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Oxidative Coupling of Aromatic Systems under the Influence of Transition Metal Compounds

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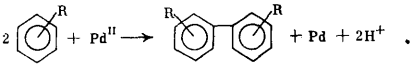
Liquid-phase reactions involving the oxidative coupling of aromatic systems (including heteroaromatic systems and aryl derivatives of the elements) to the corresponding biaryls under the influence of transition metal compounds are examined. Attention is concentrated on reactions under the influence of palladium(II) salts and complexes, which constitute the group of the most important reactions of this class. Oxidative coupling under the influence of other oxidants, including strong one-electron oxidants such as cobalt(III), manganese(III), cerium(IV), iron(III), etc., is considered for comparison. The bibliography includes 124 references.

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I. INTRODUCTION

Oxidative coupling reactions with formation of a C–C bond have been known for a long time. Interest in them increased considerably after the development of the Wacker process for the oxidation of olefins[1] and particularly in the last ten years in connection with the discovery of the coupling of aromatic compounds to biaryls under the influence of palladium salts[2].



The rapid publication of the relevant patent literature (see, for example, Refs. 3–16) indicates the potential importance of this reaction for the development of a single-stage method of synthesising biaryls, which are valuable intermediates in organic synthesis. Until recently the most universal method for the synthesis of biaryls was the technologically complex two-stage Ullmann reaction[17]. Coupling under the influence of palladium(II) salts proceeds under milder conditions via a non-radical mechanism, which creates conditions for a high selectivity. Furthermore, coupling may be achieved catalytically as a result of the regeneration of palladium(II) by means of oxidants, including O_2.

The early studies on this reaction, published before 1969, have been examined in previous reviews[1,18–20] and have been briefly discussed in other publications[21,22]†. Further research into the oxidative coupling of the aromatic systems, including heteroatomatic systems and aryl derivatives of the elements, greatly extended the applications of the reaction and deepened the understanding of its mechanism. Significant advances have been achieved in the development of oxidative coupling catalysts based on palladium(II). Numerous studies have been published recently on the oxidative coupling of aromatic compounds under the influence of other oxidants, in the first place strong one-electron oxidants such as cobalt(III), manganese(III), cerium(IV), iron(III), etc. These data are extremely useful for the understanding of the mechanism of coupling under the influence of palladium(II). Such problems are in fact the subject of the present review. which covers the literature published up to the middle of 1976. It is noteworthy that, together with the term "oxidative coupling", the terms "oxidative dimerisation", "oxidative dehydrodimerisation", and "oxidative pairing" are used in the literature. The first term is used in the review because in the author's view it is the most accurate and embraces not only symmetrical but also asymmetric coupling reactions. Stern's[18] and Moritani and Fujiwara's[23] reviews may be recommended to those who wish to become acquainted with the related oxidative coupling and olefin arylation reactions under the influence of palladium(II).

† During the preparation of this paper for the Press, the following reviews were also published: R. A. Sheldon and J. K. Kochi, Adv. Catalysis, **25**, 274 (1976); I. I. Moiseev, Zhur. Vses. Khim. Obshch. im. Mendeleeva, **22**, 30 (1977); H. W. Krause, R. Selke, and H. Pracejus, Z. Chem., **16**, 465 (1976).

II. OXIDATIVE COUPLING UNDER THE INFLUENCE OF PALLADIUM(II) COMPOUNDS

1. AROMATIC (CARBOCYCLIC) COMPOUNDS

In 1965 Van Helden and Verberg[2] reported for the first time the oxidative coupling of aromatic compounds to biaryls under the influence of palladium(II) in acetic acid:

$$2RH + Pd^{II} \rightarrow R{-}R + Pd^{0} + 2H^{+}.$$

Subsequent studies showed that the composition of the products of the reaction depends on the conditions. The coupling of benzene derivatives has been most fully investigated (see Table). Compounds of the naphthalene series and probably other aromatic condensed systems also enter into this reaction.

Depending on the substrate, when aromatic hydrocarbons are acted upon by $PdCl_2$ + NaOAc in acetic acid, biaryls are formed in yields of 25–81% [here and henceforth the yields are quoted relative to the initial amount of palladium(II)][2]. In the absence of sodium acetate the reaction does not occur. Davidson and Triggs found that, when palladium(II) is used in the form of $Pd(OAc)_2$, products resulting from the acetoxylation of the ring and the

side chain are formed together with the coupling products[24,25,27] (for further details about the acetoxylation, see Refs. 22 and 26). Thus biphenyl (66%) and phenyl acetate (16%) were obtained from benzene in acetic acid. Benzyl acetate (40–45%) was the main product from toluene. In the presence of $HClO_4$ in acetic acid the reaction is sharply accelerated and the yield of coupling products increases as a result of the suppression of the acetoxylation reaction[24,27]. The addition of alkali metal acetates also accelerates the overall reaction, but under these conditions there is an increase in the yield of acetoxylation products[24,28]. The acetoxylation of benzene and toluenee by palladium(II) acetate in acetic acid is almostly completely suppressed when the reaction is carried out under oxygen at a pressure of 50 atm.[29] when mainly coupling products are formed. When benzene was allowed to interact with $Pd(OAc)_2$ in benzene solution and with $PdSO_4$ in 20% aqueous sulphuric acid solution, only coupling products were obtained[24,27].

The oxidative coupling of aromatic systems to biaryls under the influence of palladium(II).

Substrate	Oxidant	Medium	T, °C	Time, h	Product R–R	Yield, % Pd	Refs.
		Aromatic compounds					
Benzene	$PdCl_2$	HOAc, NaOAc	90	5.5	Biphenyl	71	2
Benzene	$PdSO_4$	H_2O, H_2SO_4	80	24	Biphenyl	54	27
Benzene	$Pd(OAc)_2$	DOAc, $HClO_4$	80	0.5	Biphenyl	44	27
Benzene	$Pd(OAc)_2$	HOAc	100	16	Biphenyl	66	25
Benzene	$Pd(CF_3COO)_2$	CF_3COOH	25	24	Biphenyl	40	32
Benzene	$Pd(NO_3)_2$	HOAc	95		Biphenyl	4,5	31
Benzene	$(C_2H_4PdCl_2)_2$	HOAc, $AgNO_3$	80	20	Biphenyl	99	34
Benzene	(styrene.$PdCl_2$)2	HOAc, $AgNO_3$	80	20	Biphenyl	68	34
Benzene	$PdCl_2$	HOAc, $AgNO_3$	80	20	Biphenyl	40	34
Benzene	(cyclo-$C_6H_{10}PdCl_2)_2$	HOAc, $AgNO_3$	80	20	Biphenyl Terphenyl	3 9	34
Toluene	$PdCl_2$	HOAc, NaOAc	110	7	Bitolyl (2,3'—25%; 3,3'—20%; 3,4'—35%; 4,4'—20%)	75	2
Toluene	$Pd(OAc)_2$	HOAc, $HClO_4$	50	1.5	Bitolyl (3,4'—34%; 4,4'—42%)	37	27
Toluene	$Pd(OAc)_2$	HOAc, $HClO_4$, $Hg(OAc)_2$	25	30	Bitolyl (3,4'—27%; 4,4'—67%)	95	35
Toluene	$(C_2H_4PdCl_2)_2$	HOAc, $AgNO_3$	80	20	Bitolyl (4,4'—31%)	61	34
Ethylbenzene	$Pd(CF_3COO)_2$	CF_3COOH	25	340	Diethylbiphenyl	53	32
Cumene	$PdCl_2$	HOAc, NaOAc	110	7	Bicumenyl	81	2
Cumene	$Pd(CF_3COO)_2$	CF_3COOH	25	340	Bicumenyl (3,4'—48%; 4,4'—40%)	42	32
Anisole	$PdCl_2$	HOAc, NaOAc	110	7	Dimethoxybiphenyl	60	2
Anisole	$Pd(CF_3COO)_2$	CF_3COOH	25	340	Dimethoxybiphenyl (2,4'—35%; 3,4'—15%; 4,4'—35%)	49	32
Chlorobenzene	$PdCl_2$	HOAc, NaOAc	110	7	Dichlorobiphenyl (3,4'—40%;	56	2
Chlorobenzene	$(C_2H_4PdCl_2)_2$	HOAc, $AgNO_3$	80	20	Dichlorobiphenyl (4,4'—20%)	70	34
Nitrobenzene	$Pd(CF_3COO)_2$	CF_3COOH	70	48	Dinitrobiphenyl (2,3'—48%)	21	32
Nitrobenzene	$(C_2H_4PdCl_2)_2$	HOAc, $AgNO_3$	80	20	3,3'-Dinitrobiphenyl	60	34
Methyl benzoate	$PdCl_2$	HOAc, NaOAc	110	7	Dimethoxycarbonylbiphenyl	42	2
Phenyl pivalate	$PdCl_2$	HOAc, NaOAc	110	7	Dipivaloyloxybiphenyl	25	2
$PhC(Me)_2CH_2C(O)OMe$	$PdCl_2$	HOAc, NaOAc	110	7	Biaryl	45	2
Biphenyl	$PdCl_2$	HOAc, NaOAc	110	7	Quaterphenyl (3,4'—45%; 4,4'–22%)	40	2
o-Xylene	$Pd(OAc)_2$	HOAc, NaOAc	110	10	Bixylyl (3,4,3',4'—65%)	73	2
m-Xylene	$PdCl_2$	HOAc, NaOAc	110	7	Bixylyl	60	2
p-Xylene	$Pd(CF_3COO)_2$	CF_3COOH	25	340	2,5,2',5'-Bixylyl	19	32
p-Xylene	$(C_2H_4PdCl_2)_2$	HOAc, $AgNO_3$	80	20	2,5,2',5'-Bixylyl	38	34
m-Di-isopropylbenzene	$PdCl_2$	HOAc, NaOAc	110	7	3,5,3',5'-Tetraisopropyl-biphenyl	25	2
2,6-Di-isopropylphenol	$PdCl_2$	HOAc, NaOAc	100	3	*p,p'*-Diphenoquinone	23	30
2,6-Di-isopropylphenol	$Pd(OAc)_2$	HOAc	100	3	*p,p'*-Diphenoquinone	21	30
2,4-Di-isopropylphenol	$PdCl_2$	HOAc, NaOAc	100	3	*o,o'*-Biphenol	1	30
2,6-Dimethoxyphenol	$PdCl_2$	HOAc, NaOAc	100	3	*p,p'*-Diphenoquinone	25	30
		Heterocyclic compounds					
Furan	$Pd(OAc)_2$	HOAc	50	2	Bifuryl (2,2'—91%)	45	44
Furan	$Pd(OAc)_2$	HOAc, NaOAc	50	2	Bifuryl (2,2'—93%)	80	44
Furan	$Pd(OAc)_2$	DMF	96	3	Bifuryl (2,2'—90%)	98	44
2-Methylfuran	$Pd(OAc)_2$	DMF	98	1	Dimethylbifuryl (2,2'—90%)	48	45
Furfural	$Pd(OAc)_2$	Furfural	97	1	Diformyl-2,2'-bifuryl	62	45
2-Methoxycarbonylfuran	$Pd(OAc)_2$	HOAc	97	3	Dimethoxycarbonylbifuryl (2,2'—65%); 2,3'—35%)	40	45
2-Ethoxycarbonylfuran	$Pd(OAc)_2$	HOAc	97	3	Diethoxycarbonylbifuryl	45	45
Diacetoxyfurfural	$Pd(OAc)_2$	HOAc	97	3	Tetra-acetoxydiformyl-2,2'-bifuryl	36	45
Benzofuran	$Pd(OAc)_2$	C_6H_6—HOAc	80	6	2,2'-Bibenzofuryl	68	50
5-Methylbenzofuran	$Pd(OAc)_2$	C_6H_6—HOAc	80	6	Dimethyl-2,2'-bibenzofuryl	70	50
Thiophen	$Pd(OAc)_2$	HOAc	70	2	Bithienyl (2,2'—30%; 2,3'—65%)	69	46
Thiophen	$PdCl_2$	H_2O	50	2	Bithienyl (2,2'—95%)	21	44
Thiophen	$PdCl_2$	H_2O, $Hg(NO_3)_2$	50	2	Bithienyl (2,2'—96%)	52	44
Thiophen	$Pd(ClO_4)_2$	H_2O, $HClO_4$	69	2	Bithienyl (2,2'—58%; 2,3'—42%)	12	44
Thiophen + furan	$Pd(OAc)_2$	HOAc	35	4	2-(2-Furyl)thiophen 3-(2-Furyl)thiophen Bithienyl Bifuryl	16 4 15 9	44
Pyrrole	$Pd(OAc)_2$	DMF	70	2	2,2'-Bipyrrolyl	1	44

Table (contd.)

Substrate	Oxidant	Medium	T, °C	Time, h	Product R-R	Yield,[a] % Pd	Refs.
			Organoelemental compounds				
C_6H_5HgOAc	$Pd(OAc)_2$	HOAc, LiOAc	90	23	Biphenyl	95	35
$(p\text{-}CH_3C_6H_4)_2Hg$	$PdCl_2$	HOAc	90	0.01	4,4'-Bitolyl	100	35
$p\text{-}CH_3C_6H_4HgOAc$	$PdCl_2$	HOAc, $HClO_4$	25	0.5	Bitolyl (3,4'—35%; 4,4'—60%)	95	35
(Ferrocenyl)HgCl	Li_2PdCl_4	CH_3OH	—	—	Biferrocenyl	—	61
C_6H_5HgOAc[a] + benzofuran	Li_2PdCl_4	C_2H_5OH	25	12	2-Phenylbenzofuran	77	50
					Biphenyl	7	
C_6H_5HgOAc[a] + 5-methylbenzofuran	Li_2PdCl_4	C_2H_5OH	25	12	5-Methyl-2-phenylbenzofuran	75	50
					Biphenyl	9	
$C_6H_5Tl(OAc)ClO_4$	$PdCl_2$	HOAc, NaOAc	115	5	Biphenyl	49	63
$(C_6H_5)_2TlCl$	$PdCl_2$	HOAc, NaOAc	115	5	Biphenyl	6	63
$p\text{-}CH_3C_6H_4Tl(OAc)ClO_4$	$PdCl_2$	HOAc, NaOAc	115	5	4,4'-Bitolyl	69	63
$3,4\text{-}(CH_3)_2C_6H_3Tl(OH)ClO_4$	$PdCl_2$	HOAc, NaOAc	115	5	3,4,3',4'-Bixylyl	66	63
$p\text{-}CH_3OC_6H_4Tl(OAc)ClO_4$	$PdCl_2$	HOAc, NaOAc	115	5	4,4'-Dimethoxybiphenyl	70	63
$C_6H_5B(OH)_2$	$Pd(OAc)_2$	HOAc, $HClO_4$	60	0.08	Biphenyl	18	27
$C_6H_5B(OH)_2$	Na_2PdCl_4	H_2O, H_2SO_3	80	0.03	Biphenyl	81	27
$p\text{-}CH_3C_6H_4B(OH)_2$	$Pd(OAc)_2$	HOAc, $HClO_4$	60	0.08	4,4'-Bitolyl	—	27
$C_6H_5SO_2Na$	Na_2PdCl_4	H_2O	100	8	Biphenyl	35	65
$C_6H_5SO_2Na$	Na_2PdCl_4	H_2O, $HgCl_2$	100	8	Biphenyl	71	65
$p\text{-}CH_3C_6H_4SO_2Na$	Na_2PdCl_4	HOAc	115	8	4,4'-Bitolyl	36	65
$p\text{-}CH_3C_6H_4SO_2Na$	Na_2PdCl_4	H_2O, $HgCl_2$	100	8	4,4'-Bitolyl	63	65
$p\text{-}CH_3C_6H_4SO_2H$	Na_2PdCl_4	H_2O—C_2H_5OH	81	8	4,4'-Bitolyl	27	65
			Catalytic reactions. 1. Oxidation by metal salts				
Benzene	$Pd(CF_3COO)_2$, $Cu(OAc)_2$	CF_3COOH	25	100	Biphenyl	110	32
					Terphenyl (*o*—40%; *m*—35%; *p*—25%)	10	
Furan	$Pd(OAc)_2$, $CuCl_2$	DMF	132	6	Bifuryl (2,2'—91%)	9000	45
Furan	$Pd(OAc)_2$, $CuCl_2$	DMF-H_2O	96	3	Bifuryl (2,2'—82%)	520	45
Furfural	$Pd(OAc)_2$, $CuCl_2$	Furfural	120	3	Diformyl-2,2'-bifuryl	1350	45
Thiophen	$Pd(OAc)_2$, $CuCl_2$	HOAc	98	6	Bithienyl (2,2'—80%)	350	44
Thiophen	$PdCl_2$, $FeCl_3$	H_2O	98	2	Bithienyl (2,2'—85%)	530	44
Thiophen	$Pd(ClO_4)_2$, $Fe(ClO_4)_3$	H_2O, $HClO_4$	69	2	Bithienyl (2,3'—81%)	160	44
Thiophen	$PdSO_4$, $Fe_2(SO_4)_3$	H_2O, H_2SO_4	98	2	Bithienyl (2,3'—77%)	170	44
Thiophen + furan	$Pd(OAc)_2$, $CuCl_2$	DMF	96	2	2-(2-Furyl)thiophen	550	44
					3-(2-Furyl)thiophen	110	
					Bithienyl	460	
					Bifuryl	58	
$p\text{-}CH_3C_6H_4HgCl$	$PdCl_2$, $CuCl_2$	HOAc	24	17	4,4'-Bitolyl	650	5
$p\text{-}(CH_3)_2CHC_6H_4HgCl$	$PdCl_2$, $CuCl_2$	HOAc	24	17	4,4'-Bicumenyl	740	5
$m\text{-}NO_2C_6H_4HgCl$	$PdCl_2$, $CuCl_2$	HOAc	24	17	3,3'-Dinitrobiphenyl	810	5
$m\text{-}HOOCC_6H_4HgCl$	$PdCl_2$, $CuCl_2$	HOAc	24	17	3,3'-Dicarboxybiphenyl	670	5
$p\text{-}CH_3C_6H_4SO_2Na$	Na_2PdCl_4, $CuCl_2$	H_2O, $HgCl_2$	100	8	4,4'-Bitolyl	380	65
$C_6H_5Tl(OAc)ClO_4$	$PdCl_2$	HOAc, NaOAc	115	5	Biphenyl	380	63
			Catalytic reactions. 2. Oxidation by oxydation				
Benzene	$Pd(OAc)_2$, O_2 (60 atm)	HOAc, NaOAc	100	8	Biphenyl	160	25
Benzene	$Pd(OAc)_2$	HOAc, NaOAc	150	4	Biphenyl	3100[b]	89
Benzene	$Pd(OAc)_2$, O_2 (1 atm)	H_2O—HOAc, $HClO_4$	68	8	Biphenyl	220	87
Benzene	$Pd(ClO_4)_2$	H_2O—HOAc	25	16	Biphenyl	5700[c]	87
Benzene	$Pd(ClO_4)_2$	H_2O—HOAc	68	6	Biphenyl	700[c]	87
Toluene	$Pd(OAc)_2$, O_2 (100 atm)	HOAc, NaOAc	100	4	Bitolyl	83	25
Toluene	$Pd(OAc)_2$	Toluene	150	16	Bitolyl (3,3'—27%; 3,4'—35%; 4,4'—13%)	20600[b]	88
Toluene	$Pd(OAc)_2$	Toluene	150	4	Bitolyl	7400[b]	89
Toluene	$Pd(ClO_4)_2$	H_2O—HOAc	68	6	Bitolyl	6400[c]	87
Chlorobenzene	$Pd(OAc)_2$	Chlorobenzene	150	4	Dichlorobiphenyl	400[b]	89
Chlorobenzene	$Pd(ClO_4)_2$	H_2O—HOAc	68	6	Dichlorobiphenyl	340[c]	87
Phenyl acetate	$Pd(OAc)_2$	Phenyl acetate	150	4	Diacetoxybiphenyl	5700[b]	89
Methyl benzoate	$Pd(OAc)_2$	Methyl benzoate	150	4	Dimethoxycarbonylbiphenyl	8500[b]	89
Nitrobenzene	$Pd(OAc)_2$	Nitrobenzene	150	4	Dinitrobiphenyl	2500[b]	89
Fluorobenzene	$Pd(OAc)_2$	Fluorobenzene	150	4	Difluorobiphenyl	2300[b]	89
Trifluoromethylbenzene	$Pd(OAc)_2$	Trifluoromethylbenzene	150	4	Biaryl	700[b]	89
o-Xylene	$PdCl_2$, O_2 (1 atm)	HOAc, NaOAc	110	10	Bixylyl (3,4,3',4'—72%)	90	2
o-Xylene	$Pd(OAc)_2$	*o*-Xylene	150	4	Bixylyl	5700[b]	89
o-Xylene	$Pd(ClO_4)_2$	H_2O—HOAc	68	6	Bixylyl (3,4,3',4'—65%)	3000[c]	87
m-Xylene	$Pd(OAc)_2$	*m*-Xylene	150	4	Bixylyl	4100[b]	89
m-Xylene	$Pd(ClO_4)_2$	H_2O—HOAc	68	6	Bixylyl	870[c]	87
p-Xylene	$Pd(OAc)_2$	*p*-Xylene	150	4	Bixylyl	400[b]	89
p-Xylene	$Pd(ClO_4)_2$	H_2O—HOAc	68	6	Bixylyl	3500[c]	87
Dimethyl phthalate	$Pd(OAc)_2$	Dimethyl phthalate	150	4	Biaryl	5200[b]	89
Naphthalene	$Pd(OAc)_2$, O_2 (1 atm)	HOAc	115	400	Binaphthyl (1,1'—41%; 1,2'—49%)	1600	41
					Oligomers (tetramer—65%)	1500	
Naphthalene	$Pd(OAc)_2$	Naphthalene	150	4	Binaphthyl (1,1'—43%; 1,2'—50%)	4500[b]	89
			Catalytic reactions. 3. Oxidation by oxygen in the presence of a catalyst				
Benzene	$PdSO_4$	H_2O—HOAc	84	3	Biphenyl	1600[d]	99
Toluene	$Pd(OAc)_2$	H_2O—HOAc	70	2	Bitolyl (2,4'—21%; 3,4'—31%; 4,4'—22%)	1800[d]	99
Toluene	$Pd(OAc)_2$	H_2O—HOAc, $Hg(OAc)_2$	70	2	Bitolyl (3,4'—36%; 4,4'—36%)	1900[d]	99
Toluene	$PdCl_2$, $H_4SiW_{10}V_2O_{40}$, O_2 (1.5 atm)	H_2O—HOAc	84	3	Bitolyl	920	99
Toluene	$Pd(OAc)_2$	sulpholane	70	3	Bitolyl (3,4'—35%; 4,4'—48%)	610[d]	99
Chlorobenzene	$Pd(OAc)_2$	H_2O—HOAc	90	—	Dichlorobiphenyl (2,4'—29%; 3,4'—26%; 4,4'—21%)	—[d]	100
Chlorobenzene	$Pd(OAc)_2$	H_2O—HOAc, $Hg(OAc)_2$	90	—	Dichlorobiphenyl (2,4'—15%; 3,4'—34%; 4,4'—36%)	—[d]	100

Table (contd.)

Substrate	Oxidant	Medium	T, °C	Time, h	Product R – R	Yield,[a] % Pd	Refs.
o-Xylene	$Pd(OAc)_2$	H_2O—HOAc	50	2,5	Bixylyl (3,4,3',4'—92%)	1300[d]	99
Durene	$PdSO_4$	H_2O—HOAc	84	4	Biduryl	670[d]	99

[a]Analogous products were obtained in a yield of 70–80% in the reaction of *p*-tolyl-, *p*-anisyl-, and *m*-nitrophenylmercury(II) acetates.

[b]Reaction carried out in the substrate undergoing oxidation in the presence of acetylacetone under a pressure of 150 atm of a 1 : 1 $O_2 + N_2$ gas mixture.

[c]Reaction carried out in the presence of $Fe(ClO_4)_3$ and $HClO_4$ under O_2 pressure (1 atm).

[d]Reaction carried out in the presence of HPA-2 having the composition $H_5PMo_{10}V_2O_{40}$ under O_2 pressure (1.5 atm).

It has been established[30] that substituted phenols in acetic acid in the presence of $PdCl_2$ and sodium acetate undergo oxidative coupling with formation of a C–C bond. This process yielded biphenols (1%) and products of their subsequent oxidation–biphenoquinones (17–25%). Phenol coupling products involving the formation of a C–O bond, which are frequently produced in other catalytic systems[18], were not detected.

When $PdBr_2$ and PdI_2 are used in acetic acid solution, oxidative coupling of aromatic compounds does not occur[2]. Palladium(II) nitrate interacts with aromatic compounds in acetic acid to form acetoxylation, nitration, and oxidative coupling products[31]. Thus phenyl acetate (39%), nitrobenzene (14%), and biphenyl (4%) were obtained from benzene. The addition of water, $HClO_4$, and iron(III) sulphate increases the yield of the coupling products.

Clark et al.[32] (see also Gol'dshleger et al.[33]) found that, under the influence of palladium(II) trifluoroacetate in trifluoroacetic acid at room temperature, aromatic compounds give rise to coupling products together with a small amount of phenols, which are probably formed on hydrolysis of the corresponding aryl trifluoroacetates during the separation of the reaction mixtures. The mode of coupling depends on the nature of the aromatic substrate. Benzene and its monosubstituted derivatives give rise preferentially or exclusively to biaryls. This is also observed with *o*- and *m*-xylenes and 1,2,3-trimethylbenzene. Apart from biaryls, alkylbenzenes yield diarylmethanes (mesitylene and durene give rise exclusively to diarylmethanes in 60% yield). Arylmethylation is characteristic of strongly acid media. Similarly phenyltolylmethane was obtained in the reaction of toluene with $Pd(OAc)_2$ in acetic acid in the presence of $HClO_4$.[27]

According to Fujiwara et al.[34], the $(olefin.PdCl_2)_2$ complexes cause the effective coupling of aromatic compounds in the presence of added silver(I), mercury(II), and copper(II) salts or oxides. Best results are obtained in the presence of the $(C_2H_4.PdCl_2)_2$–$AgNO_3$ (1 : 1) system. In the absence of the palladium(II) complex, silver(I) nitrate is inactive. Gaseous products (ethylene, nitrogen dioxide, and HCl) are evolved during the reaction. The yield of biphenyl in the coupling of benzene decreases in the following sequence of palladium(II) complexes: $(C_2H_4.PdCl_2)_2 > (styrene.PdCl_2)_2 > PdCl_2 > (cyclo\text{-}C_6H_{10}.PdCl_2)_2$. It is suggested that the role of $AgNO_3$ is cooperation in the substitution of the olefin for RH in the palladium(II) complex. In addition, the nitrate ion is involved in the reaction as an oxidant, which is indicated by the evolution of nitrogen dioxide.

The influence of substituents in the aromatic substrate shows that oxidative coupling under the influence of palladium(II) has the characteristics of electrophilic substitution in the aromatic ring[2]; electron-donating substituents facilitate the reaction, while electron-accepting substituents retard it. Monosubstituted benzene derivatives give rise to all six theoretical biaryl isomers[2,27]. 2,2'-Isomers are usually formed in an insignificant amount, probably owing to steric hindrance. In the reactions involving monoalkylbenzenes the main coupling products are the 3,4'- and 4,4'-isomers of biaryls. *o*-Xylene gives a mixture of the three possible isomers of bixylyl, in which the 3,4,3',4'-isomer predominates (more than 60%)[2]. The proportions of the biaryl isomers are almost independent of added acids, salts, (for example NaOAc), and complex-forming agents. It has been shown[35] that the addition of mercury(II) salts significantly increases the yield of 4,4'-isomers in the coupling of alkylbenzenes. In this case the reaction proceeds via the intermediate formation of mercury derivatives of the aromatic compounds (see below). The proportions of the isomers depend strongly on temperature. Thus, when toluene is coupled in acetic acid under the influence of $PdCl_2$ + NaOAc at 25°C, 2,4'- and 2,3'-bitolyls are formed preferentially (in yields of 44 and 24% respectively), while at 200°C the main products are the 3,4'- and 4,4'-isomers (35 and 21%)[35].

Steric effects play a significant role in oxidative coupling. This is indicated by the inertness of the $PdCl_2$ + NaOAc system in acetic acid in relation to *p*-di-isopropylbenzene, *p*-di-(t-butyl)benzene, and mesitylene[2]. It is noteworthy that in trifluoroacetic acid polysubstituted benzene derivatives (mesitylene and durene) show the highest reactivity compared with benzene and its monosubstituted derivatives in the arylmethylation reaction and not the coupling reaction[32]; the reaction mechanism is in this case different (see below).

The coupling of benzene in acetic acid in the presence of $PdCl_2$ and NaOAc proceeds in accordance with the kinetic equation[2].

$$v = k[Pd^{II}][C_6H_6] \qquad (1)$$

It is remarkable that the rate of reaction v is independent of the sodium acetate concentration, although in the absence of the latter the reaction with $PdCl_2$ does not occur[2]. This is probably because the relevant measurements were made[2] at a fairly high sodium acetate concentration (approximately 1 M) under saturation conditions.

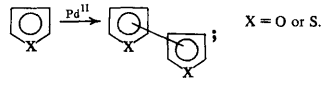
Eqn. (1) is also valid for the coupling of benzene in acetic acid[27] and in aqueous acetic acid[38] in the presence of $Pd(OAc)_2$. The replacement of C_6H_6 by C_6D_6 leads to a marked isotope effect: $k(H)/k(D) = 5.0$.[27] The rate of the reaction in acetic acid falls when water and chloride ions are added[36].

It has been established[27] that, when benzene is coupled in the presence of palladium(II) acetate at 50°C in acetic acid containing 0.5 M $HClO_4$, metallic palladium is not precipitated. The explosive red complex $[Pd(C_6H_6).(H_2O)(ClO_4)]_n$, in which the formal oxidation state of palladium is +1, was isolated instead. The complex decomposes in solution with formation of zero-valent palladium and biphenyl on heating *in vacuo* to 100°C. When chloride ions are added to the solution, palladium(I) disproportionates to bivalent and zero-valent palladium; molecular oxygen, bromine, and $KMnO_4$ oxidise palladium(I) to palladium(II). The role of the palladium(I) complex in the oxidative coupling has not so far been elucidated. The complex probably contains simultaneously bivalent and zero-valent palladium and the latter is stabilised by the benzene molecule. A complex containing palladium in the formal +1 oxidation state and having the composition (quinone).Pd_2SO_4.$3H_2O$ has been isolated in the oxidation of olefins to carbonyl compounds[37]. The zero-valent palladium formed in this reaction is stabilised in solution as a result of the formation of a complex with the olefin, for example $Pd(C_2H_4)_2$. We have suggested the involvement of palladium(I) in the coupling of benzene with ethylene under the influence of $Pd(OAc)_2$.[39]

2. HETEROAROMATIC COMPOUNDS

Like benzene and naphthalene derivatives, aromatic heterocycles undergo oxidative coupling smoothly under the influence of palladium(II). The coupling of five-membered heterocycles of the furan and thiophene series has now been investigated in detail (see Table). Presumably other heteroaromatic systems with various heteroatoms and ring sizes, which do not form inert complexes with palladium(II), would also undergo the coupling reaction. Heteroaryls differ from benzene derivatives by their higher reactivity. The coupling conditions in the heterocyclic series are on the whole analogous to those in the aromatic coupling. Limitations are imposed by the specific properties of the particular classes of heterocyclic compounds. Thus the tendency by furan derivatives to undergo solvolytic ring opening[40] restricts the application of aqueous solvents and rules out the possibility of adding inorganic acids. The coupling of thiophen is less complicated and shows the greatest similarity with the reaction of benzene.

Products of the coupling of five-membered heterocycles were detected when an attempt was made to acetoxylate thiophen[41] and to carbonylate thienyl- and furyl-mercury(II) derivatives[42] under the influence of palladium(II). The oxidative coupling of thiophen and furan derivatives has been studied[43-47]; the reaction proceeds under very mild conditions with formation of a mixture of 2,2′- and 2,3′-biheteroaryls and a small amount of the 3,3′-isomer[44]:



; X = O or S.

The coupling of thiophen proceeds in both organic and aqueous solutions, including strongly acid solutions. The yield of bithienyls increases following the addition of mercury(II) salts. The coupling of furan takes place in a wide range of organic solvents[44,45] and in basic aqueous solutions, for example, in H_2O–dimethyl formamide (DMF) mixtures. In acetic acid the yield of biheteroaryls increases after the addition of sodium acetate[44,45]. Thiophen acetoxylation products were not detected under these conditions[41]. The isomeric composition of biheteroaryls depends on the reaction conditions. In acetic acid the ratio of the yields of 2,2′- and 2,3′-bithienyls—the main reaction products—increases after the addition of sodium acetate and water and after the reduction of temperature[44,46]. The ratio of the 2,2′- and 2,3′-isomers of bithienyl increases sharply when aqueous media are used and mercury(II) is added[44].

The reactivity of 2-substituted furan derivatives in the coupling reaction under the influence of $Pd(OAc)_2$ varies as follows in the presence of various substituents: H, CH_3, $CHO > COOCH_3$, $COOC_2H_5$, $CH(OOCCH_3)_2 > COOH$.[45] The sequence was established for electrophilic substitution reactions involving all five-membered aromatic heterocycles[40].

The joint coupling of furan and thiophen makes it possible to obtain in a single stage furylthiophens mixed with bithienyl and bifuryl[44]. The main product is 2-(2′-furyl)-thiophen and a small amount of 3-(2′-furyl)thiophen. It is noteworthy that the synthesis of furylthiophens by other methods is very complex[48,49].

The interaction of benzofuran with $Pd(OAc)_2$ in a benzene–acetic acid mixture yielded 2,2′-bibenzofuryl (68%), 2-phenylbenzofuran (12%), and biphenyl (4%).[50] The ratio of the reaction products indicates a much higher reactivity of benzofuran compared with benzene. A similar result was obtained with 5-methylbenzofuran[50].

Pyrrole chars rapidly on interaction with $Pd(OAc)_2$ in acetic acid, DMF, and heptane[44] and only traces of 2,2′-bipyrrolyl are formed (1%). It may prove useful to protect the pyrrole ring by *N*-alkylation, because *N*-methylpyrrole is smoothly vinylated by olefins under the influence of palladium(II).[51] Pyridine does not undergo the coupling reaction[44], because it forms a very stable complex with palladium(II).[52]

The kinetics of the coupling of heterocycles have been studied in relation to the reaction of thiophen[46]. The coupling of thiophen under the influence of $Pd(OAc)_2$ in acetic acid proceeds in accordance with the equation

$$v = k[Pd^{II}] \cdot [C_4H_4S]/(1 + K[C_4H_4S]), \qquad (2)$$

which differs from Eqn. (1) by the presence of the denominator $1 + K[C_4H_4S]$, which indicates the formation of an intermediate palladium(II) complex of thiophen with a stability constant, $K = 0.2$ litre mole^{-1} at 70°C. In benzene a similar complex is less stable, the difference between the coordination capacities of benzene and thiophen in relation to palladium(II) being manifested. It is suggested[46] that palladium(II) forms a complex with thiophen via the sulphur atom. The kinetic isotope effect in the coupling of [2,5-D_2]thiophen in acetic acid is $k_2(H)/k_2(D) = 1.8$ [k_2 is the rate constant for the attack by palladium(II) on the 2-position in thiophen][46]. In aqueous solution the rate of reaction of thiophen with $PdCl_2$ is given by the equation[47]

$$v = k[Pd^{II}]\,[C_4H_4S]/[H^+]^a\,[\bar{Cl}]^b,$$

where $a \leq 1$ and $2 < b < 3$. A similar kinetic equation holds[1] for the oxidation of olefins by an aqueous solution of $PdCl_2$.

3. ORGANOELEMENTAL COMPOUNDS

The oxidative coupling of aryl derivatives of metals and non-metals [for example, mercury(II), thallium(II), boron(III), etc.] to biaryls under the influence of palladium(II) is discussed in this section. The coupling of organoelemental compounds takes place as a rule very readily and, in contrast to the coupling of hydrocarbons, makes it possible to obtain a unique biaryl isomer and not a mixture of isomers, the structure of the isomer depending on the organoelemental compound (see Table). These reactions proceed via the mechanism involving the substitution of the element by palladium(II),[18,19] which has been well established in the chemistry of palladium, and for this reason are of fundamental importance for the understanding of the mechanism of aromatic coupling under the influence of palladium(II).

Heck was the first to show[53,60] the considerable preparative possibilities of such reactions in relation to the arylation of olefin and acetylene derivatives. Mercury(II) compounds proved to be the most effective. Tin(IV), lead(IV), etc. compounds have also been used. It is suggested[53-60] that the short-lived intermediate RPdX plays a decisive role in the reaction:

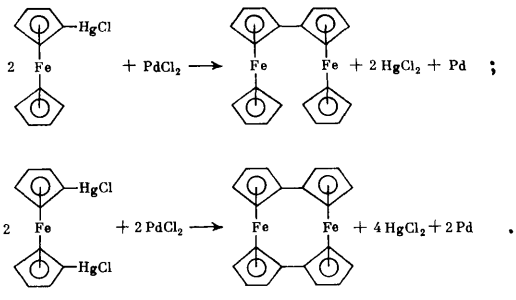
$$RHgX + PdX_2 \rightarrow RPdX + HgX_2 ,$$

$$RPdX + \underset{H}{\overset{H}{C{=}C}} \rightarrow R{-}\underset{H}{\overset{H}{C}}{-}\underset{}{\overset{}{C}}{-}PdX \rightarrow \underset{R}{\overset{}{C{=}C}} + HPdX .$$

In the absence of unsaturated compounds RPdX gives rise to oxidative coupling products:

$$2RPdX \rightarrow R{-}R + PdX_2 + Pd .$$

Oxidative coupling of RHgX derivatives (R = phenyl, *p*-tolyl, *p*-cumenyl, *m*-nitrophenyl, *m*-carboxyphenyl, etc.) takes place at 25°C with high yields of the corresponding biphenyl derivatives[5]. A new C–C bond is then formed almost exclusively at the site of the initial addition of mercury(II). The coupling of (*p*-tolyl)HgOAc in acetic acid under the influence of $(PdOAc)_2$ is fairly slow, but is sharply accelerated by the addition of $HClO_4$; $(p\text{-tolyl})_2Hg$ reacts instantaneously also in the absence of $HClO_4$.[35] Heterocyclic mercury(II) derivatives react analogously[42]. The reaction with ferrocene gave a high yield of biferrocenyl[61,62]:



Arylthallium(III) derivatives react with $PdCl_2$ in acetic acid in the presence of sodium acetate to form biaryls [Eqn. (3)][63]. As in the coupling of mercury(II) derivatives, the C–C bond is formed at the site of the initial addition of thallium(III); a small amount of side products comprising hydrocarbons RH and RCl is formed. The reaction proceeds with substitution of thallium(III) by palladium(II) in $RTl(III)$.[63] Here $PdCl_2$ is active also in the absence of NaOAc, but the addition of the latter accelerates the reaction. The inorganic products of the reaction are zero-valent palladium and thallium(I). Thallium(III), formed by reaction (3), probably oxidises metallic palladium to palladium(II), which makes the reaction catalytic in relation to palladium(II):

$$\begin{gathered} 2RTl(III) + Pd(II) \rightarrow R{-}R + Pd + 2Tl(III) , \\ Tl(III) + Pd \rightarrow Tl(I) + Pd(II) . \end{gathered} \qquad (3)$$

On reaction with palladium(II) salts, Grignard reagents give rise to coupling products with intermediate substitution of magnesium(II) by palladium(II):[64]

$$\begin{gathered} C_6H_5MgX + PdX_2 \rightarrow C_6H_5PdX + MgX_2 ; \\ 2C_6H_5PdX \rightarrow (C_6H_5)_2 + PdX_2 + Pd . \end{gathered}$$

A similar reaction takes place smoothly with aromatic and heterocyclic compounds also under the influence of copper(II), silver(I), iron(III), cobalt(II), nickel(II), ruthenium(IV), rhodium(III), etc. salts; iridium, osmium, and platinum compounds are less active[64].

The coupling of organic derivatives of non-metals (boron and sulphur) also involves the substitution of these elements by palladium(II). Benzene- and 3-methylbenzeneboronic acids give rise to biphenyl and 4,4′-bitolyl respectively after interacting for several minutes with $Pd(OAc)_2$ in acetic acid in the presence of $HClO_4$:[27]

$$2C_6H_5B(OH)_2 + Pd(II) + H_2O \rightarrow (C_6H_5)_2 + 2B(OH)_3 + Pd + 2H^+ .$$

Arenesulphinic acids and their salts are converted into biaryls in the presence of palladium(II) with liberation of SO_2 [Eqn. (4)][65]. The reaction takes place in aqueous and organic media and the addition of mercury(II) salts catalyses the coupling reaction. Similar reactions may also be expected for aryl derivatives of silicon, because phenylation of olefins by trimethylphenylsilane in the presence of palladium(II) is known[66]. For the same reason, there is probably also a possibility of aromatic coupling via a stage involving the substitution of phosphorus in triphenylphosphine and of antimony in triphenylstibine for palladium(II), since the above compounds are capable of arylating styrene with a high yield [Eqn. (5)][23]:

$$2(p\text{-}CH_3C_6H_4)SO_2Na + Pd(II) \rightarrow 4,4'\text{-}(C_6H_4CH_3)_2 + Pd + 2SO_2 + 2Na^+ ; \qquad (4)$$

$$(C_6H_5)_3P + CH_2{=}CHC_6H_5 \xrightarrow{Pd(OAc)_2} trans\text{-}\ C_6H_5CH{=}CHC_6H_5 . \qquad (5)$$

4. THE OXIDATIVE COUPLING MECHANISM

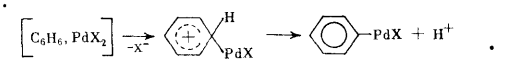
The oxidative coupling of aromatic, heteroaromatic, and organoelemental compounds under the influence of palladium(II) includes a slow stage in which the aromatic ring undergoes electrophilic substitution and proceeds via the intermediate formation of σ-arylpalladium(II).[18,19] This is preceded by the rapid formation of an intermediate arene–palladium(II) complex in accordance with Eqn. (6); this complex has been detected by kinetic methods in the thiophen coupling reaction[46]:

$$C_6H_6 + PdX_2 \rightleftarrows [C_6H_6,\ PdX_2] . \qquad (6)$$

The involvement of a σ-arylpalladium(II) is confirmed by the following data: (1) the acceleration of the reaction by electron-donating substituents and its inhibition by electron-accepting substituents: (2) the formation of coupling products when organoelemental compounds containing an aryl–element σ bond interact with palladium(II); (3) the marked kinetic isotope effect in the coupling of C_6D_6 and [2,5-D_2]thiophen; (4) the first order of the reaction with respect to palladium(II) and the substrate; (5) the

acceleration of the coupling by the addition of alkali metal acetates, which promotes the abstraction of H^+; (6) other data.

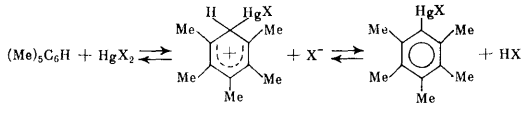
It is usually believed[67] that electrophilic substitution in the aromatic ring proceeds via mechanism(7) in two stages with formation of a cyclohexadienyl intermediate. The marked kinetic isotope effect in the oxidative coupling shows that the rate-limiting stage in reaction (7) is the abstraction of a proton from the cyclohexadienyl intermediate[27,46]:



(7)

Similar behaviour has been observed in the mercuration of aromatic compounds[67]. According to Yatsimirskii et al.[36], the anion bound to palladium(II) cooperaties in the abstraction of H^+ in reaction (7). The absence of deuterobenzene when the coupling is carried out in D_2O and DOAc shows that reaction (7) is irreversible[27]. Reaction (7) does not involve hydride transfer, because 2,2′-bibenzofuryl, obtained on coupling [2-D]benzofuran, does not contain dueterium[50].

The cyclohexadienyl intermediate in reaction (7) is an analogue of stable arenonium ions formed as intermediates in many reactions involving the electrophilic substitution of a hydrogen atom in an aromatic ring[68-70]. Nitration and halogenation of aromatic compounds, alkylation of aromatic compounds by olefins in the presence of Lewis acids, and the numerous reactions involving the migration of substituents in the aromatic molecule and their intermolecular transfer, investigated by Koptyug and coworkers[71], belong to this group of reactions. Reaction (7), involving the formation of a σ-arylpalladium(II), is analogous to the familiar reactions of arenonium ions[71], for example:



Here the cyclohexadienyl intermediate was detected by ultraviolet and ^1H NMR spectroscopy[72].

The subsequent fate of the σ-arylpalladium(II) (RPdX) is less definite. Van Helden and Verberg[2] rule out a radical decomposition of RPdX, because in an oxygen atmosphere phenol is absent from the reaction products; futhermore, the reaction is not affected by inhibitors of free radicals. The formation of coupling products at the instant of the liberation of zero-valent palladium from diarylpalladium(II) (RPdR) [Eqn. (9)] appears to be most likely:

$$RPdX + RPdX \rightarrow RPdR + PdX_2 , \quad (8)$$

$$RPdR \rightarrow R{-}R + Pd . \quad (9)$$

This hypothesis is based on the exceptional ease of formation of coupling products from diarylmercury(II) derivatives under the influence of palladium(II).[35] The synthesis and reactions of σ-aryl derivatives of nickel(II), palladium(II), and platinum(II) of the type $RM(C_6H_4F)(PEt_3)_2$, where R = Ph or Me, constitutes a direct model of reaction (9).[73] The above nickel(II) and palladium(II) compounds decompose in solution with formation of coupling products and the zero-valent metal:

$$RPd(C_6H_4F)(PEt_3)_2 \rightarrow R{-}C_6H_4F + Pd + 2PEt_3 .$$

The complex $NiBr(C_6H_5)(PEt_3)_2$ decomposes rapidly in toluene at 80°C with a quantitative yield of biphenyl; it has been suggested[73] that the reaction proceeds via a disproportionation stage:

$$2NiBr(C_6H_5)(PEt_3)_2 \rightleftarrows Ni(C_6H_5)_2(PEt_3)_2 + NiBr_2(PEt_3)_2 , \quad (10)$$

$$Ni(C_6H_5)_2(PET_3)_2 \rightarrow (C_6H_5)_2 + Ni(PEt_3)_2 . \quad (11)$$

The pathway leading to the formation of RPdR from RPdX has not been elucidated; we believe that it involves the disproportionation stage (8), similar to reaction (10). It has been suggested in a number of studies[22,32] that the substrate molecule is attacked by RPdX in accordance with the equation

$$RPdX + RH \rightarrow RPdR + HX . \quad (12)$$

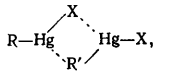
Reaction (12) does not conflict with data on the influence of the ring substituent and on isotope effects, but it is inconsistent with kinetic data. Since the electrophilic activity of RPdX must be lower than that of PdX_2, reaction (12) cannot be faster then reaction (7). One should therefore expect that stage (12) becomes rate-limiting and that the overall oxidative coupling process is of second order with respect to RH. This is inconsistent with experiment and necessitates the abandonment of the hypothesis of stage (12). Reaction (8) must be fast despite the low concentration of RPdX in the reaction mixture. There is no direct experimental confirmation of this, but numerous data for exchange reactions involving organometallic derivatives of beryllium, magnesium, cadmium, mercury, lead, zinc, and other metals have shown that reactions of type (8) are frequently very fast (for further details, see Reutov et al.[74]). In view of the profound analogy between the reactions of mercury(II) and palladium(II) with unsaturated compounds[19,74], the results for mercury(II) compounds are the most instructive. The kinetics and mechanisms of the exchange reactions of alkyl and aryl derivatives of mercury(II) have been studied in detail; the available data[74] show that such reactions proceed fairly readily, which may be an indication of the involvement of stage (8) in oxidative coupling.

Thus the principal features of the mechanisms of the oxidative coupling of aromatic compounds under the influence of palladium(II) can be represented by the sequence of reactions (6)–(9), among which reactions (7) and (8) determine the isomeric composition of the coupling products. It is possible to calculate the ratio of the rate constants for attack by palladium(II) on various positions in the substrate and to find the statistical proportions of the isomeric biaryls [i.e. the proportions obtained when the probabilities of reactions (8) are the same for different RPdX isomers]. By comparing the statistical and experimental proportions of the isomers, it is possible to obtain information about the rate of the exchange reaction (8) for different RPdX isomers. Fine polar effects of the group R in reaction (8) can be discovered in this way.

As an example, we shall consider the coupling of thiophen. When this reaction is carried out in acetic acid under the influence of $Pd(OAc)_2$ at 70°C with $[C_4H_4S]$ = 2.0 M, the experimental ratios of the 2,2′-, 2,3′-, and 3,3′-bithienyls are 6.4 : 13.8 : 1 (Kozhevnikov et al.[46]), while the statistical ratios are 3.2 : 3.6 : 1. Thus reaction (8), which leads to the asymmetric 2,3′-isomer, is much faster than the analogous reactions giving rise to the symmetrical 2,2′- and 3,3′-isomers. The concerted influence of the 2-thienyl and 3-thienyl groups, which have different electropolar properties, is probably manifested here. This effect is known for the "symmetrisation" reactions of RHgX:[74]

$$RHgX + R'HgX \rightarrow RHgR' + HgX_2 . \quad (13)$$

It has been established that reaction (13), involving the formation of asymmetric mercury derivatives, is faster than the fastest of the reactions where the symmetrical derivatives R_2Hg and R'_2Hg are formed from RHgX and R'HgX. This synergistic effect indicates the occurrence of reaction (13) [and in the case which we are considering also of reaction (8)] via the cyclic transition state



which corresponds to the S_Ei mechanism[74]. The preferential formation of asymmetric bithienyls in the reaction of thiophen with $Pd(OAc)_2$ may serve as confirmation of the occurrence of reaction (8) in oxidative coupling. More reliable conclusions require a broad analysis, for which the available data are as yet insufficient.

The mechanism discussed above refers to oxidative coupling in non-acid and moderately acid media. Coupling in strongly acid media (trifluoroacetic acid[32], acetic acid with added $HClO_4$ [27]) may proceed via a different mechanism. When alkylbenzenes are coupled in strongly acid media, diarylmethanes are formed together with biaryls. Under these conditions, polyalkylbenzenes (mesitylene, durene) yield mainly diarylmethanes[32]. Analogous products are formed when very strong oxidants [cobalt(III), cerium(IV), manganese(III), etc.)] act on alkylbenzenes. In this case coupling proceeds via a radical mechanism involving a stage in which an electron is transferred from RH to the oxidant (see Section III). In view of the similarity of the coupling products, a radical mechanism cannot be ruled out also in the case of coupling under the influence of palladium(II) in strongly acid media, particularly for reactions of polyalkylbenzenes. It is noteworthy that even thallium(III), which usually reacts with aromatic compounds via an electrophilic substitution mechanism, is capable of abstracting an electron from RH in trifluoroacetic acid with formation of a radical-cation[75] (Section III).

5. CATALYTIC REACTIONS

Catalytic oxidative coupling reactions are of greatest practical interest. For these to occur, palladium(II) must be regenerated from zero-valent palladium under the influence of an oxidant. The oxidants employed are O_2, copper(II), iron(III), vanadium(V), heteropolycompounds, etc. The most suitable industrial oxidant is oxygen; other oxidants may be used in laboratory practice, for example, the salts of metals in the highest oxidation states, hydrogen peroxide, or organic peroxides. Coupling under the influence of molecular oxygen, catalysed by palladium(II), can be divided into processes of two types: (1) those in which zero-valent palladium is oxidised by molecular oxygen and (2) those in which zero-valent palladium is reversibly oxidised by the effective oxidant, which plays the role of an agent transferring electrons from zero-valent palladium to oxygen‡; these reactions are considered separately below. Examples of catalytic reactions are presented in the Table. In the discussion of the catalytic coupling of aromatic compounds attention has been concentrated on fundamental research and only a selection of the patent literature is covered.

‡ Here and henceforth the term reversibly acting oxidant is understood to imply an oxidant whose oxidised form (Ox) can be rapidly regenerated by treating the reduced form (Red) with molecular oxygen under the reaction conditions.

(a) General Discussion

Oxidative coupling under the influence of palladium(II) results in the formation of inactive zero-valent palladium, which is then converted into metallic palladium. In order to achieve the catalytic process, it is therefore necessary to oxidise zero-valent palladium to active palladium(II):

$$2RH + Pd(II) \rightarrow R{-}R + Pd(0) + 2H^+, \quad (14)$$

$$Pd(0) + Ox \rightarrow Pd(II) + Red. \quad (15)$$

Depending on the conditions, any of the reactions (14) and (15) may be the rate-limiting stage of the catalytic process; hence follows the necessity for finding the optimum conditions. This problem was first solved successfully for the liquid-phase oxidation of olefins to carbonyl compounds[76,77] and has been examined in detail for these reactions in a number of reviews[1,18,78]. The principles underlying the selection of catalytic systems for the oxidation of olefins are largely applicable also to oxidative coupling reactions when account is taken of the specific features of the latter.

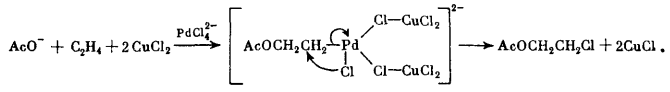
The choice of oxidants based on the oxidation potential is restricted at the lower limit by the requirement for a fairly high oxidation potential in order to regenerate palladium(II) and at the upper limit by the requirement for chemical inertness with respect to the organic substrate being oxidised. When a reversibly acting oxidant is used, the upper limit to its oxidation potential is set by the potential of molecular oxygen. The quantity $E_0[Pd_{met}/Pd(II)]$—the standard oxidation potential of the $Pd_{met}/Pd(II)$ pair whose values have been measured in various media—is usually employed as a criterion for the selection of oxidants[79]. However, this criterion is not entirely correct, because in real catalytic systems the reduced palladium is not precipitated and remains in solution in the form of zero-valent palladium complexes[78]. Such complexes, having the composition $Pd(olefin)_2$, have been detected in the oxidation reactions of ethylene and propene in aqueous palladium(II) solutions[37]. $E_0[Pd(0)/Pd(II)]$—the potential of the Pd(0)/Pd(II) pair, where Pd(0) does not refer to metallic palladium but to a zero-valent palladium complex in solution—must be regarded as a more accurate criterion[37,78]. The accurate oxidation potential of the Pd(0)/Pd(II) pair is not available, but there is not doubt that this potential is less negative than that of the $Pd_{met}/Pd(II)$ pair. For this reason, oxidants (for example, *p*-benzoquinone in the absence of Cl^- ions[37]) weaker than those which might have been thought suitable on the basis of the value of $E_0[Pd_{met}/Pd(II)]$ are also suitable for the regeneration of palladium(II). Together with the oxidation potential, an important characteristic of the oxidant is its ability to form zero-valent palladium complexes in the catalytic system[37].

The optimum reaction conditions for the given oxidant are usually selected by introducing ligands with definite coordination properties in relation to the Pd^{2+} ion[78]. The standard oxidation potential of the $Pd_{met}/Pd(II)$ pair depends significantly on the ligands present in the reaction system. In the absence of ligands capable of forming stable complexes with the Pd^{2+} ion (for example, in dilute solutions of palladium perchlorate or sulphate), the standard oxidation potential of the electrode process $Pd_{met} = Pd^{2+} + 2e^-$ is very high ($E_0 = 0.987$ V). In the presence of

ligands binding Pd^{2+} into fairly stable complexes (for example, Cl^-, Br^-, CN^-, etc.), the absolute value of the standard oxidation potential of the $Pd_{met}/Pd(II)$ pair diminishes. For example, $E_0 = 0.632$ V for the electrode process $Pd_{met} + 4Cl^- = PdCl_4^{2-} + 2e^-$.[79] Hence it follows that, for the same oxidant, the introduction into the reaction system of ligands forming stable complexes with Pd^{2+} should increase the rate of reaction (15) and reduce that of reaction (14), while exclusion of the ligands from the reaction mixture should lead to the opposite consequences. Since palladium(II) complexes are extremely labile, these thermodynamic predictions are indeed observed in practice.

The use of an oxidant with a higher potential should accelerate reaction (15), which, however, does not always happen owing to kinetic difficulties. An example is provided by molecular oxygen. The standard electrode potential of the process $2H_2O = O_2 + 4H^+ + 4e^-$ is 1.228 V.[79] Consequently direct oxidation of zero-valent palladium by oxygen is thermodynamically feasible in the presence of any ligand. However, in reality this process is very slow and requires severe conditions. The oxidation of zero-valent palladium by oxygen is significantly facilitated in the presence of reversibly acting oxidants, which are capable of effecting rapid electron transfer from zero-valent palladium to oxygen[78]. Copper(II) salts are usually employed as oxidants of this kind. The number of compounds suitable as reversibly acting oxidants in homogeneous catalysis is small. The discovery of the ability of copper salts to function as reversibly acting oxidants in relation to zero-valent palladium made it possible to achieve the catalytic oxidation of olefins to carbonyl compounds and stimulated the development of a whole series of related catalytic oxidation processes, including oxidative coupling reactions[1]. We therefore believe that it is very important to seek new reversibly active oxidants, the application of which will make it possible to extend significantly the scope of homogeneous metal-complex catalysis in partial oxidation reactions.

Before discussing studies on the catalytic oxidative coupling reactions, certain comments must be made concerning the mechanisms of the oxidation of organic compounds by palladium(II) salts in the presence of oxidants. This process was discussed above within the framework of the multistage mechanism (14)–(15) with the intermediate formation of zero-valent palladium. There is no doubt about the possibility of a multistage process, since reactions (14) and (15) may be carried out independently. At the same time it has been suggested that there is a possibility of a concerted mechanism of the oxidation process in which there is no intermediate formation of reduced palladium and electrons are transferred directly from the organic substrate to the oxidant via palladium(II),[37] the Pd^{2+} ion behaving as a bridge under these conditions. There are as yet no reliably established examples of reactions via the concerted mechanism, but many experimental data indicate its feasibility. They include the influence of the oxidant on the composition of the reaction products. Thus at a high $CuCl_2$ concentration in the oxidation of ethylene in water and acetic acid, saturated chloro-derivatives are formed as side products—ethylene chlorohydrin[80] and β-chloroethyl acetate[81] respectively. Since this happens only in the presence of $CuCl_2$, it has been suggested[81] that the reaction proceeds via the heterolytic cleavage of the C–Pd bond with transfer of the ligand:



Saturated β-halogeno-substituted coupling products were obtained similarly in the reaction of phenylmercury(II) with ethylene[82]. It has been shown[83] that in the reaction of benzene, alkylbenzenes, or their mercury derivatives with palladium(II) in the presence of acetate, chloride, etc. anions, the introduction of an oxidant (for example, $K_2Cr_2O_7$) results in substitution in the aromatic ring. In the absence of the oxidant, only oxidative coupling takes place. Thus the concerted mechanism can promote substitution in the aromatic ring or arylmethylation via the formation of R^+ in the heterolysis of RPdX induced by the oxidant. However, the involvement of the oxidant in reaction (9) leads to coupling. Presumably the former is more likely in the case of strong oxidants and the latter in the case of moderately strong oxidants. This problem requires special study.

Conclusions based on the above thermodynamic consideration of the influence of oxidants and ligands are independent of the reaction mechanism. They are valid also for the concerted mechanism. However, in the concerted mechanism the ability of the ligands to form bridge bonds between palladium(II) and the oxidant, at least in the case of cationic oxidants, is important together with the coordination properties of the ligand in relation to the Pd^{2+} ion.

(b) Oxidation by Metal Salts

The possibility of the regeneration of palladium(II) by copper(II) and iron (III) salts was already noted in the first patent of Van Helden et al.[3] Copper(II) salts are effective as oxidants for zero-valent palladium in the coupling reactions of very reactive aromatic systems, such as the thiophen and furan heterocycles and organoelemental compounds. Benzene and its derivatives are much less reactive in relation to coupling reactions under the influence of palladium(II). This is the reason for the limited applicability of copper salts as oxidants for the coupling reactions of these compounds. The Pd(II)/Cu(II) catalytic system is stable only in the presence of high concentrations of ligands forming stable complexes with palladium(II) and (or) copper(I) (these are usually Cl^- ions)[78]. The optimum concentration of Cl^- in the catalytic solution in water is approximately 1 M,[84] while in non-aqueous solutions it is less but still remains high. Under these conditions, the rate of reaction (14) is fairly high only for very reactive aromatic systems. Benzene and the majority of its derivatives are not included among these. The presence of Cl^- ions induces an appreciable side reaction involving the chlorination of organic compounds and intense corrosion of the apparatus, which also restricts the applications of the Pd(II)/Cu(II) system.

In the presence of palladium(II) as the catalyst, $CuCl_2$ effectively oxidises aryl derivatives of mercury(II) [5] and arenesulphinic acids[65] to biaryls in yields up to 800% [here and henceforth the yields are quoted in relation to palladium(II)]. The coupling of benzene in trifluoroacetic acid under the influence of copper(II) acetate is very slow[32].

The palladium(II)-catalysed oxidative coupling of furan, thiophen, and their derivatives under the influence of copper salts proceeds very readily and may be used as a convenient preparative method for the synthesis of the corresponding bifuryl, bithienyl, and furylthiophen derivatives[44,45,47,85]. Copper salts do not have a significant influence on the isomeric composition of the coupling products. The reaction proceeds in both aqueous and organic solvents (DMF, acetic acid, etc.) in yields up to

9000%. The coupling of furfural to 5,5′-diformyl-2,2′-bifuryl takes place smoothly in furfural and the yield and purity of the products increase after the addition of inert adsorbents to the system, for example, of activated charcoal[45].

The use of iron(II) salts as oxidants in palladium(II)-catalysed coupling of thiophen in aqueous solution makes it possible to obtain bithienyl in yields exceeding 700%.[44,47] The isomeric composition of bithienyl depends significantly on the presence of chloride ions in the reaction medium[47]. 2,2′-Bithienyl is formed in chloride systems with a selectivity up to 90%. In the absence of chloride ions in acid sulphate and perchlorate media 2,3-bithienyl is formed with a selectivity of about 90%, while its synthesis by other methods is extremely complex[86]. An increase of the concentrations of H^+ and Fe^{3+} increases the yield of the 2,3′-isomer, but lowers the catalytic activity. The influence of H^+ has been explained[47] by the protonation of thiophen at the sulphur atom, which entails the deactivation of the aromatic system, particularly in the 2-position of the thiophen ring. The analogous influence of the Fe^{3+} ion is probably due to its coordination to the sulphur atom. It may be that the latter favours the coupling of thiophen via the concerted mechanism[47]. The competitive influence of the Cl^- ion on the rates of stages (14) and (15) leads to an extremum in the dependence of the catalytic activity on $[Cl^-]$. In chloride-free systems the addition of mercury(II) salts sharply accelerates the reaction and leads to the exclusive formation of 2,2′-bithienyl[47]. Apart from Fe^{3+}, V_2O_5 is suitable as an oxidant in the coupling of thiophen in aqueous solution[47]. Iron(III) and vanadium(V) salts have been used as oxidants in the coupling of benzene, naphthalene, and their derivatives in sulphuric acid[6].

Palladium(II) may be regenerated also by thallium(III) compounds. This is indicated by the formation of biphenyl (in a yield of approximately 400%) when an excess of $C_6H_5Tl(OAc)ClO_4$ reacts with palladium(II)[63].

(c) Oxidation with Oxygen

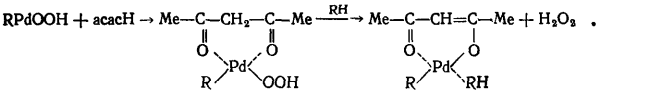
The possibility of the regeneration of palladium(II) by oxygen without cocatalysts was already noted in the first studies[2,29] on the oxidative coupling of aromatic compounds. Davidson and Triggs reported that the coupling of benzene in acetic acid in the presence of $Pd(OAc)_2$ takes place catalytically at an O_2 pressure exceeding 50 atm,[25,29] but the yield of biphenyl under these conditions is low (160% after 8 h at 100 °C)[25]. In the presence of $Pd(OAc)_2$ in acetic acid bubbled with O_2 naphthalene gives very slowly (after 400 h) catalytic yields of a mixture of isomeric binaphthyls (1600%) and naphthalene oligomers ranging from the trimer to the hexamer (1500%).[41]

$Pd(ClO_4)_2$ catalyses the coupling of benzene under the influence of oxygen (1 atm) in aqueous acetic acid in the presence of $HClO_4$.[87] The yield of biphenyl increases linearly with time (220% after 8 h at 68 °C) and depends on the $HClO_4$ concentration {the yield is a maximum when $[HClO_4] = 2-4$ M}. The activity of palladium(II) depends appreciably on the anion: $Pd(ClO_4)_2$ is twice as active as $Pd(OAc)_2$. The addition of $Fe(ClO_4)_3$ in an amount corresponding to $[Fe^{3+}]/[Pd^{2+}] = 90-200$ has a strong promoting influence. In the presence of Fe^{3+} the yield of biaryls decreases in the sequence toluene > *p*-xylene > *o*-xylene > *m*-xylene > benzene > chlorobenzene. 3,4,3′,4′-Bixylyl is formed preferentially from *o*-xylene, while toluene yields mainly 3,4′-bitolyl. The Fe^{3+} ion behaves as an oxidant in this reaction rather than as a cocatalyst, because there are no data showing the absorption of oxygen and yields of biaryls exceeding 100% (relative to Fe^{3+}) have not been achieved.

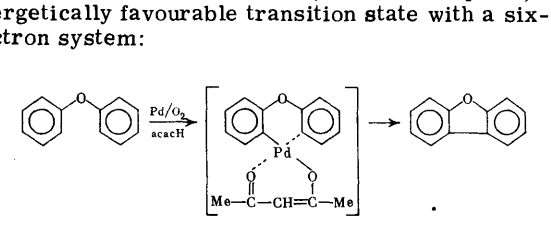
The oxidative coupling of benzene and naphthalene derivatives catalysed by palladium(II) carboxylates takes place very effectively in the substrate undergoing oxidation at an elevated temperature and a partial O_2 pressure of about 25 atm. This interesting reaction was discovered by Japanese workers, who investigated it extensively in relation to many aromatic compounds. The influence of conditions on the yield of coupling products[88,89], the relative activities of the aromatic compounds[90], and isotope effects[91] were investigated and the mechanism of the coupling reaction was considered[92,93]. The reaction is usually carried out at 150 °C using a 1 : 1 $O_2 + N_2$ mixture in order to exclude the formation of explosive mixtures of organic vapours and oxygen[88]. The yield of coupling products increases with the pressure of the gas mixture up to 50 atm and then ceases to depend on the pressure[89]. The catalytic activity of palladium(II) decreases with increase of the $Pd(OAc)_2$ concentration, although the absolute yield of biaryls increases under these conditions[91]. The yield rises when β-diketones (acetylacetone is best) and EDTA are added to the reaction mixture. The addition of polar solvents, inorganic acids, alkali metal acetates and ligands such as triphenylphosphine, bipyridyl, pyridine, chloride ions, dienes, etc. reduces significantly the yield of oxidative coupling products[89]. The catalyst exhibits a high activity for a long time. Thus, in the coupling of toluene in the presence of $Pd(OAc)_2$ and acetylacetone the yield of bitolyl was 20 600% after 16 h.[88] The influence of the substituent in the benzene ring on the yield of biaryls is typical of electrophilic substitution in the aromatic ring: toluene > *o*-xylene > *m*-xylene > *p*-xylene > mesitylene[89]. The reaction mechanism is not yet entirely clear. A scheme has been proposed for the catalytic process in which oxygen both regenerates palladium(II) and abstracts a hydrogen atom from the molecule of the aromatic compound[92,93]:

$$\begin{aligned} Pd(OAc)_2 + 2RH &\rightarrow RPdR + 2HOAc\ , \\ RPdR &\rightarrow R{-}R + Pd\ , \\ Pd + O_2 + RH &\rightarrow RPdOOH\ , \\ RPdOOH + acacH &\rightarrow RPd{-}acac + H_2O_2\ , \\ RPd{-}acac + RH &\rightarrow RPdR + acacH\ . \end{aligned} \qquad (16)$$

It is suggested that acetylacetone (acacH) promotes the reaction by forming a stable *cis*-diarylpalladium(II) complex, which then readily gives rise to coupling products[92]:



It is of interest that diphenyl ether undergoes an intramolecular coupling reaction, which has been explained[92] by the possibility of the formation, in the first place, of an energetically favourable transition state with a six-π-electron system:



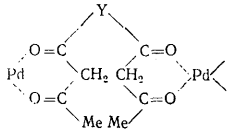
The favourable initial orientation, in one plane, of the benzene rings of the diphenyl ether (owing to conjugation via the oxygen atom) is apparently also important.

It has been suggested that this reaction may resemble the oxidation of triphenylphosphine and alkyl isocyanides by oxygen, which proceeds via zero-valent palladium complexes of molecular oxygen[94]. In this connection it has been postulated[91] that reaction (16) proceeds via a zero-valent palladium complex of O_2:

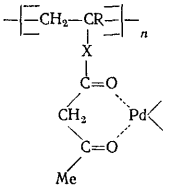
$$(C_6H_5)_4Pd + O_2 \xrightarrow[-2C_6H_5]{} (C_6H_5)_2Pd(O_2) \xrightarrow{C_6H_5} \begin{matrix} C_6H_5 \\ C_6H_5 \end{matrix}\!\!>\!Pd\!<\!\begin{matrix} OOH \\ C_6H_5 \end{matrix} .$$

The involvement of free radicals in the reaction is probably ruled out because the coupling reaction is unaffected by inhibitors of free radicals[92].

There are data in the patent literature[8-15] concerning the possible practical achievement of the oxidative coupling of aromatic hydrocarbons at elevated temperatures and under O_2 pressure. The problem of separating the catalyst from the involatile oxidative coupling product is most complex when such processes are employed. In this connection mention should be made of the very important patent of Krause and Doebler[16] for the synthesis of biphenyl derivatives in the presence of heterogeneous palladium catalysts of type (A) or polymers (B):



(A)



(B)

where Y = alkylene, arylene, etc., R = alkyl or aryl, and X = arylene of a single bond. These catalysts are in essence palladium(II) complexes of diketones fixed on the solid surface. The catalysts are chemically equivalent to the homogeneous catalysts based on $Pd(OAc)_2$ and acetylacetone, which were discussed above; this is manifested by the similarity of the conditions in the corresponding reaction. The fundamental difference is the heterogeneous nature of the catalysts, which makes it possible to separate them readily from the reaction products and return them to the cycle.

Methods for attaching metal-complex catalysts to the surface of a solid carrier have been widely developed recently[95] and are extremely promising for the improvement of the technology of oxidative coupling processes. This applies particularly to the coupling reactions discussed in this section, which take place in the substrate undergoing oxidation, in the absence of polar solvents which significantly complicate the use of fixed metal complexes.

(d) Oxidation by Oxygen in the Presence of the Cocatalyst

Direct oxidation of zero-valent palladium by oxygen requires fairly severe conditions. The process may be significantly facilitated by the introduction of a cocatalyst—a reversibly acting oxidant, capable of effecting rapid electron transfer from zero-valent palladium to O_2. The use of classical reversibly acting oxidants—copper(II) salts—in oxidative coupling reactions is limited for reasons partly indicated above. Furthermore, there exist kinetic limitations, which hinder the formation of copper salts: in aqueous solutions the oxidation of copper(I) by oxygen is very rapid, but in organic media, where oxidative coupling is usually carried out, this reaction is very slow owing to the low solubility of CuCl.[96]

Matveev and coworkers suggested that heteropolyacids (HPA) be used as new reversibly acting oxidants, suitable for employment in palladium(II)-catalysed liquid-phase oxidations of olefins[97,98], oxidative coupling of aromatic compounds[99,100], etc. It has been established[99] that many molybdenum and tungsten HPA, which have a sufficiently high potential for the oxidation of zero-valent palladium to palladium(II), can be used for this purpose, including HPA with phosphorus, silicon, arsenic, boron, etc. heteroatoms. However, the most effective compounds of this series are those in which molybdenum or tungsten are partially substituted by vanadium, for example, compounds of the type $H_{3+n}PMo_{12-n}V_nO_{40}$ (henceforth designated by HPA-n, $n = 1-8$). Vanadium-containing HPA-n have the properties of reversibly acting oxidants and therefore permit the use of molecular oxygen as the oxidant in coupling reactions. The corresponding process may be represented by Eqns. (17)–(19), in which H_2(HPA) is the reduced form of HPA:[99,100]

$$2RH + Pd(II) \rightarrow R{-}R + Pd + 2H^+ , \quad (17)$$

$$Pd + HPA + 2H^+ \rightarrow Pd(II) + H_2(HPA) , \quad (18)$$

$$\frac{H_2(HPA) + 1/2O_2 \rightarrow HPA + H_2O}{2RH + 1/2O_2 \rightarrow R{-}R + H_2O} , \quad (19)$$

It is noteworthy that reaction (19) in organic solvents proceeds faster than the corresponding reaction of copper(I) owing to the higher solubility of H_2(HPA) compared with CuCl.

HPA are of great interest as components of catalysts for oxidative coupling and other partial oxidation reactions. This is due to the comparatively simple methods for their synthesis, ready solubility in both aqueous and organic solvents, and the possibility of varying over a wide range their compositions and hence their oxidation-reduction properties. The latter possibility is at the present time just beginning to be investigated. It is very significant that, in contrast to copper salts, HPA are capable of oxidising palladium in the absence of chloride ions. This makes it possible to achieve a much higher activity of palladium(II) and to eliminate the side reaction involving the chlorination of aromatic compounds, which takes place in the presence of chloride ions. There are reviews[101,102] and a special monograph[103] on the methods of synthesis and properties of HPA. The oxidation-reduction properties of HPA have not as yet been widely discussed in connection with their employment in catalysis. Matveev and coworkers investigated the spectra[104], thermodynamics[105], and kinetics[106] of oxidation-reduction reactions of the HPA-n. However, a detailed discussion of these studies is outside the framework of the present review.

The yields of the products of the oxidative coupling of benzene derivatives under the influence of oxygen, catalysed by the Pd(II)/HPA-2 oxidation-reduction system, have been widely studied[99,100]. The reaction proceeds in aqueous acetic acid under an O_2 pressure of 1.5 atm. The yield of biaryls relative to absorbed O_2 in the coupling of benzene, toluene, o-xylene, and durene (characterised by the selectivity of the reaction) reaches 70–93%.[99] The yield calculated relative to palladium(II) exceeds 4400% in a single catalytic cycle. The catalytic coupling of aromatic compounds in the presence of HPA-2 as well as the corresponding stoichiometric reaction have the characteristic features of electrophilic substitution in the aromatic ring. The alkylbenzene activity series benzene < toluene and o-xylene > durene, determined by the polar and steric influences of the substituents, are consistent with the results of earlier studies on the stoichiometric

reaction, Neither HPA-2 nor oxygen affect the composition of the coupling products. As in the stoichiometric reaction, mercury(II) has a marked influence on the proportions of the biaryl isomers. For monosubstituted benzenes, the addition of mercury(II) increases the yield of the 4,4′- and 3,4′-isomers. Thus in the coupling of toluene the yield of 4,4′-bitolyl increases from 22 to 41% with increase of the concentration of $Hg(OAc)_2$ from zero to 0.1 M. In the coupling of *o*-xylene the yield of the 3,4,3′,4′-isomer increases in the presence of mercury(II). It is interesting that the replacement of acetic acid as a solvent by sulpholane has a similar effect on the proportions of the isomeric biaryls[99].

The kinetic data obtained for the coupling of benzene derivatives in the presence of HPA-2 [100] are also consistent with the interpretation of this reaction as electrophilic aromatic substitution: electropositive substituents [OCH_3, $N(CH_3)_2$, OC_6H_5, alkyl] accelerate the reaction, while electronegative substituents (Cl, COOH, CF_3) inhibit it. The influence of chain length (toluene–ethylbenzene > isopropylbenzene > propylbenzene) and of the number of substituents (*o*-xylene > 1,2,4-trimethylbenzene > mesitylene > durene) on the reaction rate corresponds to the usually observed steric influence in electrophilic substitution reactions involving the aromatic ring. The rate of coupling increases after the addition of mercury(II) and reaches saturation at an $Hg(OAc)_2$ concentration of 0.1 M. The orders of the reaction with respect to O_2 and HPA-2 are close to unity, while the order with respect to palladium(II) is less than unity (more precisely 0.4–0.6). These data show that the rate-limiting stage of the oxidative coupling of aromatic compounds under the influence of oxygen, catalysed by Pd(II)/HPA-2, is reaction (19), involving the oxidation of H_2(HPA) to HPA by oxygen[100].

It is very significant that coupling in the presence of HPA proceeds under very mild conditions: at 50–90°C and an O_2 pressure of 1.5 atm. This is an advantage of this process over the palladium(II)-catalysed oxidative coupling in the absence of a reversible oxidant, which takes place at an oxygen partial pressure of about 25 atm.

III. COUPLING UNDER THE INFLUENCE OF OTHER METALS

Apart from palladium(II) compounds, the compounds of many other metals, usually in high oxidation states, may be used for the coupling of aromatic systems. The preparative importance of the coupling reaction involving compounds of these metals is small. Depending on the nature of the metal and the oxidation state, which determines its oxidising properties, coupling may occur via two mechanisms: by electrophilic substitution in the aromatic ring, like the majority of the reactions in the presence of palladium(II), or via electron transfer from RH to the oxidant with formation of a radical-cation. The mechanism of oxidative coupling depends also on the nature of RH, the acidity of the medium, and other factors. The ability of the oxidant to form aryl derivatives is an essential but not sufficient condition for the reaction via the electrophilic substitution mechanism. An increase of the oxidation potential of the oxidant and of the acidity of the medium as well as a decrease of the ionisation potential of RH favour the reaction via the electron transfer mechanism with formation of a radical-cation.

1. COUPLING VIA THE ELECTROPHILIC SUBSTITUTION MECHANISM

The mechanism of these reactions has been little studied, so that only preliminary conclusions may be reached. More complete information is available about coupling under the influence of platinum(II) and platinum(IV): these reactions are very similar to coupling under the influence of palladium(II). Platinum(II) acetate interacts with benzene in an excess of the latter and with benzeneboronic acid in HOAc to form biphenyl[27]. Toluene reacts with $Pt(OAc)_2$ in acetic acid in the presence of $HClO_4$ to form phenyltolylmethane[27]. Chloroplatinic acid is active in the coupling of furan to bifuryl[45] and also readily induces the coupling of toluene in acetic acid in the presence of $Hg(OAc)_2$ and $HClO_4$ to form mainly 4,4′-bitolyl[35]. The degree of reduction of platinum(IV) depends on the $HClO_4$ concentration. In a weakly acid medium platinum(IV) is reduced to platinum(II), while in a strongly acid medium it is reduced to zero-valent platinum[35]. In the last case two moles of biaryl are formed per mole of platinum(IV). It is suggested[35] that the addition of $HClO_4$ increases the electrophilic acitivity of platinum(II) [$PtCl_2$ (Ed. of Translation)] owing to the formation of $Pt(ClO_4)_2$ [which may be more dissociated (Ed. of Translation)]. The coupling of benzene under the influence of H_2PtCl_6 proceeds with a low selectivity in relation to biphenyl in water and aqueous acetic acid[107]; the main product is chlorobenzene. Platinum(IV) is reduced under these conditions to platinum(II) and the reaction proceeds autocatalytically, since platinum(II) catalyses the coupling reaction with participation of platinum(IV).[107] A mechanism has been proposed for the coupling of benzene with the intermediate formation of σ-phenylplatinum(II).[107] The occurrence of aromatic coupling in the presence of platinum(II) via the electrophilic substitution mechanism is also indicated by the well known ability of platinum(II) to catalyse the H–D exchange involving aromatic compounds[107].

Very little is known about coupling under the influence of compounds of other noble metals and data on the mechanisms of these reactions are altogether lacking. Gold(III) sulphate causes slow coupling of benzene in aqueous sulphuric acid, while treatment of toluene with Au_2O_3 in acetic acid in the presence of $HClO_4$ results in the formation of bitolyl[27]. When benzene is coupled under the influence of gold(III) in D_2O, the deuteration is not observed, as in the case of palladium(II)[27]. Ruthenium(IV) and ruthenium(III) compounds are relatively ineffective in the coupling of benzene[30] and furan[45].

As already mentioned, copper, silver, iron, cobalt, nickel, ruthenium, rhodium, iridium, osmium, and platinum as well as palladium(II) compounds interact with Grignard reagents to form coupling products[64]. Recently biaryls were obtained in a high yield from a Grignard reagent under the influence of thallium(I)[108]. The course of the reaction may be represented by the equations

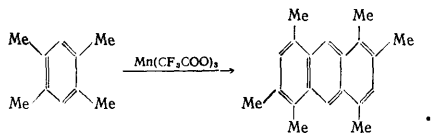
$$RMgBr + TlBr \rightarrow RTl + MgBr_2 ,$$
$$2RTl \rightarrow R{-}R + 2Tl .$$

However, the formation of a small amount of arylthallium(III) derivatives and aryl bromides indicates a more complex reaction mechanism.

2. COUPLING VIA THE ELECTRON TRANSFER MECHANISM

This class of reactions includes primarily coupling under the influence of strong one-electron oxidants in strongly acid media. These reactions have been studied in detail and their radical mechanism has been demonstrated quite reliably in many instances.

Cobalt(III), manganese(III), and cerium(IV) trifluoroacetates oxidise aromatic hydrocarbons RH in trifluoroacetic acid at room temperature with formation of a mixture of biaryls, diarylmethanes, and aryl trifluoroacetates[109,110]. The composition of the products depends on the nature of RH and the [RH]:[Me] ratio. For the ratio [RH]:[Co(III)] = 0.5, benzene gives a quantitative yield of phenyl trifluoroacetate[109]; in the presence of an excess of benzene, biphenyl was found among the products. However, its yield is insignificant, because biphenyl itself is oxidised by cobalt(III) much faster than benzene[109]. Benzene reacts similarly with cerium(IV)[111]. Toluene and *p*-xylene give rise to benzyl trifluoroacetates, diarylmethanes, and higher oligomers; anisole yields mainly 4,4′-dimethoxybiphenyl (30%). The oxidation of mesitylene results in the preferential formation of bimesityl together with diarylmethane. Durene yields diarylmethane and only traces of a biaryl. When durene was treated with cobalt(III) or manganese(II) trifluoroacetates, hexamethylanthracene was obtained in addition to biarylmethane[110]:



Under these conditions, naphthalene gives a low yield of 1,1′-binaphthyl[110]. The reactions of cobalt(III), manganese(III) and cerium(IV) with aromatic hydrocarbons exhibit considerable qualitative similarities despite certain quantitative differences between the reactivities and product ratios[110].

The heterogeneous oxidation of polymethylbenzenes by iron(III) chloride in non-polar media takes place similarly to oxidation by cobalt, manganese, and cerium compounds[112,113]. In this case chloro-derivatives of the aromatic compounds and polymers are formed together with biaryls and diarylmethanes. Alkylbenzenes react similarly with $SbCl_5$.[114]

It is of interest that the reactions of aromatic perfluorocarbonium ions in $SbCl_5$ solution also lead to coupling products—perfluoropolyaryls. For example, perfluoro-1,3,5-triphenylbenzene was obtained by the reaction between perfluorohexadiene and pentafluorobenzene (80%)[115].

The reactions of aromatic compounds with strong oxidants exhibit a low selectivity in relation to coupling and give many products, as a result of which they are not usually of synthetic value. However, certain reactions can be of preparative importance. For example, the coupling of naphthalene with mesitylene in the presence of $FeCl_3$ makes it possible to isolate 1-(2,4,6-trimethylphenyl)naphthalene in 35% yield[113].

It can be regarded as established that the reactions of aromatic compounds with strong one-electron oxidants proceed via a radical mechanism involving a slow stage in which an electron is transferred from RH to the oxidant[109–113]. This is indicated by the following data. The reactivity of RH increases in the sequence benzene < toluene < *p*-xylene < mesitylene < durene. The ionisation potential of RH diminishes in the same sequence. The above reactions are fully analogous to the electrochemical oxidation of RH, which takes place via electron transfer. The oxidation of benzene and toluene by cobalt(III) trifluoroacetate is of first order with respect to RH and cobalt(III) and there is no kinetic isotope effect. Finally aromatic radical-cations were detected directly by EPR in the reaction of RH and cobalt(III)[109,116]. The reaction mechanism may be represented by the following equations[109–113]:

$$Me^{n+} + RH \rightleftarrows [RH,\ Me^{n+}] \rightleftarrows [RH^{\cdot+},\ Me^{(n-1)+}] \rightarrow RH^{\cdot+} + Me^{(n-1)+},$$

$$RH^{\cdot+} + RH \rightarrow [HR{-}RH]^{\cdot+} \xrightarrow[-e,\ 2H^+]{Me^{n+}} \text{biaryl},$$

$$RH^{\cdot+} \xrightarrow{-H^+} R^{\cdot} \xrightarrow[-e]{Me^{n+}} R^+,$$

$$R^+ + RH \rightarrow [R{-}RH]^+ \xrightarrow{-H^+} \text{diarylmethane},$$

$$R^+ + CF_3COOH \rightarrow ROOCCF_3 + H^+ .$$

Electron transfer takes place in the molecular complex [RH.Me^{n+}], the decomposition of which yields the $RH^{\cdot+}$ radical-cation, Subsequently $RH^{\cdot+}$ may attack the RH molecule with formation of the coupling products or it may lose a proton and an electron under the influence of the base and Me^{n+} may be converted into the carbonium ion R^+. The latter gives rise to substitution and arylmethylation products.

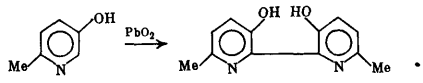
Depending on the conditions, the two-electron oxidants thallium(III) and lead(IV) may react with aromatic compounds via electrophilic substitution in the aromatic ring or via a radical mechanism involving electron transfer[110].

Benzene and toluene are coupled to biaryls under the influence of thallium(III) in aqueous $HClO_4$ and in acetic acid, the reaction being slow and having a low yield[117,118]. The addition of palladium(II) increases sharply the yield of biaryls as a result of the substitution of thallium(III) by palladium(II) in aryl derivatives of thallium(III)[117]. It is well known that thallium(III) usually reacts with aromatic compounds via the electrophilic substitution mechanism[119]. Numerous arylthallium derivatives have been isolated and characterised satisfactorily. However, Elson and Kochi reported[75] that they succeeded in detecting by EPR the durene and 4,4′-bitolyl radical-cations under the conditions of the substitution of thallium in durene and toluene by thallium(III) trifluoroacetate. This demonstrated the possibility of reactions of thallium(III) via a radical mechanism involving electron transfer from RH to thallium(III).

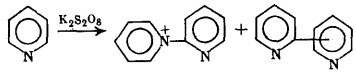
Lead(IV) readily oxidises aromatic compounds to biaryls, diarylmethanes, and aryl ethers with formation of aryllead(IV) derivatives as side products[120,121]; the composition of the product depends on the reaction conditions. In trichloroacetic acid lead(IV) gives products resulting from the metallation of RH, for example *p*-methoxyphenyl-lead(IV) was obtained from anisole in 50% yield[120]. Under more severe conditions (in trifluoroacetic acid), the reaction of lead(IV) with methylbenzenes proceeds via a radical mechanism[121], similar to that of the reactions with one-electron oxidants examined above. These data for thallium(III) and lead(IV) show that even the well-established ability of the metal ion to form aryl derivatives may prove to be an inadequate criterion for the selection of the reaction mechanism. One must also take into account the acidity of the medium and the nature of the ligands and the substrate. In this connection, Nyberg and Wistrand suggested[110] that in media more acid than trifluoroacetic acid reactions with aromatic compounds via electron transfer are not ruled out even in the case of mercury(II).

The coupling reactions of heterocyclic compounds of the pyridine series can be carried out under the influence of strong radical oxidants. Substituted 3-pyridinols react

with PbO_2 in benzene solutions to give 2,2'-bipyridyl derivatives, which are remarkable because of their fluoroescence in the visible region under the influence of ultraviolet radiation[122]:



Pyridine is oxidised by potassium persulphate in aqueous solution with formation of the pyridylpyridinium cation and a mixture of bipyridyl isomers[123]:



The ratio of the reaction products depends on the pH of the medium; in acid media the pyridylpyridinium cation is formed preferentially (90%), while in alkaline media the product is 40% of bipyridyl. The addition of silver(I) in an alkaline medium increases the yield of bipyridyl. The radical mechanism of this reaction has been reliably established by detecting the pyridinium radical-cation using EPR.

The oxidative coupling of aromatic systems has a fairly broad universality. The coupling takes place in series of aromatic, heterocyclic, and organoelemental compounds in the presence of a large range of oxidants. Naturally, with such wide variation of the conditions, the reaction mechanism does not remain the same. Having arranged the oxidants effecting the coupling reaction in order of decreasing oxidation potentials, it is possible to observe quite clearly a continuous change in this series from the radical coupling mechanism (via electron transfer with intermediate formation of an aromatic radical-cation) to electrophilic substitution in the aromatic ring and participation of an organometallic intermediate. The selectivity of the conversion of the substrate into the coupling products increases in the same sequence. Oxidative coupling under the influence of palladium(II) salts and complexes is the most important reaction among those in the above class. This is associated with its high selectivity and the possibility of its being catalytic. The latter is a decisive advantage of palladium(II) over other oxidants.

The synthetic possibilities of the reactions are fairly extensive for a wide range of aromatic systems. Among these, the coupling of benzene and its derivatives has been studied in greatest detail. The coupling of benzene to form biphenyl has no significant advantages over the non-catalytic vapour-phase pyrolysis of benzene. However, the coupling of benzene derivatives is really promising as an effective method for the preparation of the corresponding polyfunctional biphenyl derivatives, which are of interest as monomers for polycondensation[124], the synthesis of plasticisers, etc. Oxidative coupling of heterocyclic compounds, where this reaction makes it possible to obtain readily biheteroaryls whose synthesis by other methods is extremely difficult, is extremely promising. The useful properties of biheteroaryls have as yet been inadequately elucidated owing to the difficulty of their synthesis.

The most complex problem, constituting an obstacle to the practical utilisation of catalytic oxidative coupling, is the separation of the catalyst from involatile coupling products. This is a specific disadvantage of homogeneous catalytic processes. The development of metal-complex catalysts deposited on the surface of a solid carrier can probably become the most promising trend in the solution of this problem.

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