79. I. D. Sokolova and N. K. Voskresenskaya, Zhur. Fiz. Khim., 36, 955 (1962) [Russ. J. Phys. Chem., 502 (1962)].
80. N. K. Voskresenskaya, I. D. Sokolova, and E. L. Krivovyazov, in Collected Papers, "Fizicheskaya Khimiya Rasplavlennykh Solei i Shlakov" (Physical Chemistry of Molten Salts and Slags), Metallurgizdat, Moscow, 1962, p. 152.
81. M. A. Reshetnikov, Izv. Sektora Fiz.-Khim. Anal., Inst. Obshch. Neorg. Khim. Akad. Nauk SSSR, 19, 174 (1949).
82. I. D. Sokolova, E. L. Krivovyazov, and N. K. Voskresenskaya, Zhur. Neorg. Khim., 8, 2625 (1963) [Russ. J. Inorg. Chem., 1375 (1963)].
83. I. D. Sokolova, E. L. Krivovyazov, and N. K. Voskresenskaya, Zhur. Neorg. Khim., 11, 898 (1966) [Russ. J. Inorg. Chem., 484 (1966)].
84. I. D. Sokolova, Zhur. Neorg. Khim., 11, 933 (1966) [Russ. J. Inorg. Chem., 502 (1966)].
85. B. F. Markov and Yu. K. Delimarskii, Ukrain. Khim. Zhur., 19, 255 (1953).
86. E. L. Krivovyazov, N. K. Voskresenskaya, and I. D. Sokolova, in Collected Papers, "Poverkhnostnye Yavleniya v Rasplavakh i Voznikayushchikh iz Nikh Tverdykh Fazakh" (Surface Phenomena in Melts and Solid Phases Formed from Them), Kabardino-Kalkarskoe Knizhnoe Izd., Nal'chik, 1965, p. 479.
87. E. L. Krivovyazov, I. D. Sokolova, and N. K. Voskresenskaya, Zhur. Prikl. Khim., 34, 2542 (1963).
88. Wu Ting-fen, A. F. Vishkarev, and V. I. Yavoiskii, Izv. Vys. Ucheb. Zaved., Chern. Met., 3, 40 (1963).
89. S. B. Yakobashvili and I. I. Frumin, Avtomat. Svarka, 103, (10), 14 (1960).
90. S. B. Yakobashvili and I. I. Frumin, Avtomat. Svarka, 115, (10), 41 (1962).
91. Yu. P. Nikitin, V. G. Korpachev, and A. N. Safronnikov, Dokl. Akad. Nauk SSSR, 148, 160 (1963).
92. G. K. Moiseev and G. K. Stepanov, Trudy Inst. Elektrokhim. Akad. Nauk SSSR, Ural'sk. Fil., 5, 61, 69 (1964).
93. B. B. Owens and S. W. Mayer, J. Amer. Ceram. Soc., 47, 347 (1964).
94. A. N. Campbell and D. F. Williams, Canad. J. Chem., 42, 1772 (1964).
95. G. Bertozzi and G. Sternheim, J. Phys. Chem., 68, 2908 (1964).
96. G. W. Mellors and S. Senderoff, J. Electrochem. Soc., 111, 1355 (1964).
97. "Spravochnik Khimika" (Chemist's Handbook), Gostekhizdat, Moscow–Leningrad, 1951, Vol. II.
98. P. Rebinder, Z. phys. Chem., 121, 103 (1926).
99. R. E. Boni and G. Derge, J. Metals, 8, 53 (1956).
100. N. A. Trifonov, Izv. Sektora Fiz.-Khim. Anal., Inst. Obshch. Neorg. Khim. Akad. Nauk SSSR, 12, 103 (1940).
101. B. Ya. Teitel'baum, Izv. Kazansk. Fil. Akad. Nauk SSSR, Ser. Khim. Nauk, No. 2, 99 (1955).
102. O. A. Esin, in Collected Papers, "Stroenie Veshchestva i Spektroskopiya" (The Structure of Matter and Spectroscopy), Izd. Akad. Nauk SSSR, 1960, p. 111.
103. V. N. Eremenko, V. I. Nizhenko, N. I. Levi, and B. V. Bogatyrenko, Ukrain. Khim. Zhur., 28, 500 (1962).
104. N. K. Voskresenskaya, N. N. Evseeva, S. I. Berul', and I. P. Vereshchetina (Compilers), "Spravochnik po Plavkosti Sistem iz Bezvodnykh Neorganicheskikh Solei" (Handbook on Fusion in Systems of Anhydrous Inorganic Salts), Izd. Akad. Nauk SSSR, Moscow–Leningrad, 1961, Vols. I and II.
105. M. F. Lantratov and A. F. Alabyshev, Zhur. Prikl. Khim., 26, 275 (1953).
106. A. G. Bergman and N. S. Dombrovskaya, Zhur. Russ. Fiz.-Khim. Obshch., 61, 1451 (1929).
107. N. K. Voskresenskaya, Zhur. Neorg. Khim., 8, 1190 (1963) [Russ. J. Inorg. Chem., 616 (1963)].
108. F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, and I. Jaffe, "Selected Values of Chemical Thermodynamic Properties", U. S. Nat. Bur. Stand., Circ. 500, U. S. Govt. Printing Office, Washington, 1952.

Kurnakov Institute of General and Inorganic Chemistry, Moscow

U. D. C. 547.314.21 : 541.64 : 547.52./59

THE CYCLISATION OF ALKYNES AND THEIR DERIVATIVES

V. O. Reikhsfel'd and K. L. Makovetskii

CONTENTS

I. Introduction 510
II. Catalytic cyclotrimerisation of alkynes 511
1. Cyclotrimerisation in the presence of catalysts based on nickel carbonyls 511
2. Cyclotrimerisation in the presence of carbonyls of other metals 512
3. Cyclotrimerisation under the influence of organometallic catalysts 513
4. Cyclotrimerisation under the influence of complex organometallic catalysts 514
5. Cyclotrimerisation in the presence of other catalysts 515
III. Syntheses of non-benzenoid cyclic structures 516
IV. Mechanism of cyclisation of alkynes 517

I. INTRODUCTION

In recent years the polymerisation of alkynes has been attracting increasing attention with the discovery of new aspects of this diverse process. Up to recently, the polymerisation of acetylene yielded only oligomers of linear structure (vinylacetylene, divinylacetylene, etc.), or high-molecular products of the cuprene type. Instances of the cyclisation of acetylene with the formation of aromatic compounds, particularly benzene, were known, but the methods of synthesis were imperfect and the mechanism of synthesis was not clear. A review of the state of the problem may be found in the monograph of Newland and Vogt[1].

The cyclisation of acetylene and its derivatives was presented in a new light after Reppe's discovery of active catalysts that permit the selective preparation of the corresponding cyclic oligomers under mild conditions[2]. Later, numerous papers appeared in which catalysts suitable for the most diverse examples were recommended. Control of the course of the reactions and high yields made cyclisation a process of practical interest. It was

shown that a virtually unlimited variety of benzene derivatives could be synthesised, the preparation of which was extremely complicated by other methods. This applies, for example, to trivinylbenzene, substituted styrene, substituted divinylbenzene and similar products.

The theoretical significance of these reactions should also be considered; this is important because it makes possible the investigation of fine details of the mechanism of action of the complex catalysts that are used for the cyclisation of alkynes. It is well known that similar catalysts are widely used for the polymerisation of alkenes and alkadienes (ethylene, propene, buta-1,3-diene, isoprene) in the preparation of synthetic rubbers and plastics. However, a study of the mechanism of action of catalysts is difficult because of the complexity of the processes of formation of macromolecules of enormous molecular weight and with a fairly wide molecular-weight distribution. This complication is completely eliminated in the cyclisation of alkynes, in which individual low-molecular products are formed.

The monograph and review literature contains very little information on the cyclisation of alkynes, notwithstanding the obvious interest in the subject. In fact, that is only one review on the subject, that of Nagihara in the Japanese language, which is not accessible to a wide circle of chemists[3]. The present review is intended to fill this gap.

Berthelot was the first to describe the cyclisation of acetylene; he obtained benzene, naphthalene and other aromatic compounds by heating acetylene above 600°[4]. Later, Mayer and coworkers[5] obtained 60% conversion by passing acetylene with hydrogen through an electric furnace at 800°; benzene, naphthalene, anthracene, biphenyl, pyrene, and a number of other compounds were separated from the resinous product obtained. Zelinskii[6] obtained aromatic hydrocarbons in high yield by passing acetylene over activated carbon at 600–650°.

Newland and Vogt give a review of papers on the high-temperature cyclisation of acetylene[1]. In recent years, interest in this process has decreased, because of the discovery of catalytic methods of cyclisation at moderate temperatures. However, occasionally papers appear on the non-catalytic cyclisation of acetylene itself and its derivatives. Thus, Rupprecht[7] reports the preparation of hexadeuteriobenzene in 20% yield from deuterioacetylene at 700°. Harris and coworkers[8] obtained hexakistrifluoromethylbenzene from perfluorobut-2-yne at 260° and 1000 atm. Shantorovich and coworkers studied the thermal polymerisation of phenyl- and cyclohexyl-acetylenes and obtained the corresponding benzene derivatives[9].

Recently, a report appeared on the spontaneous cyclic oligomerisation of t-butylfluoroacetylene, which proceeds even at low temperatures[10]; the main product of this reaction is 1,2,3-tri-t-butyltrifluorobenzene.

As a rule, the high-temperature cyclisation of acetylene and its derivatives cannot be used for the purposeful synthesis of definite compounds; many different products, including high-molecular products, are obtained at the same time. These disadvantages are largely avoided when the reaction is carried out in the presence of catalysts. Cyclisation may lead to cyclic trimers, which are derivatives of benzene, or to non-benzenoid cyclic polymers (cyclobutadiene, cyclo-octatetraene, etc.). These two synthetic routes will be considered separately.

II. CATALYTIC CYCLOTRIMERISATION OF ALKYNES

1. Cyclotrimerisation in the Presence of Catalysts Based on Nickel Carbonyls

$[Ni(CO)_2[PPh_3)_2]$, formed by the reaction of $Ni(CO)_4$ with an alcoholic solution of $P(C_6H_5)_3$, which was proposed by Reppe, was one of the first catalysts for the preparation of benzene derivatives from acetylene[11]; when suspended in benzene, acetonitrile, or tetrahydrofuran, it cyclises acetylene to benzene (88%) and styrene (12%). The trimers of prop-2-yn-1-ol, 1,3,5- and 1,2,4-tri(hydroxymethyl)benzene, were obtained in quantitative yield with the same catalyst in boiling benzene. It is interesting that the ratio of the isomers in the reaction products was 1 : 1 instead of 3 : 1, as would be expected with mutual orientation of the alcohol molecules according to the laws of statistics.

Reppe did not succeed in preparing the cyclic trimer of butynediol, which he explained by the absence of unsubstituted acetylene hydrogen from this compound. However, somewhat later Kleinschmidt obtained hexa(hydroxymethyl)benzene on the same catalyst[12].

It was shown in subsequent papers that other alkynes and their derivatives can be cyclotrimerised in the presence of nickel-carbonylphosphine catalyst. Thus, Rose and Statham[13] carried out the cyclic trimerisation of phenylacetylene and phenylethynylmethanol to give 1,2,4-triphenylbenzene and 1,3,5-tri-(α-hydroxybenzyl)benzene respectively. They also attempted to obtain benzene derivatives from 3-methylbuty-1-yn-3-ol, *NN*-diethyl-1--methylprop-2-ynylamine, benzoylacetylene and phenylpropiolic acid, but they did not succeed in obtaining trimers.

The preparation of tri-(1-hydroxyethyl-1-methyl)benzene, triisopropylbenzene[15], and 1,2,4-trivinylbenzene on the same catalyst is described in a number of patents (cited by Meriwether and coworkers[14]). Simultaneous cyclotrimerisation of acetylene and divinylacetylene gave *o*-divinylbenzene[16], and *o*-xylene was obtained in the same way from acetylene and but-2-yne[17]. It is interesting that in a number of instances the use of the catalyst $[Ni(CO)_2.(PPh_3)_2]$ may lead to the formation of linear polymers.

Using 35 different mono- and di-substituted acetylenes, Meriwether and coworkers[14] studied reactions in the presence of $[Ni(CO)_2(PPh_3)_2]$. The catalyst (0.4 mole % of the monomer) and the alkyne compound were dissolved in a suitable solvent (benzene, cyclohexane, ethanol) and boiled under reflux for 24 hours. As a rule, the reaction yielded a mixture of isomers of benzene derivatives, and linear polymers of the general formulae

$$R{-}C{\equiv}C{-}[CR{=}CH]_n{-}CH{=}CHR,$$

and

$$R{-}C{\equiv}C{-}[CR{=}CH]_n{-}CR{=}CH_2,$$

where $n = 0$–10. The preferential formation of cyclic or linear products is mainly determined by the nature of the substituent at the triple bond. Thus, for monosubstituted alkynes, the yield of aromatic products fell from 65% for propyne to 5% and lower for hept-1-yne, although the total conversion remained almost unchanged. The ratio of 1,2,4-isomers to 1,3,5-isomers varied in the homologous series without showing definite tendencies. It was found that steric factors have a great effect on the reactions. Cyclohexylacetylene formed only a linear dimer, and t-butylacetylene did not react at all.

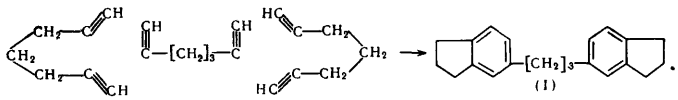
Meriwether did not succeed in polymerising more disubstituted acetylenes, conjugated diacetylenes, and also

monosubstituted acetylenes, containing t-butyl, carboxyl, amide, or nitrile groups, or halogen.

When the structures of two alkynes did not differ greatly, it was found possible to carry out simultaneous cyclotrimerisation, in particular with a mixture of hept--1-yne and pent-1-yne, or with pent-1-yne and phenylacetylene. A mixture of benzene (43%), *o*-xylene (50%), styrene, and 1,2,3,4-tetramethylbenzene was obtained by the simultaneous cyclopolymerisation of acetylene and but-2-yne.

The following qualitative order of reactivity was established for the cyclotrimerisation on $[Ni(CO)_2(PPh_3)_2]$ of alkyne ethers, esters and ketones: vinylacetylenes > > arylacetylenes > acetylene alcohols > higher alkynes > > lower alkynes, acetylene ≫ acetylenic acids.

More active monomers generally form aromatic products, and the less active more linear polymers. The cyclotrimerisation of unconjugated diacetylenes on the same catalyst is very interesting, mixed aliphatic-aromatic structures being formed[18]. Thus hepta-1,6-diyne forms, in addition to a highly unsubstituted linear polymer, an aromatic trimer, 1,3-di-(5-indanyl)-propane (I):



(I)

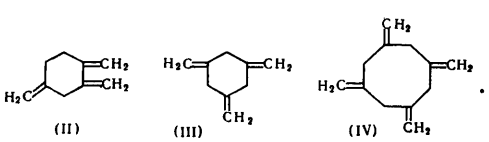
In the polymerisation of alkynes with modified catalysts, it was shown that monocarbonyltriphosphine and tetraphosphine complexes of nickel do not catalyse the cyclic polymerisation of alkynes[19]. When the phenyl group linked to phosphorus is replaced by other groups, the catalyst activity is significantly changed in the following order:

$$C_2H_4CN > C_6H_5 > H > OC_2H_5 > \text{n-alkyl} \gg OC_6H_5 \text{ and Cl.}$$

Experiments in which $Ni(CO)_4$ was used did not lead to the formation of trimers. All these results indicate the important part played by the phosphine ligands in the catalyst complex. Replacement of groups linked with phosphorus affects not only the catalyst activity but also the direction of the reaction. Thus, $[Ni(CO)_2\{P(OC_6H_5)_3\}_2]$ favours aromatisation of phenylacetylene, but $[Ni(CO)_2 \cdot \{P(C_2H_4CN)_3\}_2]$ favours linear polymerisation.

Attempts made by Meriwether and coworkers to obtain kinetic information on the cyclotrimerisation of alkynes on carbonylphosphinenickel catalysts were not successful[19]. This reaction is very rapid and has a high heat effect.

It is interesting to note that the cyclisation of allenes may be carried out on the same carbonylphosphinenickel catalysts. Benson and Lindsey[20] obtained the allene trimers (II) and (III) and the tetramer (IV) by heating allene at 105–110° in tetrahydrofuran in the presence of $[Ni(CO)_2\{P(OC_6H_5)_3\}_2]$ for 5–6 hours:



(II) (III) (IV)

The simultaneous cyclisation of allene and alkynes, which they also carried out, gave a mixture of isomeric dimethylenecyclohexenes.

Schrauzer showed that when acetylene reacts with acrylonitriles in the presence of $Ni(CO)_3(PPh_3)$, there is a considerable induction period[21]. This indicates that the true reaction catalyst is not $Ni(CO)_3(PPh_3)$. Actually, it has been shown that the reaction is more complicated:

$$Ni(CO)_3PPh_3 + 2CH_2{=}CH{-}CN \longrightarrow Ni(CH_2{=}CH{-}CN)_2 \cdot PPh_3 + 3CO.$$

In the presence of acetylene, complexes of nickel with acrylonitrile and acetylene are formed:

$$Ni(CH_2{=}CH{-}CN)_2(C_2H_2)_2 \quad \text{or} \quad Ni(CH_2{=}CH{-}CN)(C_2H_2)_2 \cdot PPh_3.$$

Similar nickel complexes were obtained with acrolein and fumaronitrile, etc.[22]

Under certain conditions the complex of $Ni(CH_2{=}CHCN)_2$ with alkyne derivatives forms aromatic nitriles (tetraphenylbenzonitrile with tolan) on decomposition, but with an excess of symmetrical alkyne hexasubstituted derivatives of benzene are formed. With acetylene itself in tetrahydrofuran under pressure, this complex gives cyclooctatetraene and benzene. However, the yields are low, which indicates the non-catalytic nature of this synthesis. The introduction of triphenylphosphine into the complex sharply increases the yields of benzene (cyclo-octatetraene is not formed at all), and the process acquires a catalytic character[22].

2. Cyclotrimerisation in the Presence of Carbonyls of Other Metals

The carbonyls of a number of transition metals and their complexes with alkynes form another large group of active catalysts for the cyclic trimerisation of alkynes. In recent years, great successes have been achieved in the chemistry of (metal carbonyl)–alkyne complexes. This subject, which is of interest in itself, has been considered in detail in a recent review by Bennett[23]. Here it should be mentioned that in many of these complexes the component alkynes form cyclic aromatic structures.

Reppe established that when acetylene reacts under pressure with the hydrogen derivative of iron carbonyl, $Fe(CO)_4H_2$, a complex if formed, decomposition of which yields hydroquinone[24]. Later, Sternberg and coworkers reported the synthesis of an $Fe(CO)_3$–duroquinone complex from pentacarbonyliron and dimethylacetylene[25]. Hübel and coworkers prepared a large number of complexes of acetylene and its derivatives with the carbonyls of iron, manganese, tungsten, and cobalt[26]. These compounds are stable, and they may be regarded as π-complexes, constructed from an organic system and one or more metal-carbonyl groups. When the complex contains more than one alkyne molecule, a ring system with conjugated double bonds (frequently with one or two carbonyl groups in the ring) is formed within the complex. In no instance could the unchanged alkyne be recovered from the complex. Decomposition of such complexes as $[Fe(CO)_4 \cdot (Ph.C \vdots C.Ph)_2]$ or $[Fe_2(CO)_7 \cdot (Ph.C \vdots C.Ph)_2]$ and $[Fe(CO)_4 \cdot (HC \vdots CPh)_3]$ or $[Fe_2(CO)_6 \cdot (HC \vdots CPh)_3]$ gives the corresponding tetraphenylcyclopentadienone and 1,3,5-trimethylbenzene.

In subsequent papers by Hübel, it is shown that mono- and di-substituted acetylenes are converted in high yield into benzene derivatives in the presence of small quantities of some metal-carbonyl compounds[27]. The yield of trimer largely depends on the nature of the metal carbonyl. Table 1 gives information on the cyclic trimerisation of tolan with various metal-carbonyl catalysts(without solvent).

TABLE 1. Cyclic trimerisation of tolan without a solvent with various catalysts[27].

Carbonyl compound	Temperature, °C	Yield of trimer
$Fe_3(CO)_{12}$	260—280	75
$Fe_2(CO)_9$	250	25
$Fe(CO)_5$	270	20
$Fe_2(CO)_6\cdot(PhC{\equiv}CPh)_2$	270	60
$[Co(CO)_4]_2Hg$	270	70
$Co_2(CO)_8$	280	60
$Co_2(CO)_6\cdot(PhC{\equiv}CPh)_2$	150	70
$Ni(CO)_4$	260	5
$Mn_2(CO)_{10}$	270	55
$Mo(CO)_6$	270	50
$W(CO)_6$	270	15

It is more convenient to carry out the reaction in a solvent; the best cyclotrimerisation catalyst are then $Co_2(CO)_8$, $[Co(CO)_4]_2Hg$, $Co_2(CO)_6RC_2R'$ or $Co_4(CO)_{10}\cdot RC_2R'$, and dioxan is the best solvent. Table 2 gives information on the cyclotrimerisation of various alkynes with these catalysts.

Unsymmetrical alkynes are cyclised exclusively to 1,2,4-trisubstituted benzenes. Prop-2-yn-1-ol is readily cyclotrimerised by Reppe's catalyst, but all attempts to carry out the reaction in the presence of cobalt-carbonyl catalysts have been unsuccessful, as have been attempts to cyclotrimerise propargyl benzoate, propargyl acetate, and benzylacetylene. Hübel also carried out the simultaneous cyclotrimerisation of various alkynes — tolan with *pp'*-dichlorodiphenylacetylene or with phenylacetylene, and phenylacetylene with acetylene. The relative reactivity of alkynes in a given reaction can be determined by carrying out the simultaneous trimerisation of equimolecular quantities of the alkynes. When the reactivities are identical, all four possible products are obtained in the statistical ratio 1 : 3 : 3 : 1 (for example, in the simultaneous trimerisation of tolan with *pp'*-dichlorodiphenylacetylene).

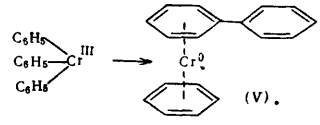
Cyclotrimerisation of alkynes in the presence of cobalt carbonyls was found to be a convenient method for the preparation of benzene derivatives containing bulky substituents. A derivative of benzene with an *ortho*-tertiary group — 1,2,4-tri-t-butylbenzene — was first obtained in this way[28]. The presence of adjacent t-butyl groups distorts the benzene ring; this is indicated by spectroscopic and thermochemical data[29]. Distortion of the benzene ring has also been noted in 1,2,4,5-tetra-t-butylbenzene, which was obtained later by a similar method[30]. It is interesting that the trimethylsilyl group does not produce this effect[29]. Cyclisation of di-isopropylacetylene in the presence of catalytic quantities of $Co_2(CO)_8$ gave hexaisopropylbenzene[31], in the molecule of which rotation of the isopropyl groups is hindered almost completely for steric reasons.

TABLE 2. Cyclic trimerisation of various alkynes with cobalt-carbonyl compounds.

Alkyne compound	Catalyst	Trimer	Temperature, °C	Yield, %
$C_6H_5C{\equiv}CH$	$[Co(CO)_4]_2Hg$	1,2,4-triphenylbenzene	101	70
$BrC_6H_4C{\equiv}CH$	»	1,2,4-tri-(*p*-bromophenyl)-benzene	101	65
$(CH_3)_3SiC{\equiv}CH$	$Co_2(CO)_6\cdot(CH_3)_3SiC_2H$	1,2,4-tris(trimethylsilyl)-benzene	90—100	55
$HOCH_2CH_2C{\equiv}CH$	$Co_2(CO)_6\cdot HOC_2H_4C_2H$	1,2,4-tri(hydroxyethyl)benzene	101	14
$CH_3OCH_2C{\equiv}CH$	$Co_2(CO)_6\cdot CH_3OCH_2C_2H$	1,2,4-tri(methoxymethyl)-benzene	101	17
$C_3H_7C{\equiv}CH$	$[Co(CO)_4]_2Hg$	1,2,4-tri-n-propylbenzene	101	11
$C_6H_5C{\equiv}CC_6H_5$	»	hexaphenylbenzene	101	90
$ClC_6H_4C{\equiv}CC_6H_4Cl$	»	hexa-(*p*-chlorophenyl)benzene	101	95
$CH_3OCOC{\equiv}CCOOCH_3$	»	hexa(methoxycarbonyl)-benzene	200	25
$C_2H_5C{\equiv}CC_2H_5$	»	hexaethylbenzene	101	75
$C_6H_5C{\equiv}CCOOH$	$Co_2(CO)_6\cdot C_6H_5C_2CO_2H$	3,5,6-triphenylbenzene-1,2,4-tricarboxylic acid	101	11
$C_6H_5C{\equiv}CCOOCH_3$	$[Co(CO)_4]_2Hg$	trimethyl 3,5,6-triphenyl-benzene-1,2,4-tricarboxylate	101	55
$C_6H_5C{\equiv}CCl$	»	1,2,4-trichloro-3,5,6-triphenyl-benzene	101	14
$C_6H_5C{\equiv}CCH_3$	»	1,2,4-trimethyl-3,5,6-triphenyl-benzene	101	90

3. Cyclotrimerisation under the Influence of Organometallic Catalysts

It was established comparatively recently that organochromium compounds obtained over 30 years ago by Hein[32] are active catalysts for the cyclisation of alkynes. Zeiss and coworkers showed that in tetrahydrofuran solution triphenylchromium forms an octahedral coordination complex with three molecules of tetrahydrofuran[33]. This complex is stable in the absence of oxygen and moisture. Removal of the tetrahydrofuran leads to the rapid conversion of the triphenylchromium into a bisarylchromium(0) complex(V):



(V).

The tetrahydrofuran ligands may be easily displaced by alkyne molecules, which undergo cyclisation with the formation of benzene and polynuclear aromatic derivatives[34]. Intermediate alkyne complexes of triphenylchromium have not been isolated. Organochromium compounds are very sensitive to the action of acid acetylene hydrogen, and monosubstituted acetylenes destroy the catalyst; for this reason, it can only be used for the cyclisation of disubstituted acetylenes.

The direction of the reaction depends on the stoichiometric ratio of alkyne to the catalyst and on the nature of the organic groups linked with chromium. Thus, in the cyclisation of but-2-yne in the presence of triphenylchromium, hexamethylbenzene or 1,2,3,4-tetramethylnaphthalene may be obtained as the main products, depending on the $(C_6H_5)_3Cr$: but-2-yne ratio; some bis(hexamethylbenzene)chromium(0) is also formed.

Table 3 shows that with all catalyst : monomer ratios the reaction products contain a naphthalene derivative. Bis(hexamethylbenzene)chromium(0) is only formed when there is a large excess of but-2-yne; it is similar in structure to ferrocene, is fairly stable, and does not catalyse the cyclic trimerisation of alkynes. If triethylchromium, or a triarylchromium with *ortho*-substituted

TABLE 3. Effect of the ratio of but-2-yne to catalyst on the yields of trimers[34].

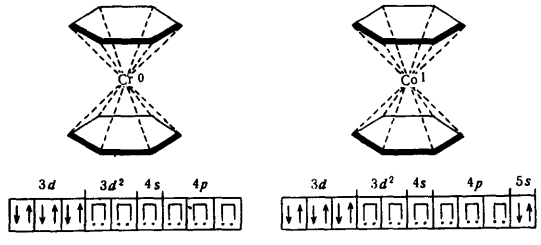
Molar ratio of $(C_6H_5)_3Cr$ to but-2-yne	1 : 1	1 : 2	1 : 3	1 : 5	1 : 20
Beginning of exothermic reaction, min	330	280	90	50	15
Yield of hexamethylbenzene, %	—	—	—	25	55
Yield of tetramethylnaphthalene, %	13	31	40	36	38

aryl groups (for example, trimesitylchromium), is used as catalyst instead of triphenylchromium, a benzene derivative is the sole reaction product.

The general character of this reaction was demonstrated by the formation of hexaphenylbenzene and 1,2,3,4-tetraphenylnaphthalene from tolan in the presence of triphenylchromium[34], and also by the formation of hexaphenylbenzene and 1,2,3,4-tetramethylphenanthrene from but-2-yne and tri-α-naphthylchromium.

Unlike chromium compounds, diphenylnickel does not react with alkynes to form naphthalene derivatives, but with tolan diethylnickel forms hexaphenylbenzene and 1,2,3,4-tetraphenylcyclohexa-1,3-diene, the latter being formed by the inclusion of the ethyl group of the catalyst in the ring[35,36].

The action of alkyl and aryl compounds of other transition metals, such as dimesityliron[37] or diphenylmanganese[38], also cyclises disubstituted acetylenes. In some respects diphenylcobalt(II) occupies a special position. Bis(hexamethylbenzene)cobalt(I), which is obtained by the reaction with but-2-yne, differs from the bisarene chromium derivatives by the presence of two electrons in excess of the complete krypton shell of the cobalt atom in this compound.



The capacity of cobalt to catalyse the reaction well outside stoichiometric proportions may be due to this special feature[38] (Table 4); in contrast, with the organochromium compounds, cyclisation occurs when the metal and the alkyne are present in stoichiometric proportions.

4. Cyclotrimerisation under the Influence of Complex Organometallic Catalysts

Ziegler's complex organometallic catalysts, which have been widely used in the polymerisation of alkenes and alkadienes, also polymerise alkynes. The polymerisation of acetylene and its homologues with the formation of linear high-molecular products was first carried out by Natta and coworkers[39]. Later, the results of more detailed study of the polymerisation of acetylene[40,41] and hexa-1-yne[42] were published. Because of the interesting properties of high-molecular alkyne polymers, a number of workers carried out the polymerisation of various alkynes in the presence of Ziegler-type[43-46] and other catalysts. Natta obtained the best results with catalysts of the type $AlR_3 + Ti(OR)_4$. Later, Hagihara and coworkers showed that with the catalytic system $Cr(t\text{-}OC_4H_9)_3 + Zn(C_2H_5)_2$ (ratio of components 1 : 3) monosubstituted acetylenes give linear dimers (vinylacetylene derivatives) in almost quantitative yield[47]. Replacement of diethylzinc by triethylaluminium led to the formation of alkylbenzenes. This shows how sensitive the alkyne polymerisation is to modifications in the catalytic system.

In 1959, Franzus and coworkers[48] first showed that cyclic trimers of disubstituted acetylenes (hexasubstituted benzenes) could be obtained with the aid of the catalytic system $Al(iso\text{-}C_4H_9)_3 + TiCl_4$; with an Al/Ti ratio within the range 1 : 1 to 3 : 1, dimethyl-, diethyl, and diphenyl-acetylene were quantitatively cyclotrimerised.

These workers note that none of the catalyst components alone catalyses cyclotrimerisation†. It was also shown that when $TiCl_4$ is replaced by $TiCl_3$ the catalytic system becomes inactive in this reaction.

Cyclic trimers of disubstituted acetylenes were also obtained by Wilke in presence of the $CrO_2Cl_2 + Al(C_2H_5)_3$ system[50]. Recently, Drefahl and coworkers made a very detailed study of the cyclotrimerisation of diphenylacetylene with Ziegler catalyst[51].

Although it was thought that monosubstituted acetylenes containing "acid" acetylene hydrogen would destroy the Ziegler catalyst, it was found that they also undergo the cyclotrimerisation reaction, forming 1,2,4- and 1,3,5-trisubstituted benzenes. A patent by Smith describes the use of a catalyst based on an organometallic compound of a non-transition metal and a transition metal halide[52]. A mixture of mesitylene (40%) and pseudocumene (60%) was obtained by the polymerisation of methylacetylene passed through a catalyst solution consisting of $Al(C_2H_5)_3$ and $TiCl_4$ in methylcyclohexane. The total yield of trimers exceeded 60%.

Lutz cyclotrimerised a number of mono- and di-substituted acetylenes in the presence of the $Al(C_2H_5)_3 + TiCl_4$ system (Table 5)[53]. He considers the use of large volumes of solvent to be the main condition for a successful synthesis. Reikhsfel'd and coworkers established that extensive dilution is not necessary, if the $Al(iso\text{-}C_4H_9)_3 + TiCl_4$ system is used as a catalyst[54]. 1,3,5-tri-n-butylbenzene was obtained from hex-1-yne, and 1,3,5-triphenylbenzene from phenylacetylene, in yields exceeding 90%. When this catalytic system is

TABLE 4. Cyclic polymerisation of but-2-yne on dimesitylcobalt[38].

But-2-yne, moles	6	8	10	20	40
$CoCl_2$, moles	1	1	1	1	1
Yield of hexamethylbenzene, % on Co	50	153	200	480	1000
Yield of π-complex, % on Co	20	20	20	20	20

TABLE 5. Cyclotrimerisation of alkynes in the presence of $Al(C_2H_5)_3 + TiCl_4$.[58]

Starting alkynes	Reaction temperature, °C	Trimers obtained	Yield, %	
			trimers	polymer
Acetylene	23—29	benzene	49.1	24.1
Methylacetylene	22—36	mesitylene	40.4	9.3
		pseudocumene	21.1	
Ethylacetylene	23—30	1,3,5-triethylbenzene	35.5	7.3
		1,2,4-triethylbenzene	17.0	
n-Butylacetylene	24—32	1,3,5-tributylbenzene	59.8	—
Dimethylacetylene	23—34	hexamethylbenzene	80.2	2.2
Diethylacetylene	24—32	hexaethylbenzene	76.5	—
Dibutylacetylene	86	hexabutylbenzene	52.2	4.6

† Under drastic conditions (pressure, temperature above 140°), Wilke obtained hexasubstituted benzenes from tolan and diethylacetylene by the action of di-isobutylaluminium hydride.

used, a change in the monomer : solvent ratio from 1 : 1 to 1 : 10 (1 : 20 according to Lutz) has no effect on the yield of trimer[55]. Replacement of $TiCl_4$ by $TiCl_3$ leads to the formation of extremely unsaturated polymers (rubber-like in the case of hex-1-yne), apparently of linear structure. Later, these workers carried out the simultaneous polymerisation of hex-1-yne and phenylacetylene[56]. With a 1 : 1 molar ratio of monomers all four possible trimers were obtained in amounts close to the statistical ratio (1 : 3 : 3 : 1). This distribution of products indicates that both alkynes have the same reactivity in the cyclotrimerisation.

A study of the effect of catalyst composition on the course of cyclotrimerisation showed that replacement of the transition metal halide in the $Al(iso\text{-}C_4H_9)_3 + TiCl_4$ system by an alkoxy-compound leads to a reduction in catalytic activity[57]; the use of tetraethoxytitanium completely deactivates the catalyst. Replacement of the alkyl group attached to aluminium by a chlorine atom has virtually no efect on the yield of cyclotrimerisation product.

Acetylenes with various substituents have been cyclotrimerised in the presence of a catalyst based on $Al(iso\text{-}C_4H_9)_3 + TiCl_4$; a number of alkynes have also been simultaneously cyclotrimerised with this catalyst[58] (Table 6).

Table 6 shows that propargyl bromide or 5-ethynyl-2-methylpyridine could not be cyclotrimerised; propargyl bromide attacks the catalyst. The direct cyclisation of t-butylacetylene was first carried out with the same catalyst, symmetrical as well as unsymmetrical isomers of tri-t-butylbenzene being obtained[59].

Hoover and coworkers used the $Al(iso\text{-}C_4H_9) + TiCl_4$ system for the cyclotrimerisation of vinylacetylene[60,61], and for the cotrimerisation of divinylacetylene and acetylene[61,62]. At -10°C vinylacetylene gave 1,2,4-trivinylbenzene in about 50% yield; when the temperature was raised to 30–50°, the yield decreased to 10%. Simultaneous cyclotrimerisation of divinylacetylene and acetylene gave *o*-divinylbenzene in 30% yield; when acetylene was replaced by methylacetylene, a mixture of trimethylbenzene isomers and dimethyl-*o*-divinylbenzene was formed. Trivinylbenzene is of interest as a cross-linking agent and as a monomer for the preparation of thermostable plastics used in rocket technology[63].

Donda and coworkers, who studied the cyclic trimerisation of phenylacetylene in the presence of $Al(C_2H_5)_3 + TiCl_4$, obtained 1,3,5- and 1,2,4-triphenylbenzene and a linear polymer[64]. The relative yields of cyclic and linear product depend mainly on the Al/Ti ratio. If this ratio was less than 4, linear polyphenylacetylene was not formed; the highest yield (75%) of aromatic compounds was obtained with an Al/Ti ratio of 2 to 4; the ratio of isomers is virtually independent of the Al/Ti ratio (60% 1,2,4-isomer and 40% 1,3,5-isomer). With higher Al/Ti ratios (4–7), the yield of benzenes fell sharply, and linear polymer was obtained as the main product. These workers point out that the solvent has an appreciable effect on the course of the reaction. The results given above refer to reactions in benzene; in heptane, with an Al/Ti ratio of unity, only oily linear polymers were obtained.

TABLE 6. Cyclotrimerisation of alkynes in the presence of $Al(iso\text{-}C_4H_9)_3 + TiCl_4$.[58]

Starting alkynes	Temperature, °C	Yield of products, %	
		cyclic	linear
Methylacetylene	20—40	60	traces
n-Butylacetylene	20—40	90	»
n-Octylacetylene	20—40	90	»
Phenylacetylene	20—40	90	»
Vinylacetylene*	0—10	37	10
Propargyl bromide	20	0	0
Furylacetylene	20—40	17.2	4.8
2-Methyl-5-ethynylpyridine	60	0	0
Triethylsilylacetylene	20—40	—	44
n-Butylacetylene + phenylacetylene	20—40	82.5	traces
n-Butylacetylene + triethylsilylacetylene	20—40	77	»
n-Butylacetylene + furylacetylene	20—40	28.5	2

* Catalyst $Al(iso\text{-}C_4H_9)_2Cl + TiCl_4$.

These workers also studied the cotrimerisation in the presence of $Al(C_2H_5)_3 + TiCl_4$ of acetylene and methylacetylene[65], and of acetylene with phenylacetylene and tolan[66]. As with pure phenylacetylene, the preferential formation of linear or cyclic polymers is determined by the Al/Ti ratio; the highest yields of aromatic trimers were obtained with an Al/Ti ratio of 3–4.

Dale used trimethylaluminium with $TiCl_4$ as a catalyst in the synthesis of 1,3,5-tris(trimethylsilyl)benzene from trimethylsilylacetylene[29]. The reaction was carried out at 60°, and a certain amount of the 1,2,4-isomer was obtained in addition to the 1,3,5-isomer.

Kambara and coworkers[67] studied the polymerisation of acetylene in the presence of various modifications of Ziegler catalyst; they noted that when one of the components of the catalytic system is a halogen derivative of a transition metal, a considerable quantity of benzene is formed with an increased degree of conversion of acetylene. Thus, with 43% acetylene conversion in the presence of $Al(C_2H_5)_3 + TiCl_4$ at 0°, 76% of the acetylene that reacts is converted into benzene. In all instances a linear polyacetylene is formed in addition to benzene; if a tetra-alkoxytitanium or a tetra-alkoxychromium is a conponent of the catalyst, the sole reaction product is a linear polyacetylene. Replacement of the titanium halide by VCl_4, $VOCl_3$, or VCl_3 leads to the exclusive formation of benzene, Starik and coworkers obtaining benzene from acetylene in up to 72% yield[68].

Recently, the results of a detailed study of the cyclisation of isopropenylacetylene in the presence of various catalytic systems was published[69]. The highest yield of cyclic products (1,3,5- and 1,2,4-tri-isopropenylbenzenes) was obtained with the catalyst $Al(C_2H_5)_3 + TiCl_4$. A change in the nature of the transition metal in the catalyst was reflected both in the tendency to form cyclic trimers and in the ratios of the isomeric cyclisation products. The ratio of 1,3,5- to 1,2,4-isomers decreased with the transition from titanium to cobalt and increased slightly with the use of nickel compounds.

5. Cyclotrimerisation in the Presence of Other Catalysts

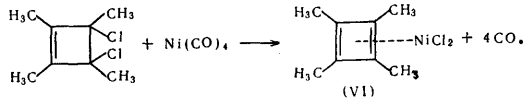
Other catalysts have also been proposed for the cyclic trimerisation of alkynes. Blomquist and Maitlis[70] found that in solvents containing no hydroxyl groups (benzene, acetone, chloroform) the complex bis(benzonitrile)palladium chloride catalyses the cyclotrimerisation of tolan in hexaphenylbenzene with a yield of 85%. The use of catalysts based on CrO_3 on aluminosilicate[71], and gel-like oxides (for example, $SiO_2 + Al_2O_3$) surface-treated with diborane[72], for the cyclisation of alkynes is described in the patent literature. Hexaphenylbenzene was obtained in

about 10% yield by the reaction of tolan with bromophenylmagnesium in a mixture of tetrahydrofuran and xylene[73]. Aromatic hydrocarbons were also obtained from acetylene derivatives by reaction of the latter with lead tetra-acetate in the dark[74].

Luttinger proposed an interesting catalytic system suitable for both the cyclisation and polymerisation of acetylenes[75]: this consists of a compound of a Group VIII metal and a hydride reducing agent; iron and metals not belonging to Group VIII are inactive. Alkali hydrides and silanes were used as reducing agents. The alkali tetrahydroborates and alkali tetrahydroaluminates were found to be the best agents. Hept-1-yne gives mainly linear polymers (dimers, trimers, and somewhat higher polymers), but other alkynes (phenylacetylene) also form aromatic products, such as 1,3,5- and 1,2,4-substituted benzenes[76]. The highest yield of benzene derivatives is obtained by the use of cobalt salts; the valence state of the metal (Co^{2+} or Co^{3+}) has no effect on the process. The usual catalyst for linear polymerisation is $NiCl_2 + NaBH_4$.

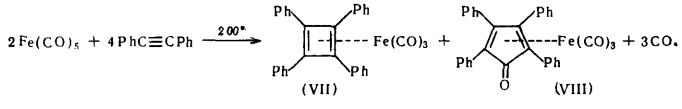
III. SYNTHESES OF NON-BENZENOID CYCLIC STRUCTURES

Under certain conditions, derivatives of cyclobutadiene, which is of great theoretical interest, may be obtained from alkynes. A compound containing the cyclobutadiene ring (VI) was first obtained by Schröder and Criegee according to the reaction[77]:



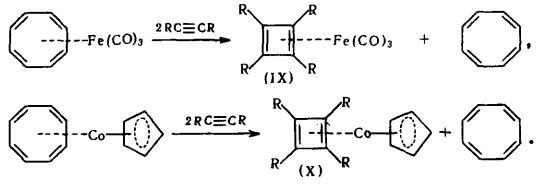
(VI)

Complex formation with compounds of a transition metal stabilises the cyclobutadiene ring. In recent years, complexes of cyclobutadiene derivatives with compounds of Fe, Co, Ag, and Pd have been obtained. Hübel and Braye[78] have reported on the reaction between $Fe(CO)_5$ and tolan, in which the tetraphenylcyclobutadiene complex (VII) is obtained in addition to other products[78]:



(VII) (VIII)

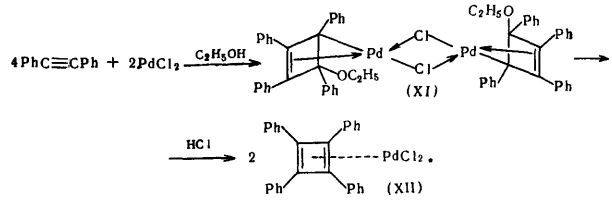
Dodge and Schomaker proved the structure of this complex from X-ray analysis[79]. Nakamura and Hagihara synthesised the same complex by the reaction of tricarbonylcyclo-octatetraeneiron with tolan[80]. Using an analogous reaction, they also synthesised the cobalt complex containing the cyclobutadiene ring (X):



(IX) (X)

Both these complexes are stable in air and they are very thermostable, being unchanged under nitrogen up to 360°; in this way they are to a certain degree reminiscent of ferrocene. Strong acids and alkalis have no action on them.

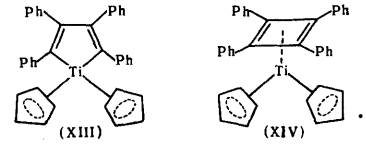
Malatesta and coworkers obtained a similar compound by the reaction of tolan with a solution of palladium(II) chloride in ethanol, with subsequent decomposition by hydrochloric acid[81]:



(XI) (XII)

Blomquist[70] confirmed Malatesta's results; by treating tolan with palladium(II) chloride in a mixture of ethanol and chloroform, he obtained the complex (XI) in 83% yield, and by passing gaseous hydrogen chloride through a solution of this in chloroform, he obtained the complex (XII) in 76% yield. The infrared and NMR spectra of the latter are very similar to the spectra of the complex of $NiBr_2$ with tetraphenylcyclobutadiene.

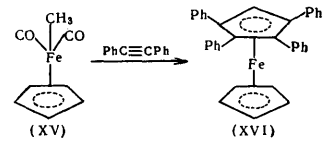
By the reaction of tolan with titanocene, Vol'pin and coworkers[82] obtained the compound π-$(C_5H_5)_2Ti(PhC{\equiv}CPh)_2$, to which structure (XIII) was assigned. Since the properties of the compound obtained are very reminiscent (stability of the pure compound and its benzene solutions, etc.) of the complexes of iron and cobalt with tetraphenylcyclobutadiene previously described, and since the electron configuration of the valence shell of the titanium atom in cyclobutadienebis(cyclopentadienyl)titanium (XIV) is similar to the inert gas configuration (like X), the compound obtained by Vol'pin and coworkers appears to have the structure (XIV):



(XIII) (XIV)

Five-membered rings may also be formed in the cyclisation of alkynes. In the cyclisation of disubstituted acetylenes in the presence of metal carbonyl catalysts, tetrasubstituted cyclopentadienones are often obtained in addition to benzene derivatives[26,31,78,83,84]. These are formed by the union of two molecules of acetylene with one of the carbonyl groups of the catalyst. As a rule, the cyclopentadiene ring formed remains in the metal carbonyl complex as an organic ligand.

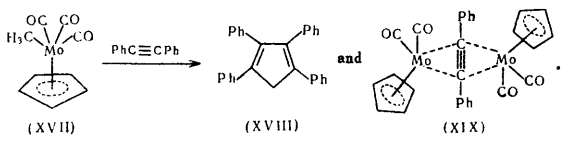
Nakamura observed an interesting reaction between carbonylcyclopentadienylalkyls of iron and molybdenum with alkynes[85]. Thus, toluene reacted with π-$C_5H_5FeCH_3$. $.(CO)_2$ (XV) to give tetraphenylferrocene (XVI):



(XV) (XVI)

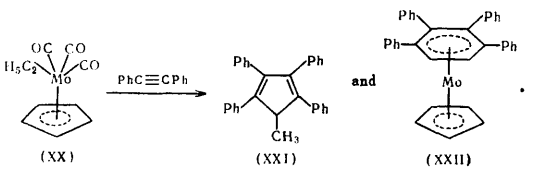
In this reaction the methyl group, which is initially linked to the iron atom, forms a cyclopentadienyl ring with two molecules of tolan. As would be expected, when tolan was replaced by acetylene, ferrocene was obtained. Ethyl and benzyl derivatives of iron carbonyl form benzene, and not ferrocene.

Cyclopentadienyl(methyl)tricarbonylmolybdenum (XVII) reacts with tolan to form tetraphenylpentadiene (XVIII) and the tolan complex (XIX), but the corresponding ethyl derivative (XX) reacts with tolan in a still more unusual manner:



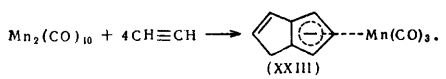
(XVII) (XVIII) (XIX)

In addition to other products, methyltetraphenylcyclopentadiene (XXI) and the "sandwich" compound cyclopentadienyl-(1,2,3,4-tetraphenylbenzene)molybdenum (XXII) are obtained, that is, in one reaction the ethyl group participates differently in the formation of a ring:



(XX) (XXI) (XXII)

Coffild and coworkers observed an unusual reaction[86]: when acetylene reacted with $Mn_2(CO)_{10}$ in tetrahydrofuran at 150° and 43 atm for 5 hours, a compound identified as tricarbonyl-π-dehydropentalenylmanganese (XXIII) was obtained:



(XXIII)

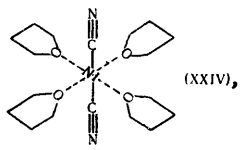
Rings containing eight and more carbon atoms may be obtained from acetylene and its derivatives. The work of Reppe[2] made an accessible one-stage synthesis of cyclo-octatetraene from acetylene possible, other cyclic higher polyalkenes being obtained at the same time in lesser quantities[2]. It is unnecessary to present well known information on the preparation of cyclo-octatetraene here; we shall merely point out that Reppe used compounds of bivalent nickel as catalysts. Later, Schrauzer showed that cyclo-octatetraene can be obtained in stoichiometric quantities by the reaction of acetylene with organic complexes of zerovalent nickel, and benzene is always obtained at the same time[22].

IV. MECHANISM OF CYCLISATION OF ALKYNES

It is generally considered that the formation of a benzene ring by the thermal cyclisation of acetylene proceeds by two successive bimolecular reactions through an intermediate stage in which vinylacetylene or its derivatives is formed[1].

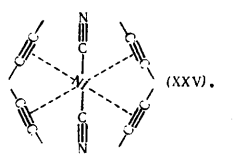
Reppe was the first to propose an explanation of the mechanism of formation of cyclo-octatetraene in the presence of catalysts[2]. According to his interpretation, the effective catalysts are unstable nickel–acetylene compounds obtained by the action of acetylene on the initial nickel compounds (for example, halides); the unstable nickel acetylide, or the metal itself, adds new molecules in such a way that 4 molecules of acetylene are arranged in coordination around the Ni^{2+} ion. This complex decomposes by way of a hypothetical intermediate biradical of four acetylene molecules to form cyclo-octatetraene and nickel compounds.

McKinley has discussed this problem in greater detail[87]. He suggests that the catalyst, for example, nickel cyanide, forms a coordination complex of type (XXIV) with tetrahydrofuran:



(XXIV),

in which four molecules of tetrahydrofuran lie in the same plane as the nickel atom, and the CN group is arranged perpendicular to this plane. Acetylene readily displaces tetrahydrofuran to give a new complex (XXV):

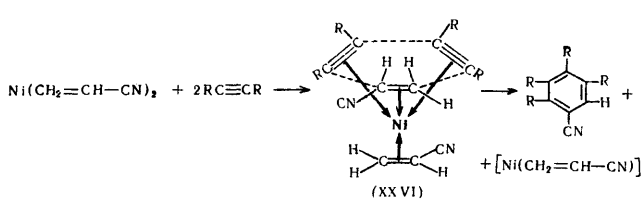


(XXV).

Since the carbon atoms of adjacent molecules are situated close to one another, it may be supposed that the electrons of the triple bond which make the bond with nickel are redistributed with the formation of simple covalent C–C bonds. The formation of octamethylcyclo-octatetraene from dimethylacetylene[87] proves that the acetylene hydrogen does not play a part in the reaction and that the metal is directly linked to the triple bond of the acetylenes. McKinley explains the exclusive capacity of nickel compounds to catalyse the synthesis of cyclo-octatetraene by favourable steric conditions for the formation of the acetylene complex, which is confirmed by the construction of Stuart–Briegleb models[87].

These ideas have been developed by Schrauzer from a more modern point of view[22,88,90]. He assumes that cyclisation reactions proceed inside metal–alkyne complexes by many-centred reactions. The first step must be considered the formation of π-complexes of the metal with the alkynes, in which a new compound is then formed on the basis of spatial proximity and geometrical arrangement. The structure of the reaction product would then be expected to depend on the structure of the π-complex transition state; this has been confirmed by experiments with bis(acrylonitrile)nickel(0)[22]. Such a complex could unite with two alkyne molecules. Since nickel here has zero valency, the complex retains the tetrahedral configuration. In the π-complex (XXVI), two molecules of alkyne are approximately coplanar with one nitrile molecule.

As would be expected, the final reaction product is benzonitrile. Under certain conditions one of the two nitrile molecules may also be displaced by an alkyne molecule with the formation of a benzene derivative.



(XXVI)

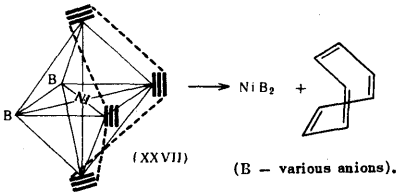
The addition of such an active electron donor as triphenylphosphine to bis(acrylonitrile)nickel(0) increases the

catalytic activity of the nickel compound in the acetylene cyclisation reaction by a factor of 100. Benzene is then the main product of the reaction.

Schrauzer and Eichler made a detailed study of the synthesis of cyclo-octatetraene on a typical catalyst, consisting of bivalent nickel with weak anion bonds, or — in the terms of modern coordination theory — with a weak ligand field[88]. They established a relationship between the structure of the complex and its magnetic properties on the one hand, and its activity in the cyclisation reaction on the other hand (Table 7).

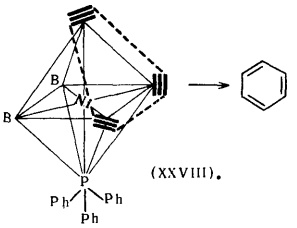
The relationship between the lability of the ligands and the catalyst activity was demonstrated in the synthesis of cyclo-octatetraene in the presence of bis(salicylaldiminato)nickel(II) and its *N*-alkyl derivatives; the methyl derivative, which is the most labile, was also found to be the most active.

Complexes with an octahedral configuration are active. The Ni^{II} ion "solvated" by acetylene molecules remains paramagnetic, because the ligand field strength (of acetylene) is insufficient for the pairing of spins of both split nickel electrons. The acetylene molecules will attempt to occupy a suitable octahedral configuration around the central field. Hence, Schrauzer and Eichler assume that the transition state in the formation of cyclo-octatetraene is a complex with four acetylene molecules with a steric arrangement suitable for the synthesis of cyclo-octatetraene (XXVII). Intermediate stages are not necessary for these molecules to form a ring:



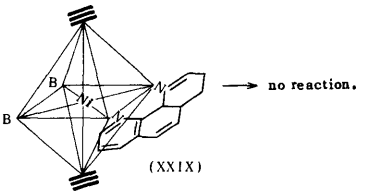
(XXVII) (B — various anions).

Experiments on the inhibition of cyclisation favour the hypothesis that cyclo-octatetraene is formed in labile acetylene complexes with an octahedral, or closely related, structure on the Ni^{II} ion[88]. Donor molecules with a strong ligand field were used as inhibitors. The addition of triphenylphosphine inhibits the formation of cyclo-octatetraene; the reaction proceeds with a tendency to form benzene, which is obviously related to blocking of one of the coordination positions in the complex (XXVIII) by a PPh_3 molecule:



(XXVIII).

The addition of compounds capable of blocking two coordination positions in the complex (*o*-phenanthroline) at once completely deactivates the catalyst:



(XXIX)

Schrauzer put forward the idea that a π-complex many-centre reaction occurs in this and similar instances. The rehybridisation of the acetylene carbon atoms from the sp- and sp^2-states, necessary for the formation of new C–C bonds, is obviously greatly facilitated by the formation of a π-complex with a transition-metal atom. The subsequent reaction of the rehybridised atom is, as a rule, not specific. Thus, with alkynes $Fe_2(CO)_{12}$ gives a large number of different organometallic complexes and organic compounds at the same time[26,27]. According to Schrauzer, nickel compounds, in contrast to compounds of other elements, can catalyse the formation of cyclo-octatetraene from acetylene, because of the difference in the energies of states in the interaction of the metal used and acetylene. In the active complexes the $3d$-terms for Ni^{II} lie in a region which favours the formation of labile compounds with acetylene molecules of just the required size. The Ni-ligand bond in these complexes shows a relatively high degree of covalency; the Ni^{II} ion carries only a weak positive charge, and therefore the energy of the $3d$-state approaches so closely to the energy of the π_g-orbitals of the acetylenes that weak dative bonds may even be formed. (In the more polar and catalytically inactive nickel halides, the energy difference between the corresponding orbitals is too great for any kind of interaction to occur between them). Analogous complexes of Co, Fe and other metals obviously do not satisfy this requirement.

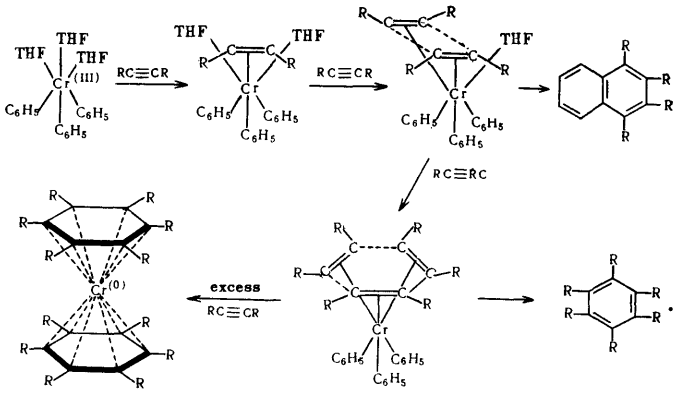
According to Schrauzer, the hypothesis previously proposed that cyclo-octatetraene results from dimerisation of cyclobutadiene, formed as an intermediate, is unsound[89]. It would be difficult to understand why catalytic quantities of cyclobutadiene produced in the presence of a large excess of acetylene would be selectively converted into cyclo-octatetraene and only give benzene in the presence of triphenylphosphine. Moreover, in its electronic structure cyclobutadiene belongs to the class of strong π-bonded ligands. The nickel complex of cyclobutadiene would therefore be more stable kinetically than the initial complex. The rate of conversion of such a complex into cyclo-octatetraene would then be the determining factor, which is not in agreement with the experimental results[90].

However, the idea of the formation of cyclobutadiene as an intermediate permits the interpretation of results on

TABLE 7. Classification of catalysts for the synthesis of cyclo-octatetraene.

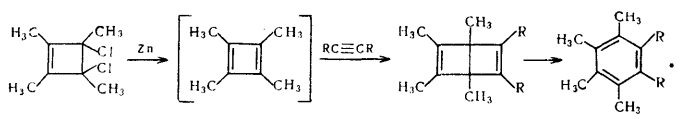
	Weak ligand field	Intermediate range	Strong ligand field
Configuration	octahedral	octahedral and planar	planar
Magnetic behaviour	paramagnetic	anomalously magnetic	diamagnetic
Exchange of ligands	rapid	moderately rapid	very slow
Catalytic activity	active	active	inactive
Examples	bis(salicylaldehydato)nickel bis(acetylacetonato)-nickel	nickel cyanide bis-(*N*-alkylsalicyl-aldiminato)nickel	nickel phthalocyanine bis(dimethylglyoximato)nickel

the cyclisation of alkynes in the presence of the alkyl- and aryl-metal catalysts of Zeiss[34]. The proposed mechanism is represented by the following scheme:



It is assumed that the alkyne molecules progressively displace the tetrahydrofuran ligands, the octahedral configuration of the complex being retained. The phenyl groups linked to chromium may take part in the reaction with an entering alkyne molecule. Although intermediate complexes with one, two, or three alkyne molecules have not been separated, under certain conditions products of the reaction of an acetylene molecule with one or two phenyl groups of triphenylchromium have been obtained; these are derivatives of styrene or stilbene[91]. But generally the displacement of tetrahydrofuran molecules goes further. As has already been mentioned, the products of the reaction of alkynes with triphenylchromium always contain naphthalene derivatives. According to Zeiss, this indicates the formation of an extremely reactive intermediate, tetra-alkylcyclobutadiene, in the chromium coordination sphere. The chromium atom in the complex can catalyse the elimination of hydrogen in the *ortho*-position of a phenyl group linked to it; dehydrobenzene is then obtained, which reacts with the tetra-alkylcyclobutadiene by an unusual intramolecular Diels–Alder reaction with the formation of tetra-alkylnaphthalene. When the reaction mixture contains sufficient alkyne, the tetra-alkylcyclobutadiene complex of triphenylchromium either loses the last molecule of tetrahydrofuran, which is replaced by alkyne, or it gives a hexa-alkylbenzene by an intermolecular Diels–Alder reaction. With a large excess of alkyne, small quantities of a bis(arene) complex are obtained as the product of further replacement of groups initially linked with chromium. When the *ortho*-position of the phenyl groups is occupied, for example, in trimesitylchromium, naphthalene derivatives are not formed.

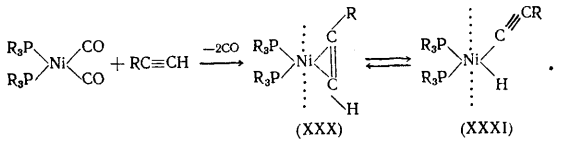
Results obtained by other workers also indicate that the cyclobutadiene ring may be formed in the cyclisation of alkynes. Berkoff and coworkers reduced 1,2,3,4-tetramethylcyclobutene in but-2-yne or dimethyl butynedioate and obtained hexamethylbenzene and dimethyl tetramethylphthalate respectively[92]. They suggest the following scheme for the reaction:



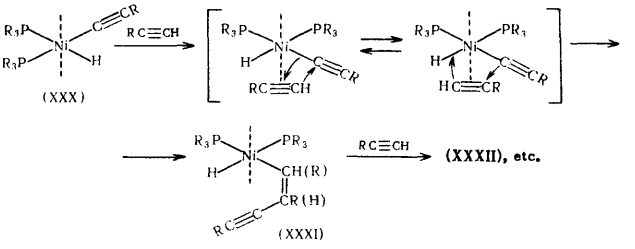
In the cyclisation of di-isopropylacetylene, Arnett and coworkers obtained, in addition to benzene and cyclopentadiene derivatives, products the formation of which is difficult to explain without the hypothesis that cyclobutadiene is produced as an intermediate[31].

Meriwether has put forward quite different interpretations on the mechanism of alkyne polymerisation and cyclisation with nickelphosphinecarbonyl catalysts[19]. Assuming the initial formation of a π-complex, he considers that the subsequent polymerisation or cyclisation steps occur with the participation of an organonickel compound having a metal–carbon σ-bond.

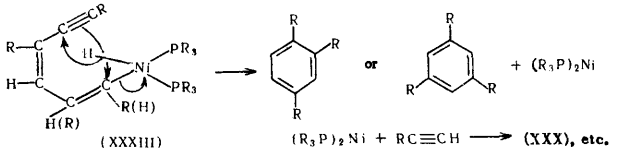
According to Meriwether, the Ni–phosphineacetylene complex obtained by replacement of carbonyl groups by acetylene molecules (XXX) is an "active" catalyst. The complex (XXX) is similar in structure to the biphosphine–Pt–acetylene complexes prepared by Chatt and coworkers[93]:



The complex (XXXI) is an active catalyst for both linear polymerisation and cyclisation. Both complexes are planar and the nickel in them has a formal valency of +2, that is, the nickel atom has a vacant p_z-orbital capable of forming π-bonds with a second acetylene molecule:

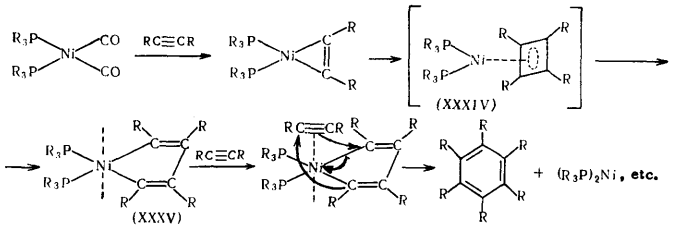


When the complex (XXXIII) has a favourable conformation, in which the first and sixth atoms of the carbon chain can approach within bonding distance, simultaneous hydrogen transfer and ring closure leads to the formation of the corresponding aromatic products:



This mechanism is not applicable to disubstituted acetylenes, since transfer of an acetylene hydrogen is its characteristic feature. Meriwether was therefore compelled to give another explanation of the polymerisation of disubstituted acetylenes. The initial type (XXX) complex formed reacts with a second acetylene molecule and, after the intermediate formation of diphosphinecyclobutadiene-nickel (XXXIV), gives a planar complex (XXXV); in this

planar complex, Ni^{2+} has a vacant *pz*-orbital and is capable of coordinating with a third acetylene molecule:

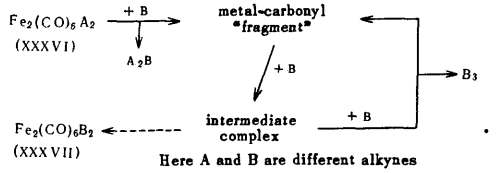


Meriwether points out that acetylene and monosubstituted acetylenes may be partly or completely polymerised by this mechanism. Meriwether's mechanism for the cyclisation of acetylenes is very artificial. This accepted scheme requires two different mechanisms for mono- and di-substituted acetylenes, which makes it doubtful.

The evidence presented in recent years that compounds of nickel with cyclobutadiene can add donor molecules (for example, the addition of triphenylphosphine or *o*-phenanthroline to tetramethylcyclobutadienenickel dichloride[94]) makes Meriwether's objection to the activation of a third acetylene molecule by the complex (XXXIV) unconvincing.

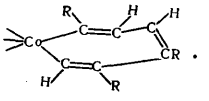
Nakamura has proposed a mechanism for the cyclisation of acetylenes which is somewhat similar to that given above; it also requires the formation of a heterocyclic compound with the metal in the ring[85].

Hübel considers that the catalytic action of metal carbonyls and their derivatives is explained by the formation of active "fragments"[27]. It is significant that the polynuclear compounds of iron and cobalt are the most active compounds. If the reaction with alkynes is carried out under conditions that exclude the formation of metal-carbonyl "fragments" (for example, with carbon monoxide under pressure), trimerisation does not occur. The following scheme is suggested:



Here A and B are different alkynes

The complex (XXXVI) reacts to only a slight degree with B, metal-carbonyl "fragments" being formed in addition to the trimer A_2B. These "fragments" react with B by way of an intermediate complex to form the trimer B_3 and new "fragments". The stable complex (XXXVII) is formed in a side-reaction. The proposed structure for the intermediate complex, for example, in the cyclotrimerisation of t-butylacetylene to 1,2,4-tri-t-butylbenzene[28], includes a non-planar seven-membered ring(bulky groups in *ortho*-positions cause bending of the plane of the ring):

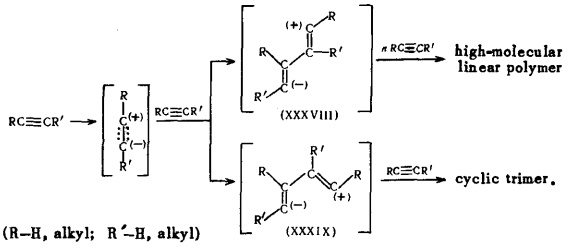


Because the ring is not planar, steric hindrance is eliminated. A benzene compound is not formed in the complex itself; this is proved by the formation of aliphatic oils when the complex is hydrogenated. The aromatic ring is closed only when the complex is decomposed (in this case, for example, by the action of bromine).

The existence of heterocyclic structures containing a metal in complexes of this kind has not been confirmed by results obtained later[95], according to which alkyne molecules in the complex can be replaced relatively easily by molecules of another alkyne present in solution. This exchange is much more probable for metal–alkyne π-complexes than for ring structures not containing triple bonds.

Ziegler's catalysts are amongst the most active in the cyclisation of alkynes. In one of the first papers in this field[53], Lutz attempted to explain the mechanism of the catalytic action of the $Al(C_2H_5)_3$–$TiCl_4$ system. Since a certain amount of linear polymers is usually obtained, according to Lutz the direction of the reaction depends on the suitability of the particular conformation of the intermediate complex. With disubstituted acetylenes, the confirmation that determines subsequent cyclisation is sterically favourable; with monosubstituted acetylenes, the probability of this route increases with the mass of the substituent.

According to Lutz, the polymerisation of alkynes is a surface-catalytic process, chain growth being effected through Al–C bonds formed by chemisorption of the alkynes on the catalyst.

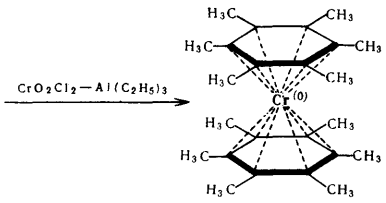


A polarised intermediate compound is formed on the catalyst, and this can react with adjacent polarised molecules by one mechanism or the other. The high selectivity shown in the cyclisation of disubstituted acetylenes indicates the importance of steric factors; steric hindrance interferes with the formation of the intermediate (XXXVIII). Even if it were formed, attack of the active end of the growing chain would be completely blocked by alkyl groups. Lutz has not solved the problem of the cyclisation of monosubstituted acetylenes. Lutz's scheme does not accomodate the catalytic system AlR_3–$TiCl_3$, which is known to have a solid surface; this, however, promotes linear polymerisation[54], that is, according to Lutz's scheme, a less probable reaction.

It is interesting to consider Wilke's point of view on the mechanism of butadiene cyclotrimerisation[96]. As is well known, when this reaction was carried out in the presence of Ziegler-type catalysts, cyclododeca-1,5,9-triene was obtained. According to Wilke, the process comprises three steps: (1) the formation of a π-complex of butadiene with a transition metal, (2) the formation of new C–C bonds of preoriented molecules with the production of a ring, and (3) separation of the cyclic trimer, or its displacement by new butadiene molecules.

This scheme has been confirmed by experiments on the cyclisation of but-2-yne with the catalytic system CrO_2Cl_2–$Al(C_2H_5)_3$, which, like $TiCl_4$–$Al(C_2H_5)Cl$, promotes the cyclotrimerisation of butadiene[96]. The "sandwich" compound bis(hexamethylbenzene)chromium(0), which is generally obtained in the presence of Zeiss arylchromium

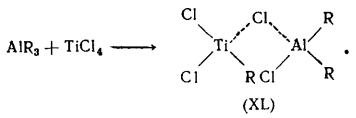
catalysts, was shown to be present in the reaction products.



This is further evidence that similar mechanisms must operate in the cyclisation of alkynes by different catalysts. Specificity in the activity of a given catalyst is determined by the nature of the metal and of the groups linked to it, and also by the reaction conditions. A general feature of all catalysts is the formation of a coordination-complex bond between the π-orbitals of the alkyne and the d-orbitals of the transition metal, together with redistribution of electrons and the formation of new C–C bonds. As Schrauzer has emphasised[88], the formation of new bonds is a non-specific reaction and nearly always occurs when an alkyne carbon atom can be brought within the sphere of action of a given transition-metal atom.

Ziegler's catalysts are no exception. On the basis of their own experiments and published results, the authors of the present review have put forward an interpretation of the mechanism of cyclotrimerisation on these catalysts[57]. Experimental results (identical course of the reaction in various solvents, identical reactivity in this reaction of acetylenes with substituents having an opposite effect on the electron density of the triple bond, etc.) suggest that the anionic mechanism usually postulated for polymerisation with Ziegler's catalysts is inapplicable. A coordination mechanism is more probable for the cyclotrimerisation of alkynes.

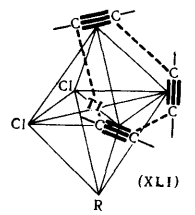
When the components of the catalytic system (for example, alkylaluminium and titanium halide) react, an active complex (XL) is formed:



(XL)

In this complex titanium is partly alkylated. The role of the alkylaluminium consists in the alkylation of titanium and the conferring of a formal charge on it. This is of great importance for the catalytic activity of the complex in cyclotrimerisation, since there is then a partial trans-hybridisation of the titanium valence electrons from the d^3s- to the sp^3-state[38]. According to the calculations of Pilcher and Skinner[97], trans-hybridisation promotes the formation of a simpler bond. It may be supposed that the main factor is the setting free in the $d^3s \rightarrow sp^3$ transition of the titanium d-orbitals, which may be used for interaction with the π-electrons of the triple bond.

The complex (XL) is highly polarised; in some papers even the possibility of the ionisation of such compounds has been considered[98-100]. It is very probable that under the reaction conditions the formation of the cyclic trimer is due to a "fragment" (an ion in the limiting case) $[TiRCl_2]$ which retains the tetrahedral configuration characteristic of both d^3s- and sp^3-hybridisation, but with one unoccupied apex. Since in the higher oxidation stages titanium has the coordination number six, the titanium atom can bind three molecules of acetylene in its coordination sphere:



(XLI)

The complex (XLI) assumes an octahedral, or close to octahedral, configuration, three molecules of acetylene being arranged approximately in the same plane. Such an arrangement facilitates the subsequent combination of the three acetylene molecules to form a ring. As Schrauzer points out[88], the transhybridisation of the alkyne carbon atoms from the sp- to the sp^2-state required for this is facilitated by the presence of a π-complex bond with the central metal atom. The benzene molecule formed in this way is very loosely bound to the remaining part of the complex and is easily displaced by new alkyne molecules. Cyclotrimerisation proceeds as a many-centred π-complex reaction (according to Schrauzer's classification). This is the most probable mechanism for the cyclisation of alkynes; however, the intermediate formation of a cyclobutadiene ring from two acetylene molecules in the coordination sphere of titanium is also possible. Because of experimental difficulties, information has not yet been obtained on the kinetics of cyclotrimerisation, which would provide a more definite answer to this question.

---o0o---

After the manuscript of this review has been submitted for publication, further reports on the cyclisation of alkynes appeared, the most interesting of which will be briefly presented here.

New catalysts for cyclotrimerisation proposed in a number of patents include: $TiCl_4$–$LiAl(C_7H_{15})_4$ and $VOCl_3$–$Al(C_3H_7)_3$[101], compounds of the bis(trialkylphosphite)nickel(0) type[102], $NbCl_5$ and $TaCl_5$[103]. Reports have been made on a detailed investigation of the cyclisation of isopropenylacetylene in the presence of Ziegler's catalyst[104], on the preparation of hexaisopropenylbenzene (a nonreactive trimer of diisopropenylacetylene)[105], the radiochemical cyclisation of methyl- and phenyl-acetylenes[106], the cyclotrimerisation of 2-methylbut-3-yn-2-ol[107], and on the synthesis in the presence of Ziegler's catalyst of [^{14}C]benzene and [$^2H_6$]benzene[108] and of trimethylbenzenes from methylacetylene for the purpose of radiocarbon analysis[109]. A number of trialkynylbenzenes were obtained by the cyclisation in the presence of cobalt carbonyls of conjugated alkadiynes in which hydrogen at the triple bond is replaced[110]. The reactions of alkadiynes and cycloalkadiynes in the presence of Ziegler's catalysts and cobalt carbonyls have been studied[111]. In nearly all instances cyclic trimers and dimers were obtained in addition to polymers. $CoCl_2$ and $(C_2H_5)_2Al$(butynyl) were observed to react in an unusual manner[112]; the reaction products included benzene, the presence of which can be explained by the elimination of but-1-yne followed by its cyclotrimerisation and dealkylation of the trimer.

Some reports deal with the preparation from alkynes of cyclobutadiene complexes of Pd[113,114], Mo, W, Co[115], and

of complexes of transition metals containing the cyclopentadienone[116] and the tropone[117] ring. When perfluorobut-2-yne reacted with π-$C_5H_5Rh(CO)_2$, π-cyclopentadienylhexakis(trifluoromethyl)benzenerhodium was obtained[118]; a study of the structure of this compound showed that only four atoms of the benzene ring are coordinated with rhodium, that is, the structure is not planar.

The addition of alkynes to cyclobutadiene derivatives[119] has been proposed as a method for the preparation of "Dewar" benzene[120]. It should be noted that great progress in the chemistry of valence isomers of benzene with non-classical Ladenburg and Dewar structures became possible when cyclic trimers of such compounds as t-butylacetylene and its derivatives had been prepared.

The observations of Schrauzer, which lead us to re-examine the mechanism of cyclisation, are of considerable interest[121]. In the reactions of alkynes in the presence of various compounds of Ni, Fe, Co, Mn and Pd, signals with a g-factor of ~2.0028 were obtained when the viscosity of the reaction medium was sufficiently high. The available information is not sufficient to enable a judgement to be made on the nature and role of this effect.

1. J.A. Newland and R.R. Vogt, "The Chemistry of Acetylene" (Translated into Russian), Inostr. Lit., Moscow, 1947.
2. W. Reppe, O. Schlichting, K. Klager, and T. Toepel, Annalen, 560, 1 (1948).
3. N. Nagihara, J. Soc. Org. Syn. Chem., Japan, 19, 20 (1961).
4. M. Berthelot, Compt. rend., 62, 905 (1866); 63, 479, 515 (1866); 140, 910 (1905).
5. R. Meyer, Ber., 45, 1609 (1912); 46, 3183 (1913); 53, 1261 (1920).
6. N.D. Zelinskii, Ber., 57, 264 (1924); Zhur. Russ. Fiz.-Khim. Obshch., 55, 140 (1923); Compt. rend., 177, 882 (1924).
7. A. Rupprecht, Acta Chem. Scand., 16, 2189 (1962).
8. J.F. Harris, R.J. Harder, and G.N. Sausen, J. Org. Chem., 25, 633 (1960).
9. M.I. Pugina and P.S. Shantorovich, Vysokomol. Soed., 4, 1784 (1962).
10. H.G. Viehe, R. Merènyi, J.F.M. Oth, and P. Valange, Angew. Chem., 76, 888 (1964).
11. W. Reppe and W.J. Schweckendick, Annalen, 560, 104 (1948).
12. R.F. Kleinschmidt, U.S.P. 2542417 (1951); see Ref. 14.
13. J.D. Rose and F.S. Statham, J. Chem. Soc., 69 (1950).
14. L.S. Meriwether, E.C. Colthup, G.W. Kennerly, and R.N Reusch, J. Org. Chem., 26, 5155 (1961).
15. C. McKeever and J.O. Van Hook, U.S.P. 2542551; see Ref. 14.
16. A.C. Cope and C.T. Handy, French P. 1213148 (1960); see Ref. 14.
17. J.C. Sauer and T.L. Cairns, J. Amer. Chem. Soc., 79, 2659 (1957).
18. E.C. Colthup and L.S. Meriwether, J. Org. Chem., 26, 5169 (1961).
19. L.S. Meriwether, M.F. Leto, E.C. Colthup, and G.W. Kennerly, J. Org. Chem., 27, 3930 (1962).
20. R.E. Benson and R.V. Lindsey, J. Amer. Chem. Soc., 81, 4247 (1959).
21. G.N. Schrauzer, J. Amer. Chem. Soc., 81, 5310 (1959).
22. G.N. Schrauzer, Chem. Ber., 94, 1403 (1961).
23. M.A. Bennett, Chem. Rev., 62, 611 (1962).
24. W. Reppe and H. Vetter, Annalen, 582, 136 (1953).
25. H.W. Sternberg, R. Markby, and I. Wender, J. Amer. Chem. Soc., 80, 1009 (1958).
26. W. Hübel, E.H. Braye, A. Clauss, E. Weiss, U. Krüerke, D.A. Brown, C.S.D. King, and C. Hoogzand, J. Inorg. Nuclear Chem., 9, 204 (1959).
27. W. Hübel and C. Hoogzand, Chem. Ber., 93, 103 (1960).
28. U. Krüerke, C. Hoogzand, and W. Hübel, Chem. Ber., 94, 2817 (1961).
29. J. Dale, Chem. Ber., 94, 2821 (1961).
30. C. Hoogzand and W. Hübel, Tetrahedron Letters, No. 18, 637 (1961).
31. E.M. Arnett and J.M. Bollinger, J. Amer. Chem. Soc., 86, 4729 (1964).
32. F. Hein, Ber., 52, 195 (1919).
33. H. Zeiss, W. Herwig, and W. Metlesics, J. Amer. Chem. Soc., 79, 6561 (1957).
34. W. Herwig, W. Metlesics, and H. Zeiss, J. Amer. Chem. Soc., 80, 2913 (1958); 81, 6203 (1959); U.S.P. 2953610.
35. H. Zeiss and M. Tsutsui, J. Amer. Chem. Soc., 81, 6090 (1959).
36. H. Zeiss and M. Tsutsui, U.S.P. 2980741.
37. M. Tsutsui and H. Zeiss, J. Amer. Chem. Soc., 82, 6255 (1960).
38. H. Zeiss (Editor), "Organometallic Chemistry", Reinhold, New York, 1960, p. 406.
39. G. Natta, G. Mazzanti, and P. Pino, Ital. P. 530758 (1955); Angew. Chem., 69, 685 (1957).
40. G. Natta, G. Mazzanti, and P. Corradini, Atti Accad. naz. Lincei, Rend. Classe Sci. fis. mat. nat., 25, 3 (1958).
41. E. Lombardi and L. Giuffre, Atti Accad. naz. Lincei, Rend. Classe Sci. fis. mat. nat., 25, 70 (1958).
42. G. Natta, G. Mazzanti, G. Pregaglia, and M. Peraldo, Gazzetta, 89, 465 (1959).
43. A.A. Berlin et al., Vysokomol. Soed., 1, 1817 (1959).
44. A.A. Berlin et al., Vysokomol. Soed., 5, 1354 (1963).
45. W.H. Watson, W.C. McMordie, and L.G. Lands, J. Polymer Sci., 55, 137 (1961).
46. J.K. Stille and D.A. Frey, J. Amer. Chem. Soc., 83, 1697 (1961).
47. N. Hagihara, M. Tamura, H. Yamazaki, and M Fujwara, Bull. Chem. Soc. Japan, 34, 892 (1961).
48. B. Franzus, P.I. Canterino, and R.A. Wickliffe, J. Amer. Chem. Soc., 81, 1514 (1959).
49. G. Wilke and H. Müller, Annalen, 629, 222 (1960).
50. G. Wilke and M. Kroner, Angew. Chem., 71, 574 (1961).
51. G. Drefahl, H.-H. Hörnhold, and H. Bretschneider, J. prakt. Chem., 25, 113 (1964).
52. W.R. Smith, B.P. 802510 (1958).
53. E.F. Lutz, J. Amer. Chem. Soc., 83, 2551 (1961).
54. V.O. Reikhsfel'd, K.L. Makovetskii, and L.L. Erokhina, Zhur. Obshch. Khim., 32, 653 (1962).
55. V.O. Reikhsfel'd, K.L. Makovetskii, and L.L. Erokhina, USSR P. 166007.
56. K.L. Makovetskii, V.O. Reikhsfel'd, and L.L. Erokhina, Zhur. Obshch. Khim., 34, 1968 (1964).
57. V.O. Reikhsfel'd and K.L. Makovetskii, Dokl. Akad. Nauk SSSR, 155, 414 (1964).
58. K.L. Makovetskii, Candidate's Thesis, Lensovet Leningrad. Technological Institute, 1964.
59. K.L. Makovetskii, B.I. Lein, and V.O. Reikhsfel'd, Zhur. Obshch. Khim., 34, 3505 (1964).
60. F.W. Hoover, U.S.P. 2951884.
61. F.W. Hoover, O.W. Webster, and C.T. Handy, J. Org. Chem., 26, 2234 (1962).
62. F.W. Hoover, U.S.P. 2933541.
63. W.C. Hourt, Ind. Eng. Chem., 52, 761 (1960).
64. A.F. Donda, E. Cervone, and M.A. Biancifiori, Rec. Trav. chim., 81, 585 (1962).
65. G. Stea and A.F. Donda, Ricerca sci. Rend., A3, 609 (1963).
66. G. Stea, E. Cervone, and G. Moretti, Ricerca sci. Rend., A3, 619 (1963).
67. S. Kambara, M. Khatano, N Sera, and K. Murai, Khim. i Tekhnol. Polim., 91 (1963).

68. I. E. Starik, Kh. A. Arslanov, and I. R. Klener, Radiokhimiya, 5, 198 (1963).
69. P. Chini, G. De Venuto, T. Salvatori, and M. De Maldé, Chimica e Industria, 46, 1049 (1964).
70. A. T. Blomquist and P. M. Maitlis, J. Amer. Chem. Soc., 84, 2329 (1962).
71. W. C. Lanning and A. Clark, U. S. P. 2 819325; Chem. Abs., 52, 5807 (1958).
72. I. Shapiro and H. G. Weiss, J. Amer. Chem. Soc., 79, 3294 (1957); U. S. P. 2 867 675; Chem. Abs., 53, 8071 (1959).
73. M. Tsutsui, Chem. and Ind., 780 (1962).
74. I. Jadot and M. Neuray, Bull. Soc. roy. Sci. Liège, 30, 52 (1961).
75. L. B. Luttinger, J. Org. Chem., 27, 1591 (1962).
76. L. B. Luttinger and E. C. Colthup, J. Org. Chem., 27, 3752 (1962).
77. G. Schröder and R. Criegee, Annalen, 623, 1 (1959); Angew. Chem., 71, 70 (1959).
78. W. Hübel and E. H. Braye, J. Inorg. Nuclear Chem., 10, 250 (1959).
79. R. P. Dodge and V. Schomaker, Nature, 186, 798 (1960).
80. A. Nakamura and N. Hagihara, Bull. Chem. Soc. Japan, 34, 452 (1961).
81. L. Malatesta, G. Santarella, L. Vallarino, and F. Zingales, Angew. Chem., 72, 34 (1960).
82. M. E. Vol'pin, V. A. Dubovitskii, O. V. Nogina, and D. N. Kursanov, Dokl. Akad. Nauk SSSR, 151, 1100 (1963).
83. G. N. Schrauzer, J. Amer. Chem. Soc., 81, 5307 (1959).
84. W. Strohmeier, H. Laporte, and D. Van Hobe, Chem. Ber., 95, 455 (1962).
85. A. Nakamura, Mem. Inst. Sci. Ind. Res., Osaka Univ., 19, 81 (1962).
86. T. H. Coffild, K. G. Ihrman, and W. Barns, J. Amer. Chem. Soc., 82, 1251 (1960).
87. C. McKinley, Ind. Eng. Chem., 44, 995 (1952).
88. G. N. Schrauzer and S. Eichler, Chem. Ber., 95, 550 (1962).
89. H. C. Longuett-Higgins and L. E. Orgel, J. Chem. Soc., 1969 (1956).
90. G. N. Schrauzer, P. Glockner, and S. Eichler, Angew. Chem., 76, 28 (1964).
91. W. Metlesics and H. Zeiss, J. Amer. Chem. Soc., 81, 4117 (1959).
92. C. E. Berkoff, R. C. Cookson, J. Hudec, and R. O. Williams, Proc. Chem. Soc., 312 (1961).
93. J. Chatt, G. A. Rowe, and A. A. Williams, Proc. Chem. Soc., 208 (1957).
94. R. Criegee and G. Schröder, Angew. Chem., 74, 703 (1962).
95. U. Kruerke and W. Hübel, Chem. Ber., 94, 2829 (1961).
96. G. Wilke, Angew. Chem., 72, 581 (1960); 75, 10 (1963).
97. G. Pilcher and H. A. Skinner, J. Inorg. Nuclear Chem., 7, 8 (1958).
98. E. Duck, J. Polymer Sci., 34, 86 (1959).
99. A. Malatesta, J. Polymer Sci., 51, S45 (1961).
100. H. Uelzman, J. Polymer Sci., 32, 457 (1958).
101. U. S. P. 3 082 269 (19th March 1963).
102. German P. 1 159 951 (2nd July 1964).
103. Austral. P. 232 995 (10th April 1964); B. P. 973 934 (4th November 1964).
104. A. Furlani-Donda and A. Guerrieri, Ricerca sci. Rend., A6, 287 (1964).
105. E. M. Arnett, J. M. Bollinger, and J. C. Sanda, J. Amer. Chem. Soc., 87, 2050 (1965).
106. A. Della-Site and A. Mele, Gazzetta, 93, 1279 (1963).
107. French P. 1 377 677 (6th November 1964); Chem. Abs., 62, 9061 (1965).
108. S. Ikeda and A. Tamani, Radioisotopes, 12, 368 (1963).
109. S. V. Butomo, V. O. Reikhsfel'd, and K. L. Makovetskii, Radiokhimiya, 7, 364 (1965).
110. W. Hübel and R. Merènyi, Chem. Ber., 96, 930 (1963).
111. A. J. Hubert and J. Dale, J. Chem. Soc., 3160 (1965).
112. M. I. Prince and K. Weiss, J. Organometal. Chem. (Amsterdam), 2, 251 (1964).
113. R. Huettel and H. Neugebauer, Tetrahedron Letters, 3541 (1964).
114. P. M. Maitlis, O. Pollock, M. L. Games, and W. J. Pryde, Canad. J. Chem., 43, 470 (1965).
115. P. M. Maitlis and A. Efraty, J. Organometal. Chem. (Amsterdam), 4, 172 (1965).
116. P. M. Maitlis and S. McVey, J. Organometal. Chem. (Amsterdam), 4, 254 (1965).
117. E. H. Braye and W. Hübel, J. Organometal. Chem. (Amsterdam), 3, 25 (1965).
118. M. R. Churchill and R. Mason, Proc. Chem. Soc., 365 (1963).
119. C. E. Berkoff, R. C. Cookson, J. Hudec, D. W. Jones, and R. O. Williams, J. Chem. Soc., 194 (1965).
120. L. Watts, J. D. Fitzpatrick, and R. Pettit, J. Amer. Chem. Soc., 87, 3253 (1965).
121. G. N. Schrauzer, in "Advances in Organometallic Chemistry" (Edited by F. G. A. Stone and R. West), Academic Press, New York, 1964, Vol. 2, p. 31.

Lensovet Leningrad Technological Institute

U.D.C. 547.659.2

COMPOUNDS OF THE β-TETRALONE SERIES

V. F. Shner and N. M. Przhiyaglovskaya

CONTENTS

I. Introduction 523

II. Methods for obtaining compounds of the β-tetralone series 524

III. Chemical properties of compounds of the β-tetralone series 526

IV. Synthesis of natural products and their analogues on the basis of compounds of the β-tetralone series 527

I. INTRODUCTION

β-Tetralone — tetralone-2 [name used throughout in Russian text (Ed. of Translation)], or 3,4-dihydro-1*H*--naphthalen-2-one, or 1,2,3,4-tetrahydro-2-oxonaphthalene — and its derivatives are characterised by high reactivity and can be used for the synthesis of various compounds. Interest in them heightened after Robinson showed that they could serve as raw materials for the synthesis of steroids and terpenes. Subsequently β-tetralone was successfully used for the synthesis of compounds similar to morphine and chrysene derivatives.

In several instances the interest lies not so much in β-tetralone itself as in various of its derivatives.

The problems of the synthesis of β-tetralone and its substituted derivatives and also the use of β-tetralone in syntheses have not been systematically covered in the