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CYCLIC ACETYLENES AND THEIR REACTIONS

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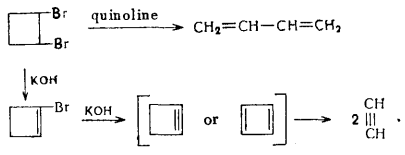
The stereochemistry of cyclic compounds has recently developed considerably. Its important achievements include the concepts of conformational analysis, non-classical strain, transannular reactions, "proximity effect", and so on. A good deal of work has also been devoted to the study of cyclic compounds with strained rings. Systems in which great strain is manifested in their chemical behaviour are particularly interesting.

Cyclic hydrocarbons containing a triple bond in the nucleus are one such group of compounds. The present review deals with the methods of synthesis, properties, and steric structure of cyclic acetylenes; it covers the literature published on this subject up to the end of 1959.

1. POLYMETHYLENE RINGS CONTAINING AN ACETYLENIC BOND

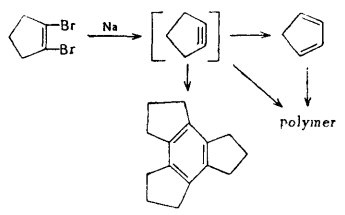
Markovnikov[1] started studying methods of preparation and structure determination of cyclic acetylenes more than sixty years ago. In 1895 he prepared a hydrocarbon, C_7H_{10}, to which he ascribed the cycloheptyne structure. As the development of stereochemistry was just beginning, this discovery aroused great interest. As a result, a number of other papers followed, which were devoted to the synthesis of cyclic acetylenes. We shall consider the subject in order of increasing number of carbon atoms in the ring.

Cyclobutyne. Willstätter[2] attempted to prepare cyclobutyne from 1,2-dibromocyclobutane:



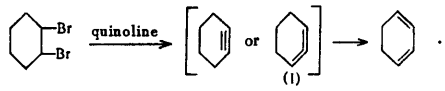
Butadiene was formed when quinoline was used in this reaction, whereas solid potassium hydroxide yielded acetylene. An unstable intermediate compound, which spontaneously undergoes rupture of the ring, is formed in this reaction, but it is impossible to say at present whether it is cyclobutyne, cyclobutadiene, or some other compound.

Cyclopentyne. Favorskii and Shostakovskii[3] studied the action of sodium on 1,2-dibromocyclopent-1-ene.

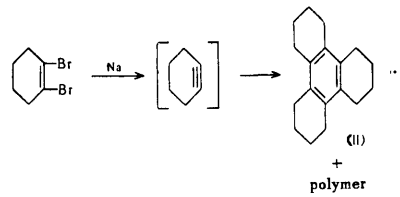


They isolated two products: tricyclopentenobenzene and cyclopentadiene, the latter only as an adduct with maleic anhydride. This indicates that the unstable cyclopentyne is formed in the reaction, but either trimerises to a benzene derivative or isomerises to cyclopentadiene.

Cyclohexyne. Crossley[4] was the first to point out the possibility of forming cyclohexyne or cyclohexa-1,2--diene (I) as intermediate products in reactions:

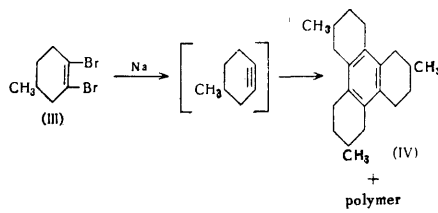


Favorskii and Bozhovskii[5] used the reaction of sodium on 1,2-dibromocyclohex-1-ene to prepare dodecahydrotriphenyl (II):

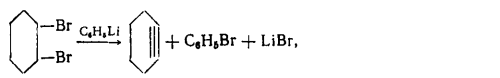


Its properties were identical with those of the material obtained previously by Mannich[6].

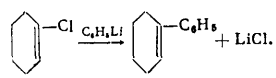
In his work with 1-methyl-3,4-dibromocyclohex-3--ene (III), Domnin[7] isolated a derivative of dodecahydrotriphenylene (IV), whose structure he determined by oxidation to mellitic acid:



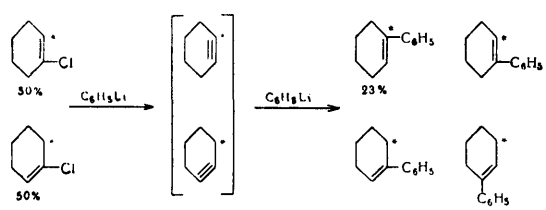
Wittig's work[8] on the reaction of phenyl-lithium with halogen derivatives of hydrocarbons also deals with cyclohexane derivatives. Phenyl-lithium does not react with fluorocyclohexane, but it removes bromine from 1,2-dibromocyclohexane:



and it substitutes phenyl for chlorine in 1-chlorocyclohex--1-ene:

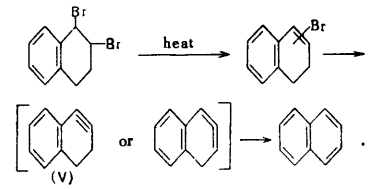


The author has not succeeded in isolating the organolithium compounds, and has ruled out the formation of cyclohexyne in this reaction owing to excessive strain. Scardiglia and Roberts[9] recently repeated the reaction of phenyl-lithium with 1-chlorocyclohex-1-ene, labelled with ^{14}C (marked in the formula by an asterisk).

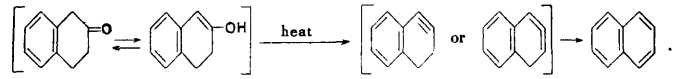


If the ^{14}C content in the starting material is 100%, then every one of the four equally probable reaction products should contain 25% ^{14}C. In fact 1-phenylcyclohex-1-ene-1--^{14}C contained 23% ^{14}C, thus confirming that the reaction proceeds through the intermediate formation of cyclohexyne.

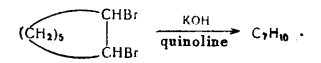
Straus and Rohrbacher[10] explain the mechanism of the elimination of hydrogen bromide from 1,2-dibromotetralin to give naphthalene by the formation of a cyclic acetylene (V);



They explain Bamberger's preparation of naphthalene by distilling β-tetralone[11] in the same way:

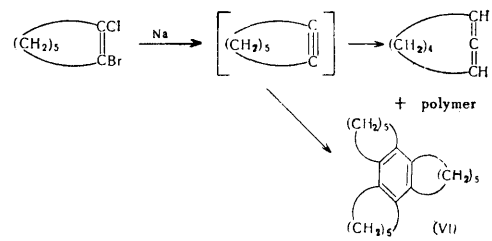


Cycloheptyne. Markovnikov[1] studied the elimination of bromine from 1,2-dibromocycloheptane by means of potassium hydroxide and quinoline:



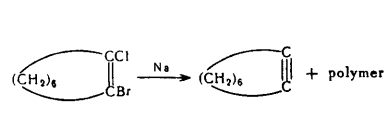
The resulting hydrocarbon had the formula C_7H_{10} and reacted with sodium, bromine, and HI. The author ascribed to it the structure of cycloheptyne. Willstätter[12] repeated Markovnikov's experiments, but obtained only traces of hydrocarbon and was not able to determine its structure.

Domnin[3] used the action of sodium on 1-chloro-2-bromocyclohept-1-ene:

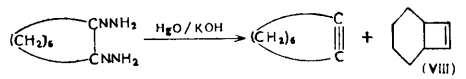


The products were cyclohepta-1,2-diene and tricycloheptenobenzene (VI), indicating that cycloheptyne is formed only as an intermediate product.

Cyclo-octyne. The first attempt to prepare cyclo--octyne, by reacting 1,2-dibromocyclo-octane with potassium hydroxide[13], failed. Cyclo-octyne was first obtained by Domnin[14,15] from the reaction of 1-chloro-2-bromocyclo-oct-1-ene with sodium:



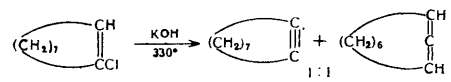
In addition to cyclo-octyne a polymer was isolated which contained tricyclo-octenobenzene (VII). In 1953 Blomquist[16,17] also obtained cyclo-octyne. To prepare cyclic acetylenes he used the Curtius method, *i.e.*, the oxidation of α-dihydrazones by mercuric oxide in the presence of alkali:



(VIII)

Cyclo-octyne is a colourless liquid which oxidises in the air, and reacts explosively with azidobenzene. An isomeric hydrocarbon was also isolated which was suggested to be bicyclo[4,2,0]oct-7-ene (VIII).

Cyclononyne was first prepared by Blomquist[17]. The action of potassium hydroxide on 1-chlorocyclonon-1--ene gave a mixture of hydrocarbons which could not be separated.

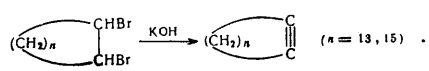


Decomposition of the cyclonona-1,2-dione dihydrazone yielded 39% pure cyclononyne. Prelog[18] obtained the same result.

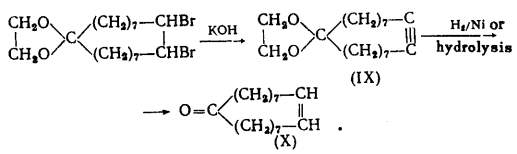
Cyclodecyne was synthesised by Blomquist[19]. Using the Favorskii method (reaction of the unsaturated chlorobromide with sodium), he obtained a 1:3 mixture of acetylene and allene; cyclodecyne was obtained in 67% yield by the decomposition of the dihydrazone. It was also prepared independently by Prelog[20].

Cycloundecyne and cyclododecyne were prepared by Prelog[21] by the decomposition of the corresponding dihydrazones.

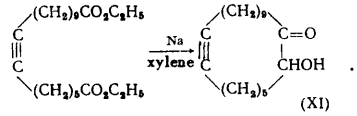
Ruzicka[13] obtained cyclopentadecyne and cycloheptadecyne by reacting the corresponding 1,2-dibromocycloalkanes with alkali:



A derivative of cycloheptadecyne (IX) was used by Stoll[22] to synthesise the compound of musk odour, civetone (X):

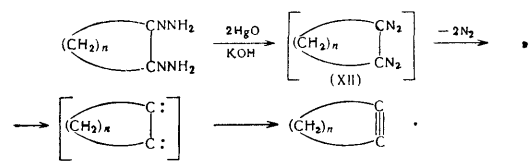


Derivatives of cyclo-octadecyne (XI) were prepared by Epsztein by cyclisation of a diester to an acyloin[23]:



(XI)

It follows from the above that there are at present three methods for the synthesis of cyclic acetylenes: 1) the classical method of elimination of hydrogen bromide from 1,2-dibromoalkanes by the action of alkali[13,22]; 2) the Favorskii method[5,14] in which halogens are removed from 1,2-dihalogenoalk-1-enes by means of sodium (the mechanism of this reaction is probably identical with that of the Würtz–Fittig reaction); 3) oxidation of the dihydrazones of α-diketones[17], a very good preparative method for pure cyclic acetylenes, giving, however, progressively smaller yields as the number of atoms in the ring decreases. A diazo compound (XII) may possibly be formed as an intermediate product in this last reaction, being subsequently converted to the acetylenic hydrocarbon with the elimination of two molecules of nitrogen:



(XII)

A comparison of the reaction products obtained by the Favorskii method and by the oxidation of dihydrazones is interesting; in the former acetylenes are always formed together with isomeric allenes, but in the latter only acetylenes. Favorskii[3] considered the formation of allenes to be the result of a rearrangement caused by strain in the acetylenes. Blomquist[19] showed, however, that the Favorskii method yielded a mixture of cyclic acetylenes and isomeric allenes even in the case of cyclodecyne, which is strainless. Consequently, either the allene is formed together with the acetylene (as a side-reaction) or the acetylene formed isomerises under the action of sodium. Favorskii[24,25] observed such an isomerisation in the case of but-2-yne:

$$CH_3C{\equiv}CCH_3 \xrightleftarrows{Na} CH_3CH{=}C{=}CH_2 \xrightarrow{Na} CH_3CH_2C{\equiv}CH.$$

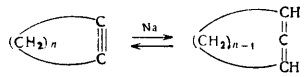
The equilibrium is shifted completely to the side of but-1--yne, because it is converted in the reaction mixture into

TABLE 1. Physical properties of cyclic acetylenes.

Compound	B.p., °C	n_D^{20}	d_4^{20}	$\lambda_{C\equiv C}$ μ	Reference
Cycloheptyne	120—1				1
Cyclo-octyne	72—6/100	n_α^{15} 1.4627	0.8407	4.73*	14,15
	157.5—8/740	1.4850	0.868	4.53	16
Cyclononyne	177—8/740	1.4890	0.8972	4.54	17
	61—2/13	n_D^{23} 1.4880			18
Cyclodecyne	203—4/740	1.4903	0.8975	4.53	19
	78.5/12	1.4950	0.8973	4.41	20
				4.58	21
Cycloundecyne		1.4875			21
Cyclododecyne	106—9/11			~4.5	13
Cyclopentadecyne	158—9/14	1.4910	0.8843		13
Cycloheptadecyne	127—8/0.25	1.4869	0.8840		

* Raman spectrum ν = 2112 cm^{-1}.

the sodium salt. It appears, therefore, that with cyclic acetylenes only the first stage of the Favorskii scheme is achieved.



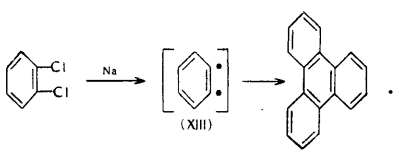
The strain in cyclic acetylenes with a small number of atoms in the ring favours isomerisation, but is apparently not a decisive factor.

The physical properties of cyclic acetylenes are given in Table 1. The cycloheptyne obtained by Markovnikov[1] was not characterised sufficiently. On the basis of boiling point (120°–121°), it could also have been cyclohepta-1,2-diene[3], b.p. 118°–119°, or cyclohepta-1,3-diene, b.p. 120°–121°.

Favorskii[3] summarised the results obtained by saying that only cyclic acetylenes with eight or more atoms can exist as monomers. Rings with fewer atoms which contain a triple bond isomerise into more stable systems. His views are, clearly, still valid.

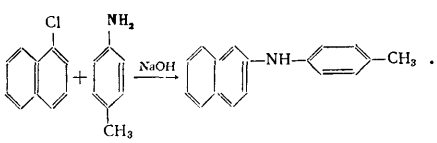
2. AROMATIC COMPOUNDS CONTAINING AN ACETYLYNIC BOND

The discovery of the triple bond in aromatic nuclei was made in connection with studies of the Würtz–Fittig reaction. In studying the action of sodium on *o*-dichlorobenzene, Bachman[26] isolated triphenylene amongst the reaction products. He considered it to result from the formation and polymerisation of the *o*-phenylene free radical (XIII):

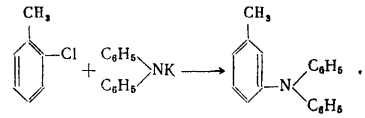


His results were confirmed by Blum-Bergman[27].

On the strength of his results with organometallic compounds, Wittig[28] later accepted the existence of benzene containing two free bonds, and suggested for this compound the name dehydrobenzene, which we shall use. The existence of dehydrobenzene as an intermediate product in reactions has been generally accepted. The concept of the transient formation of dehydrobenzene has been used to explain the reaction mechanism of certain nucleophilic substitutions in aromatic compounds. Rearrangements accompanying substitution reactions in the benzene ring were observed many years ago, the new substituent entering the position *ortho* to the group displaced. For example, Kym[29] found that the action of *p*-toluidine and alkali on 1-halogenonaphthalene gave a 2-substituted naphthalene derivative:

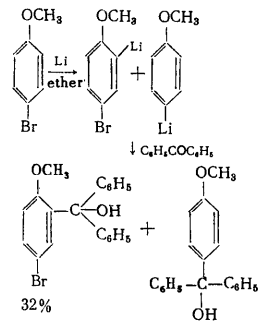


Hausermann[30] observed a rearrangement in the reaction of diphenylaminopotassium with *o*-chlorotoluene:

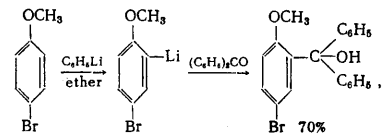


Many such examples are given in the review by Bunnet and Zahler[31]. They could not be explained using the chemical theories existing at that time, but the course of a number of such reactions is now accounted for by the properties of dehydrobenzene.

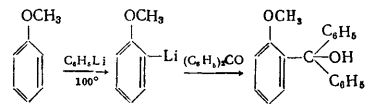
a) The discovery of dehydrobenzene arose from Wittig's observation[32] that in aromatic compounds an alkali metal is capable of replacing not only a halogen atom, but also, when the molecule contains electron-withdrawing substituents, a hydrogen atom in the position *ortho* to such substituents:



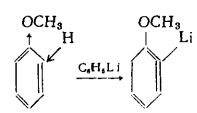
The structure of the organometallic compounds was shown by condensation with benzophenone. It was also shown that phenyl-lithium reacts more readily than lithium itself:



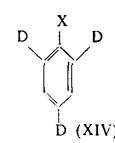
and that substitution of hydrogen is equally possible in compounds not containing a halogen:



Wittig explained the mobility of the hydrogen atom in the *o*-position of anisole by polarisation of the C–H bond under the influence of the electron-withdrawing substituent:



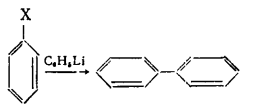
Roberts[33] confirmed the mobility of the *o*-hydrogen atom using exchange between hydrogen and deuterium in deuterated halogenobenzenes (XIV).



X = F, Cl, Br.

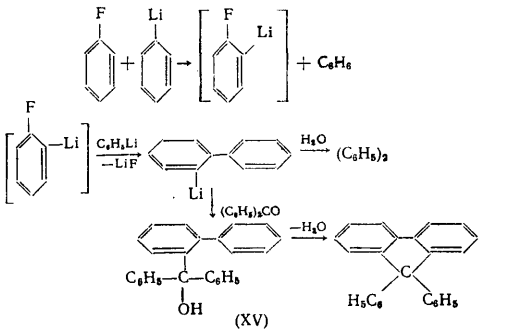
He observed that in fluorobenzene 100% of the deuterium is replaced by hydrogen, whereas under identical conditions chloro- and bromobenzene exchange only 50–70% of the deuterium. Deuterium in the *ortho*-position of fluorobenzene underwent exchange 1000 times faster than that in the *meta*- or *para*-positions[34].

Wittig verified this hypothesis[35] in the following reaction of halogenobenzenes:

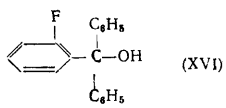


X	% $(C_6H_5)_2$
F	70
Cl	8
Br	10
I	8

The reaction with phenyl-lithium resulted in biphenyl, as would be expected from the Würtz–Fittig mechanism:



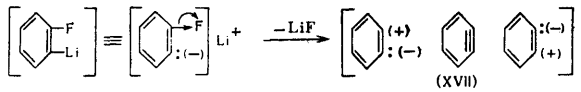
In the condensation with benzophenone, however, only (2-biphenylyl)diphenylcarbinol (XV) was isolated; *o*-fluorophenyldiphenylcarbinol (XVI), which could be expected from *o*-fluorophenyl-lithium, was absent.



(XVI)

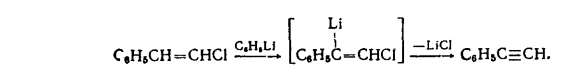
The unexpectedly high yield in the reaction with fluorobenzene is proof that a different mechanism is involved.

From these facts Wittig[28] suggested the formation of dehydrobenzene as an intermediate product. He considered that *o*-fluorophenyl-lithium is unstable and decomposes into lithium fluoride and dehydrobenzene (XVII).

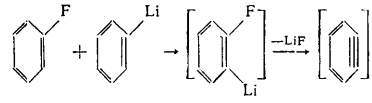


(XVII)

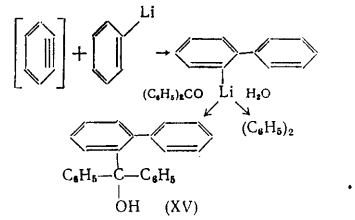
Loss of the lithium salt was assumed by analogy with his earlier work[8,36] on the reaction of β-chlorostyrene with phenyl-lithium to yield phenylacetylene:



The reaction of fluorobenzene with phenyl-lithium is at present explained as proceeding in two stages — elimination and addition:

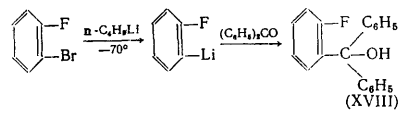


(I)



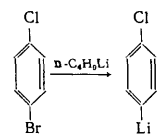
o-Fluorophenyl-lithium formed in the first stage loses lithium fluoride to yield dehydrobenzene. In the second stage dehydrobenzene adds on one molecule of phenyl-lithium giving *o*-biphenylyl-lithium, which reacts with benzophenone to give (2-biphenylyl)diphenylcarbinol (XV), and with water decomposes to biphenyl.

Gilman[37] showed that *o*-fluorophenyl-lithium is stable only at very low temperatures. At -70° a condensation product (XVIII) of *o*-fluorophenyl-lithium with benzophenone was isolated in 84% yield.

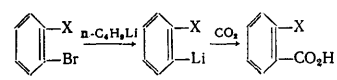


(XVIII)

It could not be obtained at -15°. However, *p*-chlorophenyl-lithium, which Gilman had prepared earlier[38], is completely stable at room temperature.



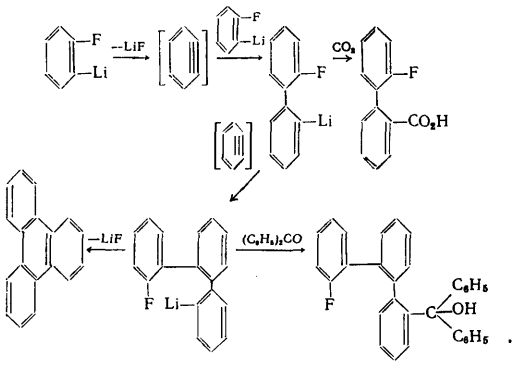
A systematic study of this reaction[39] included *o*-dihalogenobenzenes; they were reacted with butyl-lithium and the reaction product treated with solid carbon dioxide:



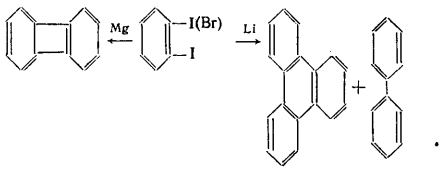
X	temp., °C	% acid
F	−60	83
Cl	−90	80
Br	−100	23

The corresponding acids were isolated in good yields. *o*-Bromophenyl-lithium proved to be very unstable even at

-100°. If the reaction mixture was heated to room temperature, 2-fluorobiphenyl and triphenylene were formed. Gilman suggested the following scheme for this reaction:

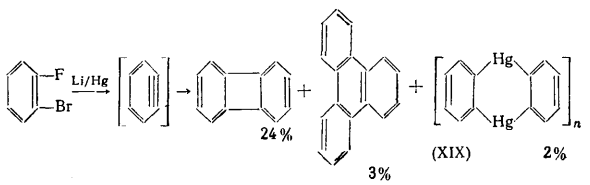


Gilman considers this stepwise formation of triphenylene more probable, from the point of view of reaction kinetics, than Bachman's mechanism, which presupposes the simultaneous interaction of three phenylene radicals. In support of his hypothesis Gilman quoted the isolation of condensation CO_2 and benzophenone, as well as the fact that in the reaction with benzophenone triphenylene was not formed. Mann and Wittig, working at about the same time as Gilman, obtained analogous results. Mann[40] used the reaction of *o*-di-iodobenzene or *o*-iodobromobenzene with lithium to obtain biphenyl and triphenylene:

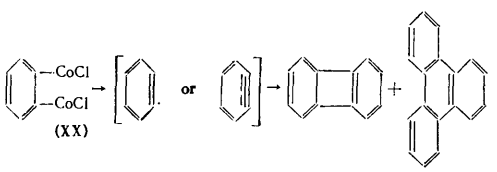


With magnesium he obtained biphenylene. The reaction with 3-bromo-4-iodotoluene gave the corresponding methyl derivatives of bi- and triphenylene[41].

From *o*-fluorobromobenzene Wittig[42] obtained biphenylene, triphenylene, and compound (XIX).

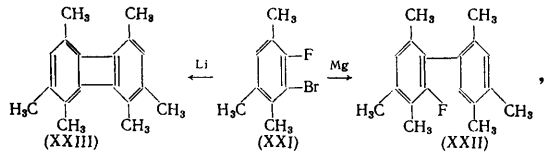


Wittig's latest work[43] showed that the Bachman mechanism cannot as yet be rejected. He isolated biphenylene and triphenylene from *o*-phenylenebiscobaltchloride (XX):



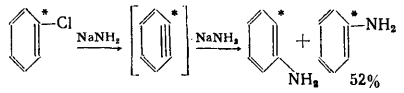
Organocobalt compounds are, of course, typical reagents which, on thermal decomposition, yield free radicals. In this case, therefore, the formation of triphenylene may well proceed by the Bachman mechanism.

Wittig[44] also studied the reaction with 1,2,4-trimethyl-5-fluoro-6-bromobenzene (XXI):



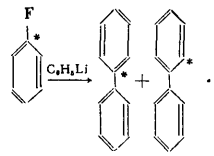
and isolated derivatives of biphenyl (XXII) and biphenylene (XXIII) but not of triphenylene. He explains the absence of a triphenylene from the reaction mixture by steric hindrance during trimerisation — the methyl groups in the triphenylene derivative would be too near to each other.

It still cannot be known for certain from the above studies whether in fact dehydrobenzene is formed in the reaction or not. Only the ^{14}C tracer studies of Roberts and his coworkers provide conclusive evidence. They studied the reaction of chlorobenzene-1-^{14}C with sodium or potassium amide in liquid ammonia[33] and analysed the resulting aniline for ^{14}C.



Two reaction products, aniline-1-^{14}C and aniline-2-^{14}C, were formed in almost equal quantities. This can only be explained by the existence of dehydrobenzene which allows for the equal probability of addition of sodium amide to either position.

The same result was obtained in the reaction of fluorobenzene-1-^{14}C with phenyl-lithium[45].

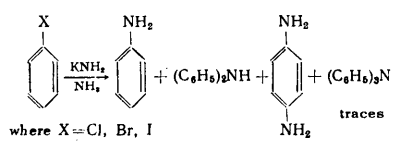


This also can be explained only as an addition of phenyl-lithium to dehydrobenzene.

Wittig obtained further such proof in his study of the reactions of diene derivatives of dehydrobenzene[42]. The diene reactions of dehydrobenzene are reviewed below (p.317).

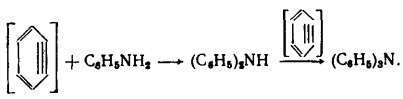
b) Addition to unsubstituted dehydrobenzene. We have already discussed several reactions of this type. In this section further examples are considered.

Bergstrom and coworkers[46] studied the action of potassium amide on halogenobenzenes in liquid ammonia:



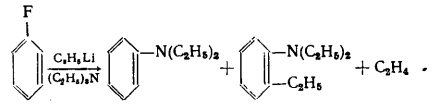
Roberts[33] accounts for the formation of aniline by addition of the metal amide to dehydrobenzene. The formation

of di- and triphenylamine can be explained by addition of the corresponding amine to dehydrobenzene:

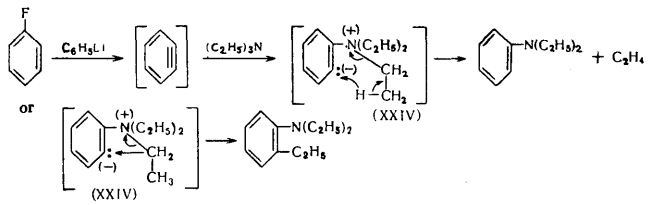


The reaction of potassium anilide with chlorobenzene can be interpreted similarly [47].

Wittig found the action of phenyl-lithium and triethylamine on fluorobenzene to be more complicated [48]:

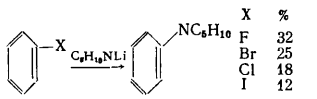


N,N-Diethylaniline, *o*-ethyl-*N,N*-diethylaniline, and ethylene were isolated. This reaction proceeds according to the following scheme:



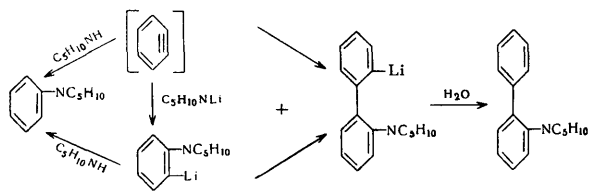
In the first stage the addition product (XXIV) is formed, and subsequently rearranges to give the final products.

Wittig [42] also studied the reaction of halogenobenzenes with lithium piperidide and found that the yield of *N*-phenylpiperidine depends considerably on the halogen present:



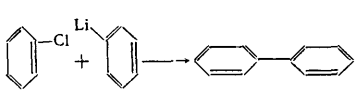
X	%
F	32
Br	25
Cl	18
I	12

Huisgen [49] studied the amination of halogenobenzenes by lithium piperidide in the presence of piperidine and showed the yield to be independent of the halogen present; this can be taken as evidence of the intermediate formation of dehydrobenzene.

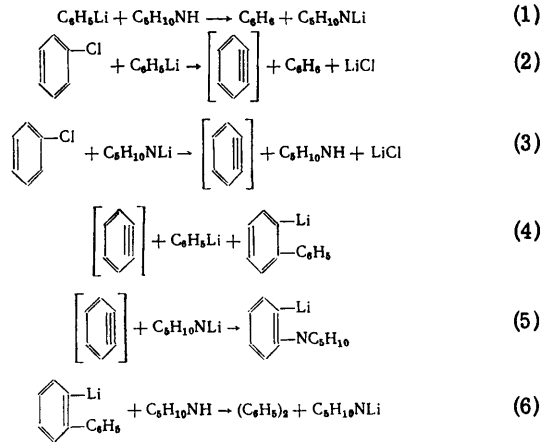


The fact that the yields were independent of the ratio of piperidine to lithium piperidide, supports the mechanism of addition of piperidine to dehydrobenzene. Similar results were obtained in the reaction with lithium diethylamide.

Huisgen [50] observed that the reaction rate of chlorobenzene with phenyl-lithium is smaller than with lithium piperidide. The addition of piperidine accelerates the former reaction and increases the yield of biphenyl form 17% to 61%.

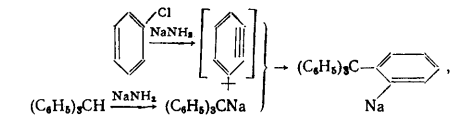


Huisgen concluded that piperidine has a catalytic effect on the reaction.

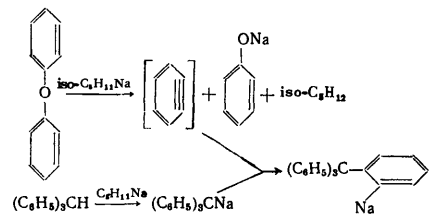


Although the concentration of phenyl-lithium in the reaction mixture is greater than that of lithium piperidide, reaction (3) is more important because it is faster. In reactions (4) and (5) phenyl-lithium reacts three times as fast as lithium piperidide, so that at high concentrations of phenyl-lithium the product is almost exclusively biphenyl. Phenyl-lithium reacts more readily because it is a stronger base than lithium piperidide.

Huisgen's recent kinetic studies [51] of the reaction of phenyl-lithium and lithium piperidide with halogenobenzenes entirely support the two-stage reaction mechanism. The formation of dehydrobenzene also explains the reaction of triphenylmethane with chlorobenzene in the presence of sodamide [52]:

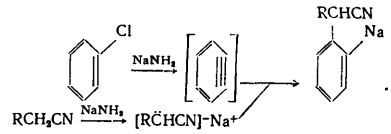


and the reaction of triphenylmethane with diphenyl ether in the presence of isopentylsodium [53]:



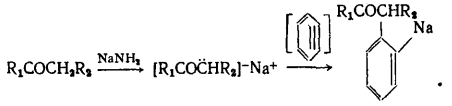
In both reactions tetraphenylmethane is formed.

Further cases of arylation by halogenobenzenes in the presence of alkali metal amides have been reported. Bergstrom [54] carried out such a reaction with nitriles:



where R = H, CH_3. Phenylacetonitrile and diphenylacetonitrile were obtained in 31 and 28% yields respectively.

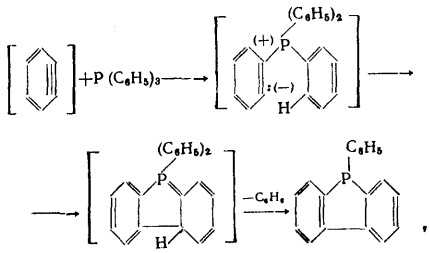
Leake[55] performed the same reaction with ketones:



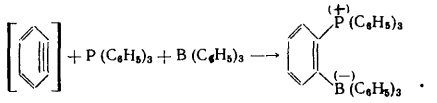
where R_1 = H or an alkyl group, and R_2 = H, alkyl, or aryl group. The esters of malonic and phenylacetic acids were also phenylated[56].

Bunnett[57] showed that the reactions of halogenobenzene with thiophenyl, piperidine, and isobutyronitrile in the presence of $NaNH_2$ gave not only aniline, diphenylamine, and triphenylamine, but also diphenyl sulphide, *N*-phenylpiperidine, and α-phenylisobutyronitrile, in 52, 29, and 23% yields respectively.

Wittig[58] studied the addition of triphenylphosphine to dehydrobenzene:



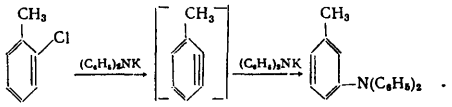
as well as the simultaneous addition of triphenylphosphine and triphenylboron:



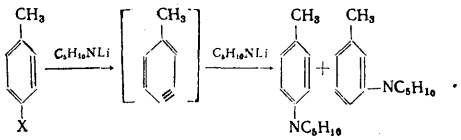
Roberts[59] compared the rates of addition of various anions to dehydrobenzene, and established that they decrease in the following order: fluorenyl anion ≃ anilide > thiophenolate ≃ triphenylmethide > acetophenone enolate anion ≃ ≃ phenylacetylide > phenolate > pyrrolate > alkoxides ≃ ≃ iodides ≃ cyanide.

c) Addition to substituted dehydrobenzenes. Reactions of this type are known as nucleophilic substitutions involving rearrangement ("kine-substitution"). They can easily be observed in substituted benzenes, by the formation of an isomer different from the starting compound. Many rearrangements of this type have been observed for substituted toluenes.

Hausermann[30] reported a rearrangement in the reaction of potassium diphenylamide with *o*-chlorotoluene:



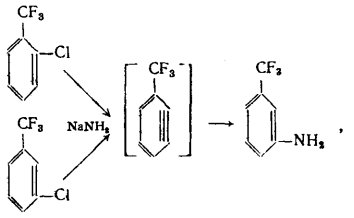
Huisgen[49] studied the reaction of *p*-halogenotoluenes with lithium piperidide and found the ratio of the resulting isomers to be independent of the halogen atom:



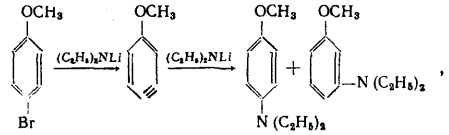
X	% meta	% para
F	53	47
Cl	55	45
Br	56	44

The constant ratio of the two isomers is evidence that the reaction proceeds *via* dehydrobenzene.

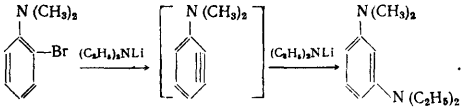
Benkeser[60] studied the reaction of trifluoromethylchlorobenzenes



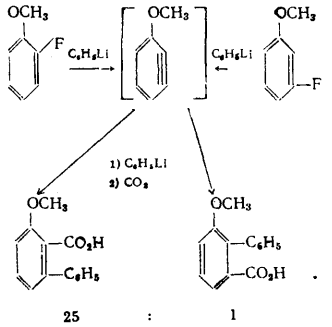
and found that rearrangement took place only in the case of *ortho* derivatives. Subsequent studies were devoted to phenolic ethers. Gilman[61] used *p*-bromoanisole



and *o*-bromo-*N*-dimethylaniline[62]:



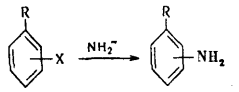
Huisgen[63] studied fluoroanisoles:



25 : 1

The reaction yielded very different quantities of isomers, probably owing to steric factors; the bulky phenyl group cannot enter the 2-position when both vicinal positions are occupied.

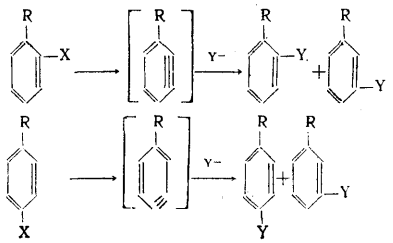
TABLE 2. Orientation in substituted halogenobenzenes.



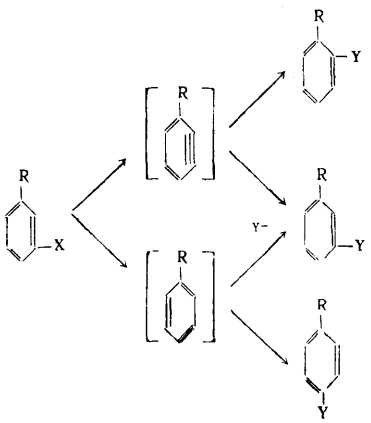
R	X	Isomer content of product, %		
		o	*m*	*p*
o-OCH_3	Br	—	100	—
m-OCH_3	Br	—	100	—
p-OCH_3	Br	—	49±1	51±1
o-CF_3	Cl	—	100	—
m-CF_3	Cl	—	100	—
p-CF_3	Cl	—	50±5	50±5
p-F	Br	—	20±1	80±1
o-CH_3	Cl	45±4	55±4	—
o-CH_3	Br	48.5±2	51.5±2	—
m-CH_3	Br	22±4	56±4	22±4
m-CH_3	Cl	40±4	52±4	8±4
p-CH_3	Cl	—	62±4	38±4

We shall discuss the reaction with diphenyl ether in the section on the synthesis of phenol by the hydrolysis of chlorobenzene.

Roberts [64] determined the quantities of the isomers formed in the above reactions and the effect of the position of the substituent on the yield of different isomers. From his results (Table 2) a number of conclusions can be drawn. First, *ortho*-isomers never give *para*-isomers, nor *vice versa*. This is explicable in terms of the formation of dehydrobenzene.

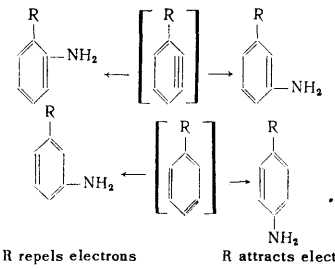


The *meta*-isomer can yield all three isomers:



The results obtained are in full agreement with theory. The fact that the *para*-isomer (which forms a dehydrobenzene without any steric hindrance) yields equal quantities of the two isomers confirms that the second stage in this reaction is an addition.

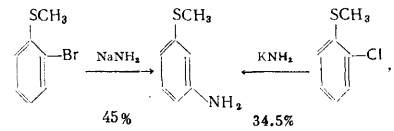
Roberts gave the following scheme for the effect of substituents on the formation of isomers:



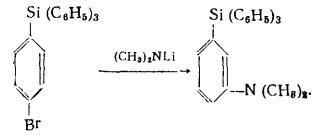
R repels electrons R attracts electrons

The decisive factor is the inductive effect of the substituent. If the substituent tends to withdraw electrons the position taken up is the further from it: in a dehydrobenzene-2,3 the NH_2^- anion enters the *meta*-position, and in a dehydrobenzene-3,4 the *para*-position. The reverse is true of substituents which repel electrons.

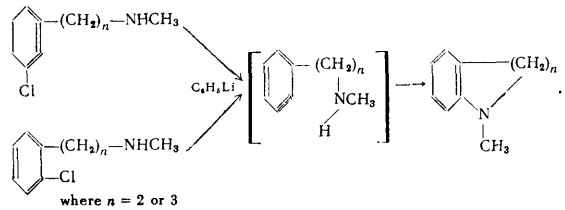
Martin [65] studied derivatives of thioanisole,



and Gilman [66] organosilicon compounds,



Addition to dehydrobenzene can also be carried out intramolecularly. Huisgen [67] accomplished the synthesis of cyclic compounds in this way.



where *n* = 2 or 3

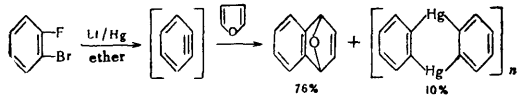
This method has recently been used for the preparation of derivatives of benzo[*b*]morpholine, tetrahydroquinoxaline, and indazoline, as well as eight- and fifteen-membered cyclic amines [68].

d) The behaviour of dehydrobenzene as a dienophile in the Diels-Alder synthesis supplies evidence of its structure and actual existence, and is in itself a remarkable discovery.

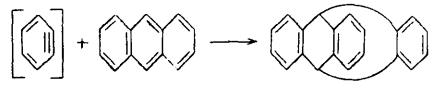
The acetylenic bond is involved in diene synthesis only if activated by neighbouring groups. Dehydrobenzene is very reactive, and readily takes part in diene synthesis. The reaction is carried out as follows [42]: an ether solution of *o*-fluorobromobenzene, lithium amalgam or metallic

magnesium, and the reacting diene is shaken under nitrogen at room temperature for several days. The condensation product is dissolved in ether, isolated by the usual procedure and then purified by chromatography.

In the first reaction which Wittig studied, furan was the diene used.

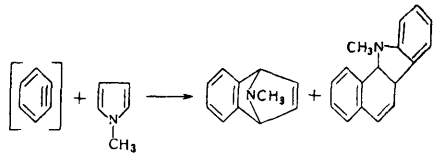


Gilman[69], as well as Müller[70] repeated Wittig's work, carrying out the reaction under conditions favourable to the stability of *o*-fluorophenyl-lithium (-70°). After heating the reaction mixture to room temperature they obtained the endo-oxide. Wittig studied diene synthesis with a number of dienes. For instance, with anthracene he obtained triptycene[71,72].



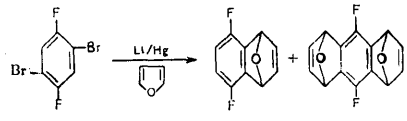
Reactions with cyclopentadiene, tetraphenylcyclopentadienone, and tetraphenylfuran were found to proceed likewise[73].

In the reaction with *N*-methylpyrrole two products were isolated[74].

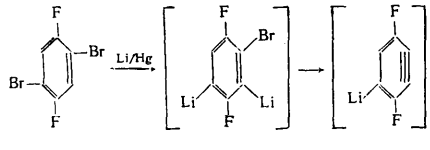


Dehydrobenzene was also treated with *N*-methylisoindole and 1,4-diphenylisobenzofuran[75]. Reactions of certain substituted halogenobenzenes with phenyl-lithium in the presence of furan were reported[44].

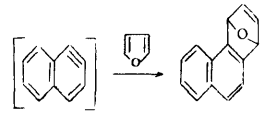
Reaction with 1,4-difluoro-2,5-dibromobenzene gave unexpected results, the fluorine atoms remaining in the molecule.



Either one molecule of lithium bromide was removed and the other bromine atom replaced by lithium, or two molecules of lithium bromide were eliminated simultaneously.

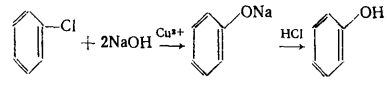


Wittig also studied the reaction of dehydronaphthalene with furan[58].



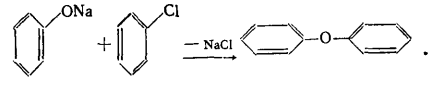
e) Synthesis of phenol from chlorobenzene. The hydrolysis of chlorobenzene by aqueous caustic soda is one of the most important industrial methods for preparing phenol. Since, in contrast to the foregoing reactions, it is carried out in aqueous solution, we shall deal with it separately.

The synthesis of phenol from chlorobenzene was discovered by Meyer and Bergius[76].

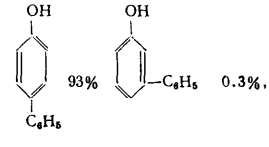


The reaction is carried out in an autoclave at 300° and 100 atm, using 10–20% NaOH solution in the presence of copper salts as catalyst. The yield of phenol is over 90%.

The first theories regarding the reaction mechanism were reviewed by Hale[77]. The mechanism is very complex, as shown by the by-products which Lüttringhaus[78] isolated. The main by-product is diphenyl ether which was earlier thought to be formed in the following reaction:

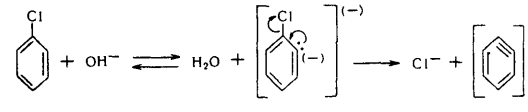


From the residue after distilling off phenol, *p*-phenylphenol and *m*-phenylphenol were isolated:



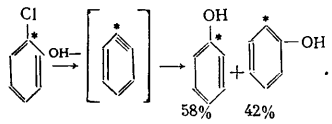
while the residue after distilling off diphenyl ether contained 30% *o*-phenylphenol, 3% *o,o*-diphenylphenol, phenyl-2-biphenylyl ether, and phenyl-4-biphenylyl ether.

Lüttringhaus proposed the following reaction mechanism involving the intermediate formation of dehydrobenzene:



The hydroxide ion attacks the hydrogen *ortho* to the chlorine atom, forming water. The equilibrium shifts to the right because the chlorobenzene anion decomposes to chloride ion and dehydrobenzene. Addition of water now yields phenol, and addition of phenoxy anion yields diphenyl ether or *o*-phenylphenol. Formation of other by-products can be explained similarly.

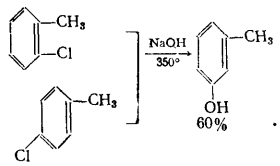
Lüttringhaus's scheme was partially proved by Roberts [79], by hydrolysing chlorobenzene labelled with ^{14}C:



A ratio of isomers close to 1 : 1 was obtained.

Lüttringhaus also studied the reaction of diphenyl ether with phenylsodium [80]. He isolated the same products as in the hydrolysis of chlorobenzene, indicating that dehydrobenzene is an intermediate also in this reaction. Wittig [42] proposed the same reaction scheme. Further proof of the intermediate formation of dehydrobenzene was the isolation of its polymerisation products, triphenylene and 4,5 : 9,10-dibenzopyrene [81] from the reaction of potassium-sodium alloy with diphenyl ether. Lüttringhaus obtained similar results in a study of phenyl-substituted diphenyl ethers and phenyl ethers derived from α- and β-naphthols [82].

The hydrolysis of chlorotoluenes was found to be accompanied by rearrangement [83,84,85]:



Roberts [79] studied the dependence of yield and isomeric composition of the reaction products on the position of the halogen atom (Table 3).

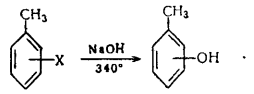
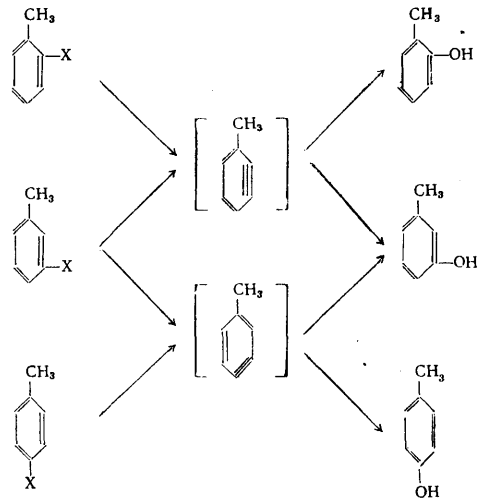


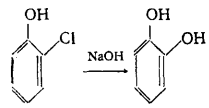
TABLE 3. Hydrolysis of isomeric halogenotoluenes.

X	Conversion, %	Product composition, %		
		o	*m*	*p*
o-Cl	68	48.2	51.8	—
m-Cl	56	21.4	63.6	15.0
p-Cl	50	—	50	50
o-Br	63	45.4	54.6	—
m-Br	60	23.9	60.2	15.9
p-Br	55	—	54.6	45.4
o-I	50	41.7	58.3	—
m-I	47	19.8	66.1	14.7
p-I	43	—	48.7	51.3

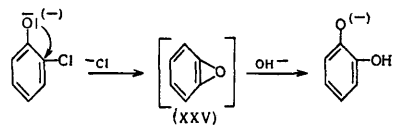
He considers two competing mechanisms possible, namely S_N2 or a dehydrobenzene mechanism. The latter is supported by the rearrangement, and the failure of *o*-chlorotoluene to give *p*-cresol (or of *p*-chlorotoluene to give *o*-cresol). Roberts suggests the following reaction scheme:



Kipriyanov [86] found that in the hydrolysis of *o*-chlorophenol the expected rearrangement did not take place, only pyrocatechol being formed.

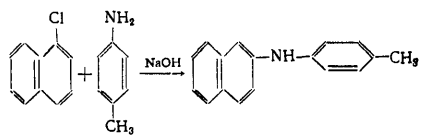


Roberts [79] explains this by intramolecular substitution resulting in "dehydrobenzene oxide" (XXV) as intermediate.



Rearrangement of 2- and 4-chlorobiphenyl was observed by Britton [85] and Moose [87].

f) Dehydronaphthalene. As early as 1894 Kym [29] observed a rearrangement in the reaction of *p*-toluidine with 1-chloronaphthalene:



Similar rearrangements, reported in several other papers [46,62,88-90], possibly indicate the existence of dehydronaphthalene.

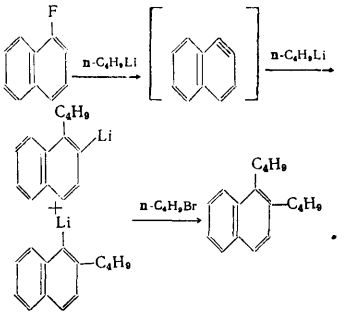
Huisgen [91] showed that constant ratios of isomers in the reaction products were obtained regardless of the position

of the halogen attached to naphthalene. The reaction of fluoro derivatives with phenyl-lithium gave:

	Naphthalene	
	α-phenyl	β-phenyl
α-$C_{10}H_7F$	36.8	63.2
β-$C_{10}H_7F$	37.6	62.4

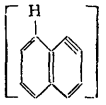
These results agree with those obtained by Bunnett[90].

Huisgen proposed addition of organometallic compounds to dehydronaphthalene for the synthesis of 1,2-dialkylnaphthalenes, which are otherwise difficult to obtain:

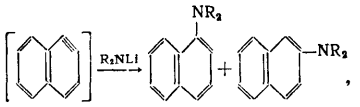


The reaction with butyl bromide gave a good yield of the expected 1,2-dibutylnaphthalene. t-Butylnaphthalenes were also prepared. The same isomer ratios were obtained whether the substituent was n- or t-butyl.

The effect of substituents on the isomer ratio has also been studied[92]. The steric effect of the hydrogen in the peri-position in dehydronaphthalene probably affects the quantity of isomers formed. For small substituents this effect is probably not important and constant ratios of isomers should be obtained. With bulky substituents the β-isomer should predominate.



The reactions of α-fluoronaphthalene with lithium alkylamides have been studied:



where R = iso-C_3H_7 or C_6H_{11}. These theoretical predictions proved correct, although it was only very bulky substituents that affected the isomer ratio.

The dependence of isomer ratio on the position and nature of the halogen has been studied in great detail[93]. In the reaction of 1- and 2-halogenonaphthalenes with lithium piperidide, constant isomer ratios were obtained for all halogens except fluorine. This can be accounted for if the reaction is assumed to proceed partly by an S_N2 mechanism.

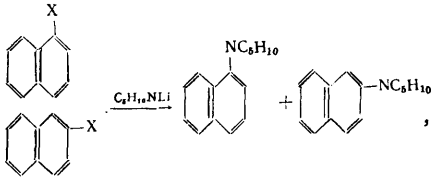
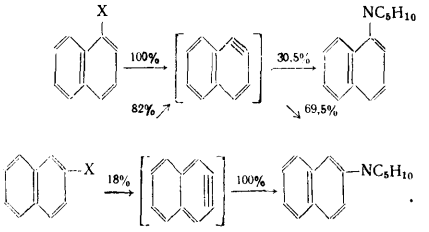


TABLE 4.

Halogenonaphthalene	Piperidinonaphthalene, %	
	1-	2-
1-F	32	68
1-Cl	30	70
1-Br	27	73
2-F	25.5	74.5
2-Cl	26.5	73.5
2-Br	23.5	76.5
Mean: 1-halogenonaphthalene	30.5	69.5
2-halogenonaphthalene	25	75

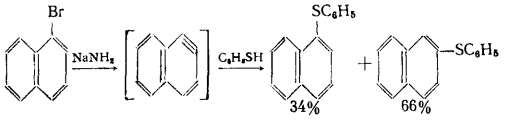
where X = F, Cl, Br, or I. Normal ratios were obtained with all halogens when the reaction was carried out in boiling piperidine (see Table 4).

From the isomer ratio it was possible to determine the course of the elimination of lithium halide from 1-lithium-2-halogeno- and 3-lithium-2-halogeno-naphthalenes, and of the addition of piperidinolithium to 1- and 2-dehydronaphthalenes. The results are:



Substitution is probably equal in the 2- and 3-positions of dehydronaphthalene-2,3, but as these positions are equivalent the products cannot be distinguished. These results were confirmed by Huisgen[94]. Similar results were also obtained with lithium diethylamide.

Bunnett[57] studied the addition of thiophenol to dehydronaphthalene.



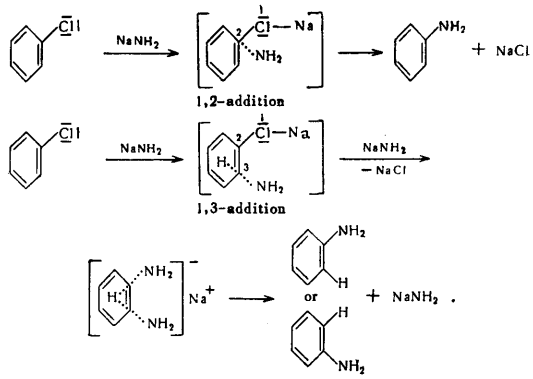
Two isomeric phenyl naphthyl sulphides were obtained in a ratio close to that established by Huisgen[93].

g) Other dehydro-systems. There is as yet no conclusive evidence for the formation of dehydro-compounds in the anthracene[95] and phenanthrene[50] systems. In the biphenyl[46,50], dibenzofuran, and dibenzothiophen systems[96,97] the substitution of halogens is accompanied by rearrangement. This indicates intermediate formation of dehydro-compounds.

The existence of dehydro-compounds may be regarded as fully established by the results described above. Three types of reactions of dehydro compounds are known at present: 1) polymerisation, to biphenylene and triphenylene, 2) addition (aromatic substitution followed by rearrangement is the best example), and 3) diene synthesis. Polymerisation is of no importance as evidence for dehydro-compounds, because it can be explained in terms of a Würtz-Fittig mechanism.

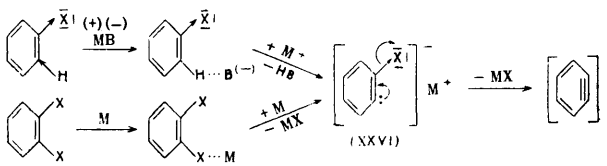
Nucleophilic substitution in the benzene ring can proceed by an S_N2 mechanism without rearrangement. If rearrangement occurs, the reaction has an elimination-addition mechanism with dehydro-compounds as intermediates. This mechanism and the existence of dehydrobenzene were confirmed by Roberts using radioactive tracers. Addition to a dehydro-compound should yield isomers in a constant ratio, independent of the reagent concentrations. The deviations observed result from the reaction proceeding by both possible mechanisms.

Morton[98] suggested another mechnism for substitution with rearrangement. He regards the reaction as a 1,2- or 1,3-addition:



After the removal of NaCl, 1,3-addition yields a cyclic complex, which on decomposition may form either a normal or a rearranged product. Which mechanism the reaction follows is still unknown.

Diene synthesis provides further strong evidence for the existence of dehydrobenzene. Dehydro-compounds can be formed by the action of anions on halogen-containing compounds, by the action of metals on dihalogeno-compounds, or by thermal decomposition of organometallic compounds. The first two methods give the same intermediate *o*-halogeno-metallo compound (XXVI).

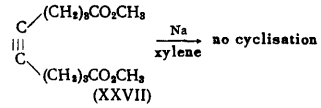


The substitution of a proton by a metal is possible owing to the electron-withdrawing properties of halogen atoms; the stronger this property is, the easier the substitution. The resulting *o*-halogenometallo-compound (XXVI) eliminates MX more easily, the more electropositive the metal. Wittig considers that the driving force of this elimination is high stability of the dehydro-compound resulting from partial overlapping of electron orbitals, although a triple bond is probably not actually formed. Thermal decomposition of organometallic compounds may yield the phenylene radical, which probably rearranges to dehydrobenzene.

The structure of dehydro-compounds will be discussed in the section on the stereochemistry of cyclic acetylenes.

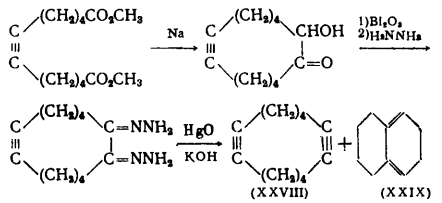
3. CYCLIC ACETYLENES CONTAINING SEVERAL MULTIPLE BONDS

The first reports of the preparation of cyclic compounds containing several multiple bonds appeared in 1956. Cram's attempt to synthesise cyclodeca-1,5-diyne did not succeed because the ester (XXVII) fails to give the acyloin[99].

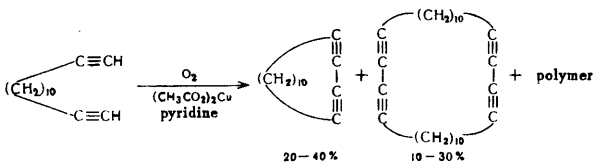


Cyclisation occurred only after reduction of the triple bond to a *cis*-double bond.

In the synthesis of cyclododeca-1,7-diyne (XXVIII) the bicyclic byproduct (XXIX) was obtained.

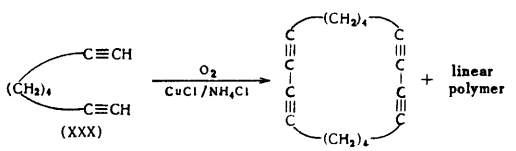


Eglington[100] obtained 1,3-diacetylenes by oxidising an α,ω-diacetylene with air in the presence of copper salts.

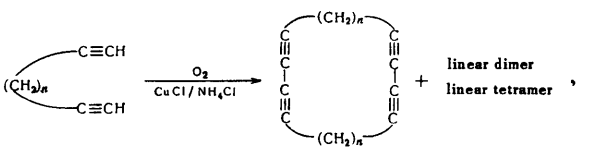


A mixture of cyclic and linear products was obtained. The yield of cyclic monomer depends on the concentration of the initial diacetylene. Cyclotetradeca-1,3-diyne absorbs oxygen from the air forming a C=O group.

Cyclisation of α,ω-diacetylenes has been thoroughly studied by Sondheimer and coworkers, who carried out first the cyclisation of octa-1,7-diyne (XXX).[101]



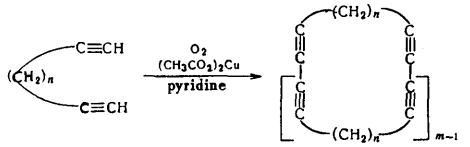
A number of other cyclic acetylenes were prepared by the same method[102].



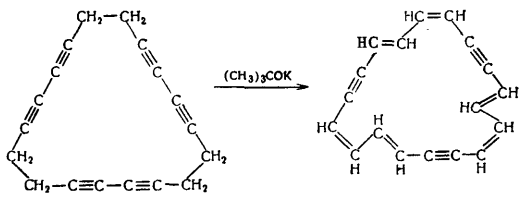
where n = 3, 4, or 5.

Cyclic products could not be obtained from hexa-1,5--diyne ($n = 2$) or deca-1,9-diyne ($n = 6$). In cyclotetradeca--1,3,8,10-tetrayne ($n = 3$) a shift of the ultra-violet absorption bands towards longer wavelenths was observed. The authors call this a "proximity effect"; its nature will be discussed in the section on the stereochemistry of cyclic acetylenes.

When Sondheimer and his coworkers used Eglington's method of oxidation[100], *viz.* very dilute pyridine solution with cupric acetate as catalyst, they isolated cyclic polymers containing several monomer units[103].

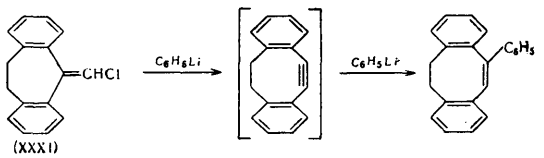


Cyclisation was also carried out with hexa-1,5-diyne-3--ol[104] and with the acetate of cyclohepta-1,6-diyne-4-ol[105]. The macrocyclic compounds cyclo-octadeca-1,3,7,9,13,15--hexayne (hexa-1,5-diyne trimer)[106], cyclotetracosa-1,3,7, 9,13,15,19,21-octayne (hexa-1,5-diyne tetramer)[107,108], and cyclotriaconta-1,3,7,9,13,15,19,21,25,27-decayne (hexa-1,5--diyne pentamer)[108] underwent Favorskii isomerisation under the effect of potassium t-butoxide giving the corresponding conjugated polyenynes.



The authors are of the opinion that these compounds can have aromatic properties.

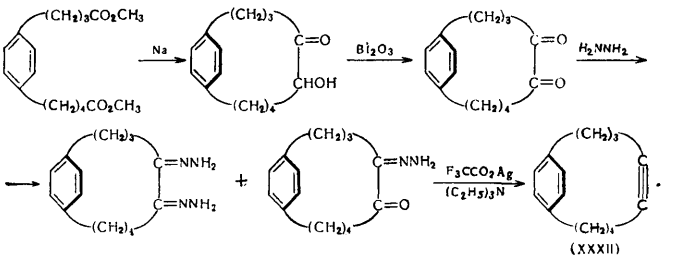
There are several papers devoted to the introduction of a triple bond into rings condensed with a benzene nucleus. Curtin[109] used the action of phenyl-lithium on 1-chloromethylene-2,3 : 6,7-dibenzocycloheptа-2,6-diene (XXXI). Rearrangement to dibenzocyclo-octyne occurred and this reacted with the phenyl-lithium.



(XXXI)

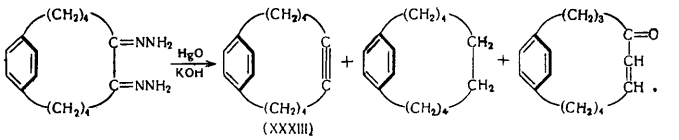
The free acetylene could not be isolated.

Cram and coworkers[110,111] studied the properties of paracyclophanes containing a triple bond; 4-[9]paracyclophyne (XXXII) was obtained from the corresponding dihydrazone:



(XXXII)

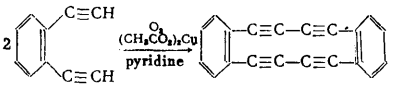
The reaction of the diketone with hydrazine gave a mixture of mono- and di-hydrazones, which could not be separated. This mixture did not react with mercuric oxide, but was decomposed by silver trifluoroacetate and triethylamine. This new method of oxidising dihydrazones was discovered by Newman. 5-[10]Paracyclophyne (XXXIII) was obtained by decomposing the dihydrazone with mercuric oxide and potassium hydroxide:



(XXXIII)

The authors think that the saturated hydrocarbon also obtained is formed by reduction of the dihydrazone according to the Wolff-Kishner method, and the unsaturated ketone by decomposition of the monohydrazone.

The compound that Eglington[112] obtained by the oxidative polymerisation of *o*-diethynylbenzene is of special note.



The structure of the cyclic compound obtained was determined by hydrogenation and from infra-red spectroscopy and X-ray analysis[113].

Oxidative condensation of α,ω-diacetylenes is one of the most important methods for the preparation of cyclic polyacetylenes. The mechanism of this reaction is probably identical with that which Klebanskii established for the coupling of linear acetylenes[114].

$$R{-}C{\equiv}CH \rightleftharpoons R{-}C{\equiv}C{:}^- + H^+$$

$$R{-}C{\equiv}C{:}^- + Cu^{2+} \xrightarrow{\text{rapid}} R{-}C{\equiv}C{\cdot} + Cu^+$$

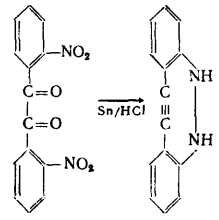
$$2R{-}C{\equiv}C{\cdot} \xrightarrow{\text{rapid}} R{-}C{\equiv}C{-}C{\equiv}C{-}R$$

$$2Cu^+ + {}^1/_2O_2 + H_2O \longrightarrow 2Cu^{2+} + 2OH^-$$

This mechanism is supported by the fact that polymerisation proceeds the faster the more acidic the acetylene. Eglington[100] considers that biradicals $\cdot C{\equiv}C(CH_2)_nC{\equiv}C\cdot$ are formed, which, depending on the reaction conditions, yield a cyclic monomer or cyclic and linear polymers.

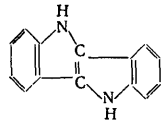
4. HETEROCYCLIC COMPOUNDS CONTAINING AN ACETYLENIC BOND

This group of compounds has received very little attention. Although Golubev obtained the first indications of the existence of these compounds as early as 1884, only a few heterocyclic acetylenes with precisely defined structure are known at present. Golubev[115] studied the reduction of *o,o'*-dinitrobenzil and obtained a compound of composition $C_{14}H_{10}N_2$, to which he ascribed the heterocyclic acetylene structure (XXXIV):



(XXXIV).

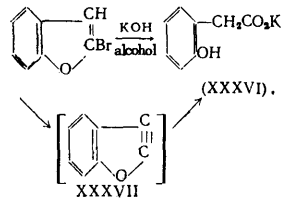
The structure (XXXIV) was not established with certainty. Kliegl[116] thinks that the compound has a completely different structure (XXXV), without the triple bond:



(XXXV).

The efforts of Ruggli[117] to obtain "Golubev's acetylene" by alkaline reduction of *o,o'*-dinitrobenzil failed.

Stoermer[118] observed cleavage of the furan ring in the action of alkali on 2-bromobenzo[*b*]furan:

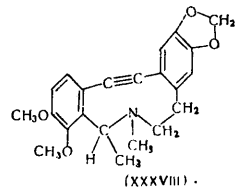


(XXXVI).

XXXVII

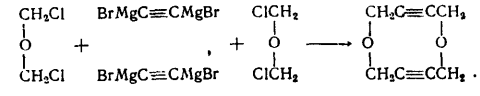
He assumed that dehydrobenzofuran (XXXVII) was formed as an intermediate product in the reaction, which subsequently yielded *o*-hydroxyphenylacetic acid (XXXVI).

Freund[119] reported the presence of a triple bond in the alkaloid des-*N*-methyldihydroberberine (XXXVIII):

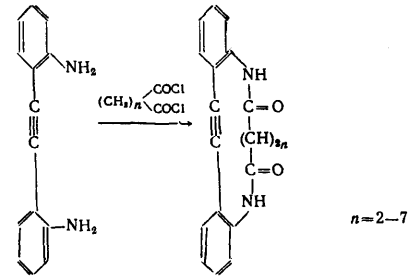


(XXXVIII).

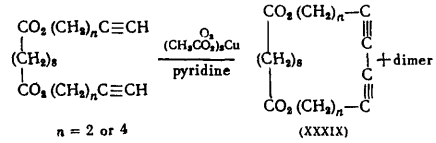
Lespieau[120] obtained a cyclic acetylene in the reaction of dichlorodimethyl ether with ethynylene di(magnesium bromide):



The structure of the above-mentioned heterocyclic acetylenes has not been established with certainty. Ruggli[117,121] obtained the first heterocyclic acetylenes of definite structure by condensation of *o,o'*-diaminotolane with acyl chlorides of dicarboxylic acids.



Eglington[100] has recently obtained the heterocyclic acetylenes (XXXIX) by oxidative polymerisation of diacetylenes:



For $n = 2$ a cyclic monomer and dimer were obtained, but for $n = 4$, only the dimer.

5. STEREOCHEMISTRY OF CYCLIC ACETYLENES

As the present review shows, cyclic acetylenes can be divided into two large groups. The first — stable compounds, whose structure is established beyond doubt — at present includes very few members. They are of especial interest to theoretical organic chemistry, being suitable for the study of spatial configuration, strain, conjugation of multiple bonds, and the possible existence of large rings with aromatic properties.

The second group comprises unstable cyclic acetylenes, the seven-, six-, and five-membered rings containing a triple bond. The possibility of temporary formation of an acetylenic bond in a four-membered ring is hardly worth considering. The structure of these compounds is still not established beyond doubt, as they cannot be isolated in the free state. They are formed only for short periods, as intermediate products, which subsequently isomerise, polymerise or react with other compounds. From the reaction kinetics and resulting products their structure was assumed to be that of cyclic acetylenes. The importance to theoretical organic chemistry of their further study can hardly be overestimated. They are especially important for the theory of the chemical bond, strain theory and in the study of reaction mechanisms.

These unstable compounds are also of great importance in chemical technology. Dehydroaromatic systems, which arise as intermediates during the hydrolysis of aromatic halogen compounds, have a decisive effect on the products. The thorough study of the mechanisms of such reactions and of the properties of dehydro-compounds is therefore not only a means of understanding and of improving the reactions used in industry at present, but also of discovering and applying new processes. This is the main task of science.

Ruzicka[13] was the first to consider the spatial configuration of cyclic acetylenes, concluding that those with ten or more atoms in the ring should be stable. Wittig[122] also examined models of acetylenes and was of the opinion that ten-membered cyclic acetylenes should have no strain in the molecule. Nine- or eight-membered rings can contain a triple bond, but are not strainless.

Favorskii[3] and Domnin[14] studied the preparation of cyclic acetylenes and arrived at the following conclusions:

1) In five-, six-, and seven-membered rings the triple bond can exist for a very short time only. Such molecules are unstable, and rapidly isomerise or polymerise.

2) The acetylenic bond can exist in eight- or nine-membered rings, but it causes strain in the molecule.

3) Cyclic acetylenes with ten-membered or larger rings are strainless.

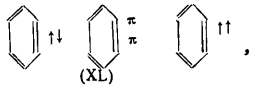
The existence of considerable strain in cyclo-octyne is indicated by the explosiveness of its reaction with azidobenzene[16]. Cyclononyne has not been studied. The infra-red spectra of both these compounds show the normal wavelength for vibration of the acetylenic bond (4.53 μ), identical with that of higher cyclic acetylenes.

Owing to the absence of data on their physical properties, the spatial configuration of cyclic acetylenes can be determined only from their chemical properties, consideration of models, and analogies with other compounds. Examination of models gave the following results. Higher cyclic acetylenes, starting with ten-membered ones, have non-planar rings, strainless or with slight strain caused by energetically unfavourable conformations of the methylene groups. Baeyer strain exists in the cyclononyne and cyclo-octyne molecules. In cyclo-octyne this is so great that it can alter the hybridisation of the atoms forming the triple bond, and cause the appearance of a dipole moment[123], *cf.* that reported by Allinger for *trans*-cyclo-octene[124]. Investigation of the structure of molecules containing a triple bond, such as dehydrobenzene, cycloheptyne, cyclohexyne and cyclopentyne is even more difficult than in the case of known strained molecules.

A good deal of attention has been given to the structure of dehydrobenzene. Bachman[26] suggested it was the phenylene radical. Roberts[33,45] accepted the existence of a triple bond in dehydrobenzene, considering that the orbitals of the second π-bond lie in the plane of the benzene ring and have no effect on the aromatic properties of the system, since they are perpendicular to the other p-orbitals (see Fig. 1). He suggested the name benzyne for dehydrobenzene.

Wittig[42] rejected this name because it implies that there is a triple bond in the molecule. He thinks that dehydrobenzene is a mesomeric molecule, with separate formulae for mesomeric states as given above (XVII), and prefers the name dehydrobenzene to benzyne because it does not presuppose the structure of the bond.

Huisgen[49] concluded that the structure of dehydrobenzene could best be represented by formula (XL):



(XL)

where π signifies partially paired electrons. This formula represents a state intermediate between the singlet and triplet states represented by the adjacent formulae.

The complexity of the problem of the structure of dehydrobenzene is shown by the fact that dehydrobenzene obtained from *o*-fluorophenyl-lithium reacts readily in diene synthesis, whereas dehydrobenzene formed by decomposition of *o*-phenylenebiscobalt chloride yields no adduct with furan, polymerising instead[43]. It is impossible to say as yet whether it is the structure of dehydrobenzene (polar or radical) or the reaction conditions which are responsible for this difference.

Some information regarding the structure of dehydro--compounds can be obtained from the work of Ingold *et al.*[125,126,127] on the excited states of acetylene. Ultra-violet spectra of photochemically excited acetylene were studied, the existence and structure of the first excited state in acetylene being established. The following results were obtained:

Stereochemical parameters

	C_2H_2 normal	C_2H_2 excited	C_6H_6 normal
C≡C bond length, Å	1.208	1.385	1.39
C–H bond length, Å	1.058	1.08	1.08
C≡C–H bond angle	180°	120.2°	120.0°
Force constants:			
C≡C stretching (dyne cm^{-1})	$15.8\cdot10^5$	$7.2\cdot10^5$	$7.6\cdot10^5$
C–H stretching (dyne cm^{-1})	$6.0\cdot10^5$	$5.1\cdot10^5$	$5.1\cdot10^5$
C≡C–H bending (dyne cm^{-1} radian^{-1})	$1.5\cdot10^{-12}$	$3.5\cdot10^{-12}$	$8.0\cdot10^{-12}$

The spatial and electronic structure of the excited molecule is shown in Fig. 2. The stereochemical parameters were obtained from moments of inertia. They show that the molecule is strictly planar and has a *trans*-configuration (centrosymmetrical). The force constants indicate that in the excited molecule it is more difficult to bend the C–H bond further than to stretch it; this leads to re-establishment of a linear molecule. These mechanical properties are exactly opposite to those of the normal acetylene molecule.

The C–C bond is a three-electron bond $\{(2sp^2)\sigma\}\{2p\pi\}$, which is identical with the aromatic bond in benzene. The C–H bonds are normal two-electron bonds $\{(C2sp^2)(H1s)\sigma\}$, as in ethylene or benzene. The π-orbital of the triple bond is converted into two unpaired $2sp^2$ orbitals which have one free place and accept one excited electron from the other π-bond. This leads to a state in which three electrons are shared among two orbitals on two carbon atoms. Ingold describes the state of these electrons as follows: "They are mainly unpaired, although each carbon atom to a certain extent binds the free electrons of the neighbouring atom and to that extent completes its octet".

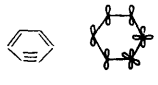


Fig. 1.

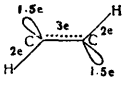


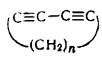
Fig. 2.

Ingold stresses the similarity in structure of the skeleton of the excited acetylene molecule to one third of a normal benzene molecule, which is supported by excellent agreement of bond lengths, valency angles and force constants. The one difference is the *trans*-arrangement of the atoms in the excited acetylene molecule. Other excited states of the acetylene molecule are also possible, but they have not yet been observed. Ingold thinks that one of those states is the *cis*-form of acetylene, which will be very similar to one third of a benzene molecule. This hypothesis is supported by the fact that acetylene forms a *cis*--transition state in the Diels-Alder reaction, just as the formation of a *trans*-transition state in addition reactions with acetylene supports the existence of the *trans*-form of the excited acetylene molecule.

Ingold considers the discovery of dehydrobenzene an additional argument in favour of the possible existence of the *cis*-form of the excited acetylene molecule, and conversely, that the structure of the triple bond in dehydrobenzene will be very similar to the *cis*-form. Arguments concerning the structure of the triple bond in the excited acetylene molecule can be applied to the molecule of dehydrobenzene. The excited triple bond has the character and spatial configuration of an aromatic bond. This is why its introduction into the benzene ring causes no appreciable change in the geometry of the molecule nor does it disturb the electronic structure and, hence, the aromatic properties. Such properties were predicted in dehydrobenzene by Roberts[33,45].

The properties of cyclo-octyne and the excited triple bond in acetylene considered above permit certain observations on the structure of the unstable cycloheptyne, cyclohexyne, and cyclopentyne. All these molecules are in a state of considerable strain, and therefore probably have a planar structure. In cyclo-octyne the strain is distributed among all the carbon atoms, changing their hybridisation and, both in the methylene groups and at the triple bond, the angles between the orbitals forming the bonds. Moreover, the strain causes accumulation of energy in the triple bond. As the number of atoms in the ring decreases, the strain becomes greater. Deformation of valency angles can no longer compensate for the shortage of ring members, so the strain on the triple bond becomes more and more pronounced, leading to the rupture of one of its component bonds, that is the triple bond becomes excited. It is difficult to say whether this is what really happens or whether dissociation of one of the simple bonds takes place earlier. Willstätter[2] observed such dissociation of a simple bond in the rupture of the four-membered ring in an attempt to prepare cyclobutyne. It follows that five-membered rings are the smallest in which a triple bond is able to exist, even for a short time. In its present form the strain theory cannot be used to predict the limiting strain tolerated for more protracted existence of a cyclic acetylene monomer. This can only be determined experimentally. Cyclic acetylenes are at present the only group of organic compounds in which the effect of strain on the structure of the molecule can be studied over a wide range of strain.

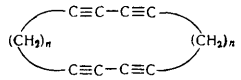
Eglington[100] made a study of models of cyclic diacetylenes with triple bonds in the 1,3-positions, concluding that twelve-membered rings of this kind (n = 8) should be relatively stable.



He did not attempt to prepare cyclododeca-1,3-diyne, but proved the existence of cyclic 1,3-diacetylenes by obtaining a fourteeen-membered ring.

The proximity effect was first observed and studied by Cram[99,110,111,128].

Sondheimer[102] observed a shift in the ultra-violet spectra of cyclic tetra-acetylenes. He showed that the long wavelength maximum for cyclotetradeca-1,3,8,10-tetrayne (n = 3) is shifted 9 mμ towards longer wavelength.



n = 3	226	238	263 mμ
n = 4 or 5	227	239	254 mμ

That this is a case of the proximity effect can be seen from the spatial structure of the tetra-acetylene molecules. A 1,3-diacetylenic group has a linear structure, and the cyclic tetra-acetylene molecule has two such "shafts" connected by methylene groups (Fig. 3).

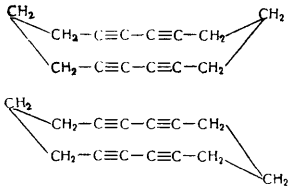


Fig. 3.

In tetradecatetrayne (n = 3) a considerable mutual approach of the triple bonds takes place, so that the shift in the ultra-violet spectra is understandable. There are two possible conformations of the ring — boat and chair. It has been shown by X-ray analysis that the molecule has a centre of symmetry and therefore exists in the chair conformation. Although the acetylenic bonds are drawn together to a considerable degree, the infra-red spectra showed triple bond absorption bands at normal frequencies. This is evidence of the absence of a transannular interaction, the possibility of which was discussed by Cram. In hexadecatetrayne (n = 4) the distance between the acetylenic groups is so great that their interaction is not observed. It should be stressed that cyclotetradeca-1,3,8,10-tetrayne (n = 3) is the first purely aliphatic compound to display the proximity effect.

Some problems of the stereochemistry of cyclic acetylenes which are still unsolved are listed below.

1. The study of the spatial structure and strain of those cyclic acetylenes known at present (especially the molecules of cyclononyne and cyclo-octyne).

2. The preparation of new cyclic acetylenes (that of cycloheptyne is especially challenging).
3. The synthesis of large rings containing several multiple bonds and the study of their aromatic properties.
4. Finally, the study of unstable cyclic acetylenes and of synthetic reactions based on them (the reactions of dehydrobenzene are of paramount importance since it is an intermediate product in certain industrial reactions, *e.g.* the manufacture of phenol from chlorobenzene under the action of alkali).

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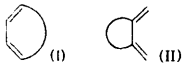
1, 2-DIMETHYLENECYCLOALKANES

Yu. A. Titov

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1. INTRODUCTION

Conjugated dienes with double bonds fixed in a cisoid position are of great importance in the study of the properties of diene systems. Such a cisoid configuration occurs in cyclic dienes of type (I) and (II).



Dienes of type (I), for instance cyclopentadiene, have been known a long time and thoroughly investigated. Compounds of type (II), 1, 2-dimethylenecycloalkanes, whose conjugated systems consist of semicyclic double bonds, have received much attention lately. More than fifty dienes of type (II) which are derived from saturated or unsaturated polymethylene rings, or aromatic (*e.g.* acenaphthene) and heterocyclic (*e.g.* dioxane) systems are already known.