13. *Macrocyclic Compounds. Part I. Synthesis of Macrocyclic Polyynes: Conformational Effects in Ring Formation and in Physical Properties.*

By Johannes Dale, A. J. Hubert, and (in part) G. S. D. King.

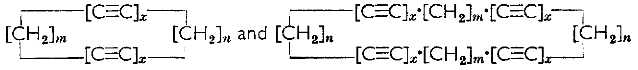
Cyclic non-conjugated diynes and tetraynes, containing 11—26 carbon atoms, have been prepared in good yields from alka-αω-diynes and αω-dibromoalkanes. By extension of the reaction to compounds containing diacetylene and triacetylene groups, cyclic conjugated tetraynes in the range of 16—26 carbon atoms have been prepared in low yields and a 22-membered hexayne in very poor yield. The cyclic non-conjugated acetylenes have been partially reduced to cyclic *cis*-olefins. Full hydrogenation has led to cycloalkanes of exceptional purity; the unknown cyclononadecane was obtained by three different routes. 1,2-Polymethylenebenzenes are formed by prototropic isomerization of the cyclic diynes.

Variations in ease of formation are explained in terms of the probability of having a conformation with the ring preformed in the final cyclization step, and variations in stability and melting point of the cyclic compounds in terms of conformational stability of the ring itself. *X*-Ray measurements support the conformations proposed for the higher-melting cyclic diynes.

The reaction between αω-dibromoalkanes and the disodium salt of acetylene or of αω-diynes in liquid ammonia has been found by Wotiz *et al.*,[1] and independently by us, to give surprisingly high yields of cyclic products even in moderately concentrated solution. A preliminary account has been published,[2] as has an extension of the method to the preparation of conjugated cyclic poly-ynes by replacement of the disodium acetylide with disodium diacetylide and disodium triacetylide.[3] In the two-step procedure which is preferred by us even for the preparation of symmetrical rings ($m = n$) the generalized reaction can be expressed as follows:

$$2\mathrm{Na{\cdot}[C{\equiv}C]}_x\mathrm{{\cdot}H} + \mathrm{Br{\cdot}[CH_2]}_m\mathrm{{\cdot}Br} \longrightarrow \mathrm{H{\cdot}[C{\equiv}C]}_x\mathrm{{\cdot}[CH_2]}_m\mathrm{{\cdot}[C{\equiv}C]}_x\mathrm{{\cdot}H}$$

$$\mathrm{Na{\cdot}[C{\equiv}C]}_x\mathrm{{\cdot}[CH_2]}_m\mathrm{{\cdot}[C{\equiv}C]}_x\mathrm{{\cdot}Na} + \mathrm{Br{\cdot}[CH_2]}_n\mathrm{{\cdot}Br} \longrightarrow$$



(I) (II)

Sodium acetylide ($x = 1$) was prepared by passing acetylene into liquid ammonia containing sodamide, whereas the diacetylide ($x = 2$) and the triacetylide ($x = 3$) were prepared *in situ* from 1,4-dichlorobut-2-yne and 1,6-dichlorohexa-2,4-diyne, respectively.[4] Thereafter the dibromide was introduced and stirring continued for 2—7 days depending on the particular substance. When the reaction was performed in two steps, the intermediate open-chain diyne ($x = 1$) was usually isolated by distillation; its disodium salt was then prepared, and another mole of dibromide introduced. The intermediate conjugated tetraynes ($x = 2$) were not isolated as on distillation they explode violently.

The yields of cyclic products (Tables 1 and 2) are in general reasonable for the non-conjugated compounds ($x = 1$); the simple diynes (I) are obtained with ring sizes ranging from 11 to 22 carbon atoms (Table 1). The higher limit is probably determined by insolubility of the reactants, whereas the lower limit reflects well-known medium-ring tension. The lower yields of the smaller rings are compensated by correspondingly higher yields of

---

[1] Wotiz, Adams, and Parsons, *J. Amer. Chem. Soc.*, 1961, **83**, 373.

[2] Hubert and Dale, *Chem. and Ind.*, 1961, 249.

[3] Hubert and Dale, *Chem. and Ind.*, 1961, 1224.

[4] Armitage, Jones, and Whiting, *J.*, 1952, 1993; Armitage, Cook, Jones, and Whiting, *J.*, 1952, 2010.

cyclic tetra-ynes (II) which crystallize from the distillation residues, whereby ring sizes from 22 to 26 carbon atoms are obtained (Table 2). The concentration of αω-diyne in the final cyclization step was usually 0·1M, which is far from being called "high-dilution." Further dilution might well increase the yields, as it was found that the yield of cyclotetradeca-1,8-dyne (I; $m = n = 5$) increased from 20% to 57% when the concentration of nona-1,8-diyne was decreased from 0·5M to 0·1M. The yield of cyclic diyne (Table 1)

TABLE 1.

Cyclic diynes (I; $x = 1$).

		Reaction	Yield *	M. p.			Found (%)			Required (%)	
m	n	time (days)	(%)	Found	Lit.[1]	B. p./mm.	C	H	Formula	C	H
2	5	7	1	3—5°		45°/0·1	90·1	9·9	$C_{11}H_{14}$	90·35	9·65
4	4	2	7	37—38	39°	65—70°/10^{-4}	—	—	$C_{12}H_{16}$	89·9	10·1
4	5	2	14 }	7—8	7°	70—80°/10^{-3}	89·3	10·4	$C_{13}H_{18}$	89·6	10·4
5	4	2	40 }								
4	6	3	16 }	30	liq.	100—110°/10^{-3}	89·3	10·7	$C_{14}H_{20}$	89·3	10·7
6	4	3	19 }								
5	5	3	57	97—98	100°	100—110°/10^{-3}	89·45	10·6	$C_{14}H_{20}$ †	89·3	10·7
5	6	3	45 }	38	40°	105—115°/10^{-3}	89·3	11·1	$C_{15}H_{22}$	89·0	11·0
6	5	3	24 }								
5	7	7	10	27·5		110—125°/10^{-3}	88·7	10·9	$C_{16}H_{24}$	88·8	11·2
6	6	3	23	−3·5		110—120°/10^{-3}	89·0	10·9	$C_{16}H_{24}$ †	88·8	11·2
5	8	7	19	41—43		120—130°/10^{-3}	88·5	11·15	$C_{17}H_{26}$	88·6	11·4
8	5	7	0								
7	7	7	32	97		160—180°/3	88·6	11·2	$C_{18}H_{28}$ †	88·45	11·55
5	10	7	12	−8		118—134°/10^{-3}	—	—	$C_{19}H_{30}$	88·3	11·7
8	7	7	22	56		124—150°/10^{-3}	88·4	11·4	$C_{19}H_{30}$	88·3	11·7
8	8	4	20	38—39		145—147°/10^{-2}	88·35	11·7	$C_{20}H_{32}$ †	88·2	11·8
9	9	7	10	106·5		198—202°/10^{-3}	87·7	11·95	$C_{22}H_{36}$	87·9	12·1
5	A ‡	5	38	128		120—125°/10^{-2}	81·8	9·4	$C_{13}H_{18}O$	82·1	9·5
B ‡	5	5	0								

* 0·1M-Solution of αω-diyne in NH_3. † Mol. wts.: Found (Rast) for $C_{14}H_{20}$, 188 ± 3; reqd., 188. Found (Rast) for $C_{16}H_{24}$, 225 ± 6; reqd., 216. Found (Hill–Baldes) for $C_{18}H_{28}$, 226 ± 7; reqd., 244. Found (Hill–Baldes) for $C_{20}H_{32}$, 273; reqd., 272. ‡ A = $(Br{\cdot}CH_2{\cdot}CH_2)_2O$; B = dibut-3-ynyl ether.

TABLE 2.

Cyclic non-conjugated tetraynes (II; $x = 1$).

		Yield *	M. p.		Found (%)			Required (%)		Mol. weight	
m	n	(%)	Found	Lit.[1]	C	H	Formula	C	H	Found	Calc.
2	5	11	146°	—	90·2	9·4	$C_{22}H_{28}$	90·35	9·65	308 ± 3	292
3	5	13	74—75	—	90·0	10·0	$C_{24}H_{32}$	89·9	10·1	384 ± 12	321
4	4	3	69	71°			$C_{24}H_{32}$	89·9	10·1		
4	5	>6	86·5	—	89·6	10·45	$C_{26}H_{36}$	89·6	10·4	338 ± 4	349
5	4	>1									

* Conditions as in Table 1.

TABLE 3.

Cyclic conjugated tetraynes (I; $x = 2$).

		Reaction	Yield (%)		M. p.		Crystal	Found (%)			Required (%)	
m	n	time (days)	0·2M *	0·07M *†	Found	Lit.	form	C	H	Formula	C	H
4	4	7	0	0·1	163° ‡	163° §	Plates			$C_{16}H_{16}$		
5	4	4 + 4	7	—	165 ‡		,,	91·5	8·2	$C_{17}H_{18}$	91·8	8·2
5	5	7	7	—	210	212 §	,,			$C_{18}H_{20}$		
5	6	4 + 4	5	—	160 ‡		,,	91·1	9·0	$C_{19}H_{22}$	91·1	8·9
6	6	7	0	4	81	82 §	Needles			$C_{20}H_{24}$		
7	7	5	2	—	171		Plates	90·6	9·5	$C_{22}H_{28}$	90·35	9·65
8	8	7	0	0·3	85		Needles	89·95	9·75	$C_{24}H_{32}$	89·9	10·1
9	9	7	2	1·0	142		Plates	89·7	10·4	$C_{26}H_{36}$	89·6	10·4
10	10	—	—	—	—	102 ¶	Needles			$C_{28}H_{40}$		

* Concn. of each reactant in liquid NH_3. † Isolation by chromatography on alumina. ‡ With decomp. § Sondheimer, Amiel, and Wolovsky, *J. Amer. Chem. Soc.*, 1957, **79**, 6263. ¶ Eglinton and Galbraith, *J.*, 1959, 889.

is a maximum for this compound; it is also high for the unsymmetrical diynes when $m = 5$ and $n = 4$ or 6, but, surprisingly, much lower if the same compounds are prepared in the inverse sense ($m = 4$ or 6, $n = 5$) starting from an even-numbered αω-diyne (compare also the pair $m = 5$, $n = 8$, and $m = 8$, $n = 5$). When both m and n are even (6 and 4) the yield does not appreciably depend on the reaction sequence. An explanation in terms of preferred conformations will be offered below. Table 1 also includes a heterocyclic ring, oxacyclotetradeca-4,11-diyne, obtained in good yield from nona-1,8-diyne ($m = 5$) and 2,2′-dibromodiethyl ether, but not at all from dibut-3-ynyl ether and 1,5-dibromopentane ($n = 5$); the explanation is again sought on a conformational basis.

The yields of conjugated cyclic compounds ($x = 2$) were much lower (Table 3) and only the simple tetraynes (I) could be isolated; no cyclic octaynes (II) were obtained. Again the yield was a maximum with five methylene groups (m) in the intermediate αω-tetrayne. The effect of increasing dilution is shown in Table 3, and a notable yield alternation is observed for the symmetrical members ($m = n$); in fact, for the higher (0·2M) concentration no cyclic product was obtained at all when $m(=n)$ was even. Some symmetrical tetraynes of this type have already been prepared by Eglinton and Galbraith [5] and by Sondheimer and his co-workers [6-8] using oxidative coupling of terminal diacetylenes; in that method the yields with even- and odd-numbered chains are comparable Thus the present method seems to be less general; on the other hand, the isolation of the product is simpler as in most cases no other crystalline product is formed. Furthermore, it would hardly be practicable to prepare the unsymmetrical tetraynes by oxidative coupling. A clue to the reason for the consistently lower yields of the conjugated cyclic tetraynes (I; $x = 2$) than of the non-conjugated cyclic diynes (I; $x = 1$) was found in the isolation of a crystalline by-product (m. p. 70°) from the one-step reaction between disodium diacetylide and 1,8-dibromo-octane. Analysis, ultraviolet spectrum, and complete hydrogenation to hexadecane were in agreement with the expected intermediate $HC{\equiv}C{\cdot}C{\equiv}C{\cdot}[CH_2]_8{\cdot}C{\equiv}C{\cdot}C{\equiv}CH$, but the infrared spectrum showed the absence of terminal acetylene groups. Presumably, the conjugated diyne grouping is more mobile in the presence of sodamide and migrates irreversibly from the monosubstituted end-position to a disubstituted position in the chain where it is more stable and is no longer available for further reaction.

Only one macrocyclic conjugated hexayne, cyclodocosa-1,3,5,12,14,16-hexayne (I; $x = 3$, $m = n = 5$) was prepared. It decomposed explosively at about 200° without melting. The yield was only 0·3% although the saturated chains have the favourable length of five carbon atoms. The limit of the reaction has probably been reached here, the yield for compounds (I; $m = n = 5$) dropping from 57% to 7% to 0·3% when x varies from 1 to 2 to 3. No attempts were therefore undertaken to prepare further members of this new class of ring compound not obtainable by oxidative coupling.

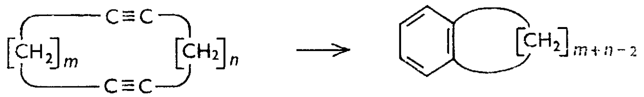
Several attempts to extend the reaction to the preparation of non-conjugated cyclic diynes (I; $x = 1$) with m and n higher than 9 by increasing the solubility and the reaction temperature, either by adding organic solvents to the ammonia or by replacing it with amines, have failed. When working in ethylenediamine and with lithium acetylide (instead of sodium acetylide), the yield of nona-1,8-diyne was only 20% and the yield in the cyclization to cyclotetradeca-1,8-diyne 10%, as compared with 80% and 57%, respectively, in liquid ammonia.

Chemical Properties.—The macrocyclic poly-ynes are remarkably stable and undergo some reactions much more sluggishly than open-chain analogues. Thus, the acetylenic nature of cyclotetradeca-1,8-diyne was not immediately recognized when it was first obtained inadvertently in a preparation of nona-1,8-diyne; it was only slowly attacked by permanganate and by bromine, and the very weak symmetry-forbidden infrared band at

---

[5] Eglinton and Galbraith, *J.*, 1959, 889; *Chem. and Ind.*, 1956, 737.
[6] Sondheimer and Amiel, *J. Amer. Chem. Soc.*, 1957, **79**, 5817.
[7] Sondheimer, Amiel, and Wolovsky, *J. Amer. Chem. Soc.*, 1957, **79**, 6263.
[8] Sondheimer, Amiel, and Wolovsky, *J. Amer. Chem. Soc.*, 1959, **81**, 4600.

4·5 μ was overlooked. The same diyne is extremely stable thermally and distils unchanged at 290° under atmospheric pressure of nitrogen. When it is heated to 500° *in vacuo* in a sealed tube a 40% yield of a liquid was obtained which had the same molecular weight and elemental composition and showed double-bond, but no triple-bond, absorption in the infrared spectrum; it is believed to contain a mixture of decahydroanthracenes formed in a transannular reaction. On the other hand, treatment of non-conjugated diynes and tetraynes ($x = 1$) with a strong base (potassium t-butoxide) below 100° gave no trans-annular-reaction product; only acetylenic bonds separated by two CH_2 groups (II; $x = 1$, $m = 2$, $n = 5$) undergo some isomerization (cf. Sondheimer[9]), the other diynes being recovered unchanged. At 160—200° the cyclic diynes were finally transformed exclusively into 1,2-polymethylenebenzenes, the product expected by analogy with the recently reported[10] aromatization of open-chain diynes:



In this way several hitherto unknown 1,2-polymethylenebenzenes were prepared (see Experimental part).

The stability of the cyclic diynes may vary with their constitution as does ease of formation, m. p., etc. (see below). In the conjugated cyclic tetraynes (I; $x = 2$) such a variation becomes more evident; the higher-melting members ($m = n = 5$ and 7) are stable at the m. p. (210 and 171°), whereas some lower-melting members ($m = n = 4$; $m = 5$, $n = 4$ or 6) decompose at the m. p. (~160°). On the whole, all these cyclic tetraynes are comparatively stable and do not give coloured products on storage, as do corresponding open-chain compounds containing the diyne grouping.

TABLE 4.

Macrocyclic non-conjugated *cis*-olefins obtained by partial hydrogenation of (I and II; $x = 1$).

m	*n*	Yield (%)	M. p.	Found (%)		Formula	Required (%	
				C	H		C	H
Dienes from (I; $x = 1$)								
4	4	95	0°	88·2	12·0	$C_{12}H_{20}$	87·7	12·3
4	5		−9	86·65	12·3	$C_{13}H_{22}$	87·6	12·4
4	6	80	0	87·3	12·6	$C_{14}H_{24}$	87·4	12·6
5	5	77	46	87·6	12·45	$C_{14}H_{24}$	87·4	12·6
5	6		18—20	87·0	12·6	$C_{15}H_{26}$	87·3	12·7
6	6		18·5	87·1	12·5	$C_{16}H_{28}$	87·2	12·8
7	7	85	38·5	87·0	12·8	$C_{18}H_{32}$	87·0	13·0
8	7		−2	86·5	12·8	$C_{19}H_{34}$	86·9	13·1
8	8	75	38—39	87·0	12·9	$C_{20}H_{36}$	86·9	13·1
9	9	70	60—63	86·65	13·15	$C_{22}H_{40}$	86·8	13·2
5	A *		45	80·35	11·2	$C_{13}H_{22}O$	80·35	11·4
				O : 8·5			O : 8·2	
Tetraenes from (II; $x = 1$)								
2	5		37—40	87·9	11·9	$C_{22}H_{36}$	87·9	12·1
4	4		25—27	—	—	$C_{24}H_{40}$	—	—
4	5		9	88·0	12·2	$C_{26}H_{44}$	87·6	12·4

* A = $(Br{\cdot}CH_2{\cdot}CH_2)_2O$.

Treatment of the cyclic diynes with methanol and boron trifluoride–mercuric oxide as catalyst leads in a normal manner to ketones; thus cyclotetradeca-1,8-diyne gave a 15% yield of cyclotetradecane-1,8-dione, m. p. 145—146°, together with one or more oily isomers.

---

[9] Sondheimer *et al.*, *J. Amer. Chem. Soc.*, 1959, **81**, 1771, 4755; 1960, **82**, 754; 1961, **83**, 1259.

[10] Eglinton, Raphael, and Willis, *Proc. Chem. Soc.*, 1960, 247.

The symmetrical cyclic diynes all give crystalline 1 : 1 complexes with silver nitrate. Under the same conditions corresponding open-chain non-terminal acetylenes do not precipitate complexes. This is useful for the purification of low-melting diynes, as the hydrocarbons are regenerated simply by treating the complex with a sodium chloride solution or by heating it in benzene in which silver nitrate is insoluble.

Partial hydrogenation of the non-conjugated cyclic poly-ynes to *cis*-polyenes on a Lindlar catalyst proceeds quickly and cleanly; the absorption of hydrogen stops practically at the calculated quantity. The compounds obtained are listed in Table 4. In contrast, Lindlar hydrogenation of the conjugated poly-ynes continued beyond the calculated value; even so some starting material was recovered, and no definite partial-reduction product was isolated. Partial reduction of the cyclic diynes to corresponding *trans-trans*-dienes with sodium in liquid ammonia was tried, but the starting material was recovered unchanged. A slow, incomplete reaction takes place when the solvent is replaced by a mixture of ether, pentane, and ammonia. Nevertheless, the *trans*-dienes seem to be much more stable than the *cis*-dienes; thus, some of the *cis*-dienes have been treated with selenium at 150°, and the equilibrium found to be almost completely on the side of the *trans,trans*-diene. A closer study of the positional and *cis–trans*-equilibria of these cyclic dienes is in progress. It should be noted that the *trans,trans*-dienes just mentioned do not form silver nitrate complexes, whereas the symmetrical cyclic *cis,cis*-dienes under the same conditions all form such complexes. This may again be a reflection of the instability of the *cis*-compounds, as it has been observed[11] that in smaller cyclic olefins the most highly strained isomers form the most stable silver nitrate complexes. There is a notable alternation in composition of the symmetrical macrocyclic *cis,cis*-diene complexes; those with odd-numbered methylene chains ($m = n = 5, 7, 9$) give 1 : 1 complexes (two double bonds per silver atom) and those with even-numbered chains ($m = n = 6, 8$) give 1 : 2 complexes (one double bond per silver atom). The alternation may not be very significant, because

TABLE 5.

Cycloalkanes obtained by full hydrogenation of macrocyclic poly-ynes.

	Obtained from:				M. p.	
Formula	Cpd.	x	m	n	Found	Highest in lit.
$C_{12}H_{24}$	I	1	4	4	61°	62—63° *
$C_{13}H_{26}$	I	1	4	5	22	23·5 †
$C_{14}H_{28}$	I	1	4	6	54—55·5	54 †
	I	1	5	5	55—55·5	
$C_{15}H_{30}$	I	1	5	6	65—66	62 †
$C_{16}H_{32}$	I	1	6	6	62—63	60—61 ‡
$C_{17}H_{34}$	I	1	5	8	66—67	65 §
	I	2	5	4	64—65	
$C_{18}H_{36}$	I	1	7	7	74—75	72 ‡
$C_{19}H_{38}$	I	1	5	10	80—81	
	I	1	8	7	81—82	
	I	2	5	6	79—80	
$C_{20}H_{40}$	I	1	8	8	61·5	61—62 ‡
$C_{22}H_{44}$	I	1	9	9	51—53	46 §
	II	1	2	5	52—53	
	I	2	7	7	51—52	
$C_{24}H_{48}$	II	1	3	5	50—51	47 ‡
	II	1	4	4	49—51	
	I	2	8	8	49—51	
$C_{26}H_{52}$	II	1	4	5	45	44 §
	I	2	9	9	44—46	
$C_{13}H_{26}O$	I	1	5	A¶	25—27	

* Prelog, Frenkiel, Kobelt, and Barman, *Helv. Chim. Acta*, 1947, **30**, 1741. † Ruzicka, Plattner, and Wild, *ibid.*, 1946, **29**, 1611. ‡ Sondheimer, Amiel, and Wolovsky, *J. Amer. Chem. Soc.*, 1960, **81**, 4600. § Ruzicka and Giacomello, *Helv. Chim. Acta*, 1937, **20**, 548. ¶ A=$(Br{\cdot}CH_2{\cdot}CH_2)_2O$.

---

[11] Cope *et al.*, *J. Amer. Chem. Soc.*, 1953, **75**, 3212; 1956, **78**, 2812; 1960, **82**, 4663.

when the 1 : 2 complexes are recrystallized from ethanol, 1 : 1 complexes are formed. Also we have found that cyclohexa-1,4-diene ($n = 1$) gives a 1 : 2 complex and from the literature it is known [12] that *cis,cis*-cyclo-octa-1,5-diene ($n = 2$) forms a 1 : 1 complex.

The cyclic poly-ynes were all quantitatively hydrogenated on platinum to the corresponding cycloalkanes, identified by m. p. and infrared spectrum (Table 5). The melting points, after a single crystallization, are in most cases somewhat higher than those of the same products prepared by other methods,[8, 13–15] indicating a very high purity obtainable by the present synthetic route. The previously unknown 19-membered ring was obtained from three different poly-ynes; it completes the series up to C_{24}, and shows the highest melting point of all cycloalkanes below C_{50}, thus invalidating speculations relating high melting point with the presence of a highly composite number of ring atoms [14] (cf. following papers in this series).

Physical Properties.—The infrared spectra of the cyclic poly-ynes show no unusual features; in fact, the bands in the C≡C stretching region (4—5 μ) of the ring compounds which contain the conjugated diyne or triyne system are practically superimposable on the spectra of similar open-chain compounds. The symmetrically disubstituted C≡C bonds in the non-conjugated diynes and tetraynes of course absorb only very weakly at 4·5 μ, but as has been shown by Mannion and Wang,[16] the presence of such triple bonds gives rise to very strong bands at 7·5 μ, which disappear on partial or complete hydrogenation. Their interpretation in terms of CH_2 wagging vibrations, whose intensity is reinforced by the inductive effect of the triple bond, appears reasonable. The cyclic *cis*-olefins all show strong absorption at about 14 μ (out-of-plane CH) and a band at 7·1 μ, both of which disappear completely on hydrogenation or isomerization to the *trans*-isomer. The C=C stretching band in the olefins at 6·0 μ is somewhat weak and often split into a doublet. Fermi resonance with some overtone is indicated because of the observed variation of the intensity ratio in the different compounds and because the band becomes single when it is displaced in position by formation of a silver nitrate complex.

The silver nitrate complexes show interesting changes in infrared absorption. The spectra had to be measured as mineral oil mulls, as the complexes reacted with potassium bromide so that discs gave the superimposed spectra of the free hydrocarbon and potassium nitrate. The mull spectra of the complexes of cyclic diynes do not show the weak C≡C stretching band at 4·48 μ; instead there is a somewhat stronger band at 4·59 μ, indicating a slight reduction of the multiple-bond character and a *cis*-like deformation of the linear C–C≡C–C system. In the spectra of the complexes of cyclic *cis,cis*-dienes there is a similar but larger displacement and a simplification of the split C=C stretching band near 6 μ. The shift is slightly different for the two complex types: the band moves to 6·23 μ for the 1 : 1 complexes (one-half silver atom per double bond) and to 6·30 μ for the 1 : 2 complexes (one silver atom per double bond). The CH out-of-plane deformation at 14 μ has become reduced in intensity, and may perhaps be identified with a band near 13·5 μ.

The ultraviolet spectra of the cyclic conjugated poly-ynes are again practically identical with those of the open-chain analogues containing the diyne or triyne chromophore, as regards both position and intensity (see Experimental part). Thus, there seems to be no spectroscopic evidence for transannular interaction between the acetylenic systems, as has been invoked by Wotiz *et al.* to explain the stability of certain cyclic diynes.[1]

By far the most interesting physical property of the cyclic poly-ynes is the melting point. In Fig. 1 the melting points for the symmetrical cyclic diynes (I; $x = 1$, $m = n$) and tetraynes (I; $x = 2$, $m = n$) have been plotted against ring size. Exceptionally high melting points are observed whenever the two equal saturated chains contain an odd

---

[12] Cope, Stevens, and Hochstein, *J. Amer. Chem. Soc.*, 1950, **72**, 2510.
[13] Ruzicka and Giacomello, *Helv. Chim. Acta*, 1937, **20**, 548.
[14] Ruzicka, Plattner, and Wild, *Helv. Chim. Acta*, 1946, **29**, 1611.
[15] Prelog, Frenkiel, Kobelt, and Barman, *Helv. Chim. Acta*, 1947, **30**, 1741.
[16] Mannion and Wang, *Spectrochim. Acta*, 1961, **17**, 990.

number of CH_2 groups; in fact, the melting-point alternation is stronger than in any other homologous series known to us. Molecular models show that strain-free conformations containing only staggered bonds (Fig. 2) can be found for the higher-melting compounds, but none for the lower-melting ones. As will be discussed in more detail in Part III of this series,[17] the predominance of one preferred conformation in the liquid as well as in the crystal lattice means that the entropy of fusion will be low, leading to a high melting point ($T_m = \Delta H_m/\Delta S_m$). If there is no preference, the liquid will contain a mixture of conformations, whereas a single one is selected by the crystal lattice; hence the entropy of fusion will be high and the melting point low. There is also an alternation in crystal form in both series; the compounds with equal odd-numbered polymethylene chains always crystallize as thin plates (cf. Table 3), whereas those with even-numbered chains

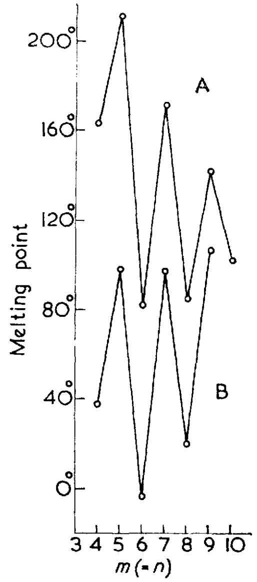


FIG. 1. Melting points of symmetrical (A) diynes (I; $x = 1$) and (B) tetraynes (I; $x = 2$).

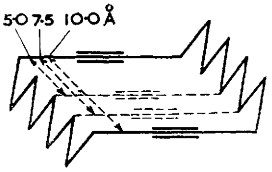


FIG. 2. Probable centrosymmetrical conformations for the high-melting cyclic diynes (I; $x = 1$, $m = n =$ odd).

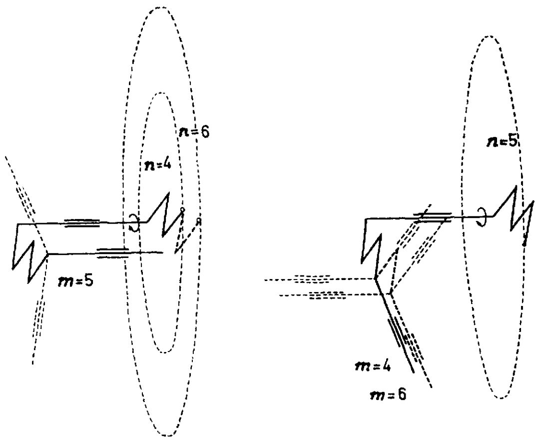


FIG. 3. Strain-free conformations in the final cyclization step in the synthesis of cyclic diynes from alka-αω-diynes and αω-dibromoalkanes.

---

[17] Dale, *J.*, 1963, 93.

which have been crystallized form needles (except I, $x = 2$, $n = m = 4$). As it is known that many other homologous series of oblong isostructural molecules (for instance, normal paraffins, polyphenyls,[18] and polyacenes [19]) crystallize with their long axis roughly perpendicular to the leaflet plane and have unit cells in which only the longest dimension changes, corresponding to the elongation of the molecule, it was expected that those cyclic diynes with odd-numbered polymethylene chains might form such a series if they have the conformations shown in Fig. 2. A determination of the unit cells for the compounds (I; $x = 1$, $m = n = 4$, 5, 7, and 9) was therefore undertaken and the results which are given in Table 6 fully confirm the predictions. The compound $m = n = 4$ crystallizes in the monoclinic system and differs from the others, which form orthorhombic crystals. The last three molecules seem to be isostructural since they form a series in which the *a*- and the *b*-axis are practically constant. The increment of the *c*-axis would be expected to be 2 × 2·5 Å = 5·0 Å (Fig. 2); as it is in fact somewhat smaller, and the *a*- and the *b*-axis are larger than expected from models, the molecules may be tilted with respect to the *c*-axis. The space group requires that the molecules have a centre of symmetry, so that the two triple bonds must be parallel and the molecules must have the chair-form (as in Fig. 2), and not the boat form which would be predicted by considering the triple bond as three " bent bonds " and applying the principle of staggered bonds.[20] This result agrees with conclusions drawn from unit-cell determinations of two closely related acetylenic ring compounds.[7,21] Another series of compact conformations with a centre of symmetry is possible, but the regular increment of the *c*-axis would then not be explained, and the saturated chains contain too many unfavourable *gauche*-oriented bonds. The results also disprove any transannular interaction between the triple bonds which has been invoked by Wotiz *et al.*[1] to explain the chemical stability and the abnormally low heat of combustion found for cyclotetradeca-1,8-diyne. The explanation should rather be sought in terms of conformational stability: the heats of combustion of the open-chain acetylenes were compared with those of n-alkanes which are free to contain a majority of the more stable *trans*-oriented bonds, whereas the cyclic diyne was compared with cyclotetradecane which is obliged to have a majority of the bonds in the less stable *gauche*-orientation (probably 8 *gauche* and 6 *trans*; see Part III of this series [17]). Furthermore, the four *gauche*-bonds of the conformations in Fig. 2 are not dialkyl-substituted but alkyl-ethynyl-substituted and may even have a lower energy than in the *trans*-position. This is generally true when one or both of the substituent atoms carry no or fewer hydrogen atoms than a

TABLE 6.

Crystal data for cyclic diynes (I; $x = 1$, $m = n$)

m	4	5	7	9
Solvent	Ethanol	Ethanol	Butanone	Heptane
M	160·2	188·3	244·4	300·5
a (Å)	12·57 ± 0·06	9·15 ± 0·05	9·36 ± 0·05	9·31 ± 0·05
b (Å)	9·27 ± 0·05	9·45 ± 0·05	9·51 ± 0·05	9·50 ± 0·05
c (Å)	9·16 ± 0·05	13·73 ± 0·07	17·72 ± 0·1	22·03 ± 0·1
β	108° ± 0·5°	—	—	—
V (Å^3)	1014	1187	1637	1948
D_m (by flotation)	1·02 ± 0·01	1·00 ± 0·01	1·01 ± 0·01	1·01 ± 0·01
Z	4	4	4	4
D_i	1·05	1·05	0·99	1·02
Space group	$P2_1/c$	$Pbca$	$Pbca$	$Pbca$

---

[18] Dhar, *Indian J. Phys.*, 1932, **7**, 43; Clark and Pickett, *J. Amer. Chem. Soc.*, 1931, **53**, 167; Pickett, *Proc. Roy. Soc.*, 1933, **142***A*, 333; *J. Amer. Chem. Soc.*, 1936, **58**, 2299.

[19] Robertson and his co-workers, *Acta Cryst.*, 1949, **2**, 233; 1950, **3**, 245; 1961, **14**, 697, 705; 1962, **15**, 289.

[20] Pauling, in " Theoretical Organic Chemistry," Kekulé Symposium, London, 1958, p. 1 (Butterworths Scientific Publns., 1959).

[21] Sondheimer, Gaoni, and Bregman, *Tetrahedron Letters*, 1960, No. 26, 25.

saturated carbon atom, for example, chlorine, fluorine, hydroxyl, and nitrile groups.[22] An indication of *gauche*-preference, or at least lack of *trans*-preference, with an ethynyl substituent has been obtained by determination of the dipole moment of hexa-1,5-diyne in benzene (0·68 D as compared with a calculated value of 1·3 D for the *gauche*-form and zero for the *trans*-form), and a study of the infrared and Raman spectra of the same compound.[23]

Preferred Conformations and Cyclization Probability.—From the preceding discussion it has become clear that *trans*-preference of the interior bonds in the polymethylene chain keeps it straight, *gauche*-preference at the end-bonds imposes a turn of the chain at the corners, and both together make the ideal conformations in Fig. 2 so favoured that they must be practically preformed in the final cyclization step, and the yields are consequently high. It also explains the curious dependence of the yields on the sequence of the reaction steps (Table 1). As shown in Fig. 3 the best conformation for ring closure in the case of nona-1,8-diyne has an end-to-end distance which fits ideally a C_5 chain, but also reasonably well a C_4 or C_6 chain; on the other hand, octa-1,7-diyne and deca-1,9-diyne, even in their best conformations, have end-to-end distances which are too long for a C_5 chain and, what is more important, are out of direction for any chain-length.

One important feature of the preformed bent-back conformations favourable to cyclization is the stretched polymethylene chain, which is of course still more favoured at the low temperature (—33°) at which the reaction takes place. Replacement of a CH_2 group by oxygen loosens such a chain, and the two CH_2–O bonds as well as the two neighbouring alkoxy-alkyl-substituted CH_2–CH_2 bonds tend to become *gauche*-oriented.[22,24] The effect on the cyclization probability will evidently depend very much on the position of the ether linkage. In the case of compound (I; $x = 1$, $m = n = 5$), if the oxygen is introduced into the dibromide, the probability should be only slightly decreased, since it is only a question of closing a preformed short gap, and the yield remains high; but oxygen in the diyne greatly reduces the probability of the conformation with this short end-to-end distance, since the number of other conformations with an unfavourable orientation in space increases so much; the yield actually drops to zero (Table 1). On the other hand, it is conceivable that when there is no conformation favourable to cyclization, a loosening of a stretched-out chain by introduction of ether linkages may actually increase the probability of cyclization. Ziegler and Holl [25] have reported two such cases in the high-dilution cyclization of dinitriles:

Dinitrile	Cyclization yield (%)	Dinitrile	Cyclization yield (%)
$NC{\cdot}[CH_2]_9{\cdot}CN$	<0·5	$NC{\cdot}[CH_2]_{12}{\cdot}CN$	12
$NC{\cdot}[CH_2]_4{\cdot}O{\cdot}[CH_2]_4{\cdot}CN$	5	$NC{\cdot}[CH_2]_4{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}[CH_2]_4{\cdot}CN$	70

Although the authors' explanation in terms of a reduction of the number of crowded hydrogen atoms in the interior of the 10-membered cycle may be of some importance, it fails to explain the decreased yields observed in our case.

Similar considerations explain the yield alternation $m(=n)$ odd–even which is observed for symmetrical diynes (Table 1) and is even more pronounced for the conjugated tetraynes (Table 3). In the latter case the stereochemistry should be essentially unchanged by elongation of the linear acetylenic portions of the molecule, and all the arguments above can be used in this series and explain the alternation in melting point, stability, and yield.

From Table 2 it will be seen that, except for cyclotetracosa-1,7,13,19-tetrayne (II; $x = 1$, $m = n = 4$), all the isolated non-conjugated tetraynes contain two five-membered polymethylene chains facing one another. It may be very significant that the best possible

---

[22] See, for example, Sheppard, *Adv. Spectroscopy*, 1959, **1**, 288.

[23] Dale and Toussaint, unpublished work.

[24] Davison, *J.*, 1955, 3270; Kuroda and Kubo, *J. Polymer Sci.*, 1957, **26**, 323.

[25] Ziegler and Holl, *Annalen*, 1937, **528**, 143.

strain-free and compact * conformations for tetraynes are of this type, with two C_5 chains providing the " corner " *gauche*-bonds and two other equal chains of any length containing only *trans*-bonds. They are exemplified in Fig. 4 for the two subseries m = even (drawn for $m = 2$) and m = odd (drawn for $m = 3$).

The melting points of the symmetrical cyclic *cis,cis*-dienes have been plotted in Fig. 5. The melting points of the three lower members have been taken from the literature (cyclohexa-1,4-diene[26] —49°; *cis,cis*-cyclo-octa-1,5-diene[12] —70°; and *cis,cis*-cyclodeca-1,6-diene[27] 23°). The observed alternation odd–even, although less pronounced and less regular, suggests a similar conformational situation as in the cyclic diynes. With molecular models strain-free ring skeletons with the two double bonds bridging the two odd-numbered saturated chains can in fact be constructed, but there is some strain introduced by the hydrogen atoms, which presumably renders these conformations less stable and less preferred. Details of conformations of cyclic olefins will be discussed in Part III.[17]

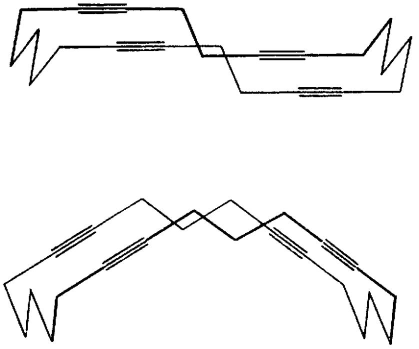


FIG. 4. Compact conformations of some cyclic tetraynes (II; $x = 1$).

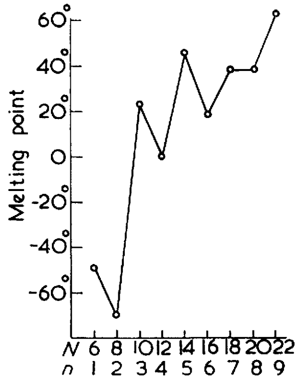
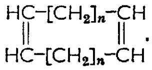


FIG. 5. Melting points of symmetrical cyclic *cis,cis*-dienes,



$$\begin{array}{c} HC-[CH_2]_n-CH \\ \| \qquad\qquad \| \\ HC-[CH_2]_n-CH \end{array}.$$

N = Total no. of carbon atoms.

EXPERIMENTAL

αω-Dibromoalkanes.—These were either commercial products (dibromo-butane, -pentane, and -decane) or were prepared from the corresponding alkane-αω-diols by the action of phosphorus tribromide. These diols were either commercial products (hexamethylene glycol) or were prepared from the corresponding dicarboxylic esters by the reduction with lithium aluminium hydride. 2,2′-Dibromodiethyl ether was similarly prepared from diethylene glycol.[28]

Alka-αω-diynes.—Hepta-1,6-diyne and the higher members were obtained by the standard method:[5, 29] reaction between monosodium acetylide and the αω-dibromoalkane in liquid ammonia. The following are new compounds: undeca-1,10-diyne (yield 70%), b. p. 93—94°/20 mm.; dodeca-1,11-diyne (yield 83%), b. p. 104°/15 mm.; trideca-1,12-diyne (yield 81%), b. p. 125—127°/14 mm. Dibut-3-ynyl ether was similarly prepared from 2,2′-dibromodiethyl ether.[28] Hexa-1,5-diyne was obtained by dehydrobromination of 1,2,5,6-tetrabromohexane with sodamide in liquid ammonia.[30]

---

* Strain-free conformations exist also for cyclotetracosa-1,7,13,19-tetrayne, but they are less compact and have a low symmetry and awkward shape.

[26] Wibaut and Haak, *Rec. Trav. chim.*, 1948, **67**, 85.

[27] Cram and Allinger, *J. Amer. Chem. Soc.*, 1956, **78**, 2518.

[28] McCusker and Kroeger, *J. Amer. Chem. Soc.*, 1937, **59**, 213.

[29] Henne and Greenlee, *J. Amer. Chem. Soc.*, 1945, **67**, 484; Lauer and Gensler, *ibid.*, 1945, **67**, 1171; Bader, Cross, Heilbron, and Jones, *J.*, 1949, 619.

[30] Pomerantz, Fookson, Mears, Rothberg, and Howard, *J. Res. Nat. Bur. Stand.*, 1954, **52**, 51.

Cyclic Diynes (I; $x = 1$).—The alka-αω-diyne (0·1 mole) was added to a stirred solution of the theoretical amount of sodamide (0·2 mole) in liquid ammonia (1 l.). An hour later the corresponding quantity (0·1 mole) of αω-dibromoalkane was introduced, and the stirring continued for several days under a condenser cooled by solid carbon dioxide. The ammonia was then evaporated, the residue dissolved in water, and this solution extracted with ether. The ether extracts were dried and evaporated, and the residue distilled *in vacuo*. When the cyclic compounds were obtained as solid fractions, they were further purified by recrystallization from ethanol or ethanol–propanol. Liquid fractions were more difficult to purify; after careful refractionation the last traces of linear compounds containing the terminal acetylenic group (and at the other end either bromine or a vinyl group produced therefrom) were eliminated by treatment with Nessler's reagent in the presence of alcohol to increase solubility of the hydrocarbon. The precipitate was filtered off, and the filtrate diluted with water and extracted with hexane. The hexane solution was filtered through a column of active alumina, the hexane evaporated, and the residue redistilled. In the case of cycloeicosa-1,11-diyne (I; $x = 1$, $m = n = 8$), probably owing to the relatively short reaction time and presence of intermediate products, it was necessary in order to obtain a correct analysis to pass the hexane solution through a column packed with two layers of adsorbent; the upper layer was alumina which had been saturated with Nessler's reagent and thoroughly washed with alcohol, benzene, and hexane; the lower layer was activated alumina. The linear intermediate, 19-*bromononadeca*-1,11-*diyne*, b. p. 145°/10^{-3} mm., was isolated in 40% yield when $m = 8$, $n = 7$, and the reaction was stopped after 2 days. After retreatment with the necessary amount of sodamide in liquid ammonia for another 5 days, the cyclononadeca-1,10-diyne was obtained in 56% yield.

In certain cases ($m = n = 3$; $m = 3$, $n = 5$; and $m = n = 10$), no cyclic diyne was obtained.

Yields, m. p., b. p. and analyses of these *cycloalkadiynes* are given in Table 1. The infrared spectra, as liquid films or KBr discs, show the absence of C≡CH bands at 3·0 and 4·7 μ; there is a very weak band at 4·46—4·48 μ (C≡C), sometimes followed by a second band at 4·37—4·40 μ. The CH_2 scissoring bands have usually two maxima at about 6·85 and 7·0 μ, but are further resolved into three or four bands for some of the longer chains. In the region 7·3—7·6 μ there are 2—4 surprisingly intense bands, the strongest of which is always very close to 7·50 μ; it has already been proposed as diagnostic of a dialkyl-substituted triple bond.[16] At longer wavelengths the spectra show more individual differences. In the cases investigated, solid and solution spectra are very similar; also the spectra of KBr discs and solid films are the same, except in the case of oxacyclotetradeca-4,11-diyne for which orientation during solidification is indicated by marked weakening of certain bands in the film spectrum.

Cyclic Non-conjugated Tetraynes (II; $x = 1$).—After distillation of the cyclic diynes above, the residues were left for several days. In some cases crystals appeared; they were filtered off and recrystallized from ethanol or ethanol–propanol. Only cyclodocosa-1,5,12,16-tetrayne was purified by sublimation at 10^{-3} mm. Some of the residues which had not crystallized were purified by chromatography and treatment with Nessler's reagent, but remained oily (*e.g.*, $m = n = 5$).

Yields, m. p.s, and analyses of these *cycloalkatetraynes* are given in Table 2. The infrared spectra are very similar to those of the corresponding diynes.

Cyclic Conjugated Tetraynes (I; $x = 2$).—A solution of disodium diacetylide was prepared [4] by adding 1,4-dichlorobut-2-yne (0·2 mole) to a suspension of sodamide (0·8 mole) in liquid ammonia; then the αω-dibromoalkane (0·2 mole) was introduced, and the mixture stirred for a week. In the preparation of the unsymmetrical cyclic tetraynes, sodamide just sufficient for the formation of the monosodium salt (0·6 mole) was used in the first step with one dibromoalkane (0·1 mole); 4 days later the rest of the sodamide (0·2 mole) was introduced as a separately prepared suspension in liquid ammonia, and the other dibromoalkane (0·1 mole) added; stirring was then continued for another 4 days. The ammonia was evaporated, and the residue taken up in ether and benzene. The solvents were evaporated at room temperature and, when the residue was semi-solid, it was suspended in methanol and filtered off. The crystals were then dissolved in cyclohexane, containing enough benzene to make a clear solution, and filtered through an alumina column which was finally washed with cyclohexane and benzene; in this way coloured impurities were removed. The solvents were evaporated and the product was recrystallized from benzene–ethanol.

When the crude product was oily ($m = n = 4$, 6, 8, and 9) the isolation had to be done by careful chromatography on alumina, with a fraction collector and hexane–benzene as eluting solvent. The cyclic tetrayne was then always in the first solid fraction eluted. As a control, cyclotetracosa-1,3,13,15-tetrayne (I; $x = 2$, $m = n = 8$) was also prepared in 3% yield by oxidative coupling of dodeca-1,11-diyne with cupric acetate in pyridine according to Sondheimer's method;[8] it had m. p. and mixed m. p. 84—85° [M (Rast), 277 ± 3. Calc. for $C_{24}H_{32}$; M, 320].

In one case ($m = n = 8$) a crystalline by-product, m. p. 69—70°, was eluted after the cyclic tetrayne (yield after crystallization from ethanol 1·3%). It proved to be an isomer of the intermediate hexadeca-1,3,13,15-tetrayne (Found: C, 91·1; H, 8·5%; M, 214 ± 15. $C_{16}H_{18}$ requires C, 91·4; H, 8·6%; M, 210) as it gave n-hexadecane, m. p. 18—18·5°, on hydrogenation over platinum dioxide in propanol but showed no acetylenic-hydrogen absorption in the infrared region. Lack of infrared bands for allenic and double bonds, presence of bands at 4·55 and 4·65 μ, and an ultraviolet spectrum in hexane with maxima at 216, 226, 238, and 253 μ and intensities (ε = 600, 770, 710, and 410) twice the normal values, established the presence of two diacetylenic chromophores in the molecule. The absence of other isomers suggests that the substance may be *hexadeca*-2,4,12,14-*tetrayne*.

Yields, m. p., and analyses of the cycloalkatetraynes are given in Table 3. The infrared spectra show bands at 4·4 and (stronger) at 4·60 μ (diacetylene); the CH_2 scissoring bands have mostly two maxima at 6·8—6·85 and 7·0 μ; and the CH_2 wagging bands have three maxima between 7·3 and 7·6 μ, with the strongest peak very close to 7·55 μ (instead of 7·50 μ for the non-conjugated cyclic poly-ynes). The ultraviolet spectra in hexane are practically identical for all these compounds, with maxima at 216, 227, 241, and 255 mμ [ε(average) 520, 700, 680, and 460)].

Cyclodocosa-1,3,5,12,14,16-*hexayne* (I; $x = 3$, $m = n = 5$).—A solution of disodium triacetylide was prepared[4] by adding 1,6-dichlorohexa-2,4-diyne (0·15 mole) to a solution of sodamide (0·60 mole) in liquid ammonia (2 l.). Then 1,5-dibromopentane (0·15 mole) was introduced during 15 min., and the mixture was stirred for 4 days. After evaporation of most of the ammonia, benzene and water were added. The organic layer was washed with water, and the aqueous phases were extracted with benzene. The combined benzene solutions were dried (Na_2SO_4) and evaporated at room temperature. All these operations were carried out under nitrogen. The yellow crystalline residue was suspended in hexane, filtered off, and recrystallized from benzene–hexane. The yield was 0·15—0·3% of slightly yellow plates which explode without melting at ~200° (Found: C, 93·4; H, 7·1. $C_{22}H_{20}$ requires C, 92·9; H, 7·1%). The *compound* is relatively stable, but slowly becomes brown at 0°. The infrared spectrum shows a very strong band at 4·52 μ (triacetylene), CH_2 scissoring bands at 6·83 and 7·03 μ, and a very strong band at 7·38 μ (CH_2 wagging?). Ultraviolet maxima of dioxan solutions were at 243, 257, 272, 290, 301, and 312 mμ (ε 210, 300, 410, 420, 220, and 260).

Cyclic Non-conjugated cis,cis-*Dienes and* cis,cis,cis,cis-*Tetraenes*.—The cyclic diyne (I; $x = 1$) or tetrayne (II; $x = 1$) (1—5 g.) was dissolved in benzene (~50 ml.) containing the Lindlar catalyst[31] (~2 g.). The mixture was stirred under hydrogen until the theoretical amount had been absorbed, at which moment the speed of hydrogenation dropped sharply to about a twentieth. The catalyst was filtered off, the benzene evaporated, and the olefin either recrystallized or distilled. M. p. and analyses are given in Table 4. The infrared spectra of the *cycloalkadienes* show olefinic bands at 3·30—3·35 μ (CH stretching), 6·03 μ (C=C stretching) (usually accompanied by another band at about 5·90 μ of equally low or lower intensity), 7·10, and ~14 μ (strong, broad) (CH out-of-plane + CH_2 rocking). In addition there are one to three resolved CH_2 scissoring bands between 6·75 and 7·0 μ. The unsymmetrical dienes show a band at 10·35 μ (*trans*-olefin?) in addition to the *cis*-absorption at 14·0 μ. The infrared spectra of the cyclic tetraenes are very similar to those of the corresponding dienes.

Cycloalkanes.—The poly-yne (0·1—2 g.) was dissolved in ethanol, propanol, or dioxan (depending on solubility) which contained platinum dioxide (0·1—0·3 g.) and had been saturated with hydrogen. When the absorption of hydrogen stopped, the catalyst was filtered off and the solvent evaporated. The cycloalkane was taken up in hexane and filtered through alumina. After evaporation of the hexane, the cycloalkane was recrystallized from methanol, ethanol, or propanol. In Table 5 the m. p.s are compared with those reported in the literature. Two of these compounds are new: *cyclononadecane* [Found: C, 85·4; H, 13·9%; M (Rast), 281 ± 6.

---

[31] Lindlar, *Helv. Chim. Acta*, 1952, **35**, 446.

$C_{19}H_{38}$ requires C, 85·6; H, 14·4%; *M*, 266], and *oxacyclotetradecane* (Found: C, 78·7; H, 13·1; O, 8·2. $C_{13}H_{26}O$ requires C, 78·7; H, 13·2; O, 8·1%).

Thermal Isomerization of Cyclic Diynes.—Cyclotetradeca-1,8- and -1,7-diyne (I; $x = 1$, $m = n = 5$; and $m = 4, n = 6$) distilled under nitrogen at ~290°/760 mm. without decomposition or rearrangement. When cyclotetradeca-1,8-diyne was heated *in vacuo* in a sealed tube at 500° for 20 min., a liquid was isolated in 40% yield on distillation. It had the same analysis (Found: C, 89·1; H, 10·6. Calc. for $C_{14}H_{20}$: C, 89·3; H, 10·7%) and molecular weight (Found: 192 ± 5. Calc.: 188) as the starting material, but a completely different infrared spectrum with olefinic bands at 3·35, 6·06, and 6·24 μ. Further out, the spectrum showed a high background absorption and broad absorption regions, indicating a mixture of isomers.

Prototropic Isomerization of Cyclic Diynes.—When the cyclic diynes (I; $x = 1$) were heated with N-potassium t-butoxide in t-butyl alcohol at temperatures below 100°, they were recovered unchanged, except that cyclohendeca-1,5-diyne (and the corresponding tetrayne) gave ill-defined products. At higher temperatures (160—200°) a reaction took place: a tube containing the cyclic diyne (~1 g.) and N-potassium t-butoxide in t-butyl alcohol (50 ml.) was sealed under nitrogen and kept for 24 hr. at 160°. After cooling, the solution was poured into water and extracted with ether. The solvents were then evaporated, and the residual oil was distilled.

From cyclododeca-1,7-diyne ($m = n = 4$) a liquid was obtained in 70% yield, which was not quite pure, but showed ultraviolet and infrared absorption typical of 1,2-disubstituted benzenes, like all the following compounds.

From the two cyclotetradecadiynes ($m = n = 5$; and $m = 4$, $n = 6$) solids, m. p. 24—26° and 22—25°, mixed m. p. 22—25°, were obtained in 60—65% yield. They had identical spectra and proved the compound to be *benzocyclodecene* (I.U.P.A.C. rule A–23.5) (Found: C, 89·1; H, 10·4. $C_{14}H_{20}$ requires C, 89·3; H, 10·7%).

From cyclo-octadeca-1,10-diyne ($m = n = 7$) an 80% yield of *benzocyclotetradecene* (I.U.P.A.C. rule A–23.5), m. p. 58—59°, was obtained (Found: C, 88·4; H, 11·4. $C_{18}H_{28}$ requires C, 88·45; H, 11·55%).

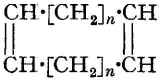
From cyclodocosa-1,12-diyne ($m = n = 9$) an impure oil was obtained, which was spectrally very similar to the above.

The ultraviolet spectra in hexane had maxima at 266 and 273 μ (ε 360 and 345). The infrared spectra showed aromatic bands at 3·26, 3·32, 6·22, 6·33, and 6·70 μ; between 12·5 and 14·5 μ there are for the solids several intense bands, the most constant strong band being at 13·25—13·38 μ.

Silver Nitrate Complexes.—To a solution of the unsaturated hydrocarbon (0·1 g.) in 5 ml. of ethanol (or propanol for the higher members) was added 1 ml. of 30% aqueous silver nitrate, A precipitate was formed immediately and filtered off. The crystals were analysed (C, H, N, or Ag) and the infrared spectra taken in Nujol. The complexes were rapidly decomposed by alkali halides in alcohol or water, or in boiling benzene where silver nitrate is precipitated; in both cases the hydrocarbon was recovered. Thermal destruction takes place above 150°.

The cyclic diynes (I; $x = 1$) all formed 1 : 1 complexes. The very weak C≡C stretching band at 4·48 μ in the hydrocarbon had been displaced in the complex to 4·59 μ and become somewhat stronger. The linear analogue, trideca-3,10-diyne, under the same conditions gave no precipitate.

The cyclic *cis,cis*-dienes formed either 1 : 1 or 1 : 2 complexes. In the symmetrical series,



$$\begin{array}{c}\mathrm{CH{\cdot}[CH_2]_{\mathit{n}}{\cdot}CH}\\ \|\qquad\qquad\| \\ \mathrm{CH{\cdot}[CH_2]_{\mathit{n}}{\cdot}CH}\end{array}$$

,yAgNO$_3$, $y = 1$ when n is 2, 5, 7, or 9, and $y = 2$ when n is 1, 6, or 8. In the infrared spectra the C=C stretching band, weak at 6·03 and 5·9 μ in the macrocyclic hydocarbon, has been displaced to 6·23 μ for the 1 : 1 complexes and to 6·30 μ for the 1 : 2 complexes; in both cases it was a single and more intense band. The olefinic CH out-of-plane deformation at about 14 μ in the hydrocarbon had lost its high intensity; instead several moderately intense bands were found between 13 and 14 μ. Other olefinic bands, at 3·3 and 7·1 μ in the hydrocarbon spectra, were concealed by the Nujol and nitrate absorption. The 1 : 2 complexes were transformed into 1 : 1 complexes on recrystallization from ethanol. *trans,trans*-Cyclotetradeca-1,8-diene under the same conditions gave no precipitate with silver nitrate.

Cyclotetradecanediones.—Cyclotetradeca-1,8-diyne was treated with boron trifluoride–mercuric oxide in methanol according to a standard procedure [32] and gave on hydrolysis an

---

[32] Hennion and Nieuwland, *J. Amer. Chem. Soc.*, 1935, **57**, 2006.

oil from which cyclotetradecane-1,8-dione (15%), m. p. 145—146° (lit.,[33] 148°), was isolated (Found: O, 14·5. Calc. for $C_{14}H_{24}O_2$: O, 14·3%). The mother-liquor probably contained positional isomers.

Crystallographic Examination of Cyclic Diynes (I; $x = 1$; $m = n = 4, 5, 7,$ *and* 9) [G.S.D. KING].—The compound with $m = 4$ crystallized from ethanol as volatile monoclinic needles which had to be sealed in glass capillary tubes for *X*-ray examination. Measurements were made of oscillation and Weissenberg photographs for the four compounds taken with nickel-filtered copper-$K\alpha$ radiation ($\lambda = 1{\cdot}5418$ Å). The results are given in Table 6.

We thank Mr. Marcel Hubert for his untiring assistance in the preparative work, and Miss Anne Holme for help with the *X*-ray determinations.

UNION CARBIDE EUROPEAN RESEARCH ASSOCIATES,
95 RUE GATTI DE GAMOND, BRUSSELS 18, BELGIUM.

[*Received, May* 23*rd*, 1962.]

[33] Blomquist and Spencer, *J. Amer. Chem. Soc.*, 1948, **70**, 30.