572. *Macrocyclic Compounds. Part IX.*[1] *Triple-bond Migration in Macrocyclic Alkadiynes*

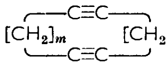
By A. J. Hubert and Johannes Dale

When macrocyclic alkadiynes (C_{12}—C_{20}) are treated with potassium t-butoxide in dimethyl sulphoxide at 40 and 80° extensive triple-bond migration takes place. Except for the smallest ring (C_{12}), the intermediate allenic compounds are only present in small amounts, and a stationary "equilibrium" state is established between diynes having the triple bonds separated by more than two CH_2-groups. The distribution of isomers in this quasi-equilibrium corresponds to that expected by conformational considerations. Finally, the diyne isomers are transformed into tricyclic olefins; this occurs rapidly when the triple bonds are close or when the ring is strained (C_{12}).

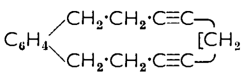
Other macrocyclic hydrocarbons (aromatic diacetylenes, cycloalkadienes) were also isomerised with the same base system.

It was shown previously[2] that a macrocylic hydrocarbon which contains two multiple bonds can have ideal conformations without angular or torsional strain and with a minimum of *gauche*-bonds only when the multiple bonds are of the same kind (either two triple bonds, or two *cis*- or two *trans*-double bonds) and when they are placed diametrically in 14-, 18-, 22-, 26-, etc., membered rings. Isomerisation of cycloalkadienes in the presence of triethylborane at 200° gave a composition of the equilibrium mixture[3] in agreement with this prediction, although the results were obscured by the concurrent *cis,trans*-isomerisation and migration, and the presence of a substantial portion of the not directly comparable conjugated dienes together with the non-conjugated dienes. It also proved to be difficult to effect equilibration over a temperature range large enough to permit evaluation of thermodynamic quantities.

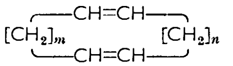
Clearly, the triple bond would be more suitable for a study of positional isomerism, as no stereoisomerism is possible, and also since the conjugated cycloalkadiyne, requiring a collinear arrangement of 6 carbon atoms, is likely to be absent in most of the rings involved, at least up to C_{16}. The base-catalysed migration of triple bonds in cycloalkadiynes at low temperatures has now been realised and is the subject of the present Paper. On the other hand, the pure *cis,trans*-isomerisation, without migration, of defined positional isomers of cycloalkadienes should also give a simplified picture and is currently being studied.



(I)



(II)



(III)

Treatment of macrocyclic diynes (I) with potassium t-butoxide in t-butyl alcohol was found[4] to be without effect at low temperatures and led to aromatisation above 160°. When the triple bond is separated by only two CH_2-groups from an unsaturated system, isomerisation to the conjugated 1,3-diene takes place already at 125° in large ring systems,[5] and at 65—70° in certain open chains.[6] On the other hand, it is known that in simple monoacetylenic hydrocarbons the triple bond can migrate from the terminal position to the 2-position by the influence of alcoholic potassium hydroxide[7,8] at 125—175°, or of

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[1] Part VIII, Dale, *J.*, 1965, 72.

[2] Part III, Dale, *J.*, 1963, 93.

[3] Part V, Hubert and Dale, *J.*, 1963, 4091.

[4] Part I, Dale, Hubert, and King, *J.*, 1963, 73.

[5] Part VI, Dale and Hubert, *J.*, 1963, 5475.

[6] Sondheimer, Ben-Efraim, and Wolovsky, *J. Amer. Chem. Soc.*, 1961, **83**, 1675.

[7] Jacobs, Akawie, and Cooper, *J. Amer. Chem. Soc.*, 1951, **73**, 1273.

[8] Wojtkowiak and Romanet, *Bull. Soc. chim. France*, 1962, 805.

sodamide,[9] and that the equilibrium is established through the intermediate 1,2-diene; [7,8] no conjugated dienes are formed although they are more stable than allenes. With potassium t-butoxide in t-butyl alcohol the equilibrium between the acetylenic and the allenic system in 9- to 11-membered rings could be established [10] at 80—120°, but of course one cannot here conclude whether migration has occurred or not. With the same base at 196° migration occurs [11] all through an open chain (C_7), and again the equilibrium mixture consists only of non-terminal acetylenes and allenes, and no conjugated diene.

In recent years extraordinary rate increases of carbanion reactions have been observed when the alcoholic solvent is replaced by dimethyl sulphoxide or similar aprotic proton-accepting solvents. Many reactions, which otherwise require drastic conditions, can thus be made to proceed at room temperature, *e.g.*, isomerisation of simple olefins [12] and of polyunsaturated fatty acids,[13] rearrangement of allyl ethers,[14] hydrogen exchange in α-position to nitriles, amides, esters, and phenyl groups,[15] Wolff–Kishner reduction,[16] etc.

We now find that the larger macrocyclic alkadiynes are readily isomerised with potassium t-butoxide in dimethyl sulphoxide at 40° to a stationary quasi-equilibrium mixture of diyne and allene isomers, without the formation of recognisable quantities of conjugated diene or tetraene systems in the unchanged monocyclic skeleton. As only small amounts of allenes are present in this " equilibrium " when the ring size is larger than C_{12}, the method is well suited for a study of triple-bond migration. In the 12-membered ring the amount of allenic isomers is much higher, and such products undergo secondary (transannular) reactions so rapidly that a diyne " equilibrium " is never reached. Such side reactions occur also finally in the higher members, but usually (see below) very slowly compared with the time needed for establishment of the diyne " equilibrium."

To follow the progress of the isomerisation two complementary methods were used. The hydrocarbon mixture was first analysed directly by gas chromatography; only in simple cases were the individual diynes sufficienty resolved to allow identification by comparison with pure isomers obtained by synthesis, but the amount of intermediate (allenic) and final secondary products could always be determined. The distribution of diyne isomers was then determined by ozonolysis of the corresponding diene mixture obtained after partial reduction; the ozonisation products were reduced with sodium borohydride and the acetylated diols analysed by gas chromatography.[17] For the ring sizes C_{14} and C_{16} it was verified that the same " equilibrium " was reached starting from different positional isomers; only when the triple bonds are too close ($m = 2$) were the secondary products formed so fast that no diyne equilibrium could be reached.

The results at 40° are given in Table 1 and partly in the form of typical gas chromatograms in Figure 1. The expected strong preference for the symmetrical isomer in the 14-membered ring, the somewhat less conspicuous preference in the larger and more flexible 18-membered ring, as well as the expected lack of preference for the symmetrical isomer in the 16- and 20-membered rings, are all convincingly borne out and support the unique ideal conformations of type (*a*) in Figure 2, possible only when $m = n$ in (I) is odd. For the 16- and 20-membered rings one might have expected a similar preference for the unsymmetrical isomers having odd $n = m + 2$, as these can have conformations of the type (*b*) in Figure 2 which are strain-free, although open and containing two unfavourable *gauche*-bonds within the saturated chain. It was found, however, that the next isomer, having even $n = m + 4$, is about as preponderant at equilibrium, although its best

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[9] Bainvel, Wojtkowiak, and Romanet, *Bull. Soc. chim. France*, 1963, 978.

[10] Moore and Ward, *J. Amer. Chem. Soc.*, 1963, **85**, 86.

[11] Smadja, *Compt. rend.*, 1963, **256**, 2426.

[12] Schriesheim *et al.*, *J. Amer. Chem. Soc.*, 1961, **83**, 3731; 1962, **84**, 3160, 3164; *Tetrahedron Letters*, 1962, 405.

[13] Ugelstad, Jenssen, and Mörk, *Acta Chem. Scand.*, 1962, **16**, 323.

[14] Price and Snyder, *J. Amer. Chem. Soc.*, 1961, **83**, 1773.

[15] Cram *et al.*, *J. Amer. Chem. Soc.*, 1960, **82**, 6412; 1961, **83**, 3678, 3688.

[16] Cram, Sahyun, and Knox, *J. Amer. Chem. Soc.*, 1962, **84**, 1734.

[17] Part IV, Hubert, *J.*, 1963, 40.

TABLE 1

Isomerisation at 40° of cycloalkadiynes (I) with potassium t-butoxide in dimethyl sulphoxide

Ring size	Starting diyne (I) *m*-*n*	Re-action time (hr.)	Approx. distribution (%) of all isom. products (by direct gas chromatography) Total diynes	" Allenic " inter-mediates	Final products	Distribution (%) of diyne isomers (by ozonolysis)						
						m-*n*:	4—5	3—6	2—7	1—8		
C_{13}	4—5	¼	90	3	7		97	3	—	—		
		½	85	4	11		96	4	—	—		
		1	83	4	13		97	3	—	—		
		2	78	4	18		93	6	2	—		
		4	72	4	24		92	5	3	1		
		8					95	5	—	—		
		24	16	—	84		91	9	—	—		
						m-*n*:	5-5 *	4—6	3—7	2—8		
C_{14}	5—5 (4—6)	¼	92(95)	8(6)	—(—)		96(25)	4(70)	—(4)	—(1)		
		½	95(91)	5(9)	—(—)		96(44)	4(50)	—(4)	—(2)		
		1	93(91)	7(9)	—(—)		96(64)	4(33)	—(3)	—(1)		
		2	93(93)	7(5)	—(2)		95(79)	5(16)	—(3)	—(2)		
		4	90(91)	6(3)	4(6)		94(84)	6(12)	—(1)	—(2)		
		8	87(87)	8(2)	5(11)		92(88)	8(11)	—(1)	—(—)		
		24	78(78)	5(1)	17(21)		91	9				
						m-*n*:	5—5 *	4—6	3—7	2—8		
C_{14}	2—8 (3—7)	¼	35	45 ‡	20		7	5	15	72		
		½	10	55	35							
		1	1	50	50							
		2	0(74)	35(1)	65(25)		—(73)	—(19)	—(8)	—(—)		
						m-*n*:	5—6	4—7	3—8	2—9		
C_{15}	5—6	½	91	9 †	—		96	4	—			
		1	90	10	—		90	10	—			
		2	88	12	—		83	13	4			
		4	86	12	2		83	14	3			
		8	82	13	5		82	15	3			
		24	63	9	28		80	16	4			
		48	39	9	52							
						m-*n*:	6—6 *	5—7	4—8	3—9		
C_{16}	6—6 (4—8)	½	83(86)	17(14) †	—(—)		91(2)	9(13)	—(80)	—(5)		
		1	86(83)	13(15)	1(2)		84	16	—	—		
		2	86(80)	12(15)	2(5)		66(3)	29(26)	5(61)	—(11)		
		4	82(74)	14(14)	4(12)		44(4)	41(37)	14(52)	2(8)		
		8	70(57)	11(12)	19(31)		22(7)	47(45)	28(41)	4(7)		
		24	56	9	35		10(9)	42(46)	38(38)	11(8)		
						m-*n*:	7—7 *	6—8	5—9	4—10	3—11	
C_{18}	7—7	½	90	8 †	2		90	10	—	—	—	
		1	89	9	2		89	11	—	—	—	
		2	88	9	3		82	18	—	—	—	
		4	83	10	7		69	28	2	—	—	
		8	83	8	9		58	26	9	7	—	
		24	60	9	31		53	27	8	~9	3	
		48	42	6	52		49	29	11	~7	4	
						m-*n*:	8—8 *	7—9	6—10	5—11	4—12	3—13
C_{20}	8—8	½					89	11	—	—	—	—
		1					77	19	3	2	—	—
		2					49	41	7	4	—	—
		4					29	49	19	4	—	—
		8					19	37	27	11	4	2
		48					11	37	31	12	6	3

* The symmetrical isomers are statistically half as probable as the asymmetrical ones. † This fraction may also in part contain diyne isomers as the allenic infrared abs. intensity is low. ‡ Several additional intermediate products were observed with this isomer, but the final product was the same.

conformation of type (*c*) in Figure 2 has a somewhat strained skeleton. It is likely that this disadvantage is compensated by its compact structure (favourable internal van der Waals' contacts) and the presence of only one unfavourable *gauche*-bond within the saturated chain. The two odd-membered rings, C_{13} and C_{15}, follow quite closely the behaviour of the neighbouring 14-membered ring (although the symmetrical isomers are relatively less favoured energetically considering the different statistical factor) and not that of the 12- and 16-membered rings, respectively. At least in the latter case this may be taken as a demonstration that the two main isomers of the 16-membered ring have less favourable conformations than the main isomer of the 14-membered ring.

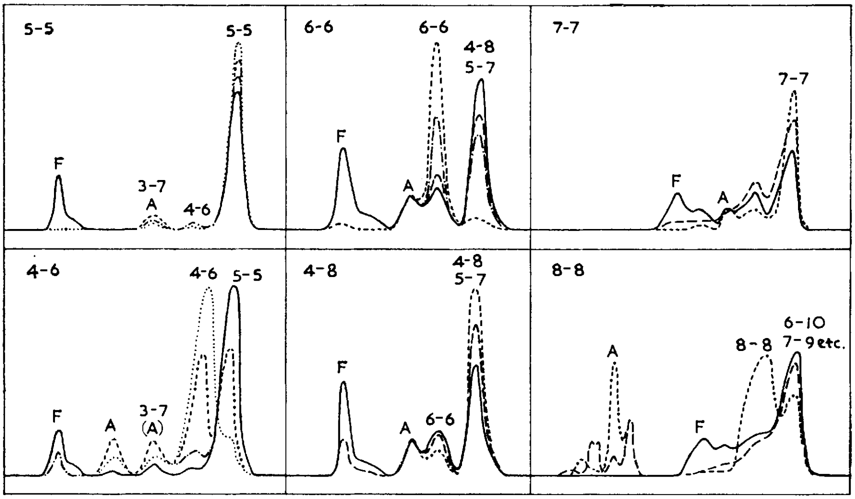
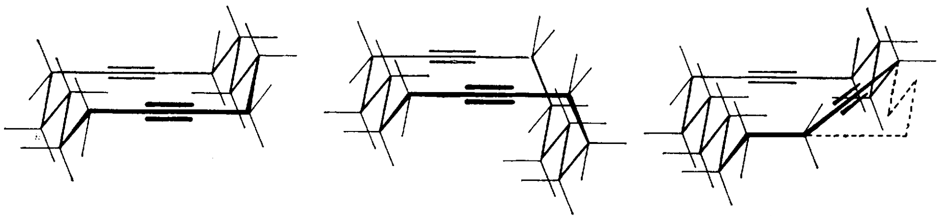


FIGURE 1. Typical gas chromatograms of the hydrocarbon mixtures obtained after isomerisation of cycloalkadiynes (I) with potassium t-butoxide in dimethyl sulphoxide at 40° for 5 min.) (· · · ·), 1 hr. (– – – –), 4 hr. (— · — · —), 8 hr. (— — —), and 24 hr. (———). The starting isomer is designated (*m*-*n*) in the upper left corner; the peaks due to diyne isomers are marked with the corresponding *m*-*n*; allenic intermediates are marked (A), and final products (F)



(*a*) (odd) $n = m$ (*b*) (odd) $n = m + 2$ (*c*) (even) $n = m + 4$

FIGURE 2. Suggested conformational types of thermodynamically favoured cycloalkadiynes (I), exemplified by (*a*) cyclotetradeca-1,8-diyne ($m = n = 5$), by (*b*) cyclohexadeca-1,8-diyne ($m = 5$, $n = 7$), and by (*c*) cyclohexadeca-1,7-diyne ($m = 4$, $n = 8$)

The 14- and 16-membered cycloalkadiynes have been isomerised also at 80° (Table 2). The reaction was much faster and the " equilibrium " was reached in one hour instead of in 24 hours at 40°. In the 14-membered ring the equilibrium composition is quite sensitive to the temperature, and a rough estimation gives as a result that the symmetrical isomer ($m = n = 5$) is more stable (in enthalpy) than the next isomer ($m = 4$; $n = 6$) by as much as 4·6 kcal./mole, although the free energy difference at 60° is only 1·3 kcal./mole. This

TABLE 2

Isomerisation at 80° of symmetrical cycloalkadiynes (I; $m = n$)

Ring size	Starting diyne ($m = n$)	Reaction time (min.)	Distribution (%) of diyne isomers (by ozonolysis)				
			m-n:	5—5	4—6	3—7	
C_{14}	5	10		83	17	—	
		20		82	12	6	
		80		79	18	4	
			[Equil. at 40°:	91	9	—]	
			m-n:	6—6	5—7	4—8	3—9
C_{16}	6	10		22	44	31	3
		20		15	46	35	3
		80		13	43	38	7
			[Equil. at 40°:	10	44	38	9]

means that the symmetrical isomer is disfavoured by a much lower entropy (10·1 e.u.), of which only a small part ($\boldsymbol{R}\ln 2 = 1{\cdot}4$ e.u.) is due to the different statistical factor. Thus, the symmetrical isomer proves to be more rigid and/or conformationally more homogeneous, as already postulated. On the other hand, the equilibrium composition for the 16-membered ring was, within the experimental error, the same at the two temperatures. This means, of course, that enthalpy differences between these isomers must be small, but also the entropy differences turn out to be much smaller here. Hence, none of the observed isomers of this ring size is very much more stable or rigid than any other.

In the gas-chromatographic behaviour (Figure 1) it is of interest to note that the more stable diyne isomers of all ring sizes are also those with the longest retention times. It may be that a stronger polarity of the triple bond in the stable isomers results from its location close to " corners," that is, in the " bridges " in a cisoid or gauchoid conformation (Figure 2), and that the less favourable isomers have the triple bonds less exposed in a transoid conformation in the " long-chains."

It should also be noted that within those isomer sets of which several members have been synthesised, there is a striking parallelism between preponderance at equilibrium of an isomer and its melting temperature (Table 3), proving the point made earlier [2] that, in the absence of intermolecular polar forces, a high melting point is to a very large extent a consequence of conformational stability. It is particularly important that the melting point of the symmetrical cyclohexadecadiyne isomer is lower than the melting points of the known unsymmetrical ones. Also the yield in the synthesis of these isomers under comparable conditions follows the same trend (Table 3) in the case of the 14-membered ring, in agreement with the idea [2,4] that when a ring has a good conformation, it may be almost preformed in the last cyclisation step.

TABLE 3

Relation between melting point, preponderance in equilibrium, and yield in synthesis of cycloalkadiyne isomers (I)

C_{14}	m-n:	5—5 [4]	4—6 [4]	3—7	2—8 [3]	
	Yield in synthesis (%):	57	16—19	1	7	
	M. p.:	98°	30°	liq.	10—12°	
	% in equilibrium:	90	10	~1	(0)	
C_{16}	m-n:	6—6 [4]	5—7 [4]	4—8	3—9	2—8
	Yield in synthesis (%):	23	10	13		
	M. p.:	−3·5°	27·5°	27—30°		
	% in equilibrium:	10	44	38	9	(0)

The allenic nature of the intermediate products was proved by the infrared absorption [18] at 5·10 and 11·45 μ of gas-chromatographically isolated fractions (peaks A of Figure 1).

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[18] Moore and Bertelson, *J. Org. Chem.*, 1962, **27**, 4182.

The final products form more rapidly the less diametrically the triple bonds are placed (Table 1) and the fact that the diyne (I; $m = 2$, $n = 8$) is not a constituent of, and does not produce, the diyne equilibrium mixture, but gives rapidly the final product, indicates that this isomer is the direct precursor, or is very close to it. In the case of this 14-membered ring the final product (peak F of Figure 1) was isolated by preparative gas chromatography and adsorption chromatography on alumina and shown by infrared and ultraviolet spectroscopy, as well as by quantitative hydrogenation, and by analysis and n.m.r. spectroscopy of the hydrogenated products, to contain a tricyclic skeleton and a non-aromatic chromophore. Logically, this chromophore should be a diene, but the ultraviolet maxima at 210 and 258 mμ (ε 16,500, 3600) resemble more those of a cycloheptatriene system,[19] as do the infrared spectral bands at 6·15 and 6·50 μ.[20] The final isomerisation product from the 16-membered ring was also shown by infrared spectroscopy to contain double bonds, and no allene, acetylene, or aromatic systems. In the 12-membered ring, the intermediate formation of large amounts of an allenic hydrocarbon was followed by at least three final products; these are also olefinic, and the spectral similarities with the product from the 14-membered ring are striking. It is remarkable that benzocycloalkenes, which are the only end products when the isomerisation is carried out in t-butyl alcohol at 160°,[4] are not observed when dimethyl sulphoxide is the solvent. It may well be that this is connected with the absence of conjugated di- and tetra-enes, which in particular cases have been shown [5] to precede aromatisation when t-butyl alcohol is the solvent. As the triple bonds are close when the final product is formed, it is also difficult to see how aromatisation can be avoided after the first transannular bridge has been formed, if one ring is 6-membered. One may therefore have to look for a reaction mechanism by which the first bridge is formed between positions 1 and 5 or 1 and 7, or by which two bridges are formed at the same time.

A striking difference in the nature of the reaction in the two solvents is also observed for the aromatic macrocyclic diynes of the type (II). It has already been established [5] that potassium t-butoxide in t-butyl alcohol converts first the $\cdot CH_2\cdot CH_2\cdot C{\equiv}C\cdot$-group into a *cis,cis*-CH=CH·CH=CH-group, which starts out being conjugated with the aromatic nucleus and then migrates to a larger or lesser extent. Two members (*p*-phenylene, $m = 6$; *o*-phenylene, $m = 8$) were now treated with t-butoxide in dimethyl sulphoxide at 40°. Maximal ultraviolet absorption was observed after 4 hr., and direct ozonolysis in the presence of an added internal standard showed that approximately the same fragments are formed (triple bonds are not ruptured under these conditions), but in smaller quantities than after isomerisation in t-butyl alcohol until maximal ultraviolet absorption was reached (Table 4). On the other hand, when the remaining triple bonds were partially reduced to double bonds before ozonolysis, it was found that the additional fragments corresponded to a mixture of isomeric diynes and dienynes. The exact distribution of isomers was difficult to establish because of overlapping peaks in the gas chromatogram of the diol fragments. It is clear, however, that in this case the triple bonds migrate as such faster than they can be isomerised to conjugated dienes. As no conjugated diene systems are formed at all in simple acetylenic compounds, it may be concluded that this

TABLE 4

Maximum amount of tetraenes by potassium t-butoxide isomerisation of aromatic diynes (II)

	4 hr. at 40° in dimethyl sulphoxide	4 hr. at 125° in t-butyl alcohol
From IV, *p*-phenylene, $n = 6$	~20%	~100%
From IV, *o*-phenylene, $n = 8$	~20	~70

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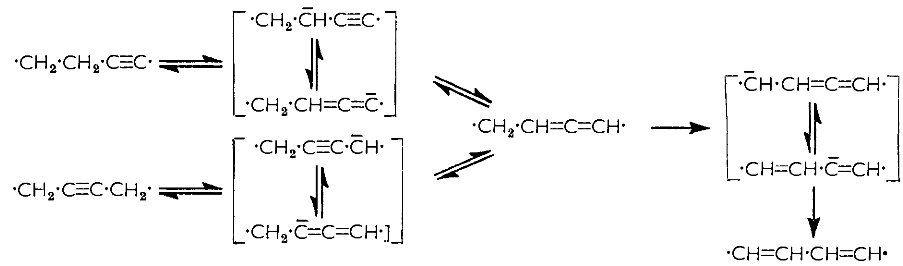
[19] Cope and D'Addieco, *J. Amer. Chem. Soc.*, 1951, **73**, 3419; Cope, Nelson, and Smith, *ibid.*, 1954, **76**, 1100; Alder, Kaiser, and Schumacher, *Annalen*, 1957, **602**, 82.

[20] Evans and Lord, *J. Amer. Chem. Soc.*, 1960, **82**, 1876.

occurs only when an intermediate allene is separated from the aromatic nucleus by one doubly activated CH_2 group. In the following Scheme for the reaction mechanism[7] of the migration process,



this means that while normally a hydrogen atom in α-position to the intermediate allene is less acidic than the olefinic hydrogen of the allene itself, a double activation makes the acidities comparable, and the more stable conjugated diene is formed irreversibly. As hydrogen atoms on normal double bonds are less acidic than those in α-position, the high acidity of allenic hydrogens is at first surprising, but considering that the anion formed is identical with the anion formed from an acetylene, it may simply be a consequence of the recognised higher activity of propargylic, compared with allylic, hydrogen.[21] Similarly, the irreversibility of the formation of the conjugated diene may be linked with the low acidity of the olefinic hydrogens compared with those in α-position; the favoured pentadienyl anions can only lead to migration of the group, or deconjugation.

The macrocyclic alkadienes (III) were finally also treated with potassium t-butoxide in dimethyl sulphoxide, but, in contrast with medium ring alkadienes, which are isomerised[22] at 70°, it was necessary to work at 100° in order to get sufficiently extensive migration, and at that temperature some decomposition both of the solvent and of the dienes occurs. The conjugated cycloalkadienes (m = 0) are especially sensitive, and when these were the starting materials, only ~5% of hydrocarbons could be recovered after 24 hr. The results in Table 5 do not therefore represent a true equilibrium composition as do the results obtained earlier with triethylborane at 200°, but the distribution of non-conjugated isomers in the stationary state is nevertheless strikingly similar to that obtained with triethylborane, and indicates that these isomers are in true equilibrium with each other, and that no specific action of the catalyst influences the equilibrium.

TABLE 5

Isomerisation of cycloalkadienes (III) with potassium t-butoxide in dimethyl sulphoxide for 24 hr. at 100°

Ring size	Starting diene (V) *m-n*	Volatile by-product (% of recovered hydrocarbons)		Distribution of diene isomers (% by ozonolysis)							
			m-n:	4—5	3—6	2—7	1—8	0—9			
C_{13}	4—5	11		27	27	23	2	21			
			m-n:	5—5	4—6	3—7	2—8	1—9	0—10		
C_{14}	5—5	0		49	25	10	5	3	10		
			m-n:	6—6	5—7	4—8	3—9	2—10	1—11	0—12	
C_{16}	6—6	9		16	36	32	9	3	0	3	
			m-n:	7—7	6—8	5—9	4—10	3—11	2—12	1—13	0—14
C_{18}	7—7	0		25	28	21	16	6	1	0	3

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[21] Peiffer, *Compt. rend.*, 1963, **257**, 3605.

[22] Devaprabhakara, Cardenas, and Gardner, *J. Amer. Chem. Soc.*, 1963, **85**, 1553.

EXPERIMENTAL

Preparation of Cycloalkadiynes (I).—Most of these have been described already,[4] but two additional members have now been prepared by the same method. *Cyclotetradeca*-1,6-*diyne* (I; $m = 3, n = 7$) was obtained (1%) from hepta-1,6-diyne and 1,7-dibromoheptane as a liquid, b. p. $\sim$100°/0·01 mm., showing no infrared bands for ·C≡CH, but containing probably a little bromide (Found: C, 87·6; H, 10·5. $C_{14}H_{20}$ requires C, 89·3; H, 10·7%). *Cyclohexadeca*-1,7-*diyne* (I; $m = 4$, $n = 8$) was obtained (13%) from dodeca-1,11-diyne and 1,4-dibromobutane. After recrystallisation from ethanol it melted at 27—30° and showed no infrared bands for C≡CH (Found: C, 88·8; H, 11·1. $C_{16}H_{24}$ requires C, 88·8; H, 11·2%). After partial reduction on a Lindlar catalyst and ozonolysis with subsequent reduction and acetylation [17] only the fragments AcO·$[CH_2]_6$·OAc and AcO·$[CH_2]_{10}$·OAc were detected by gas chromatography.

Isomerisation Procedure.—A saturated solution (90 ml.) of sublimed potassium t-butoxide in dimethyl sulphoxide [12] was added to a solution of the cycloalkadiyne ($\sim$2 g.) in pyridine (10 ml.), the pyridine being needed to avoid precipitation of the higher diynes in pure dimethyl sulphoxide. A deep blue-red colour appeared within a few minutes; this colour development was characteristic for each particular diyne. It was slower for the higher diynes than for those of lower molecular weight, and in the 14-membered set, as an example, the less stable 1,7-isomer gave an instantaneous deep coloration, whereas the more stable 1,8-isomer required a longer time to develop colour. The mixture was kept under argon in a thermostat at the required temperature. Samples were withdrawn at intervals with a pipette under a current of argon and poured into water. The resulting milky suspension was extracted with ether (when hexane was used the recovery was incomplete, and erratic results were obtained) and the extract analysed by isothermal gas chromatography [F & M, 500 instrument, thermal conductivity detector, ¼ in. × 8 ft. poly(diethylene glycol succinate) column (40% on 60—80 mesh Embacel) at 180—210°] and also by ozonolysis after partial reduction of the triple to double bonds; the "ozonides" were as usual [17] reduced by sodium borohydride and acetylated before gas chromatography on a Silicone gum rubber column using temperature programming.

Reproducibility of the catalyst system was difficult to achieve; two different preparations can show quite different activity towards the same acetylenic compound and the time required to reach equilibrium may vary widely. When a set of positionally isomeric cycloalkadiynes was available (C_{14}, C_{16}) the same catalyst preparation was used in order to simplify comparison.

To verify that there was no loss of hydrocarbon (*e.g.*, by polymerisation or reaction with the solvent) the isomerisation was in several cases (Table 6) carried out in the presence of an inert internal standard which had a volatility suitable for the subsequent gas-chromatographic analysis.

TABLE 6

Recovery of hydrocarbons from isomerised cycloalkadiynes (I) as determined by gas chromatography

Cycloalkadiyne (I)		Internal standard	Total isomerised hydrocarbons recovered (%) after x minutes at 40°								
m	n		$x = 5$	10	30	60	120	240	500	1400	4300
5	5	Acenaphthene	96	—	—	96	101	103	91	98	98
4	6	,,	106	102	97	98	96	108	109	104	100
6	6	Diphenylbutane	97	97	101	98	98	95	93	81	73
7	7	Bibenzyl	—	107	100	100	106	100	95	81	60

The gas chromatograms of the ozonolysis products were in some cases complicated by a too-strong intensity of one of the two fragments to which one particular unsymmetrical diyne isomer (after reduction) gives rise. This is probably due to the ozonolysis of allenic intermediates, or olefinic substances. In the case of cycloeicosa-1,11-diyne (I; $m = n = 8$) a group of non-diynic isomerisation products (peak A in Figure 1) was isolated by gas chromatography; it showed allenic absorption at 5·10 μ and olefinic absorption at 6·10 μ and gave in fact an ozonolysis product with retention time corresponding to the anomalously strong peak of the mixture. Similarly, after 6 hours' isomerisation at 40°, in addition to a diyne fraction, the intermediate product from cyclohexadeca-1,9-diyne (I; $m = n = 6$) was also isolated (peak A in Figure 1); it showed allenic infrared bands at 5·11 and 11·44 μ. However, in most of these cases (except the 12-membered ring) the quantity of allenes present was small and rarely disturbed the analysis of diynes. Only in the case of cyclododeca-1,7-diyne (I; $m = n = 4$) was it impossible to determine the diyne equilibrium. The diyne decomposed by direct gas chromatography as such, and already after 20 min. isomerisation at 40°, a large amount (56%) of an allenic liquid substance was isolated by gas chromatography on poly(diethylene glycol succinate). The infrared spectrum showed the typical [18] allene bands at 5·10, 11·43, and 13·87 μ; other strong bands were at 12·36 and 12·53 μ. Three weak peaks appeared in front of the "allene peak"; already after isomerisation for 4 hr. these were the main peaks and the allene had almost disappeared.

Characterisation of the Final Isomerisation Products.—(*a*) *Cyclododeca*-1,7-*diyne.* Whether isomerisation at 40° lasted for 5, 18, or 64 hr., the gas chromatograms were very similar. The three main peaks, eluted first, were collected together. They showed no allenic infrared band, as did the fourth peak (now very weak), but olefinic bands at 3·35 and 6·20 μ, and further bands at 6·55, 10·40, 12·25, 13·65 (strong), 14·0, and 14·4 μ. Ultraviolet maxima (in hexane) were at ~210sh and 257 mμ (ε 6200, 1350).

(*b*) *Cyclotetradeca*-1,8-*diyne.* After isomerisation for 72 hr. at 40° the crude product showed ultraviolet maxima at 210 and 260 mμ (ε 14,000, 3200). Gas chromatography showed, in order of decreasing retention time (cf. Figure 1), the presence of 52·5% 1,8-diyne, 2·5% 1,7-diyne, 2·0% 1,6-diyne (and allenic intermediate), and 43·5% of the unknown final product. By absorption chromatography on alumina (activity 1) this products was eluted first with hexane. It showed by gas chromatography one large peak with a shoulder; infrared bands typical for double bonds at 3·33 and 6·15 μ, another band at 6·50, and strong bands at 12·7, 13·1, 13·3, and 13·5 μ; and ultraviolet maxima (in hexane) at 210 and 258 mμ (ε 16,500, 3600). Complete hydrogenation on PtO_2 in hexane gave a liquid which also showed a shoulder in the gas chromatogram; the skeletons of the two products are therefore different and different from cyclotetradecane. Analysis showed the skeleton to be tricyclic (Found: C, 87·3; H, 12·7. $C_{14}H_{24}$ requires C, 87·4; H, 12·6%). Only traces of olefinic infrared bands and no ultraviolet absorption was found. The n.m.r.-spectrum was not well resolved but the ratio of tertiary to secondary protons was about 4 to 20, to be expected for a tricyclic skeleton.

(*c*) *Cyclohexadeca*-1,9-*diyne.* Preparative gas chromatography allowed the isolation of the final product, eluted first (peak F of Figure 1), which appeared after long reaction times (72 hr.). It could also be isolated by chromatography on alumina and was eluted first with hexane. Olefinic infrared bands were at 3·35sh, 6·00, and 6·34 μ; stronger bands were at 13·4 and 13·6 μ.

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