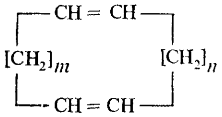
Macrocyclic Compounds. Part XIII.[1] Isomerisation of Macrocyclic Alkadienes by Potassium Dispersed on Alumina

By **A. J. Hubert** and **Johannes Dale,** Union Carbide, European Research Associates, 95 Rue Gatti de Gamond, Brussels 18, Belgium

Data for the isomerisation at 25° of cyclic alkadienes with ring sizes from C_{10} to C_{26} complements the data obtained earlier (200°) with triethylborane as catalyst. Although no true equilibrium could be reached on the potassium–alumina catalyst used (the conjugated isomer was slowly reduced to the cyclic alkene), the positional isomer distribution in the stationary state confirms that conformational preferences for certain isomers are more accentuated at this low temperature.

THE combined positional and configurational isomerisation of the double bonds in macrocyclic alkadienes (I) at 200°, in the presence of triethylborane, led to an equilibrium mixture the nature of the components of which depended on the original ring size, in agreement with conformational predictions.[2] However, we wished [2] to establish the equilibrium at a lower temperature in order to permit calculation of enthalpy and entropy differences between the various isomers of each ring size. It was expected that conformational preferences would be more pronounced at this lower temperature.



(I)

In the meantime the problem has been simplified by studying on the one hand the pure positional isomerisation of the triple bonds in macrocyclic alkadiynes at 40 and 80° in the presence of potassium t-butoxide in dimethyl sulphoxide,[3] and on the other hand the pure configurational isomerisation of the double bonds in symmetrical, or diametrical, macrocyclic alkadienes (I; $m = n$) at 25 and 75° by irradiation in the presence of diphenyl disulphide.[1] In both cases the conformational effects were more striking and clearcut.

Of several catalysts tried the only one which isomerised olefins at room temperature sufficiently rapidly was the so-called 'high-surface sodium,' a dispersion of sodium on alumina.[4,5] With the macrocyclic alkadienes this catalyst was less active, but a dispersion of 2—5% potassium on alumina was satisfactory. Unfortunately, the conjugated isomer was reduced slowly to the cyclic alkene, and this side reaction, which has been studied more completely and developed into a catalytic partial hydrogenation method for conjugated diolefins, prevented the attainment of a true equilibrium. Thermodynamic quantities could not therefore be calculated. Nevertheless, in an atmosphere of nitrogen, after the side reaction had exhausted the alumina of active hydrogen, a stationary 'equilibrium state' between the diene isomers was obtained at 25°. Quantitative ozonolysis [6] indicated the amount of alkene as well as the diene isomer distribution, which provided information about relative stabilities of the positional isomers. The erratic values for the conjugated dienes and the alkenes are probably due to the heterogeneity of the reaction mixture; solid potassium derivatives might have furnished more or less of these compounds after hydrolysis. The kinetic results are presented in the Table, and the isomer composition is compared with that obtained [2] for the equilibrium at 200°.

The data in the Table show that the situation at 25° is in general not greatly different from that at 200°. Those rings which gave the highest proportion of conjugated isomer at 200° gave even more at 25°, even if this isomer were the one removed from the equilibrium by reduction to the alkene. This suggests that production of the conjugated isomer is favoured more by a low enthalpy than by a high entropy. In the series of even-membered rings, the conjugated isomers with 14, 18, and 22 ring atoms, for which relatively strain-free conformations are possible,[7] seem more dominant in the 'equilibrium' than those with 12, 16, and 20 members, for which strain-free conformations are not possible. The largest rings produce almost exclusively the conjugated isomer, like the acyclic alkadienes. From the 10-membered ring no conjugated isomer was formed under these conditions.

Among the non-conjugated isomers the 'diametrical' one ($m = n$) is the most stable from the 14-, 18-, 22-, and even the 26-membered ring (considering the statistical factor of $\frac{1}{2}$ for this isomer) and is formed in higher proportion than at 200°. This agrees with earlier conclusions [8] that only the diametrical *trans,trans*-isomers with these rings sizes can have a completely strain-free conformation and should therefore have low enthalpies (lack of tension) and low entropies (rigid and unique conformations). The fact (Table) that the diametrical isomer is not the dominant one from the 16-, 20-, and 24-membered rings, where it can have no strain-free conformation in either configuration also agrees with this. Instead, from these rings the two

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Isomerisation of cycloalkadienes (I) in heptane (2 g./100 ml.) on potassium–alumina (1·5 g./10 g.) at 25° under nitrogen

Ring size $(m + n + 4)$	Starting isomer		Distribution of positional isomers [a] after								
			¼ hr.	½ hr.	1 hr.	2 hr.	4 hr.	8 hr.	24 hr.	48 hr.	(At 200°) [b]
		m,n									
10	*cis,trans*-1,5-Diene $(m = 2, n = 4)$	3,3		100	100	100 (30°)					
		2,4									
		1,5									
		0,6									
		m,n									
12	*cis,cis*-1,7-Diene $(m = n = 4)$	4,4		77	62	51		44 (10 hr.)	25	7	(11)
		3,5		6·5	10	4		10	10	8	(16)
		2,6		13	22	39		44	68	75	(57)
		1,7						3			(6)
		0,8		3	6	5			1	10	(10)
		(Alkene [c])		(3)	(3)			(7)	(14)	(39)	
		m,n									
13	*cis,cis*-1,7-Diene $(m = 4, n = 5)$	4,5					7·5	7·5	8		(16)
		3,6					12	11	15		(23)
		2,7					11	10	13		(30)
		1,8					2	3	5		(6)
		0,9					68	68	58		(25)
		(Alkene [c])					(18)	(16)	(34)		
		m,n									
14	*cis,cis*-1,8-Diene $(m = n = 5)$	5,5	72	72	63	54	46	27	21	19	(14)
		4,6	9		8·5	6·5	5	3·5	3	3	(8)
		3,7	5·5		4	2·5	2·5	2	2·5	2·5	(6)
		2,8	4·5		3·5	3	3	3	3	2·5	(15)
		1,9								1·5	(7)
		0,10	8·5		22	34	44	64	69	72	(50)
		(Alkene [c])	(6)		(4)	(7)	(13)	(11)	(12)	(26)	
		ε_{236} [d]	1900	3000	4200	7900		13,600		14,100	
		m,n									
14	*cis,cis*-1,5-Diene $(m = 2, n = 8)$	5,5		15	23	28	25	22	14		
		4,6		7·5	6	5	4·5	3	2·5		
		3,7		29	15	6	3	2·5	1·5		
		2,8		17	13	6	3	2·5	2·5		
		1,9		0·5	0·1	0·1	1·5	1·5	2		
		0,10		32	43	55	63	68	78		
		(Alkene [c])		(8)	(8)	(16)	(15)	(18)	(35)		
		ε_{236} [d]		5800	8500	11,200		12,700	11,500		
		m,n									
14	*cis,trans*-1,3-Diene $(m = 0, n = 10)$	5,5					3	4	6		
		4,6					1·5	2	4		
		3,7					1	1			
		2,8					2	2·5	4·5		
		1,9					1·5	2·5	4		
		0,10					92	88	81		
		(Alkene [c])					(12)	(20)	(40)		
		m,n									
15	*cis,cis*-1,8-Diene $(m = 5, n = 6)$	5,6		35	28	18	10	8	7		(16)
		4,7		14	12	7	4	5·5	4·5		(9)
		3,8		14	4	3	3·5	3	2·5		(8)
		2,9		6	5	4·5	4	5	4·5		(10)
		1,10		1	2	3	3·5	4	2·5		(5)
		0,11		30	49	63	75	75	78	100	(52)
		(Alkene [c])		(8)	(11)	(14)	(21)	(28)	(42)	(77)	
		ε_{236} [d]		3900	7800	10,000	10,300	13,000	11,100	8100	
		m,n									
16	*cis,cis*-1,9-Diene $(m = n = 6)$	6,6	8	6	5·5	5	5·5	5·5	8		(5)
		5,7	31	28	26	17	11	8·5	13		(12)
		4,8	46	47	39	29	18	13	17		(14)
		3,9	7	7	5·5	4	2	2·5	7		(6)
		2,10	2·5	2·5	2	2	1·5	2·5	6		(9)
		1,11				1	1·5	2·5	6		(5)
		0,12	5	11	22	43	60	66	43		(48)
		(Alkene [c])	(24)	(26)	(30)	(32)	(38)	(52)	(68)		
		ε_{236} [d]	930	2000	3100	6000	9000	7500	3700		
		m,n									
18	*cis,cis*-1,10-Diene $(m = n = 7)$	7,7		26	22	16	7·5	3			(7)
		6,8		15	12	10	5	2·5			(9)
		5,9		8·5	8	6·5	3	2			(10)
		4,10		12	12	10	5·5	3·5			(10)
		3,11		5	6	5	2·5	1·5			(8)
		2,12		2·5	2	1·5	1·5	1			(9)
		1,13		0·5	1	1	1·5	1·5			(4)
		0,14		30	37	51	74	85	100		(45)
		(Alkene [c])		(4)	(6)	(7)	(9)	(15)	(40)		
		ε_{236} [d]			8300	14,500		20,300	13,300		

TABLE (*Continued*)

Ring size ($m + n + 4$)	Starting isomer		Distribution of position isomers[a] after								
			$\frac{1}{4}$ hr.	$\frac{1}{2}$ hr.	1 hr.	2 hr.	4 hr.	8 hr.	24 hr.	48 hr.	(At 200°)[b]
		m,n									
20	*cis,cis*-1,11-Diene ($m = n = 8$)	8,8		11	10	7·5	7·5	5·5	(7)		(5)
		7,9		31	29	25	24	21	(22)		(11)
		6,10		35	54	31	29	26	(27)		(11)
		5,11		11	10	10	10	9	(11)		(10)
		4,12		6	7	7·5	8·5	7·5	(9)		(8)
		3,13		3·5	4·5	5·5	5·5	5·5	(7)		(7)
		2,14		1	1	1·5	1	2	(6)		(9)
		1,15									(4)
		0,16		2	4	11	15	24	(11)		(35)
		(Alkene[c])		(2)	(4)	(6)	(10)	(22)	(77)		
		ε_{236}[d]		550	1250	1950	3650		2700		
		m,n									
22	*cis,cis*-1,12-Diene ($m = n = 9$)	9,9		20	19	14	9	7			(3)
		8,10		21	18	14	8	5·5			(6)
		7,11		14	13	11	8	3			(7)
		6,12		17	17	13	10	4·5			(7)
		5,13		10	8·5	7·5	3	3			(6)
		4,14		6·5	4	4	2·5	1·5			(5)
		3,15		3	3	2	1	0·5			(6)
		2,16		1	1·5	0·5	0·1				(10)
		1,17		0·5		0·5					(5)
		0,18		8	16	34	56	77	100		(45)
		(Alkene[c])		(6)	(6)	(12)	(16)	(30)	(57)		
		ε_{236}[d]		2000		8600	12,200				
		m,n									
24	*cis,cis*-1,13-Diene ($m = n = 10$)	10,10			7·5	5·55	4				
		9,11			21	14	9				
		8,12			20	13	8				
		7,13			11	7	4				
		6,14			9	6·5	4				
		5,15			8	5	3				
		4,16			4	3	2				
		3,17			2	1·5	1				
		2,18			0·5	0·5	0·5				
		1,19				0·5	0·5				
		0,20			17	43	63		100		
		(Alkene[c])			(4)	(6)	(10)		(52)		
		ε_{236}[d]		3500	7000	10,000	1,5600	11,300	7800		
		m,n									
26	*cis,cis*-1,14-Diene ($m = n = 11$)	11,11		13	12	8	9	6			
		10,12		22	16	16	12	9			
		9,13		17	14	14	10	6·5			
		8,14		16	14	14	11	9			
		7,15		11	12	11	7	5			
		6,16		6·5	7·5	7	5	3·5			
		5,17		5·5	7	6	4·5	3			
		4,18		2·5	3·5	2·5	2	2			
		3,19		1	1	1	0·5	0·5			
		2,20		0·5	0·5						
		1,21									
		0,22		4	13	21	39	56	100		
		(Alkene[c])	(1)	(7)	(10)	(25)	(32)	(32)	(58)		
		ε_{236}[d]		2300	3100	4300	6900		4400		

[a] Per cent. of total dienes, excluding formed alkene. [b] With triethyl borane as catalyst. [c] Per cent. of total hydrocarbons. [d] Determined on total hydrocarbons.

'next-to-diametrical' isomers ($n = m + 2$ and $n = m + 4$) are predominant, exactly as was found for the corresponding macrocyclic alkadiynes.[3] In fact, the similarity between the positional isomer distribution observed for the equilibrium of non-conjugated cyclic alkadienes and that for the corresponding cyclic alkadiynes suggests that the double bonds have mainly the *trans*-configuration, because this configuration, with a centre of symmetry, is sterically most similar to the triple bond.

The situation for the 14-membered ring is of particular interest, as in all previous studies of this series this is the ring size where conformational effects show up most strikingly. For this ring it was demonstrated that an 'equilibrium state' could be approached starting from five different isomers (Table); even the conjugated isomer could be in part deconjugated, in spite of the side reaction this isomer undergoes. The data in the Table show that the ratio between the concentrations of the conformationally 'good' isomers ($m = 0$, $n = 10$, and $m = n = 5$) and the conformationally 'bad' ones is increased greatly by lowering the temperature. This means that at 200° the high entropy of the latter isomers starts to compete with the low enthalpy of the former in determining the equilibrium.

An interesting phenomenon was revealed by the kinetic data in the Table for the *cis,cis*-cyclotetradeca-1,5-diene ($m = 2$, $n = 8$). The 1,6-isomer ($m = 3$, $n = 7$) accumulated during the early stages of the reaction, and its concentration even surpassed that of the 1,5-isomer, although in the final 'equilibrium' its concentration is smaller. It appears that, while in the initial stage the *cis,cis*-1,5-isomer may be isomerised particularly easily into a 1,6-isomer of some particular configuration, the dominant configurations of these positional isomers may at the end be entirely different. Similar effects have been observed in the isomerisation of but-1-ene,[4,9] pent-1-ene,[4] and some n-octenes;[10] thus, but-1-ene gives initially 96% of *cis*-but-2-ene,[9] although *trans*-but-2-ene is by far the most preponderant in the equilibrium. It is also seen (Table) that the 1,7- and 1,8-isomers are first formed from cyclotetradeca-1,5-diene in amounts greater than the equilibrium quantities, whereas this is not the case for the formation of 1,4- and 1,3-dienes. It thus appears that there is a larger barrier on the short path to the conjugated isomer than on the longer path to the diametrical isomer.

Similarly, during the early stages of the isomerisation of *cis,cis*-cyclodocosa-1,12-diene ($m = n = 9$) the quantity of 1,11-isomer formed ($m = 8$, $n = 10$) slightly exceeds that of the 1,12-isomer, although at 'equilibrium' it is the other way round (Table). Here the explanation would be that at equilibrium only 2·8% of the 1,12-isomer has the original *cis,cis*-configuration, as shown earlier.[1]

For the 10-membered system, the only isomer present at equilibrium was the cyclodeca-1,6-diene ($m = n = 3$), and it proved to have the *cis,cis*-configuration. The particular conformational stability of this isomer has already been discussed;[4] it was formed quickly and quantitatively from the *cis,trans*-1,5-diene on the potassium–alumina catalyst (Table).

EXPERIMENTAL

Materials.—The *cis,cis*-cycloalkadienes were prepared as already described [1,2,11] by Lindlar reduction of the corresponding diynes. *cis,trans*-Cyclotetradeca-1,3-diene was isolated from the isomer mixture.[2] *cis,trans*-Cyclodeca-1,5-diene was prepared from butadiene and ethylene on 'naked nickel.' [12]

Catalyst.—Dispersions of alkali metals on alumina were prepared as described by Haag and Pines.[4]

Isomerisation.—A solution of the cycloalkadiene (2 g.) in heptane (100 ml.) was added to a dispersion of potassium (1·5 g.) on alumina (10 g.) at 25°. The mixture was stirred under nitrogen, and samples of the solution (18 ml.) were taken at intervals, poured into propanol and ozonolysed directly. Reduction by sodium borohydride, and acetylation and analysis by gas chromatography [6] of the fragments, gave the isomer distribution. The ultraviolet absorption intensity at 236 mμ of the sample before ozonolysis was also determined (Table) as an extra check on the amount of conjugated diene present.

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