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ASYMMETRIC BROMINATION OF 4-METHYLCYCLOHEXENE IN THE PRESENCE OF DIHYDROCINCHONINE

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Abstract—The asymmetric bromination of 4-methylcyclohexene (**1**) in the presence of dihydrocinchonine gave a levorotatory mixture of *trans*-3-*cis*-4- (**2**) and *cis*-3-*trans*-4-dibromo-1-methylcyclohexane (**3**), containing an excess of (−)-**2** and (−)-**3**. The steric course and optical yields of the reaction were completely analyzed, on the basis of polarimetric, chromatographic and NMR methods, and the absolute configurations of **2** and **3** were deduced from the results of the bromination of (+)-**1**. The hypothesis that the bromination of alkenes with bromine-dihydrocinchonine gives an excess of the (*R*:*R*)-enantiomer was thus confirmed. Partial asymmetric bromination of (±-**1** gave (−)-**2** of higher optical purity, and the recovered olefin was dextrorotatory. The thermal isomerization of **2** to **3** was also investigated.

IT HAS been shown[1] that bromination of alkenes in the presence of *Cinchona* alkaloids leads to optically active dibromides, an excess of the (+)-enantiomers being formed from acyclic olefins and an excess of the (−)-enantiomers from cyclohexene and cyclopentene, when cinchonine or dihydrocinchonine are used as the asymmetric catalysts. It had also been assumed, even if not conclusively proved, that the enantiomer formed in excess had the (*R*)- or (*R*:*R*)-configuration. The present work was undertaken in order to control the previous deductions about the absolute configurations of cyclic dibromides, by extending them to asymmetric olefins, and to calculate the optical yield of the asymmetric bromination in such a case. 4-Methylcyclohexene (**1**) was chosen as the first asymmetric substrate, its absolute configuration being known.[2]

RESULTS AND DISCUSSION

Two isomeric dextrorotatory dibromides were obtained by Mousseron[3] on bromination of (*R*)-(+)-4-methylcyclohexene, but no indication was given regarding their configuration. Since this point was of essential interest for the present work, we have re-examined in detail the bromination of (*R*)-(+)-4-methylcyclohexene (**1b**). From a sample having $[\alpha]_D$ +7·90°, a mixture of dibromides (**2b** and **3b**) was obtained, with α_D +5·51°. The IR spectrum of this mixture showed strong bands at 696 and 646 cm^{-1} (axial C–Br)[4] and very weak ones at 718 and 683 cm^{-1} (equatorial C–Br).[4] The mixture contained a very large amount of the *trans*-diaxial isomer* as deduced from its NMR spectrum; the ratio between the signals at δ 4·60 (equatorial H, α to Br)[7] and at δ 3·96 (axial H)[7] was about 96:4. Heating the mixture caused

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* We assume that the preferred conformations of 2 and 3 are chair forms with equatorial Me groups. This assumption is based on the conformational energies of methylcyclohexane[5] and *trans*-1,2-dibromocyclohexane[6] and particularly on NMR spectra. The chemical shifts of the protons α to Br in 2 and 3 are practically the same as those of the corresponding stereoisomers of 3,4-dibromo-t-butylcyclohexane.

partial conversion of the diaxial into the diequatorial dibromide, with simultaneous decrease of optical activity. Isomerization of diaxial to diequatorial dibromides had been described for dibromocholestanes,[8] dibromodecalins[9] and 3,4-dibromo-t-butylcyclohexane.[10] Based on the mechanism proposed for such transformations[8d] and the results obtained with steroid dibromides, it can be assumed that the dextrorotatory dibromide **2b** (whose configuration, 1*R*:3*S*:4*S*, can be deduced from that of the starting olefin) undergoes inversion on C-3 and C-4, yielding the levorotatory isomer **3b** (configuration 1*R*:3*R*:4*R*). Racemization was very unlikely, also because no evidence was obtained for the formation of *cis*-dibromides, while other types of reactions were excluded on the basis of IR and NMR spectra, and GLC analysis. From the rotations of the mixtures and the concentrations of the components, obtained after different heating time intervals, if one assumes $[\alpha]_D$ +106·2° as the maximum rotation of (*R*)-(+)-4-methylcyclohexene,[11] it is possible to calculate (Experimental) that the maximum rotations of **2b** and **3b** should be, within a reasonable approximation, respectively +85° and −165° (neat, 1 dm). Evidently, the dextrorotatory values of +57·6° and +32·5° reported by Mousseron,[3] should correspond to mixtures of **2b** and **3b**.

Racemic 4-methylcyclohexene was brominated in chloroform solution, in the presence of dihydrocinchonine to obtain a mixture of four dibromides **2a**, **2b**, **3a** and **3b**. Distillation of this mixture at a temperature at which isomerization of **2** to **3** is not observed, yielded levorotatory fractions, whose rotations progressively increased in absolute value; IR and NMR spectra indicated that the amount of **3** was greater in the higher boiling fractions. Moreover, column chromatography of the original mixture permitted separation of diastereoisomerically pure **2**, which had a negative rotation. This indicates that both **2** and **3**, as obtained by asymmetric bromination of **1**, contain an excess of the levorotatory enantiomers. From the composition of the original mixture, known from GLC and NMR analyses, and from the rotation of **2** deduced after column chromatographic separation, the rotation of **3** and the optical yield of the asymmetric reaction can easily be calculated (Table 1). Another important deduction may be drawn from the data reported above; the levorotatory enantiomers of **2** and **3**, formed in excess by asymmetric bromination, have respectively configurations **2a** (1*S*:3*R*:4*R*) and **3b** (1*R*:3*R*:4*R*). This is in perfect agreement with the previous assumption[1] about the absolute configuration of the dibromides formed in the asymmetric bromination. Whereas almost coincident results were obtained when the brominations were carried out in the presence of dihydrocinchonine or cinchonine, optical yields more than doubled when the reaction temperature was changed from 0 to 25°.

When the bromination was stopped after the addition of one half of the equimolar amount of bromine, the optical yield of **2** increased, and that of **3** decreased; the recovered olefin from the partial bromination was dextrorotatory [(*R*)-configuration], and its optical purity was about 1·1% ($[\alpha]_D$ +1·2°). Since analogous results were obtained in the partial bromination of 4-t-butylcyclohexene,[12] this method could possibly be applied more widely for determining configurations of chiral alkenes.

Guetté and Horeau[13] have recently shown that in a kinetic asymmetric transformation, when the substrate is racemic and the reaction is complete, the optical purities of the two diastereoisomeric products should be inversely proportional to their relative amounts. Moreover, when the substrate is partially resolved the difference between the products of the mole fractions and the optical purities of the diastereoisomers should be equal to the optical purity of the substrate. The results obtained in the present work for the asymmetric total bromination of racemic 4-methylcyclohexene are in fairly good agreement with the assumption that $P_2C_2 = P_3C_3$ (Table 1),

TABLE 1. BROMINATIONS OF (±)-4-METHYLCYCLOHEXENE IN THE PRESENCE OF DIHYDROCINCHONINE[a]

t (°C)	C_2	C_3	α_2 (30°)	α_3 (30°)	P_2	P_3	P_2C_2	P_3C_3	P_2C_2–P_3C_3	P_1
0	0·96	0·04	−0·24°	−8·5°	0·28	5·15	0·268	0·206		
25	0·94	0·06	−0·56°	−17·76°	0·66	10·76	0·620	0·646		
27[b]	0·95	0·05	−1·70°	−12·56°	2·00	7·60	1·90	0·38	1·52	1·13

[a] C_2, C_3 = molar fractions of **2** and **3**; α_2, α_3 = optical rotations of **2** and **3** (neat, 1 dm); P_2, P_3, P_1 = optical purities of **2**, **3** and recovered **1**.

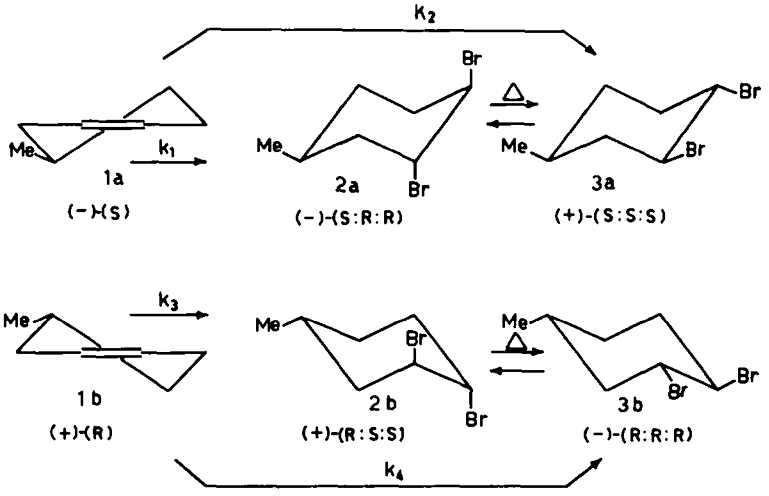
[b] Partial bromination.

particularly for the reaction at 25°. The asymmetric half-bromination should be equivalent to the total bromination of an olefin having an optical purity equal and sign opposite to that of the recovered olefin; therefore P_2C_2–P_3C_3 should correspond to the optical purity of the recovered olefin (P_1). The agreement between the calculated value of 1·5 and the experimental one of 1·1, although not too good, is still acceptable.

The formation of optically active dibromides by bromination of alkenes in the presence of *Cinchona* alkaloids was attributed[1] to the action of an alkaloid–bromine complex as an asymmetric reagent; however, other mechanisms were not rigorously excluded. The data reported above are in better agreement with the hypothesis involving the alkaloid–bromine complex, since with other mechanisms (such as the preferential capture of carbonium ions or dibromides by the alkaloid) the conversion of the alkene into the dibromide would not be complete, and the inverse relationship between optical purities and relative amounts of dibromides would not be verified.

A qualitative kinetic analysis of the asymmetric bromination would be difficult, also because a competition between the alkaloid–bromine complex and free bromine as brominating agents in the process cannot be excluded; this competition could perhaps be responsible for the difference in optical yields when the reaction is carried out at 0°, or at 25°. The formation of an excess of one of the enantiomers in the case of the asymmetric bromination of cyclohexene could be explained with a preferential reaction of the alkaloid–bromine complex with one of the two enantiomeric dissymmetric monoplanar[14] (half-chair) conformations **4a** and **4b**. If it is admitted that the bromination takes place essentially by a *trans*-diaxial addition, conformation **4a** should give the (*R*:*R*)-dibromide (**5a**), conformation **4b** the (*S*:*S*)-dibromide, if the principle of minimum modification is respected.

The situation is more complicated if, as in the case discussed in this paper, the molecule contains a chiral carbon, since each of the two enantiomers can exist in two diastereoisomeric monoplanar conformations. However, if one considers only the two conformations with equatorial Me groups (**1a** and **b**) the situation is not very different from that of the unsubstituted cyclohexene, except for the important fact that in this case **1a** and **1b** are not interconvertible like **4a** and **4b**. In a case of this type, in which the four dibromides **2a**, **3a**, **2b** and **3b** are formed through four independent reactions with rate constants k_1, k_2, k_3 and k_4, when the reaction is complete asymmetric induction can only be observed if $k_1 - k_2$ is different from $k_3 - k_4$. The fact that an excess of **2a** is formed and that partial asymmetric bromination gives a higher optical yield for **2a** further indicates that $k_1 - k_2 > k_3 - k_4$, and $k_1 > k_3$. The latter fact is in perfect agreement with the finding that also cyclohexene gives an excess of the (R:R) dibromide **5a**, since in **1a** the ring has the same chirality as in **4a** (3, 4M, according to the helicity rule.[15]) The recovery of a dextrorotatory olefin in the partial bromination further confirms that the more reactive enantiomer towards the asymmetric brominating agent is **1a**. The possibility that the dibromides **3a** and **3b** may be formed through diaxial attack on the monoplanar conformations of **1** having an axial Me group seems to be ruled out on the basis of the results obtained in the bromination of 4-t-butylcyclohexene,[12] in which such conformations should be



1a (−)-(S)

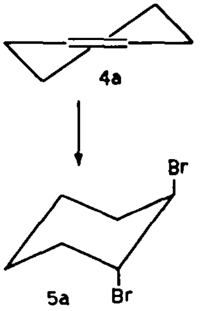
2a (−)-(S:R:R)

3a (+)-(S:S:S)

1b (+)-(R)

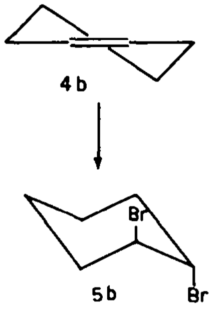
2b (+)-(R:S:S)

3b (−)-(R:R:R)



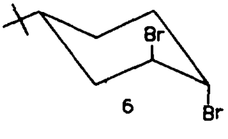
4a

5a



4b

5b



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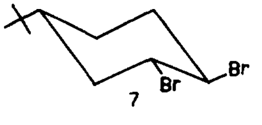

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highly unfavoured. The relative amounts of diaxial and diequatorial dibromides were in the latter case almost identical with those of the 4-methylcyclohexene dibromides. Therefore, it may be safely concluded that **3a** and **3b** are formed directly by diequatorial attack on conformations **1a** and **1b**.

Equilibrations and racemizations of vicinal dibromides

In the thermal equilibration between *trans*-3-*cis*-4-dibromo-t-butylcyclohexane (**6**) and *cis*-3-*trans*-4-dibromo-t-butylcyclohexane (**7**)[10,16] it was found that equilibrium corresponds to a nearly 50:50 composition. Our results, obtained by NMR analysis of the mixtures formed on heating dibromide **6** (containing a little of **7**) at 120° and 200° (under 120° equilibrium is reached with extreme slowness), indicated that the ratio of **6** to **7** does not appreciably vary in the above temperature interval, and has a value very near to 65:35. The equilibrium mixture of **2** and **3**, obtained by heating **2** at 140° and 190°, contained the two dibromides in the ratio 63:37, determined both by NMR and GLC techniques. Havinga *et al.*[6] have recently studied the conformational equilibrium of *trans*-1,2-dibromocyclohexane, and found that the percentage of the diequatorial conformer is 21 in carbon tetrachloride and 35 in benzene. The latter value is very near to those found by us for the isomeric equilibrium of neat *trans*-3,4-dibromo-1-alkylcyclohexanes. Heating of (−)-*trans*-1,2-dibromocyclohexane (**5a**)[1] and (+)-1,2-dibromopentane[1] produced racemization of the two compounds. It is very likely that this process follows a mechanism analogous to that leading to the epimerization of the dibromides **2** and **6**. Preliminary results indicated that the racemization rate was slower for (+)-1,2-dibromopentane than for **5a**. Possibly, the absence of a cyclic structure, and the fact that one of the Br atoms is attached to a primary C atom makes the formation of the bromide–bromonium ion couple,[8d] which, very probably, is the intermediate responsible for the racemization, more difficult.

EXPERIMENTAL

Optical rotations—Perkin–Elmer photoelectric polarimeter, mod. 141; unless stated otherwise, the values given are observed rotations for neat liquids in a 1-dm tube, and are accurate within ±0·005°. GLC—Fractovap C. Erba mod. C.V., column 1% NPGS on Chromosorb W 80–100 mesh, carrier gas N_2. IR spectra—Perkin–Elmer, mod. 257 grating spectrophotometer; spectra registered on liquid films, thickness 0·1 mm. NMR spectra—Varian DA-60-IL spectrometer; spectra registered on pure liquids for **2** and **3**, and on CCl_4 solns for **4** and **5**, TMS as internal standard.

$CHCl_3$ was purified by washing with 2N NaOH, conc H_2SO_4, H_2O, and distillation. Pet ether refers to the fraction of boiling range 30–50°.

Olefins. (±)-4-Methylcyclohexene was prepared[17] by dehydration of mixed *cis*- and *trans*-4-methylcyclohexanols with $KHSO_4$. (*R*)-(+)-4-Methylcyclohexene was obtained by pyrolysis of (+)-*cis*-4,N-dimethyl-N-phenylcyclohexylamine-N-oxide.[18]

Bromination of (R)-(+)-*4-methylcyclohexene.* To a soln of (*R*)-(+)-4-methylcyclohexene (1·0 g, 0·01 mole), $[\alpha]_D^{25}$ + 7·9 and Et_3N (1·0 g, 0·01 mole) in $CHCl_3$ (50 ml), a 10% excess of a 0·26M soln of Br in $CHCl_3$ was added slowly, with stirring at 0–5°. After washing with $NaHSO_3$aq, 2N HCl, $NaHCO_3$aq, H_2O and drying ($CaCl_2$), the solvent was evaporated at 30–40° (rotating evaporator) and the residue (2·2 g) distilled; b.p. 100°/7 mm, α_D^{30} +5·514°, α_{546} + 6·342°, α_{436} + 11·388°, α_{365} + 19·086°. (Reported: rac. dibromide, b.p. 94–95°/12 mm;[17] active dibromide, b.p. 100–103°/10 mm[3]). IR spectrum, C–Br stretching bands at 696 (s), 646 (s), 718 (w) and 683 (w) cm^{-1}; NMR spectrum, multiplets at δ 4·60 ($\frac{1}{2}$W 6 c/s, diaxial dibromide) and 3·96 ($\frac{1}{2}$W 16 c/s, diequatorial dibromide) ppm. Integration showed that the ratio of **2b** to **3b** was about 96:4.

Isomerization of **2b** *to* **3b**. The above product was heated at 140° under N_2 for 4 hr in a sealed tube, then distilled; b.p. 100°/7 mm, α_D^{30} +1·532°, α_{546} +1·768°, α_{436} +3·194°, α_{365} +5·486°; composition (NMR), 74% **2b** and 26% **3b**. On heating again at 150° for 5 hr the mixture (b.p. 57°/1·5 mm, n_D^{22}1·5356, α_D^{30} −0·240°, α_{546} −0·268°, α_{436} −0·414°, α_{365} −0·524°) contained 64·5% **2b** and 35·5% **3b**. The IR spectrum showed a strong increase in intensity of the bands at 718 and 683 cm^{-1}. The optical rotations of **2b** ($\alpha_2 = +6{\cdot}38°$) and **3b** ($\alpha_3 = -12{\cdot}27°$) may be deduced by solving the two equations: (i) $0{\cdot}740\ \alpha_2 + 0{\cdot}260\ \alpha_3 = 1{\cdot}532$ and (ii) $0{\cdot}645\ \alpha_2 + 0{\cdot}355\ \alpha_3 = -0{\cdot}240$, of which (i) refers to the initial and (ii) to the final mixture. Since the optical purity of the starting olefin was 7·43%, the maximum rotations of **2b** and **3b** (at 30°) are respectively +85° and −165°.

Total asymmetric brominations of (±)*-4-methylcyclohexene*

(1) *In the presence of dihydrocinchonine.* (a) *At* 0°. To a stirred soln of (±)-4-methylcyclohexene (6·0 g, 0·062 mole) and dihydrocinchonine (6·0 g, 0·020 mole) in $CHCl_3$ (800 ml), a 1·8M soln of Br in $CHCl_3$ (36 ml, 0·065 mole) was added in 1 hr, with cooling at 0°. After extraction of the alkaloid with 2N HCl, the soln was washed with $NaHSO_3$aq, dried ($CaCl_2$) and evaporated as previously described. The residue was distilled to give a 96:4 mixture of **2** and **3** (10 g), b.p. 61–62°/2 mm, α_D^{30} −0·569°, α_{546} −0·652°, α_{436} −1·150°, α_{365} −1·819°. A part of this material (5 g) was chromatographed over neutral SiO_2 (100 g, Woelm, grade I, column diam. 2 cm) using pet ether as the eluant and collecting 10-ml fractions. Fractions 17–20 afforded on evaporation pure **2** (0·8 g), b.p. 62°/2 mm, n_D^{22} 1·5388; α_D^{30} −0·240°, α_{546} −0·270°, α_{436} −0·492°, α_{365} −0·814°. The optical purity of **2a** was therefore 0·28%. Fractions 21–28 contained a mixture of **2** and **3** (1·7 g), α_D^{30} −0·185°, α_{546} −0·219°, α_{436} −0·440°, α_{365} −0·752°. From fractions 29–46 a mixture was obtained (0·6 g), α_D^{30} +0·050°, α_{546} +0·060°, α_{436} +0·100°, α_{365} +0·152°. The amount of **3** in the mixture was high, as shown by a strong increase of the IR bands at 718 and 683 cm^{-1}; the positive rotation was due to partial epimerization of **2a** to **3a** (this holds also for fractions 21–28) during chromatography. The diequatorial dibromide formed directly by asymmetric bromination is levorotatory (see below).

From the rotations of pure **2** (α_D^{30} −0·240°, optical purity of **2a** 0·28%) and of the original mixture (α_D^{30} −0·569°), it may be deduced that the rotation of **3**, formed in 4% yield by asymmetric bromination, is α_D^{30} −8·5° (optical purity of **3b** 5·15%).

In another experiment, (±)-4-methylcyclohexene (2·3 g, 0·024 mole) was brominated in the presence of dihydrocinchonine (2·0 g, 0·007 mole) as described, and the product was distilled at 2 mm to give two fractions: I, 2·2 g, b.p. 64–65°, α_D^{27} −0·63°, α_{546} −0·72°, α_{436} −1·32°, α_{365} −2·20°; II, 2·8 g, b.p. 65–66°, α_D^{27} −1·00°, α_{546} −1·15°, α_{436} −2·10°, α_{365} −3·49°. The IR bands at 718 and 683 cm^{-1} (diequatorial dibromide) were stronger in fraction II.

(b) *At* 25°. The olefin (10 g, 0·104 mole) was dissolved in 1·6 l. $CHCl_3$ and brominated at 25° in the presence of dihydrocinchonine (18 g, 0·061 mole). The product (24·6 g), isolated as described under (a), had b.p. 57°/1·5 mm, n_D^{22} 1·5386; α_D^{30} −1·592°, α_{546} −1·830°, α_{436} −3·269°, α_{365} −5·368°; the ratio of **2** to **3** was 94:6, as determined by NMR. Pure **2** (b.p. 62°/2 mm, n_D^{22} 1·5388, α_D^{30} −0·560°, α_{546} −0·640°, α_{436} −1·161°, α_{365} −1·952°) was obtained by chromatography of the mixture over SiO_2. The calculated rotation of **3** in the original mixture was therefore α_D^{30} −17·76°, and the optical purities of **2a** and **3b** were respectively 0·66 and 10·76%.

(2) *In the presence of cinchonine.* (±)-4-Methylcyclohexene (3·0 g, 0·031 mole) and cinchonine (5·3 g, 0·018 mole) dissolved in $CHCl_3$ (700 ml) were treated, at 0–5°, with a 1·82M soln of Br in CCl_4 (30·9 ml, 0·056 mole). After the usual treatment 5 g of mixture of **2** and **3** were obtained, b.p. 62–63°/2 mm, α_D^{30} −0·526°.

Partial asymmetric bromination. The olefin (10 g, 0·104 mole) and dihydrocinchonine (10 g, 0·034 mole) were dissolved in $CHCl_3$ (1·7 l.) and treated, while stirring at 27°, with a 1·66M soln of Br in $CHCl_3$ (30 ml, 0·050 mole); addition was carried out in 1 hr. After remotion of the alkaloid and drying, most of the solvent was distilled through a 1-m fractionating column packed with glass helices. The last fractions were collected at 40°/20 mm and consisted of unreacted olefin mixed with solvent (condenser and collecting flask cooled at −15°). From the residue, by distillation at 2 mm, 10·2 g of **2** and **3** (95:5) were obtained, b.p. 63°, α_D^{30} −2·243°, α_{546} −2·568°, α_{436} −4·589°. The fractions of olefin-containing solvent were again fractionated through the same column at ordinary press. to yield pure 4-methylcyclohexene (0·7 g), b.p. 103–104°, $[\alpha]_D^{27}$ +1·2° (optical purity 1·13%). This product and the whole solvent from the bromination were combined and treated with Br. The dibromides (4 g) so formed were chromatographed over SiO_2 to give pure **2**, α_D^{30} +1·056°, α_{546} +1·201°, α_{436} +2·128° (optical purity of **2b**, 1·24%). A part of the original mixture of dibromides obtained by partial asymmetric bromination (5·5 g) was chromatographed over SiO_2. Pure

2 was obtained (2·8 g), α_D^{30} −1·700°, α_{546} −1·967°, α_{436} −3·540°, α_{365} −5·918° (optical purity of **2a**, 2%). The rotation of **3** in the original mixture was therefore α_D^{30} −2·243° (optical purity of **3b**, 7·6%).

Equilibration of dibromides

Samples of the mixed dibromides (**2** + **3**, or **6** + **7**, 2 g each) in which the content of diaxial isomers was higher than 90%, were heated in Pyrex tubes sealed under N_2 for a time sufficient to reach constant composition. The samples occupied half of the total volume. Analysis of the equilibrated mixtures was effected by NMR spectrometry on crude liquids and, after distillation, on CCl_4 solns. The data, reliable within ±2%, are reported in Tables 2 and 3.

TABLE 2. EQUILIBRATION OF **2** AND **3**

T (°K)	% **2**	Time (hr)
416	63[a]	20
463	63	8

[a] GLC retention times (injection block 140°, column 100°, flow rate, 52 ml/min), **2**, 4 min 30 sec, **3**, 12 min 50 sec. Ratio of **2** to **3** (from peak areas), 63 : 37.

TABLE 3. EQUILIBRATION OF **6** AND **7**

T (°K)	% **6**	Time (hr)
393	65·5[a, b]	44
473	65	2

[a] NMR signals at δ4·62 (½W 10·5 c/s, diaxial dibromide) and 3·90 (½W 16 c/s, diequatorial dibromide) ppm (in CCl_4).

[b] GLC retention times (injection block, 160°, column 135°, flow rate 46 ml/min), **6**, 3 min 45 sec, **7**, 11 min. Ratio of **6** to **7** (from peak areas), 65 : 35.

Thermal racemizations

(a) (−)-trans-1,2-*Dibromocyclohexane*. The dibromide **5a**,[1] α_D^{25} −6·13° was heated at 145° in a tube sealed under N_2. After 5 hr a product, b.p. 102–103°/14 mm was obtained, whose IR spectrum was identical with that of the starting material. The dibromide was completely inactive.

(b) (+)-1,2-*Dibromopentane*. The dibromide,[1] α_D^{25} +0·89°, was heated in the same conditions as above. After definite time intervals the product was distilled (b.p. 76–77°/22 mm) and its optical rotation measured; α_D^{25} (hr): 0·89° (0), 0·71° (1), 0·56° (2), 0·43° (3), 0·34° (4), 0·20° (6), 0·08° (9).

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REFERENCES

[1] G. Berti and A. Marsili, *Tetrahedron* **22**, 2977 (1966).

[2] S. I. Goldberg and Fuk-Luen Lam, *J. Org. Chem.* **31**, 240 (1966).

[3] [a] M. Mousseron and R. Granger, *C.R. Acad. Sci., Paris* **205**, 327 (1937); [b] M. Mousseron, R. Granger and J. Valette, *Bull. Soc. Chim. Fr.* 244 (1946).

[4] E. L. Eliel, N. L. Allinger, S. J. Angyal and G. A. Morrison, *Conformational Analysis* p. 144. Interscience, New York (1965).

[5] Ref. 4, p. 439.

[6] C. Altona, H. R. Buys, H. J. Hageman and E. Havinga, *Tetrahedron* **23**, 2265 (1967).

[7] J. W. Emsley, J. Feeney and L. H. Sutcliffe, *High Resolution Nuclear Magnetic Resonance Spectroscopy* p. 698. Pergamon Press, Oxford (1965–1966).

[8] [a] J. Mauthner and W. Suida, *Monatsh.* **15**, 91 (1894); [b] J. Mauthner, *Ibid.* **27**, 421 (1906); [c] D. H. R. Barton and E. Miller, *J. Am. Chem. Soc.* **72**, 1066 (1950); [d] C. A. Grob and S. Winstein, *Helv. Chim. Acta* **35**, 782 (1952); [e] G. H. Alt and D. H. R. Barton, *J. Chem. Soc.* 4284 (1954); [f] H. Kwart and L. B. Weisfeld, *J. Am. Chem. Soc.* **78**, 635 (1956); [g] D. H. R. Barton and A. J. Head, *J. Chem. Soc.* 932 (1956).

[9] W. Hückel and H. Waiblinger, *Liebigs Ann.* **666**, 17 (1963).

[10] E. L. Eliel and R. G. Haber, *J. Org. Chem.* **24**, 143 (1959).

[11] M. Mousseron, R. Richaud and R. Granger, *Bull. Soc. Chim. Fr.* 218 (1946).

[12] G. Bellucci, G. Berti, C. Giordano and A. Marsili, *Chim. Ind. Milan* **50**, 255 (1968).

[13] J. P. Guetté and A. Horeau, *Bull. Soc. Chim. Fr.* 1747 (1967).

[14] R. Bucourt and D. Hainaut, *Ibid.* 1366 (1965).

[15] R. S. Cahn, C. Ingold and V. Prelog, *Angew. Chem.* Internat. Edit. **5**, 385 (1966).

[16] Ref. 4, p. 69.

[17] C. Harries, *Liebigs Ann.* **395**, 253 (1913).

[18] G. Berti and G. Bellucci, *Tetrahedron Letters* 3853 (1964).