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An Empirical Relationship between the Molecular Rotations of Optically Active 2-Halogenoalkanes

By B. A. Chaudri, D. G. Goodwin, and H. R. Hudson,* Department of Chemistry, Northern Polytechnic, Holloway Road, London N.7

Values for the optical rotations of enantiomerically pure 2-halogenopentanes are determined. Molecular rotations for these halides and for the previously prepared 2-halogenobutanes and 2-halogeno-octanes are reported at five wavelengths in the region 365-589 nm. and an empirical relationship between them is established.

VARIOUS attempts have been made to correlate molecular rotation with molecular structure, in particular with the polarizabilities of the groups present.¹ The methods of Boys² and of Brewster³ both enabled correct predictions of the sign of rotation of an optically active alkyl halide to be made, although the accuracy with which the magnitude of rotation could be predicted was less certain, since values for the rotations of the optically pure halides had not then been verified experimentally.

phorus trichloride or chlorodiphenylphosphine (Table 1), and the bromide by the dealkylation of the corresponding trialkyl phosphite with a restricted quantity of hydrogen bromide (Table 2). As described in other systems,^{4,5} the optically active iodide was best prepared from the dialkyl hydrogen phosphite and phosphorus tri-iodide. Maximum rotations for the halides were also determined by stereospecific conversion into (+)- or (-)-ethyl 1-methylbutyl sulphide (Table 3).5,6

Observed, specific, and molecular rotations for the

TABLE 1 Reactions of (+)- or (-)-pentan-2-ol with phosphorus halides

| Pentan-2-ol | Halide | Addn. temp. | ROH recovered | 2 | -Halogenopen | tane |
|--|--|---|--|---|-------------------------|--|
| $\begin{array}{cccc} & & & & \\ \hline (g.) & & & & \\ 4\cdot 2 & + 4\cdot 46^{\circ} \\ 7\cdot 2 & + 4\cdot 46 \\ 8\cdot 9 & + 4\cdot 26 \end{array}$ | $ \begin{array}{c} (g.) & (m. \\ Ph_2PCl & 10.5 & 1.0 \\ PCl_3 & 3.8 & 0.3 \\ PBr_3 & 10.0 & 0.3 \end{array} $ | bl.) (°C) -10 -10^{a} -10^{a} -10^{f} | (g.) (mol.) 0·8 0·2 0·1 0·01 1·3 0·15 | $\begin{array}{c} \text{(g.)} (\text{mol.)} \\ \textbf{3} \cdot 2 \textbf{0} \cdot \textbf{63} \\ \textbf{1} \cdot \textbf{5} \textbf{0} \cdot \textbf{17} \\ \textbf{3} \cdot \textbf{0} \textbf{0} \cdot \textbf{20} \end{array}$ | $\alpha_{D}^{20} a$ | $ \begin{array}{r} \alpha_{\rm D}^{20}({\rm corr.}) \ b \\ - 38.15^{\circ} \\ - 37.92 \\ - 47.89 \end{array} $ |

• After g.l.c. purification. ^b Corrected for optically pure pentan-2-ol, $\alpha_D^{20} + 11\cdot26^\circ$. • $n_D^{20} 1\cdot4061$, $\alpha_D^{23} - 14\cdot98^\circ$ (Found: Cl, 33·1. Calc. for C₅H₁₁Cl: Cl, 33·3%), 100% 2-isomer. ^d Residue (5·7 g.) distilled to give *di-1-methylbutyl hydrogen phosphile* (3·8 g., 0·21 mol.), b.p. 69°/0·1 mm., $n_D^{20} 1\cdot4240$, $\alpha_D^{22} + 10\cdot42^\circ$ (Found: P, 13·9. C₁₀H₂₃O₃P requires P, 14·0%), [³¹P δ (p.p.m.) -4·3 doublet, $J_{\rm PH}$ 687 Hz]. • $\alpha_D^{23} - 14\cdot90^\circ$ (Found: Cl, 33·2%), 100% 2-isomer. ^f Residue afforded di-1-methylbutyl hydrogen phosphile (2·9 g., 0·13 mol.), b.p. 51°/0·01 mm., $\alpha_D^{25} + 10\cdot08^\circ$ (Found: P, 13·9%). • $n_D^{20} 1\cdot4408$, $\alpha_D^{27} - 17\cdot82^\circ$ (Found: Br, 53·2. Colored Cl, Br, Far, 50°/0·1 mm., $\alpha_D^{25} + 10\cdot08^\circ$ (Found 2) browners (29%) Calc. for $C_5H_{11}Br$: Br, 53.0%), containing 2-bromopentane (98%) and 3-bromopentane (2%).

Rotations for the optically pure 2-halogenobutanes⁴ and 2-halogeno-octanes^{5,6} have recently been established and values for the 2-halogenoare now reported. The chloride and pentanes

TABLE 2

Reactions of (+)-tri-1-methylbutyl phosphite with hydrogen halides

| | | Adda | 2-H | alogenoper | ntane |
|--|---|---|---|--|---|
| Phosphite • | Halide | temp. | <u>~</u> | | aD ²⁰ |
| (g.) | (g.) (m | ol.) (°C) | (g.) (mol.) | α_D^{20} | (corr.) ^b |
| 5.1 0] | HBr 1.3 0. | 92 0 | $1.9 \ 0.72$ | +14.21° d | $+52.63^{\circ}$ |
| 4 ∙3 ° | HI 1.70 | ·90 0 | $2 \cdot 1 \ 0 \cdot 72$ | +19.54f | +72.38 |
| ^a From pure pent (1.0 g.). Br, 52.8% (0.8 g.). 1.4940 (F containing | pentan-2-c an-2-ol, α_D ^{<i>a</i>} After g $\langle \rangle$, 100% ^{<i>f</i>} Purified $\langle \rangle$ ound: I, g trace (<0 | $\begin{array}{l} l, \alpha_D{}^{20} - 3 \cdot \\ {}^{20} - 11 \cdot 26^{\circ} \\ .1.c. \ purifiq \\ 2 \text{-isomer.} \\ by \ distill \\ 63 \cdot 65. \ C \\ \cdot 5\%) \ 3 \text{-iode} \end{array}$ | 04°. b Con- cation, $n_{\rm D}$ b Mixed ation at alc. for Coppentane. | rrected for with dia. 20 1.4405 with dia. $^{20^{\circ}}/0.5$ m $_{5}H_{11}I$: I, | optically lkyl ester (Found: kyl ester $n_{\rm m.}$, $n_{\rm D}^{20}$ $64\cdot1\%$), |

bromide were prepared without loss in optical purity by previously described procedures: 5 the chloride by interaction of optically active pentan-2-ol with phos2-halogenoalkanes RCHXMe (I) (R = Et, Pr^n , or n-hexyl) are given at wavelengths in the range 365-589 nm., over which plain o.r.d. curves are obtained (Table 4). The values quoted, which are averages of the highest rotations obtainable in alcohol-phosphorus trihalide and related systems and those derived by stereospecific conversion into the ethyl sulphides, are within $\pm 0.3\%$ (Cl) and ± 1 —1.5% (Br and I) of those found experimentally by either method.

It was assumed in Brewster's calculations that for a 2-substituted alkane (I) there would be (to a first approximation) no dependance of molecular rotation on R, provided that Me and X were similar in size.³ This would be most nearly true for X = Cl but even in this case it is clear that [M] increases appreciably with increasing chain length. The molecular rotations determined at 589 nm. (Table 4) indicate errors of between 20 and 67% in the calculated values, which are 55, 60, and 95 (based on Brewster's 'observed conformational rotatory powers') or 39.5, 66, and 104 (based on his calculated conformational rotatory powers'), for the

E. L. Eliel, 'Stereochemistry of Carbon Compounds,' McGraw-Hill, New York, 1962, pp. 398-412.
 S. F. Boys, Proc. Roy. Soc., 1934, A, 144, 655.
 J. H. Brewster, J. Amer. Chem. Soc., 1959, 81, 5475.

⁴ D. G. Goodwin and H. R. Hudson, J. Chem. Soc. (B), 1968, 1333.

 ⁵ E. J. Coulson, W. Gerrard, and H. R. Hudson, J. Chem. Soc., 1965, 2364; H. R. Hudson, Synthesis, 1969, 1, 112.
 ⁶ H. M. R. Hoffmann, J. Chem. Soc., 1964, 1249.

2-chloro-, 2-bromo-, and 2-iodo-alkanes respectively. Closer agreement cannot be expected, since the calculated values depend heavily on the proportions of the different conformers which are assumed to be present. Whilst these calculated rotations are interesting in that they rotations of the chloride, bromide, and iodide are in a remarkably constant ratio to one another. The ratios for any one of the three alkyl groups under investigation lie within $\pm 1\%$ of the mean values (Table 5) and increase slightly with decreasing wavelength. Similarly,

TABLE 3

Reactions of (+)- or (-)-2-halogenopentanes with sodium ethyl sulphide

| | C ₅ H ₁₁ X tal | xen | Ets | SNa | EtOH | Temp. | | C.H.,SEt @ | Calc. max b for $C_5H_{11}X$ |
|---------------|--------------------------------------|-----------------|--------------|--------|-------|-------|-------|-----------------|-----------------------------------|
| x | (g.) | αD^{20} | (g.) | (mol.) | (ml.) | (°C) | Time | α_D^{20} | α_D^{20} |
| Cl | 2.4 | +6.68° | 17.6 | 9.3 | 100 | 60 | 6 hr. | -4·12° | |
| \mathbf{Br} | 3.1 | +11.19 | 12.6 | 7.3 | 100 | 60 | 1 | -4.84 | -54.19 |
| 1 | 6.5 | -56.87 | $22 \cdot 2$ | 8.1 | 100 | 60 | 1 | +17.53 | +76.04 |

^a After purification by g.l.c. ^b Calculated for optically pure ethyl 1-methylbutyl sulphide, α_D^{20} 23.44°.

TABLE 4

Observed,^a specific,^b and molecular rotations of the 2-halogenoalkanes RCHXMe

| 2 X | | R = Et | | | $R = Pr^n$ | | | R = n-hexyl | | |
|-------|----|-------------------------|--------------------|-------------------|-----------------------|------------------------|-------------------|------------------|--------------------|-------------------|
| (nm.) | ~~ | $\alpha_{\lambda^{20}}$ | [α]λ ²⁰ | [M] ₂₀ | $\alpha \lambda^{20}$ | $[\alpha]\lambda^{20}$ | [M] ₂₀ | αλ ²⁰ | [α]λ ²⁰ | [M] ₂₀ |
| 589 | Cl | 31.0 | 35.5 | 32.9 | 38.1 | 43.8 | 46.7 | 31.6 | 36.5 | 54.3 |
| 578 | | 32.1 | 36.8 | 34.1 | 39.9 | 45.9 | 48.9 | 33.0 | 38.1 | 56.6 |
| 546 | | 36.7 | 42.0 | 38.9 | 45.1 | 51.8 | 55.2 | 37.4 | $43 \cdot 2$ | 64.2 |
| 436 | | 62.0 | 71.0 | 65.7 | 75.5 | 86.8 | 92.5 | 62.9 | 72.6 | $107 \cdot 9$ |
| 365 | | 96.6 | 110.7 | 102.5 | 116-6 | 134.0 | $142 \cdot 8$ | 97.4 | 112.5 | 167.3 |
| 589 | Br | 43.3 | 34.5 | 47.3 | 53·4 | 44.3 | 66-9 | 44 ·2 | 40 ·0 | 77.3 |
| 578 | | 45.2 | 36.0 | 49.3 | 55.7 | 46.2 | 69.8 | 46.2 | 41.8 | 80.7 |
| 546 | | 51.4 | 40·9 | 56.0 | 63.3 | $52 \cdot 5$ | 79.3 | 52.5 | 47.5 | 91.7 |
| 436 | | 88.5 | 70.5 | 96.6 | 108.3 | 89.9 | 135.8 | 89.9 | 81.3 | 157.0 |
| 365 | | 141.9 | 113.0 | 154.8 | $172 \cdot 1$ | 142.8 | 215.7 | 142.9 | $129 \cdot 2$ | 249.5 |
| 589 | I | 60.9 | 38.1 | 70.1 | 75.0 | 50.0 | 99.0 | 63.9 | 48·3 | 116.0 |
| 578 | | 63.7 | 39.9 | 73.4 | 78.6 | $52 \cdot 4$ | 103.8 | 66.9 | 50.6 | 121.5 |
| 546 | | $73 \cdot 2$ | 45.8 | 84.3 | 90.1 | 60.0 | 118.8 | 76.7 | 58.0 | 139.3 |
| 436 | | 133-1 | 83.3 | 153.3 | 1 63 ·0 | 108.6 | 215.1 | 138.3 | 104.6 | 251.2 |
| 365 | | $236 \cdot 2$ | 147.8 | 272.0 | 289.6 | $192 \cdot 9$ | 382.0 | 243.4 | 18 4·1 | 442·1 |

^a Calculated for halides prepared from optically pure alcohols.¹¹ ^b Calculated from reported densities d_4^{20} for the halides in which R = Et (Handbook of Chemistry and Physics, 46th edn., Chemical Rubber Co., Ohio, 1965), Pr^n (ref. 8), and n-hexyl.⁸

might be regarded as being of the correct order of magnitude (cf. ref. 1) they are of little practical value. Calculations of the molecular rotation of 2-bromobutane on the basis of Boys's formula have given values of [M] 227.6 and 162.4 which are more seriously in error.^{2,7} It is clear also from the present results that the relationship suggested by Brauns,⁸ viz., that for halides in which the halogen atom is attached to the asymmetric carbon atom ' the differences of their specific rotations, (Cl-F), (Br-Cl), and (I-Br), have the same numerical relation as the respective differences of the radii of the covalentbonded atoms (41:17:21)' does not hold even approximately for the halides under investigation. Had such a relationship been established at any particular wavelength it would have been entirely fortuitous as it clearly has no theoretical basis.

An empirical correlation between the molecular rotations which have now been determined can nevertheless be made. Thus, for any one alkyl substituent (I; R = Et, Pr^n , or n-hexyl) and any given wavelength in the region examined (365-589 nm.), the molecular

⁷ M. Maestro, Gazzetta, 1964, 94, 1122.

⁸ D. H. Brauns, J. Res. Nat. Bur. Stand., 1943, **31**, 83; Rec. Trav. chim., 1946, **65**, 799. for a given halogen, the molecular rotations of the 2halogenoalkanes (I) containing different alkyl substituents R are in constant ratio to one another, within

TABLE 5

Ratios of molecular rotations for different halogens X in 2-halogenoalkanes (I) ^a

| III 2-maiogenoarkanes (1) | | | | | |
|---------------------------|------|------|------|--|--|
| λ (nm.) | Cl | Br | I | | |
| 589 | 1.00 | 1.43 | 2.13 | | |
| 578 | 1.00 | 1.44 | 2.14 | | |
| 5 46 | 1.00 | 1.44 | 2.16 | | |
| 436 | 1.00 | 1.46 | 2.33 | | |
| 365 | 1.00 | 1.50 | 2.66 | | |

^a Values for individual substituents R(Et, Prⁿ, or n-hexyl) all lie within $\pm 1\%$ of these figures.

| TABLE | 6 |
|-------|---|
|-------|---|

Ratios of molecular rotations for different substituents R in 2-halogenoalkanes (I) ^a

| λ (nm.) | Et | Pr ⁿ | n-hexyl | | |
|---------|------|-----------------|---------|--|--|
| 589 | 1.00 | 1.41 | 1.64 | | |
| 578 | 1.00 | 1.42 | 1.65 | | |
| 546 | 1.00 | 1.42 | 1.65 | | |
| 436 | 1.00 | 1.41 | 1.64 | | |
| 365 | 1.00 | 1.40 | 1.62 | | |

 a Values for individual halogens X (Cl, Br, or I) all lie within $\pm 1\%$ of these figures.

less than $\pm 1\%$. At 589 nm., the ratio is 1.00: 1.41:1.64, for R = Et, Pr^n , and n-hexyl respectively, and is similar at other wavelengths (Table 6). The molecular rotations of the various halides in this series are therefore quite simply interrelated, at least within the limits of experimental error, by equation (1) in which the factors $f_{\lambda}(\mathbf{R}^2/\mathbf{R}^1)$ and $f_{\lambda}(\mathbf{X}^2/\mathbf{X}^1)$ are the ratios at wavelength λ

 $[M]_{\lambda}(\mathrm{R}^{2}\mathrm{MeCHX}^{2}) =$

$$[M]_{\lambda}(\mathrm{R}^{1}\mathrm{MeCHX^{1}}) \cdot f_{\lambda}(\mathrm{R}^{2}/\mathrm{R}^{1}) \cdot f_{\lambda}(\mathrm{X}^{2}/\mathrm{X}^{1})$$
 (1)

for the two alkyl substituents \mathbb{R}^2 and \mathbb{R}^1 (Table 6), or the two halogens X^2 and X^1 (Table 5) in question. It must be stressed that this relationship is purely empirical for the wavelengths investigated and cannot hold for example in the region of a Cotton effect.⁹ It would be of interest to determine whether similar relationships hold for types of alkyl halide other than the 2-halogenoalkanes but few reliable data are available. Calculation from recent values 10 for the rotations of optically pure 1-chloro- and 1-bromo-phenylethane (I; R = Ph, X = Cl or Br) at 589 nm., shows the specific and molecular rotations of these halides to be $[\alpha]_{D}^{20}$ 117.6, $[M]_{D}^{20}$ 165.2 (chloride) and $[\alpha]_{D}^{20}$ 124.9, $[M]_{p}^{20}$ 231.1 (bromide). The molecular rotations are thus in the ratio 1.00: 1.40, which is little different from that now reported for the 2-halogenoalkanes at 589 nm. No obvious correlation can be made between the molecular rotations of the halides and those of 2-substituted alkanes containing different types of functional group (e.g., I; X = OH or SEt). Intermolecular hydrogen-bonding and/or conformational factors presumably complicate the situation in these compounds.

EXPERIMENTAL

Optically active 2-halogenobutanes and 2-halogenooctanes were prepared as described.4,5 Pentan-2-ol was resolved by the hydrogen phthalate method, with brucine.¹¹

Polarimetry.-Optical rotations were measured with a Bellingham and Stanley model A polarimeter at room temperature, or in thermostatted cells on a Perkin-Elmer 141 photoelectric polarimeter. All are quoted for l 1 dm. and are corrected to 20 °C where necessary. Variations of rotation with temperature have been reported for the 2-halogenobutanes.⁴ For the 2-halogenopentanes and 2halogeno-octanes variation was also linear over the range 15-25 °C as follows (circular degrees per °C for 2-halogenoalkanes of maximum rotation). 2-Halogenopentanes: 0.106 (Cl); 0.125 (Br); 0.162 (I). 2-Halogeno-octanes: (0.080 (Cl); 0.100 (Br); 0.126 (I). Hence, $\alpha_{\rm D}^{\ t} = \alpha_{\rm D}^{\ 20}$ [1 + (20 - t)x], where for the 2-halogenopentanes x = 0.00278 (Cl), 0.00234 (Br), or 0.00216 (I); for the 2-halogeno-octanes x = 0.00253 (Cl), 0.00226 (Br), or 0.00197 (I).

Gas Chromatography.—Optically active 2-chloropentane and 2-bromopentane were purified, without loss in rotatory power, in a 4 ft \times 5/8 in. glass column containing 15% squalane or 10% polyethylene glycol 400 on 85-100 mesh Celite at 50 °C (N₂ flow-rate 200 ml./min.); both were

⁹ L. Bartlett, B. A. Chaudri, D. G. Goodwin, H. R. Hudson, and P. M. Scopes, J. Chem. Soc. (C), 1970, 1329. ¹⁰ H. M. R. Hoffmann and E. D. Hughes, J. Chem. Soc., 1964,

1244.

shown to be isomerically pure by g.l.c. on squalane.¹² Ethyl 1-methylbutyl sulphide was purified on the polyethylene glycol column at 70°. At least two passes were necessary since separation from diethyl disulphide was more difficult than for the s-butyl compound.⁴ Racemization did not occur.

Tri-1-methylbutyl Phosphite.-Phosphorus trichloride (5.75 g., 1 mol.) in light petroleum (b.p. 30-40°) (10 ml.) was added dropwise (20 min.) with shaking to a solution of pentan-2-ol (11-0 g., 3 mol.), $\alpha_D^{\ 20}$ –5-66° and dimethylaniline (15.2 g., 3 mol.) in the same solvent (150 ml.) at -10° . Filtration at room temperature afforded dimethylanilinium chloride (18.8 g., 2.85 mol.) (Found: Cl, 22.3. Calc. for $C_8H_{12}NCl$: Cl, 22.5%) and a liquid which was distilled to give (i) 1.0 g., b.p. up to $114^{\circ}/0.5$ mm.; (ii) 5.5 g., b.p. 114—118°/0.5 mm., n_D²⁰ 1.4313; (iii) tri-1-methylbutyl phosphite (2.5 g., 0.21 mol.), b.p. 118-119°/0.5 mm., $n_{\rm D}^{20}$ 1·4319, $\alpha_{\rm D}^{20}$ +1·315° (Found: C, 62·2; H, 11·1; P, 10·4. $C_{15}H_{33}$ OP requires C, 61·6; H, 11·3; P, 10·6%) [³¹P δ (p.p.m.) -140 singlet]. Fraction (ii) contained the triester (82%) and di-1-methylbutyl hydrogen phosphite (18%) [³¹P δ (p.p.m.) -4·3 doublet, $J_{\rm PH}$ 687 Hz.] In a further similar preparation pentan-2-ol (13·7 g.), $\alpha_{\rm D}^{20}$ -3.04° gave a mixture (11.9 g.), b.p. 70-76°/0.1 mm., $n_{\rm p}^{20}$ 1·4314, $\alpha_{\rm p}^{20}$ +0·002° (Found: P, 11·1%), containing the tri- (84%) and di- (16%) esters.

2-Chloro- and 2-Bromo-pentane.--Interaction of optically active pentan-2-ol with the phosphorus halides, of tri-1methylbutyl phosphite with the hydrogen halides, and isolation of the products were as described for the s-butyl systems.4

2-Iodopentane.—Phosphorus tri-iodide (11.7 g., 1.1 mol.) in carbon disulphide (35 ml.) was added (45 min.) to di-1methylbutyl hydrogen phosphite (5.5 g., 1 mol.) (from pentan-2-ol, α_{D}^{20} -3.04°) at 0°. After 48 hr. at 20° water was added. The organic layer was washed, dried (K_2CO_3) , and carbon disulphide was removed at 20°/17 mm. The residue was distilled at $20^{\circ}/0.5$ mm. and trapped (-80°) to give a condensate consisting of 2-iodopentane with traces of carbon disulphide. The latter was removed by prolonged shaking at 15 mm. to leave 2-iodopentane (2.1 g., 0.43 mol.), $n_{\rm p}^{20}$ 1.4951, $\alpha_{\rm p}^{20}$ +19.96° ($\alpha_{\rm p}^{20}$ +73.92° corrected for optically pure pentan-2-ol) (Found: I, 63.4. Calc. for $C_5H_{11}I$: I, 64.1%).

(+)-Ethyl 1-Methylbutyl Sulphide.—Pentan-2-ol (3.2 g.), $\alpha_{\rm p}^{20}$ -5.645°, was converted into the methanesulphonate as described for the 1-methylheptyl ester.⁶ The undistilled ester (5.4 g.) was then heated (90 min./60°) with sodium ethyl sulphide (12.3 g., 4.5 mol.) in ethanol (90 ml.). The product was extracted with light petroleum (b.p. 30-40°) (100 ml.), washed, dried (MgSO₄), and purified by g.l.c. to give ethyl 1-methylbutyl sulphide (Found: C, 64.8; H, 12.1; S, 24.6. C₇H₁₆S requires C, 63.6; H, 12.1; S, 24.2%), $n_{\rm D}^{20}$ 1.4500, $\alpha_{\rm D}^{20}$ +11.75° ($\alpha_{\rm D}^{20}$ +23.44° corrected for optically pure pentan-2-ol).

Conversion of (+)- or (-)-2-Halogenopentanes into Ethyl 1-Methylbutyl Sulphide.-The 2-halogenopentanes were heated at 60 °C with sodium ethyl sulphide in ethanol as specified (Table 3); the products were extracted and purified as described above.

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 R. H. Pickard and J. Kenyon, J. Chem. Soc., 1911, 45.
 B. A. Chaudri, H. R. Hudson, and W. S. Murphy, J. Chromatog., 1967, 29, 218.