

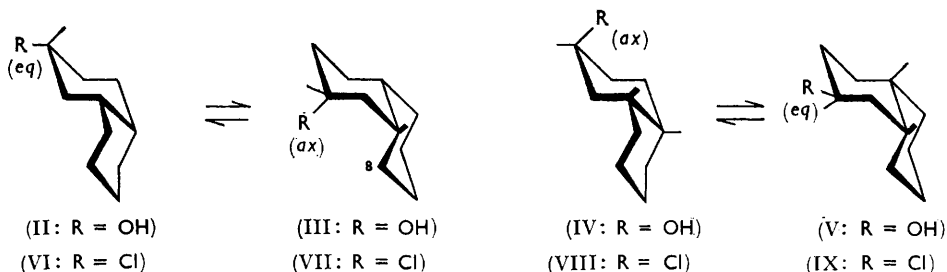
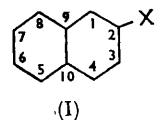
608. Molecular Polarisability. Steric Courses for the Replacement of Hydroxyl by Chlorine in *cis*-2-Decalol.

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Dipole moments, molar Kerr constants, refractivities, etc., are reported for *cis*-2-decalol (m. p. 104–106°), and for three samples of *cis*-2-decalyl chloride, prepared by treatment of the alcohol with phosphorus pentachloride, hot concentrated hydrochloric acid, or thionyl chloride, respectively. Values of $\infty(mK_2)$ for the three halides are compared with those calculated, from polarisability data, for rival space formulæ, and, on the basis of a previous assignment of configuration to *cis*-2-decalol (m. p. 104–106°), steric courses for the three reactions are discussed. Phosphorus pentachloride and hydrochloric acid substitute largely with inversion of configuration, and thionyl chloride with retention; observed $\infty(mK_2)$ values for the halides prepared with hydrochloric acid and thionyl chloride, however, are compatible with some degree of racemisation.

THE configurations of 2-substituted decalins (I) are expressed, by convention, in terms of the relative positions of the hydrogen atoms at C-9 and C-10 and C-9 and C-2; *cis*-conformations have the hydrogen atoms at positions 9 and 10 on the same side of the molecule, and may be either *cis,cis*, if the 2-hydrogen is also on that side, or *cis,trans*, if the 2-hydrogen is *trans* to the 9-hydrogen.¹

cis,cis- and *cis,trans*-2-Decalol both exist as an equilibrium mixture of two chair-chair conformations,² the hydroxyl group being attached equatorially in the one, and axially in the other [structures (II),(III) and (IV),(V), respectively]. From scale molecular models, it is evident that there is marked steric interaction of the substituent and the axial-hydrogen at position 8 in structure (III);^{1,3} conformational analysis has, therefore, been based on the assumption that *cis,cis*-2-decalol should possess a more equatorial character than the *cis,trans*-epimer. Since the hydrogen phthalate of *cis*-2-decalol (m. p. 105°) is hydrolysed at 1.5 times the rate of the hydrogen phthalate of the



isomer (m. p. 18°),⁴ the former is assigned the *cis,cis*-conformation (II),(III), a conclusion substantiated by studies of the catalytic hydrogenation and subsequent elimination reactions of 2-naphthoic acids.⁵ If this is so, conformational analysis of the *cis*-2-decalyl chlorides, obtained from *cis*-2-decalol (m. p. 105°) by use of different substituting agents, should demonstrate, in addition, the steric courses of the different reactions. Molar Kerr constants have, therefore, been measured for *cis*-2-decalol (m. p. 104–106°), and for

¹ Daubin, Tweit, and Mannerskantz, *J. Amer. Chem. Soc.*, 1954, **76**, 4420.

² Bastiensen and Hassel, *Nature*, 1946, **157**, 765.

³ Mills, *J.*, 1953, 260.

⁴ Hückel, Havekoss, Kumstat, Ullmann, and Doll, *Annalen*, 1938, **533**, 128.

⁵ Linstead, Doering, Davis, Levine, and Whetstone, *J. Amer. Chem. Soc.*, 1942, **64**, 1985.

three samples of *cis*-2-decalyl chloride (prepared with phosphorus pentachloride, hot concentrated hydrochloric acid, and thionyl chloride, respectively), as solutes in benzene.

EXPERIMENTAL

Apparatus, procedures, notation, and methods of calculation are described in refs. 6 and 7; symbols and equations required for the treatment of observational data have been summarised before.⁸

Solvent.—The solvent used was freshly-distilled sodium-dried benzene, ϵ^{25} 2.2725, d_4^{25} 0.87378, n_D^{25} 1.4973, $10^7 B_D^{25}$ 0.410.

Solutes.—*cis*-2-Decalol (m. p. 104–106°) was prepared from 2-naphthol by Raney nickel-catalysed hydrogenation at 140°/130 atm.^{9,10} Phosphorus pentachloride was added to a solution of *cis*-2-decalol (m. p. 104–106°) in dry chloroform, containing calcium carbonate in suspension.¹¹ The mixture was shaken at room temperature overnight, poured into water, and extracted with ether; the washed ether extract yielded *cis*-2-decalyl chloride, b. p. 112–116°/15 mm. (Found: C, 69.2; H, 9.7; Cl, 20.9. C₁₀H₁₇Cl requires C, 69.5; H, 9.9; Cl, 20.5%). A second sample was obtained by heating *cis*-2-decalol (m. p. 104–106°) with concentrated

TABLE I.

Kerr effects, dielectric constants, etc., of solutions in benzene at 25°.

cis-2-Decalol (m. p. 104–106°)										
$10^5 w_2$	678	862	1218	2084	2896	3446				
ϵ^{25}	2.2884	—	2.3003	2.3204	2.3379	2.3519				
d_4^{25}	—	0.87471	0.87506	0.87597	0.87670	0.87756				
$10^4 \Delta n$	0	0	-1	-1	-1	-2				
$10^7 \Delta B$...	—	—	0.004	0.004	0.007	0.009				
whence $\Sigma \Delta \epsilon / \Sigma w_2 = 2.29$; $\Sigma \Delta d / \Sigma w_2 = 0.106$; $\Sigma \Delta n / \Sigma w_2 = -0.004_5$; $10^7 \Sigma \Delta B / \Sigma w_2 = 0.25$.										
cis-2-Decalyl chloride (from PCl ₅)										
$10^5 w_2$	391	550	597	641	730	815				
ϵ^{25}	—	2.2901	2.2914	2.2917	—	—				
d_4^{25}	—	0.87453	—	—	—	—				
$10^7 \Delta B$...	0.018	—	0.027	—	0.032	0.037				
$10^5 w_2$	862	982	1204	1442	1517	2763				
ϵ^{25}	—	—	2.3076	2.3159	2.3192	2.3574				
d_4^{25}	—	0.87510	0.87528	0.87567	0.87581	0.87753				
$10^7 \Delta B$...	0.038	0.042	—	0.063	—	0.121				
whence $\Sigma \Delta \epsilon / \Sigma w_2 = 3.05$; $\Sigma \Delta d / \Sigma w_2 = 0.133$; $10^7 \Sigma \Delta B / \Sigma w_2 = 4.40$.										
cis-2-Decalyl chloride (from HCl)										
$10^5 w_2$	410	583	1189	1400	1775	1997	2641	3346		
ϵ^{25}	2.2848	—	—	—	2.3281	2.3348	2.3560	2.3753		
d_4^{25}	—	0.87957	0.87535	0.87560	—	—	0.87715	0.87809		
$10^7 \Delta B$...	—	0.023	0.049	0.057	0.071	0.077	0.102	—		
whence $\Sigma \Delta \epsilon / \Sigma w_2 = 3.11$; $\Sigma \Delta d / \Sigma w_2 = 0.129$; $10^7 \Sigma \Delta B / \Sigma w_2 = 3.95$.										
cis-2-Decalyl chloride (from SOCl ₂)										
$10^5 w_2$	514	666	817	823	870	951	1109	1512	1514	1824
ϵ^{25}	—	2.2935	2.2974	2.2973	—	2.3007	2.3072	—	—	—
d_4^{25}	0.87443	0.87461	—	0.87489	—	0.87504	0.87529	—	—	—
$10^7 \Delta B$...	—	—	—	—	0.029	—	—	0.050	0.048	0.060
whence $\Sigma \Delta \epsilon / \Sigma w_2 = 3.06$; $\Sigma \Delta d / \Sigma w_2 = 0.132$; $10^7 \Sigma \Delta B / \Sigma w_2 = 3.14$.										

⁶ Le Fèvre and Le Fèvre, (a) *Rev. Pure Appl. Chem. (Australia)*, 1955, **5**, 261; (b) *J.*, 1953, 4041; (c) chap. XXXVI in "Physical Methods of Organic Chemistry," ed. Weissberger, Interscience, New York and London, 3rd edn., 1960, vol. I, p. 2549; (d) *J.*, 1956, 3549.

⁷ Le Fèvre, "Dipole Moments," Methuen, London, 3rd edn., 1953, ch. 2.

⁸ Le Fèvre and Sundaram, *J.*, 1962, 1494.

⁹ Musser and Adkins, *J. Amer. Chem. Soc.*, 1938, **60**, 664.

¹⁰ Stork and Hill, *J. Amer. Chem. Soc.*, 1957, **79**, 495.

¹¹ Shoppee and Summers, *J.*, 1952, 1790.

TABLE 2.

	$\alpha\epsilon_1$	β	γ	δ	${}_{\infty}P_T$ (c.c.)	R_D (c.c.)	μ (D) *	$10^{12} {}_{\infty}(mK_2)$
<i>cis</i> -2-Decalol (m. p. 104—106°)	2.29	0.121	-0.003	0.6	112.6	45.0	1.7 _g	5
<i>cis</i> -2-Decalyl chloride (PCl ₅)	3.05	0.152	0.000	10.7	149.0	49.1	2.1 _g	133
<i>cis</i> -2-Decalyl chloride (HCl)	3.11	0.148	0.000	9.6	151.2	49.3	2.2 _o	118
<i>cis</i> -2-Decalyl chloride (SOCl ₂)	3.06	0.151	0.000	7.7	149.4	49.1	2.1 _g	92

* Calc. for distortion polarisations of $1.05R_D$ (c.c.).

hydrochloric acid in a sealed tube at 125° for 10 hr.;¹² when the reaction mixture was worked up in the usual way, *cis*-2-decalyl chloride, b. p. 114—118°/19 mm. was obtained (Found: C, 69.8; H, 9.7; Cl, 20.8%). A third sample, b. p. 119—124°/20 mm. (Found: C, 69.7; H, 10.0; Cl, 19.7%) was prepared, using thionyl chloride as substituting agent; ¹ a solution of *cis*-2-decalol (m. p. 104—106°) in purified thionyl chloride was allowed to stand overnight at room temperature, warmed at 70° for 2 hr., and the mixture worked up as before.

Measurements.—These are listed in Table 1; quantities calculated therefrom, including dipole moments and molar Kerr constants at infinite dilution, are in Table 2. For the concentrations used, differences (Δn) between the refractive indices of solution and solvent were beneath the limit of detection for all three chlorides.

DISCUSSION

Standard computational procedures exist^{6,13} for calculating *a priori* the molar Kerr constant of a molecular structure having specifiable geometry. Initial data required are the longitudinal, transverse, and vertical polarisabilities (b_L , b_T , and b_V) of bonds involved. In the present work, the following values are taken (for the C—H,^{6a} C—C,^{6a} and C—Cl^{6d} bonds, respectively): $10^{23}b_L$ 0.064, 0.099, 0.382; $10^{23}b_T$ 0.064, 0.027, 0.185; $10^{23}b_V$ 0.064, 0.027, 0.185. For each bond, the three polarisabilities are related to Cartesian axes (X , Y , Z), arbitrarily set up within the molecular framework, by nine direction cosines from which the polarisability of every bond along the X , Y , Z directions can be determined and totalled for the whole molecule. The estimate, referred to X , Y , Z , which results is conveniently summarised by a symmetric matrix, Q , which, by an appropriate orthogonal transformation, affords the diagonal matrix, $\text{diag. } (b_1b_2b_3)$, representing induced moments with respect to principal axes (1, 2, 3). The principal semi-axes of the molecular polarisability ellipsoid and their locations within X , Y , Z are, therefore, given by the eigenvalues and three orthonormal eigenvectors of the matrix, Q .

Molar Kerr constants are thus calculated for axial and equatorial forms of both *cis,cis*- and *cis,trans*-2-decalyl chloride [structures (VI),(VII) and (VIII),(IX), respectively]. All interbond angles have been taken as tetrahedral; in models (VI) and (VIII), axes (X , Y , Z) are located with X and Y in the plane of C-1, C-9, C-3, and C-4, and the X -axis parallel to the 1,9-link, and in models (VII) and (IX) with X and Y in the plane of C-1, C-2, C-4, and C-10, and the X -axis parallel to the 1,2-link. Expected molecular polarisability semi-axes (b_1 , b_2 , b_3) and resolutes (μ_1 , μ_2 , μ_3) of the observed dipole moment, as calculated, are in Table 3; from these, molar Kerr constants for conformations (VI)—(IX) emerge as in the last column. Observed molar Kerr constants are subject to standard deviations of the order of 5 units, so that the three values (footnote § in Table 3) are, therefore, significantly different. Although the ratio of equatorial to axial form in the *cis,trans*-epimer is uncertain, conclusions of a general nature can still be drawn.

¹² Borsche and Lange, *Annalen*, 1924, **434**, 225.

¹³ Eckert and Le Fèvre, *J.*, 1962, 1081.

TABLE 3.

Polarisability semi-axes, dipole moment components, etc., for *cis*-2-decalyl chloride.

	Principal polarisability semi-axes *	Direction cosines with †			Dipole moment components ‡	10 ¹² mK (calc.) §
		X	Y	Z		
(VI)	1.998	0.9421	-0.2628	-0.2084	-2.05	68
	1.905	0.2991	0.9394	0.1677	-0.65	
	1.800	0.1517	-0.2203	0.9636	-0.33	
(VII)	1.998	0.1174	-0.2629	0.9577	-2.05	68
	1.905	0.2577	0.9394	0.2263	-0.65	
	1.800	0.9591	-0.2202	-0.1781	-0.33	
(VIII)	1.998	0.1174	0.2629	0.9577	2.05	68
	1.905	-0.2578	0.9393	-0.2263	-0.65	
	1.800	0.9590	0.2203	-0.1781	0.33	
(IX)	2.113	0.2955	0.8591	-0.4178	2.17	170
	1.826	-0.4963	0.5117	0.7013	0.17	
	1.764	0.8163	0.0001	0.5776	0.00	

* Listed in descending order as b_1 , b_2 , and b_3 , in units of 10^{-23} c.c. † See text for location in molecular framework. ‡ Listed in descending order as μ_1 , μ_2 , and μ_3 (in D). § The observed values from the three methods of preparation are: 133 (PCl₅); 118 (HCl); 92 (SOCl₂).

Steric Course of the Substitution with Phosphorus Pentachloride.—The observed mK of *cis*-2-decalyl chloride, prepared from *cis,cis*-2-decalol by treatment with phosphorus pentachloride, corresponds to 50–70% content of (IX); substitution has, therefore, been accompanied by predominant inversion of configuration; 50–70% inversion if the *cis,trans*-chloride is 100% equatorial, 100% inversion if the equatorial : axial ratio is 0.5–0.7. The latter, characteristic of an S_N2 mechanism, conforms more to the pattern of previous experience with phosphorus pentachloride substitutions,¹⁴ and would, in addition, confirm the suggestion of Mills,³ that the two forms of *cis,trans*-2-substituted decalins do not differ greatly in stability.

Steric Course of the Substitution with Hydrochloric Acid.—The observed mK of *cis*-2-decalyl chloride, obtained with hot concentrated hydrochloric acid as substituting agent, differs from that observed for the sample prepared with phosphorus pentachloride by a little more than the experimental error. The lower value, however, is consistent with the increased racemisation that would be expected to accompany a coupled S_N1 mechanism.

Steric Course of the Substitution with Thionyl Chloride.—An observed mK of 92×10^{-12} is compatible with 20–30% content of (IX); if an equatorial : axial ratio for the *cis*- to the *trans*-isomer of 0.5–0.7 is accepted, it may be concluded that chlorination of *cis,cis*-2-decalol with thionyl chloride has proceeded with 25–50% inversion. The retention of configuration, normally associated with an S_Ni mechanism is indicated but is evidently incomplete.

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¹⁴ Ingold, "Structure and Mechanism in Organic Chemistry," Cornell Univ. Press, Ithaca, New York, 1953, p. 306 *et seq.*