solutions of the radical obeyed Beer's law. The maximum rate of flow through the spectrophotometric cell (volume, 0.1 cc) was 12 ml/min at 300 mm. Solutions of the pure radical could be kept in the cell for periods up to 1 hr with no detectable change in radical concentrations.

The rate of disappearance of the 2,4,6-tri-*t*-butylphenoxy radical is a pseudo-first-order process as demonstrated by plotting the logarithm of the absorbance *vs.* time. Figure 1 illustrates the decay of the hindered phenoxy radical at three different concentrations of 3-*t*-butylphenol. Good first-order plots were obtained for all of the unhindered phenols studied. Initial concentrations of radical were in the range 1–20 $\times$ 10^{-4} mole $l.^{-1}$. Phenol concentrations were chosen to give convenient rates of reaction, 5 $\times$ 10^{-4}–100 $\times$ 10^{-4} mole $l.^{-1}$, except for *p*-cyano- and *m*-cyanophenol where concentrations up to 200 $\times$ 10^{-4} mole $l.^{-1}$ were used.[20]

The rate of the reaction of 2,4,6-tri-*t*-butylphenoxy radical with *p*-methoxyphenol was too fast to measure by this method, but was readily determined by esr. The esr spectrometer was of conventional design, operating at 9600 MHz and employing 100-kHz field modulation. The esr cavity was cylindrical and was operated in the TE 011 mode. The data were read into a Varian C-1024 time-averaging computer. The reactions were carried out in the mixing stop-flow apparatus as described. The solutions were mixed at a point 4 cm above the esr cavity and allowed to flow through a signal free quartz tube, 2-mm bore, clamped on the axis of the cavity. Immediately upon attainment of equilibrium, the flow was stopped and the computer scan was simultaneously initiated (5-sec scan time). The spectrometer time constant was 0.01 sec.

Isotope Effect.—The kinetics were carried out as described above, except that the solutions of *p*-phenylphenol contained 0.1% (by volume) methanol-OD. Similar experiments were done in the presence of 0.1% undeuterated methanol.

(20) Hydrogen bonding was not detected at these concentrations from infrared spectroscopy.

Acknowledgment.—The authors are indebted to Dr. T. Cole for assistance with the esr measurement and to Mr. J. Beers for his enthusiastic approach to the solution of our glass blowing problems.

Conformational Preferences in Diastereomers. II

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An nmr study of the coupling constants of protons located at the two asymmetric centers in two systems is reported. In the 1,2-diphenyl-1-propyl system, increasing the size of the substituent leads to large coupling constants for both the *erythro* and *threo* isomers. A correction for electronegativity changes is made and the rotamer populations are compared with *A* values. In the substituted dihalopropane system, the use of dipole moment data in conjunction with the nmr data positively identifies the predominant rotamers. A large discontinuity is reported upon changing the substituent from isopropyl to *t*-butyl.

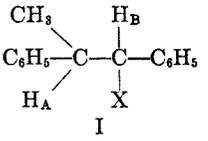
The observation that the vicinal coupling constant determined in nmr spectra is related to the dihedral angle[1] described by the H–C–C–H bonds has opened up a wide field of inquiry into the conformational preferences of large organic molecules.[2]

The observed vicinal coupling constant is a weighted mean derived from the populations of the two *gauche* rotamers (each J_{AB} = 1–3 cps) and the *trans* rotamer (J_{AB} = *ca.* 11–13 cps).

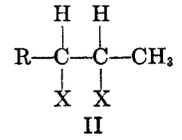
The effect of moving from one substituent to a more electronegative substituent has been shown to decrease the vicinal coupling constant.[3–6]

Bond-angle deformations also affect the vicinal coupling constant.[1,7] For example, cyclopropyl and cyclobutyl systems show somewhat anomalous coupling constants.[8,9]

With these reservations in mind, the conformational preferences of two new sets of diastereomers were studied, the 1,2-diphenyl-1-propyl system[10,11] (I) and



I



II

the substituted dihalopropane system (II). Once again the size of the substituents was systematically varied.

Results and Discussion

1,2-Diphenyl-1-propyl Series.—Table I records the nmr chemical shifts and coupling constants of the system in question. The variation in chemical shifts of the vicinal protons is small and will not be considered further. However, in the *erythro* series the chemical shift of the methyl substituent consistently falls at *ca.* 1.2 ppm. In the *threo* series this group appears at *ca.* 1.5 ppm. Examination of molecular models shows that the methyl group in the *erythro* isomer lies slightly above the plane of the two phenyls and probably suffers partial shielding due to the aromatic ring current. This effect is much less apparent in the *threo* model.

Partial nmr spectra of *threo*- and *erythro*-III are shown in Figure I.

The vicinal coupling constants listed in Table I show a fairly steady increase with increasing size of the substituent X. For example, when X is chloro the *erythro* isomer exhibits a coupling constant of 8.7 cps. This increases to 9.7 for bromo and 10.5 cps for iodo.

Discussion of conformational preferences will be aided by reference to Newman projections shown in

(1) (a) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959); (b) M. Karplus, *J. Am. Chem. Soc.*, **85**, 2870 (1963).

(2) (a) A survey of the literature has been given in part I of this series: C. A. Kingsbury and W. B. Thornton, *J. Org. Chem.*, **31**, 1000 (1966); (b) D. J. Pasto, C. Cumbo, and J. Frazer, *J. Am. Chem. Soc.*, **88**, 2194, 2201 (1966); (c) M. Buza and E. I. Snyder, *ibid.*, **88**, 1161 (1966).

(3) R. E. Glick and A. A. Bothner-By, *J. Chem. Phys.*, **25**, 362 (1956).

(4) C. N. Banwell and N. Sheppard, *Mol. Phys.*, **3**, 351 (1960).

(5) K. L. Williamson, *J. Am. Chem. Soc.*, **85**, 516 (1963).

(6) J. Cavanaugh and D. P. Dailey, *J. Chem. Phys.*, **34**, 1099 (1960).

(7) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press Ltd., London, 1959, p 86.

(8) H. S. Gutowsky, M. Karplus, and D. M. Grant, *J. Chem. Phys.*, **31**, 1278 (1959).

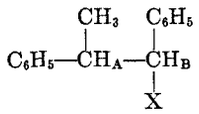
(9) S. Borcic and J. D. Roberts, *ibid.*, **87**, 1056 (1965).

(10) D. J. Cram and F. A. Elhafez, *J. Am. Chem. Soc.*, **74**, 5052 (1952).

(11) D. J. Cram, F. D. Greene, and C. H. DePuy, *ibid.*, **78**, 790 (1956), and earlier papers.

TABLE I

CHEMICAL SHIFTS AND COUPLING CONSTANTS IN THE 1,2-DIPHENYL-1-PROPYL SYSTEM[a]



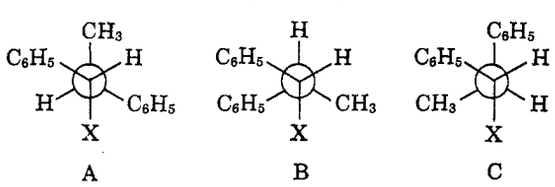
X	Compd	H_A, ppm	H_B, ppm	J_{AB}, cps	Mp, °C
OH	*erythro*-III[b]	2.84	4.41	8.4[b]	53
	threo-III	2.88	4.51	6.0	Liquid
OAc	*erythro*-IV	3.29	6.05	8.7	108
	threo-IV	3.18	5.84	7.8	Liquid
Cl	*erythro*-V	3.32	4.96	8.7	139
	threo-V	3.34	4.97	8.4	53
Br	*erythro*-VI	3.49	5.07	9.7	159
	threo-VI	3.43	5.06	9.5	58
I	*erythro*-VII	3.50	5.12	10.5	125
	threo-VII[c]	3.50	5.18	*ca.* 10.1	131
OTs	*erythro*-VIII			8.0	91
OPNB[d]	*erythro*-IX	3.42	6.10	8.1	107
OPNB[d]	*threo*-IX	3.47	6.14	7.4	144

[a] Spectra were run on a Varian A-60 *vs.* tetramethylsilane as an internal indicator taken as 0 ppm. Approximate concentration 10% by weight per volume in $CDCl_3$. [b] This value is relatively insensitive to concentration. [c] Approximate value. [d] PNB is *p*-nitrobenzoate.

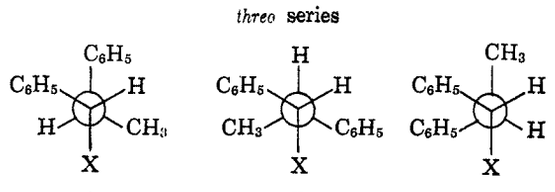
Chart I. It is apparent from Table I that the *erythro* isomer consistently has a higher coupling constant than the *threo* isomer, although with large substituents the difference is small. Thus rotamer A (*trans* protons) for the *erythro* isomer is more highly populated than B and C, whereas in the *threo* isomer A is less important relative to the *gauche* rotamers B and C. Steric replusions between the two large phenyl rings may destabilize rotamer A of the *threo* isomer relative to B and C.

CHART I

erythro series



threo series



In both the *erythro* and *threo* cases rotamer A involves two *gauche* interactions between large groups, whereas B and C are associated with three *gauche* interactions (*e.g.*, C_6H_5–C_6H_5, C_6H_5–X, and CH_3–X in *erythro*-B). Thus the reduction of energetically unfavorable *gauche* interactions may be responsible for the dominance of A. Similar ideas have been expressed by other authors,[12-15] in largely theoretical discussions of this problem.

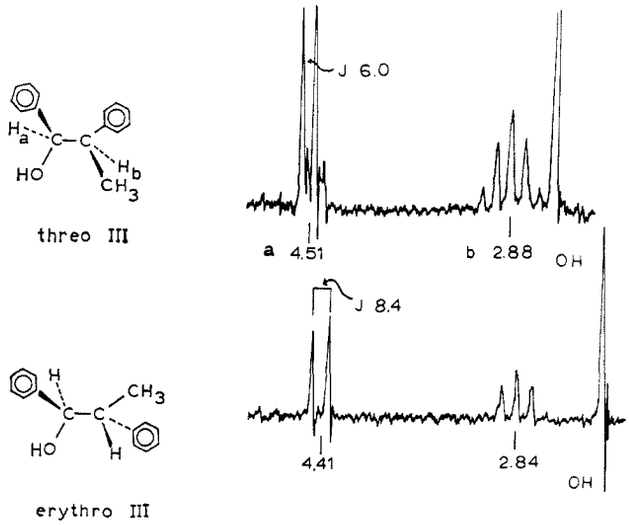


Figure 1.—Partial nmr spectra of *erythro*- and *threo*-1,2-diphenyl-1-propanol (III).

It is possible to make some rough calculations of the importance of rotamers with *trans* protons (*i.e.*, rotamer A) relative to rotamers with *gauche* protons (*i.e.*, rotamers B and C). From previous work[16,17] 12 cps seems to be a reasonable estimate for the coupling constant of rotamer A, whereas 2 cps will be used for the *gauche* cases (B and C). Also assuming that the observed coupling constant is a weighted mean of *gauche* and *trans* contributions, the following rotamer fractions may be calculated, *e.g.*, for the *erythro* isomer, where X is OH.

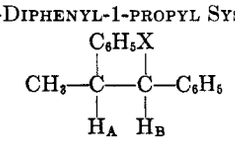
$$12X + 2(1 - X) = 8.4$$
$$X = 0.64$$
$$K = 0.64/0.36 = 1.8$$

It should be noted that this method is fraught with difficulty since the equilibrium constants so calculated are strongly dependent on the assumed *trans* and *gauche* coupling constants.

The ratios A/(B + C) are listed in Table II. An electronegativity correction has been applied for other substituents relative to hydroxyl by the Karplus

TABLE II

RELATIVE ROTAMER POPULATIONS IN THE 1,2-DIPHENYL-1-PROPYL SYSTEM



X	Compd	K = [rotamers A/(rotamers B + C)]	$-\Delta F°$, cal	*A* values, cal
OH	*erythro*-III	1.8	360	400 to 900
	threo-III	0.7	−220	
OAc	*erythro*-IV	3.4	740	400 to 700
	threo-IV	2.1	460	
Cl	*erythro*-V	1.8	350	300 to 500
	threo-V	1.6	270	
Br	*erythro*-VI	2.0	430	200 to 700
	threo-VI	1.7	310	
I	*erythro*-VII	2.0	430	400

(12) D. Y. Curtin, *Rec. Chem. Progr.* (Kresge-Hooker Sci. Lib.), **15**, 111 (1954).
(13) J. L. Mateós and D. J. Cram, *J. Am. Chem. Soc.*, **81**, 7756 (1959).
(14) M. Newman, *J. Chem. Educ.*, **32**, 844 (1955).
(15) D. J. Millen, "Progress in Stereochemistry," Vol. 3, Butterworth and Co. (Publishers) Ltd., London, 1962, p 159.
(16) N. Sheppard and J. J. Turner, *Proc. Roy. Soc.* (London), **A252**, 506 (1959).
(17) C. N. Banwell, N. Sheppard, and J. J. Turner, *Spectrochim. Acta*, **16**, 294 (1960).

method,[1b] using Williamson electronegativity values.[5,6] In our opinion this is an overcorrection. The equilibrium constants probably should be larger for the bromo and iodo cases. On this basis the acetate would have the strongest conformational preference.

Treating these ratios as equilibrium constants, the free-energy differences between *gauche* and *trans* rotamers can be calculated. These data are roughly comparable to A values, which, of course, are measures of the tendency for a substituent to occupy the equatorial position relative to the axial position in a cyclohexane system.[18] The A values would seem to show that the chloro group has approximately as large a conformational preference as the larger iodo group. A similar conclusion results from this study. As Jensen[19,20] and co-workers have pointed out the greater bond length of the iodo group tends to offset its greater size.

Inspection of Table I will show that the *erythro* isomer has the higher melting point as well as the higher J_{AB} value. This is rather common phenomenon.[10] The *p*-nitrobenzoate IX is the only exception in this study.

The basis for this correlation may lie in entropy differences between the solid state and the melt. Compounds which have several rotamers populated in solution (J_{AB} = 5–8 cps) but only one in the solid state gain considerable entropy on melting. A low melting point is thought to be the result. Other compounds which have a single rotamer populated in the solid, and largely the same rotamer populated in solution have little to gain on melting. A high melting point is the result.[21]

Substituted 2,3-Dihalopropanes.—Increasing the size of the substituent increased J_{AB} for both *erythro* and *threo* isomers in system I. In an earlier study[2a] increasing the size of the substituent resulted in increasing J_{AB} for the *erythro* isomer but decreasing J_{AB} for the *threo* isomer. With no clear trend in the data observable the nmr studies were extended to system II. Again the variation of the vicinal coupling constant was measured in a series of compounds with increasing size of the alkyl substituent R. Compounds with both vicinal chloro and bromo substituents were investigated. As Table III shows, the type of halogen substituent does not greatly affect the vicinal coupling constant.

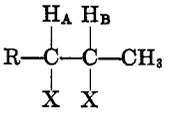
The variation in the vicinal coupling constants is best discussed in terms of the three rotamers given in Chart II.

As the size of the R group increases it will be noticed that J_{AB} in the *threo* series steadily decreases, going from 3.1 (DL-X) to 1.4 cps (*threo*-XV). The populations of rotamers B and C increase at the expense of A.

On the other hand, the *erythro* series shows a discontinuity as the bulk of R is increased. The vicinal coupling constant moves from 8.8 in *meso*-X (R is methyl)[22,23] to 10.6 cps in *erythro*-XII (R is isopropyl) indicative of the increasing dominance of rotamer A.

TABLE III

COUPLING CONSTANTS AND DIPOLE MOMENTS IN THE ALKYL-SUBSTITUTED 2,3-DIHALOPROPANE SYSTEMS

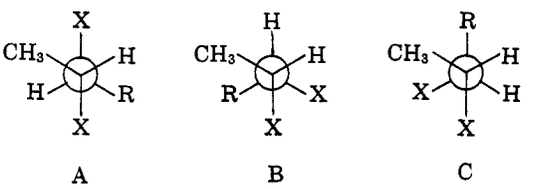


Compd	R	X	J_{AB}, cps[a]	Dipole moment, D.[b]
meso-X[c]	CH_3	Br	8.81	1.75[d]
DL-X[c]			3.11	1.63[d]
meso-XI[c]	CH_3	Cl	7.4	
DL-XI[c]			3.45	
erythro-XII	$(CH_3)_2CH$	Br	10.6[e]	0.85[f]
threo-XII			3.5	2.21
erythro-XIII	$(CH_3)_2CH$	Cl	9.2[e]	0.95
threo-XIII			3.7	2.40
erythro-XIV	$(CH_3)_3C$	Br	2.02	2.66
threo-XIV			1.60	2.50
erythro-XV	$(CH_3)_3C$	Cl	2.36	2.43
threo-XV			1.40	2.51

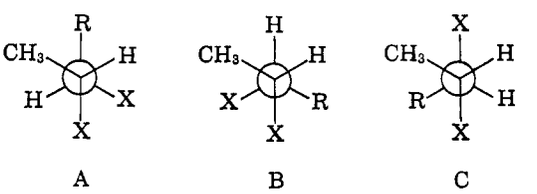
[a] Coupling constants were determined from expanded spectra taken on a Varian A-60 instrument *vs.* tetramethylsilane. Approximate concentration was 140 mg/ml of CCl_4. [b] Dipole moments ±0.05 D. [c] Reference 4. [d] Reference 24, p 111. [e] An approximate value determined from spin decoupled spectra. [f] Approximately 5% of *threo*-XII was present.

CHART II

erythro series



threo series



However, in *erythro*-XIV (R is *t*-butyl), the near-minimum coupling constant is found, 2.0 cps, indicative of a very small population of rotamer A.

Dipole moment data for compound X–XV are also given in Table III. These data corroborate the nmr data in every way. Partial nmr spectra of *threo*- and *erythro*-XV are given in Figure 2.

In *erythro*-XII and -XIII a large J_{AB} value is coupled with a small dipole moment, usually *ca.* 0.9 D. Thus rotamer A is dominant in these compounds. The large J_{AB} requires *trans*-vicinal protons, whereas the small dipole moment suggests predominantly *trans* halogens.

Other compounds, especially *erythro*-XIV, which have small coupling constants showing a dominance of rotamers B or C, also show large dipole moments (2.66 D. for *erythro*-XIV). In these compounds the two halogens as well as the two vicinal protons are *gauche*. The group moments of the two halogens in part are additive and a high dipole moment is the result. From the fact that the *t*-butyl group has a

(18) E. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 236.

(19) (a) F. R. Jensen and L. Gale, *J. Org. Chem.*, **25**, 2075 (1960); (b) *J. Am. Chem. Soc.*, **81**, 6367 (1959).

(20) E. Eliel and R. Haber, *ibid.*, **81**, 1249 (1959).

(21) J. Hildebrand and R. C. Scott, "The Solubility of Nonelectrolytes," Reinhold Publishing Corp., New York, N. Y., 1950, p 59.

(22) A. A. Bothner and C. Naar-Colin, *J. Am. Chem. Soc.*, **84**, 743 (1962).

(23) F. A. L. Anet, *ibid.*, **84**, 747 (1962).

slightly larger group moment than the methyl group[24] (by 0.1 to 0.3 D.), C is perhaps the more probable.

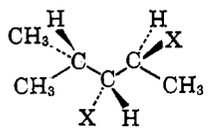
Angle deformation does not seem to be the reason for the stability of rotamer C.[25,26] The C^{13}–H coupling constant was determined from a neat sample of *erythro*-XIV. This value (152 cps) is very similar to that of bromomethane (150 cps), showing interorbital angles are probably similar in the two compounds.

The temperature dependence of *erythro*-XIV is quite normal. At 130° J_{AB} increased to 2.3 cps from 2.0 cps showing that rotamer A probably increases in importance. Rough values for $\Delta H°$ (*ca.* 800 cal) and $\Delta S°$ (1.9 eu) may be calculated from these data.

For the *threo* series of diastereomers, the combination of dipole moment data with nmr data provide an exact identification of the dominant rotamer. In *threo*-XIV and -XV the low coupling constant and high dipole moment are only consistent with the presence of rotamer B. In fact if one calculates the dipole moment expected from the presence of 100% of rotamer B, the result, 2.7 D., is very close to that experimentally observed, *ca.* 2.5 D.

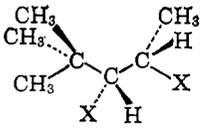
To summarize the previous data, for the *threo* isomers rotamer B appears to become increasingly important with increasing size of R. For the *erythro* isomers rotamer A is dominant where R is isopropyl but (probably) rotamer C is present where R is *t*-butyl. Thus an unexpected inversion of order has occurred.[27]

The reason for the difference in behavior between the *erythro*-XII and *erythro*-XIV may lie in the balance between 1,2 (*i.e.*, *gauche*) and 1,3 steric repulsions. In the isopropyl compound, *erythro*-XII, 1,2 interactions appear to be the most important. The large J_{AB} and the small methine H–H_B coupling constant (*ca.* 3 cps) show that the following over-all conformation is probably important. The 1,3 interactions involve an eclipsed hydrogen and a bromo group and also a



erythro-XII, rotamer A

hydrogen–methyl interaction. Neither interaction is extremely unfavorable. Going to the *t*-butyl compound, *erythro*-XIV, the methine proton is replaced by a methyl and a severe 1,3 methyl–bromo interaction results. It appears to be energetically favorable to rotate about the bond joining the asymmetric centers, even though the resulting rotamer C suffers three *gauche* 1,2 interactions between large groups rather than two such interactions which would be present in the erythro rotamer A. A methyl–methyl 1,3 interaction remains in C.



erythro-XII, rotamer C

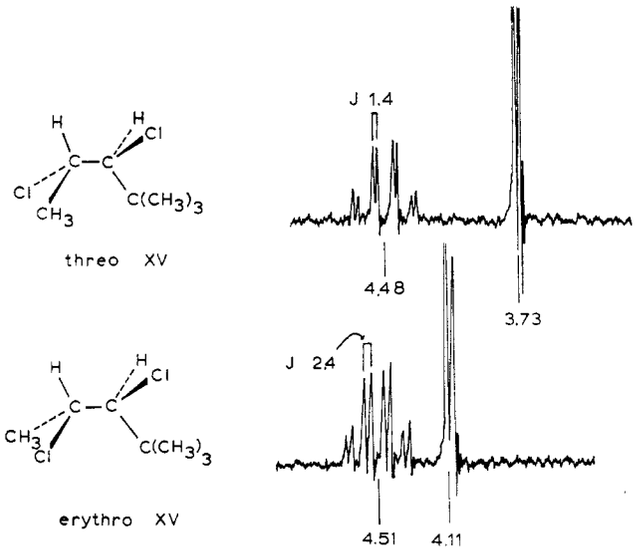


Figure 2.—Partial nmr spectra of *erythro*- and *threo*-4,4-dimethyl-2,3-dichloropentane (XV).

It seems surprising that a 1,3 bromine–methyl interaction can be that much worse than a 1,3 methyl–methyl interaction. The bromine van der Waals radius is 1.95 A, while that of chlorine is 1.8 A.[28] The methyl van der Waals radius is *ca.* 2.0 A, somewhat greater than the above values. The ability of the methyl hydrogens to stagger themselves may be the principal factor in reducing steric repulsions in rotamer C. Also there is some indication from molecular models that the *t*-butyl group may rotate more freely in rotamer C than in rotamer A, thus giving an entropy advantage to C.

Theoretically there should be a consistent set of rules whereby one may predict the most stable rotamer in any compound. These rules are as yet obscure particularly in systems involving heteroatoms. For example there was no way of predicting *erythro*-XII would have *trans* halogens, but that *erythro*-XIV would have *gauche* halogens. At any rate, the rather common practice of choosing the most stable rotamer from Newman projections or even with the aid of molecular models is perhaps undesirable.[29]

Experimental Section

erythro- and *threo*-1,2-diphenyl-1-propanol were prepared by the method of Cram and Elhafez.[10] The tosylate and *p*-nitrobenzoates were similarly synthesized.

erythro- and *threo*-1,2-diphenyl-1-propyl acetate were prepared from the corresponding alcohol as follows. To a solution of 3 g (0.014 mole) of *erythro* alcohol dissolved in 50 ml of anhydrous ether containing *ca.* 8 g of pyridine was added 2.0 g (0.025 mole) acetyl chloride with stirring. The reaction mixture was refluxed for 1 hr. The reaction mixture was diluted with water and extracted with ether. The ether layer was washed with dilute HCl, then with saturated $NaHCO_3$, and finally with water. The ether layer was dried over $MgSO_4$. Evaporation of the ether yielded crystals. The crystals were recrystallized from hot pentane, mp 107–108°. The *threo* acetate was distilled; the fraction distilling from 127 to 129° (0.25 mm) was used for nmr purposes. The spectra of these compounds showed the expected resonance absorptions.

(24) A. L. McClellan, "Table of Experimental Dipole Moments," W. H. Freeman and Co., San Francisco, Calif., 1963, p 251, 360.

(25) N. Muller and D. Pritchard, *J. Chem. Phys.*, **31**, 768 (1959).

(26) G. J. Karabatsos and C. Orzech, Jr., *J. Am. Chem. Soc.*, **86**, 3574 (1964).

(27) See, however, ref 2b.

(28) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, pp 257, 92.

(29) H. C. Brown, K. Morgan, and F. Chloupek, *J. Am. Chem. Soc.*, **87**, 2137 (1965).

TABLE IV
PHYSICAL CONSTANTS AND SPECTRAL DATA
$RCH_BCH_ACH_3$
X X

Compd	R	Bp, °C (mm)	Chemical shifts, ppm[a] CH_3	H_A	H_B	R
erythro-XII	$(CH_3)_2CH$	63–65 (5)	1.92	4.38	4.05	Complex
threo-XII		66–68 (1.5)	1.77	4.30	3.74	
erythro-XIII		23 (0.7)	1.67	4.16	3.78	
threo-XIII		37 (1.7)	1.60	4.32	3.64	
erythro-XIV	$(CH_3)_3C$	60 (1.2)	1.79	4.52	4.32	1.13
threo-XIV		66–67 (1.3)	1.80	4.46	3.90	1.16
erythro-XV		40 (1.6)	1.61	4.52	4.11	1.10
threo-XV		53 (2.5)	1.62	4.47	3.73	1.13

[a] *Vs.* tetramethylsilane as an internal indicator taken as 0 ppm. Solutions were 140 mg/ml of carbon tetrachloride.

erythro- and *threo*-1,2-diphenyl-1-propyl chloride were prepared by treatment of the alcohol with HCl. To 10.0 g (0.047 mole) of the *threo* alcohol 25 g (0.59 mole) LiCl plus 50 ml of concentrated HCl were added. The heterogeneous mixture was vigorously stirred for 2 hr at room temperature. The mixture was diluted with 100 ml of water and extracted with ether. The ether layer was washed with water until no test for chloride ion was evident and then dried over $MgSO_4$.

Filtering and evaporation yielded mixed crystals of *erythro* and *threo* chlorides. Fractional crystallization using pentane–chloroform solvent yielded *erythro* chloride, mp 138–139°, and *threo* chloride, mp 52–53°. These constants were very similar to the literature values.[10]

erythro- and *threo*-1,2-diphenyl-1-propyl bromide were prepared by a method similar to the chloride, yielding *erythro* bromide, mp 157–159° (lit.[10] mp 159–160°), and *threo* bromide, mp 57–59° (lit.[10] mp 60–61°). The nmr spectra again were consistent in every way with the structure.

Treatment of *threo*-1,2-diphenyl-1-propanol with HI–LiI yielded only *erythro* iodide, mp 124–125° (lit.[10] mp 126°). The *threo* iodide was prepared by the method of Cram and Elhafez,[10] mp 130–131°.

The preparation of the dibromides and dichlorides in the dihalopropane system involved addition of the halogen to *cis* and *trans* commercial olefins (Columbia Organic Chemical Co.). It was assumed that *trans* addition occurred in each case. The basic procedure was a modification of that of Lucas, Simpson, and Carter.[30]

The apparatus consisted of a 250-ml, three-necked flask fitted with an addition funnel, a mercury-sealed stirrer, and a glass tube leading to a gas trap which contained a sodium thiosulfate solution. The reaction flask was protected from light.

A solution of 10 g (0.119 mole) of *trans*-4-methyl-2-pentene dissolved in 50 ml of pentane was placed in the reaction flask. To this solution, cooled to −50° and under nitrogen, a solution of 18.2 g (0.115 mole) of bromine in 75 ml of pentane was added dropwise with stirring. After the bromine color had disappeared, the reaction mixture was poured into ice. The organic layer was washed with cold, dilute $Na_2S_2O_3$ and then washed three times with water. The organic layer was dried over $MgSO_4$ and the solvent was evaporated yielding an oil which was distilled. The fraction distilling from 49 to 52° (1.9 mm), 20.7 g, was used for spectral purposes.

(30) H. Lucas, M. Simpson, and I. Carter, *J. Am. Chem. Soc.*, **47**, 1465 1925).

The other halogenations were carried out similarly. The physical constants of the dibromides are very similar to those reported by Boord and co-workers.[31]

The chlorinations were similar to the brominations except that a gas inlet tube was used. Chlorine was introduced periodically until the yellow color persisted for 20 min. The dichlorides are not reported in the literature. The spectral data and physical constants are summarized in Table IV.

Dipole Moment Measurements.—The basic technique was that described by Weissburger.[32]

Dielectric constants were measured with a transistorized heterodyne beat apparatus which was built by R. W. King and J. G. Verkade and will be described in a future publication by these authors. Dipole moments were calculated from the dielectric constants by utilizing the relations[33]

$$\mu = \frac{(9kTP_t)0.5}{4N\pi}$$

$$P_t = \frac{3(\mathrm{MW})}{d(\epsilon + 2)^2}\left[\frac{\partial \epsilon}{\partial x} - 2n_\infty \frac{\partial n}{\partial x}\right]$$

where μ = dipole moment in D. NLTS, P_t = total molar polarizability, d = density of solvent, ϵ = observed dielectric constant, $\partial\epsilon/\partial x$ = slope of plot of ϵ *vs.* mole fraction, and MW = molecular weight of solvent.

Five solutions differing in mole fraction were made up using cyclohexane as the solvent and P_t was determined from the slope of the straight line obtained by plotting the observed dielectric constant *vs.* mole fraction of solute. A least-squares analysis by computer techniques was applied to each set of data. Since $\partial n/\partial x$ is very small, the quantity of $2N_\infty \partial n/\partial x$ makes a negligible contribution to P_t and was therefore neglected.

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(31) (a) C. G. Schmitt and C. E. Boord, *ibid.*, **54**, 751 (1932); (b) I. Schuman and C. E. Boord, *ibid.*, **55**, 4930 (1933).

(32) A. Weissburger, "Technique of Organic Chemistry," Vol. I, 3rd ed, Interscience Publishers, Inc., New York, N. Y., 1960, p 2602.

(33) H. B. Thompson, *J. Chem. Ed.*, **43**, 66 (1966).