Polar Addition of Olefins. Part I. Stereochemistry of the Halogenation of *cis*- and *trans*-2-t-Butylstyrene. Rotational Isomerism of the Products

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Halogenation of *cis*- and *trans*-2-t-butylstyrene in carbon tetrachloride occurs by a non-stereospecific addition. The stereochemistry of dibromide formation depends strongly on the starting olefin, but the same ratio (50%) of dichloro-compounds is obtained from either *cis*- or *trans*-olefin. The results provide further support for an unsymmetrical bridged bromonium ion intermediate in the bromination reaction, but indicate that an open carbonium ion is involved in the chlorination reaction. The coupling constants obtained for the dihalogeno-compounds show that conformers with *gauche* t-butyl and phenyl groups are substantially populated in both the *threo*- and the *erythro*-compounds. This observation is shown to have analogies with the rotamer populations in halogenoethanes.

THE electrophilic addition of chlorine and bromine to olefins is well documented.[1-4] In non-polar solvents, addition of these halogens to symmetrical dialkyl olefins (*cis*- and *trans*-but-2-ene,[5-8] *cis*- and *trans*-di-t-butyl-ethylene [9]), which are not capable of forming highly stabilised carbonium ions, proceeds stereospecifically and *trans*. This has been attributed to the formation of the cyclic ion intermediate originally postulated by Roberts and Kimball.[10]

In contrast a less stereospecific addition (predominantly, though not exclusively, *trans* in non-polar solvents but less stereospecific in more polar solvents) has been observed in aryl-substituted olefins such as *cis*- and *trans*-1-phenylpropenes,[7,11] *cis*- and *trans*-stilbene,[12,13] and styrenes.[14] This lack of stereo-specificity has been ascribed to an unsymmetrical structure of the transition state, which resembles a benzylic cation more than a bridged halogenium ion.[11]

It is thus clear that the structure of the starting olefin exerts a considerable influence on the nature and structure of the transition state involved in the halogen addition.

In the course of preparing some sterically hindered ethanes in order to study their coupling constants, we investigated the additions of chlorine and, particularly, bromine to *cis*- and *trans*-2-t-butylstyrene. The results demonstrate the influence of the bulky t-butyl group (which might be expected to impose severe conformational restraints in the transition state) on the stereochemistry and course of halogen addition to olefins.

The couplings and rotational preferences shown by the t-butyl-substituted ethanes also throw light on the factors which affect rotational energies in these compounds; these will also be considered.
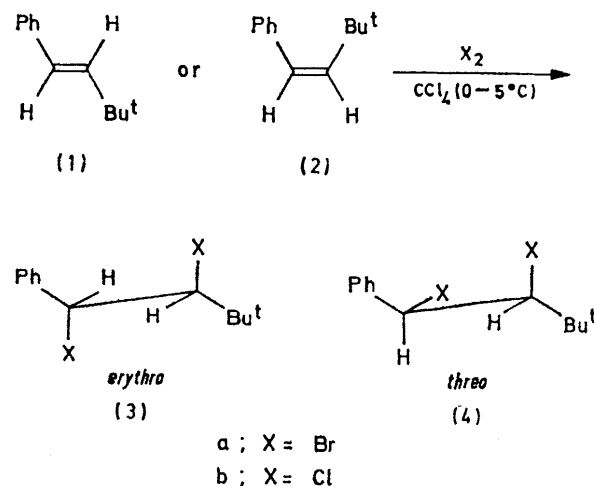
SCHEME 1

Results.—Addition of halogen to either *trans*- (1) or *cis*- (2) 2-t-butylstyrene in carbon tetrachloride, yields a mixture of *erythro*- and *threo*-1,2-dihalogeno-3,3-dimethyl-1-phenylbutane [(3) and (4)].‡ The assignments of *erythro*- and *threo*-configurations were made on the basis of the n.m.r. spectra (Table 1). The vicinal coupling constant ($^3J_{HH}$) is larger for the *erythro*- than

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[1] G. Williams, *Trans. Faraday Soc.*, 1941, **37**, 749.

[2] P. B. D. de la Mare, *Quart. Rev.*, 1949, **3**, 126.

[3] P. Sykes, 'The Search for Organic Reaction Pathways,' Longmans, London, 1972, p. 140.

[4] R. C. Fahey, *Topics Stereochem.*, 1968, **3**, 180.

[5] H. J. Lucas and C. W. Gould, *J. Amer. Chem. Soc.*, 1941, **63**, 254.

[6] M. L. Poutsma, *J. Amer. Chem. Soc.*, 1965, **87**, 2172.

[7] R. Fahey and C. Schubert, *J. Amer. Chem. Soc.*, 1965, **87**, 5172.

[8] J. Rolston and K. Yates, *J. Amer. Chem. Soc.*, 1968, **91**, 1469.

[9] R. Fahey, *J. Amer. Chem. Soc.*, 1966, **88**, 4681.

[10] J. Roberts and G. E. Kimball, *J. Amer. Chem. Soc.*, 1937, **59**, 947.

[11] R. Fahey and H. J. Schneider, *J. Amer. Chem. Soc.*, 1968, **90**, 4429.

[12] R. Buckles, J. Bader, and R. Thurmaier, *J. Org. Chem.*, 1962, **27**, 4523.

[13] G. Heubleim, *J. prakt. Chem.*, 1966, **31**, 84.

[14] J. Rolston and K. Yates, *J. Amer. Chem. Soc.*, 1969, **91**, 1469.

for the *threo*-isomers, as seen clearly from Table 2. The stereochemical results for the addition reactions (Scheme 1) are shown in Table 3, which includes for

TABLE 1

Chemical shifts (δ) [a] and couplings (Hz) in *erythro*- and *threo*-PhCH$_A$X·CH$_B$XBu^t

		δ_A	δ_B	δ(Bu^t)	J_{AB} n-Pentane	CCl$_4$	Me$_2$CO
X = Br	erythro	5·42	4·52	1·03	4·58	4·54	4·25
	threo	5·40	3·99	1·20	2·00	2·08	2·28
X = Cl	erythro	5·18	4·23	1·00	4·84	4·74	4·38
	threo	5·30	3·83	1·18	1·83	1·82	2·02

[a] In CCl$_4$ solution.

TABLE 2

Vicinal coupling constants in R^{1}CHX·CHXR^2

				$^3J_{HH}$/Hz		
R^1	R^2	X	Solvent	erythro	threo	Ref.
Me	Me	Cl	Neat	6·26	3·28	16
			CS$_2$	7·39	3·45	16
Ph	Me	Cl	CCl$_4$	8·0	5·7	7
Ph	CO$_2$Me	Cl	CCl$_4$	11·0	8·6	17
Ph	Bu^t	Cl	n-Pentane	4·84	1·83	a
			CCl$_4$	4·74	1·82	a
			Me$_2$CO	4·38	2·02	a
Bu^t	Bu^t	Cl	CCl$_4$	5·2	0·8	9
Me	Me	Br	Neat	7·87,	3·03,	16,
				7·85	3·15	18
			CS$_2$	8·81	3·11	16
Ph	Me	Br	CCl$_4$	10·2	5·3	10
Ph	Bu^t	Br	n-Pentane	4·58	2·06	a
			CCl$_4$	4·54	2·08	a
			Me$_2$CO	4·25	2·28	a
p-MeO·C$_6$H$_4$	Me	Br	CCl$_4$	10·0	5·4	10

[a] This paper.

TABLE 3

Stereochemistry of halogen addition to 2-alkyl-substituted styrene

		Cl$_2$ Addition (%)		Br$_2$ Addition (%)		
PhCH : CHR		erythro	threo	erythro	threo	Ref.
R = Me	cis	61—64	27—30	17	83	7, 11
	trans	38—39	45—46	88	12	7, 11
R = Bu^t	cis	46 [b]	46	62·3 [c]	37·7 [c]	a
	trans	46 [b]	46	87·3	12·7	a

[a] This paper. [b] Up to 8% of substitution products were also present. [c] Calculated percentage from a mixture of cis- (83·9%) and trans- (16·1%) olefins.

comparison the literature results for the analogous 1-phenylpropenes.[11]

Mechanism of Halogen Addition.—The results (Table 3) demonstrate the non-stereospecific addition of halogens to 2-t-butylstyrene and also the pronounced effect of the t-butyl as compared to the methyl substituent. According to Buckles,[15] the mechanism of bromination of olefins in CCl$_4$ is as follows:

$$S + Br_2 \rightleftharpoons S \cdots Br_2 \quad \text{(i)}$$
$$S \cdots Br_2 + Br_2 \longrightarrow [SBr^+Br_3^-] \quad \text{(ii)}$$
$$[SBr^+Br_3^-] \longrightarrow SBr_2 + Br_2 \quad \text{(iii)}$$
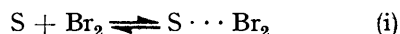
The initial rapid and reversible process gives the charge-transfer complex S $\cdots$ Br$_2$. This is followed by ionis-

[15] R. E. Buckles, J. L. Miller, and R. J. Thurmaier, *J. Org. Chem.*, 1967, **32**, 888.

ation (assisted by bromine) to give the intimate ion pair [SBr$^+$Br$_3^-$], which under the reaction conditions used here (non-polar solvent, absence of added bromide salt, and low concentrations of bromine) decomposes unimolecularly to products.

The stereochemical results of the bromination reaction (Table 3) can now be explained (Scheme 2). This scheme is based on the observation [11] that the intermediate more resembles an open benzylic cation than a bridged bromonium ion. It may be regarded either as a very
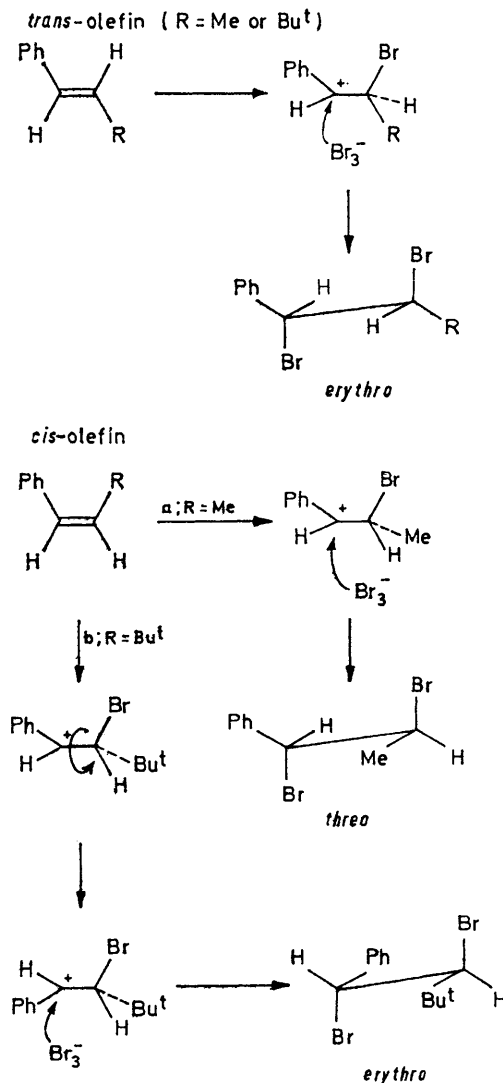
SCHEME 2

unsymmetrical bromonium ion (*i.e.* with a long bond between the bromine and carbonium atoms) or as a constrained carbonium ion. In either case, the preferred conformation will be as shown in Scheme 2, there will be fairly rapid rotation about the central C–C bond (see later), and the breakdown of the intimate ion pair (SBr$^+$ Br$_3^-$) will occur by a predominantly *trans* coplanar migration.

For the *trans*-olefin, the intermediate cation is in its most stable conformation with the phenyl and R groups

almost *trans*, thus the usual attack of Br_3^- produces the *erythro*-compound in much the greater proportion (88 and 87·3% for R = Me or Bu^t, respectively).

In the case of the *cis*-olefins, the reaction path differs for the methyl and t-butyl cases. For the *cis*-1-phenyl-propene (R = Me in Scheme 2) the path is essentially identical with that of the corresponding *trans*-olefin, resulting in a similar proportion of the *threo*-isomer (83% *threo* vs. 88% *erythro*, cf. Table 3).

However, in the t-butyl case (R = Bu^t, Scheme 2) although the formation of the intermediate cation occurs as before there is now considerable steric strain between the *cis* phenyl and t-butyl groups in the transition state. This can be relieved most easily by rotation about the central C–C bond to the other stable conformer, and this will give finally the *erythro*-compound. The large proportion of the *erythro*-isomer obtained (62%; Table 3) suggests that rotation about the central carbon bond is faster than the rate of attack of the Br_3^- ion. This is supported by the results of Collins and Benjamin,[16] who found that the rate of rotation about the $\overset{+}{C}$–C bond in (5) was comparable to the rate of nucleophilic attack (of OH^-) at the carbonium ion centre.

It is interesting to compare the behaviour toward isomerization of the unsymmetrical bromonium ion with the results reported by Fahey.[9] He has demonstrated the striking stability to isomerisation of the intermediate bridged chloronium ion (6), where the severe steric interaction between the two bulky t-butyl groups is unable to produce rotation. Our results, which show isomerisations (even with Br which is a better bridging atom than Cl), clearly demonstrate the unsymmetrical charge distributions and consequently much lower barrier toward rotation than in the chloronium ion (6).
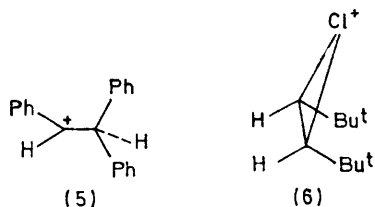
The results in Table 3 cannot be ascribed to isomerisation of the starting olefin, or to secondary isomerisation of the product dibromides. In fact, both starting olefins and product dibromides have been shown to be stable under the reaction conditions. However, isomerisation of the dibromides is observed at very high bromine concentration, or when the products are left for 96 h in contact with an excess of bromine. For this reason we have used short reaction times (<7 min) and mild conditions (low concentration of halogen).

Chlorine Addition.—The chlorine addition is basically similar, but the intermediate cation (7) in the chlorination of the *trans*-olefin will have a decreased conformational preference and therefore a much more rapid rate of rotation about the $\overset{+}{C}$–C bond, than the corresponding bromine ion. If the rotation is very fast

compared with the attack of Cl_3^- (or decomposition of the intimate ion pair) then the proportions of the products will be equal, and this is observed for compounds (1) and (2) and also for the *trans*-methylstyrene
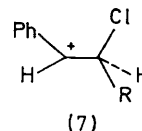
(Table 3). Only in the case of the *cis*-methylstyrene is there any significant inequality in the product proportions.

Chlorine addition to olefins in non-polar solvents has been shown by Poutsma[6,17] to proceed by a predominantly free-radical mechanism at high olefin concentrations even at low temperatures and in the dark. However at the low olefin concentrations used here
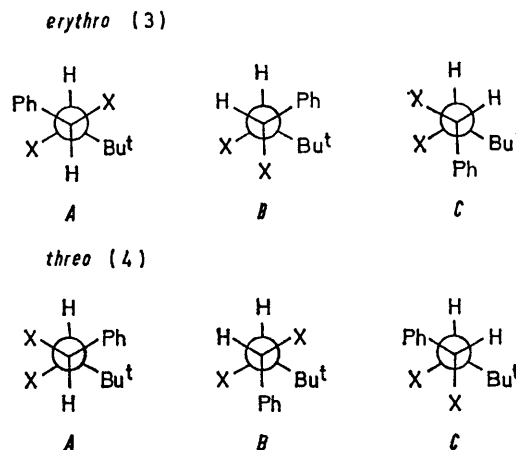

FIGURE The individual rotamers of *erythro*- (3) and *threo*- (4) 1,2-dihalogeno-3,3-dimethyl-1-phenylbutanes

(<4 × 10⁻²M) the chlorination reactions studied by Poutsma all proceeded by the usual electrophilic mechanism; further we see no products corresponding to a free-radical attack.

Rotamer Populations.—The rotational isomers of the *erythro*- (3) and *threo*- (4) dihalides are shown in the Figure; these, when considered with the $^3J_{HH}$ values (Table 1) and dipole moment data enable the rotamer populations to be obtained, as follows.

The observed coupling in any solvent is the weighted mean of the couplings in the rotamers, *i.e.*

$$J_{obs} = \sum_{i=A,B,C} n_i J_i \qquad (iv)$$

where $\Sigma n_i = 1$

Thus it is necessary first to estimate the rotamer couplings J_i. It is a common procedure in such studies to consider merely one *gauche*- and one *trans*-oriented

[16] C. J. Collins and B. M. Benjamin, *J. Org. Chem.*, 1963, **85**, 2519.

[17] M. L. Poutsma, *J. Amer. Chem. Soc.*, 1965, **87**, 2161.

coupling.[18] This procedure takes no account of the orientation dependence of the effect of substituents on such couplings, which results in considerable variations of J_g.[19] However, these can easily be estimated from the equations given previously for such couplings [19] taken together with the observed couplings in similar systems.

We note that all alkyl groups have similar substituent effects on $^3J_{HH}$ ($^3J_{HH}$ in EtX is 7·35, 7·62, and 7·52 Hz for X = Me,[20] Ph, and CMe_2Et,[21] respectively). The couplings for (3; X = Br) may therefore be taken directly from the observed couplings in *meso*-dibromobutane (8), obtained following the procedure of ref. 22

Me   Me
H⟍⤬⟋Br   Br⟍⤬⟋Me
Br⟋⤬⟍H   Br⟋⤬⟍H
   Me   H

(8)
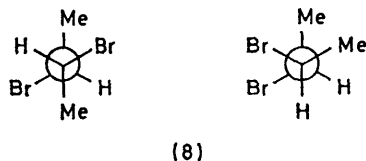
but using an improved model,[23] of 10·8 (J_t) and 1·9 Hz (J_g). The values for (3; X = Cl) can be obtained from these by using the equations of ref. 19 (J_t^t and J_g^g) to give J_g 10·4 and J_g 1·6 Hz.*

The values of J_t may be safely transferred to the *threo*-compounds (4) but the orientation of the halogen atoms with respect to the coupling protons is markedly different in (4B) and (4C) and must be considered explicitly. The observed coupling in the t-butyl analogue (9) of (4C) of 0·8 Hz [8] may be taken as the

Bu^t
Cl⟍⤬⟋H
Cl⟋⤬⟍H
Bu^t

(9)
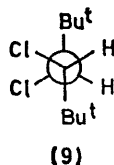
value for (4C; X = Cl), and from the equations of ref. 19 (J_g^g) the corresponding coupling for (4C; X = Br) is 1·4 Hz.

The couplings for (4B) are markedly different as in this orientation the electronegative substituents increase the coupling. We note that the orientation of the substituents with respect to the coupling protons in (3B) [and (3C)] is the average of those in (4C) and (4B) and thus the couplings can also be considered to be the corresponding averages. This gives couplings in (4B) of 2·4 Hz for X = Cl and Br, and this is also reasonably consistent with the predictions of ref. 19.

To summarise, we use values for the rotamer couplings of (3A), (3B), and (3C) of 10·8, 1·9, and 1·9 Hz (X = Br) and 10·4, 1·6, and 1·6 Hz (X = Cl) and of (4A), (4B), and (4C) of 10·8, 2·4, and 1·4 Hz (X = Br) and 10·4, 2·4, and 0·8 Hz (X = Cl). These values can be inserted

in equations (iv) with the observed couplings to relate the rotamer populations. However, this does not immediately give all the rotamer populations as there are too many unknowns for the number of equations, but use can be made also of the observed dipole moments of compounds (3) and (4) (X = Br) of 3·03 and 1·92 D. In this case equation (iv) can be re-written as

$$\mu^2_{obs} = \sum_{i = A,B,C} n_i \mu^2_i \qquad \text{(v)}$$

The values of the rotamer dipole moments were estimated from those calculated for 1,2-dibromoethane by use of our latest value of the C–CHBr–C bond moment of 2·03 D.[23] This gave μ_g 3·37, μ_t 0·0 D.

For compounds (3) both the coupling constants and dipole moments of (3B) and (3C) are identical, and therefore only the population of (3A) can be determined. Equation (iv) and the observed couplings (Table 1) give values of n_A of 0·30, 0·29, and 0·26 (X = Br) and 0·37, 0·33, and 0·30 (X = Cl) for solutions in n-pentane, carbon tetrachloride, and acetone. The proportion of the more polar isomers (3B) and (3C) increases as the solvent dielectric constant increases, as expected.

The observed dipole moment when inserted into equation (v) gives, for the pure liquid, n_A (X = Br) 0·20 in reasonable agreement with the coupling constant calculations.

For compounds (4), the three isomers all have either different couplings or different dipole moments, thus the combination of these measurements provides enough data to determine all the rotamer populations. From the foregoing values of the rotamer couplings and dipole moments and values of μ_{obs} and J_{obs} of 1·92 D and 2·1 Hz, we obtain n_A 0·00, n_B 0·68, and n_C 0·32.

These results thus show that for compounds (3) there is *ca.* 30% of (3A; X = Br) and slightly more for X = Cl. This corresponds to energy differences ($E_A - E_{B,C}$) of +0·1 (X = Br) and −0·1 kcal mol^{-1} (X = Cl). For (4; X = Br), (4B) is the predominant rotamer and the energy differences are $E_A - E_B > 1·5$ and $E_C - E_B$ 0·4 kcal mol^{-1}.

The results show unambiguously that the rotamers with *gauche* phenyl and t-butyl groups are substantially populated, indeed in both compounds (3) and (4) this is the major rotamer. This conclusion is unaffected by any reasonable variation in the rotamer couplings. The observation of a small vicinal coupling, taken together with the known range of values of J_t (>10 Hz) leads unequivocally to the conclusion that the major rotamers are (3B) or (3C). This is to be contrasted with the comparable situation in cyclic compounds, *e.g.* cyclohexanes, where conformations with axial t-butyl groups essentially are forbidden. However, these results are in

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* Note that the equations of ref. 19 are used here merely to calculate the difference between X = Cl and X = Br in any configuration and are thus much more reliable used in this way than in the calculation of any given coupling.

[18] W. F. Reynolds and D. J. Wood, *Canad. J. Chem.*, 1969, **47**, 1295.

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[20] R. C. Ferguson and D. W. Marquardt, *J. Chem. Phys.*, 1964, **41**, 2087.

[21] S. Ebersole, S. Castellano, and A. A. Bothner-By, 1964, *J. Phys. Chem.*, 1964, **68**, 3430.

[22] R. J. Abraham, *J. Phys. Chem.*, 1969, **73**, 1192.

[23] R. J. Abraham and E. Bretschneider, ' Structure of Molecules and Internal Rotation,' ed. W. J. Orville-Thomas, Wiley, London, 1973, ch. 13.

line with recent determinations of rotamer populations [24] and barriers to rotation [25] in substituted ethanes, which demonstrate clearly that the values for relative sizes of substituents cannot be transferred from cyclic to acyclic compounds.

The rotamer energies obtained can be compared with those from other ethanes; for example, the relative rotamer energies for a number of 1,2-disubstituted ethanes CH_2X-CH_2Y have been determined. For the pairs of substituents (Ph,Bu^t), (Bu^t,Br), (Ph,Br), and (Br,Br) these energy differences, $E_g - E_t$, are 1·7, 1·3, 0·5, and 1·3 * kcal mol^{-1}, respectively.[19,23,26] The small value of the *gauche* phenyl–bromide interaction is noteworthy and is consistent with results from barrier heights [27] and relative rotamer populations in other halogenoethanes [24] which both suggest that phenyl lies between chlorine and bromine in effective size in these systems.

If the foregoing values are considered as a measure of the repulsive interactions between *gauche* substituents in ethanes then the relative rotamer energies in compounds (3) and (4) may be calculated as the sum of these contributions. This gives for the bromo-compounds relative energies of 1·8, 4·3, and 3·5 kcal mol^{-1} for (3A), (3B), and (3C), and of 3·0, 3·5, and 3·1 kcal mol^{-1} for (4A), (4B), and (4C). Comparison with the observed energies shows that those for (4B) and (4C) are of the right order (δE_{BC} obs. −0·4; calc. −0·4) but that rotamer A is far less stable than predicted (δE_{AC} obs. >1·5; calc. −0·1). A similar anomaly is found for compounds (3) (δE_{AC} obs. 0·1; calc. −1·7); thus in both cases the rotamers with *trans*-protons are destabilised by *ca.* 1·5 kcal mol^{-1} with respect to predictions from 1,2-disubstituted ethanes.

This anomaly has an exact analogy in the well-documented halogenoethanes. The *gauche*-to-*trans* energy difference in 1,2-dichloroethane (1·20 kcal mol^{-1}) [28] predicts the same value in 1,1,2,2-tetrachloroethane. The observed energy difference is 0·0 kcal mol^{-1}.[28] This discrepancy has been shown to be due to the non-tetrahedral angles in these molecules and molecular mechanics calculations based on heavy atom angles of 111° can quantitatively account for the rotamer stabilities in all the halogenoethanes.[29]

A similar explanation could well hold in the molecules studied here, as the normal C–C–C− angles are also non-tetrahedral (*ca.* 111°). If this is the case then the trisubstituted compound should exist virtually all in one form, analogous to the case of 1,1,2-trichloroethane ($E_g - E_t$ *ca.* 2·0 kcal mol^{-1}).[28] An investigation of these systems is in progress.

EXPERIMENTAL

N.m.r. spectra were obtained on Varian HA100 and A56/60 spectrometers (probe temperatures 27 and 40 °C,

* In n-pentane solution.

respectively). In each case the average of three calculated spectra (measured by the side-band technique) was taken and the r.m.s. errors were 0·05 Hz when averaged over the entire spectrum.

The dipole moments of two mixtures of (3) and (4) (X = Br), containing 38·5 and 81% of (3) (measured by n.m.r. integration) were obtained in benzene solution by the method and with the apparatus described in ref. 30, based on the Halverstadt–Kumler equation.[31] Extrapolation to infinite dilution gave P_{20} values of 188·4 and 240·5 cm^3 for the two mixtures, which gave dipole moment values of 2·41 and 2·89 D [using d^{20} and n_D^{20} values of 1·549 and 1·5645 as measured for a mixture of (3) and (4)]. These with the foregoing percentage compositions gave dipole moments of 3·03 and 1·92 ($\pm$0·1) D for (3) and (4) (X = Br), respectively.

Benzyltriphenylphosphonium Chloride.—Benzyl chloride (3·5 g, 3·2 ml) and triphenylphosphine (6·5 g) were dissolved in nitromethane (5 ml). The solution was refluxed for 1·5 h, then cooled and washed with ether (100 ml). The product (9·4 g; m.p. 314—315 °C) was filtered off and used in the next stage without recrystallisation.

cis- *and* trans-2-*t*-*Butylstyrene.*—To a stirred suspension of benzyltriphenylphosphonium chloride (38·85 g, 0·10 mol) in dry benzene (500 ml) under nitrogen was added 2·25N-n-butyl-lithium in n-hexane (48 ml, 0·10 mol). The resulting deep red solution was cooled to 8—10 °C and pivalaldehyde (7·9 g, 0·092 mol) in dry benzene (100 ml) was added slowly during 0·5 h, with the temperature kept between 8 and 10 °C. After stirring for 2 h at room temperature, the mixture was refluxed for 3 h. Then water (250 ml) was added, and after shaking and separation the water layer was extracted with benzene (2 × 100 ml). The benzene layers were combined, dried (MgSO$_4$), and evaporated to 200 ml. The solution was treated with light petroleum (b.p. 60—80°; 200 ml) and the precipitate was filtered off. Evaporation of the solution and elution (with light petroleum) through a column of grade 3 alumina (550 g) gave a 1 : 1 mixture of pure products (10·9 g, 73·7%). Pure *cis*-olefin was obtained by column chromatography on grade I alumina. Quantitative yields of pure *trans*-olefin were obtained by refluxing a 1 : 1 mixture of *cis*- and *trans*-2-t-butylstyrene in carbon tetrachloride containing iodine.

Halogen Additions.—In a typical reaction, to a stirred solution of olefin (0·10 g, 0·625 mmol) in carbon tetrachloride (15 ml) was added (in the dark and at 0 —5 °C) a solution of halogen (1·0 g of bromine per 10 ml of solution or a saturated solution of chlorine) (2·5 ml, 1·6 mmol). The halogen colour was removed by treatment with an excess of aqueous sodium sulphite; the organic layer was separated and dried (MgSO$_4$). The solvent was distilled off and a yield of crude liquid dihalides of *ca.* 0·2 g (100%) was consistently obtained. The compositions of these crude mixtures are summarised in Table 3.

Stability of Mixtures of erythro- *and* threo-1,2-*Dibromo-*

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[31] I. F. Halverstadt and W. D. Kumler, *J. Amer. Chem. Soc.*, 1942, **64**, 2988.

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3,3-*dimethyl*-1-*phenylbutane*.—Solutions of various mixtures of *erythro*- and *threo*-dibromo-compounds in carbon tetrachloride were placed in n.m.r. tubes and an excess of pure bromine was added to each. Isomerisation was observed after 4 h in daylight to give an equilibrium mixture of 56·9% *threo* and 43·1% *erythro*. The isomerisation reactions were followed by n.m.r., using the t-butyl signals of the dibromo-compounds.

Only a little isomerisation (<10%) of the dibromo-

products was observed after 96 h in the dark and under the reaction conditions.