Polar Addition to Olefins. Part II.[1] Stereochemistry of Addition of Deuterium Bromide to *cis*- and *trans*-t-Butylstyrene. Rotamer Populations of Sterically Crowded Trisubstituted Ethanes

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Addition of deuterium bromide to *trans*- and *cis*-β-t-butylstyrene in methylene chloride, at 0 °C, gives *erythro*- and *threo*-1-bromo-3,3-dimethyl-1-phenylbutane, the polar addition products. With the *trans*-olefin 81% of *cis*-addition was found, whereas with the *cis*-olefin 67% of *cis*-adduct is formed. The mechanistic implications of these results are discussed. The vicinal proton couplings for the addition product and for the related 2-hydroxy-(and acetoxy-)3,3-dimethyl-1-phenylbutanes are reported. Although the rotamers with *gauche* phenyl and hydroxy-groups are overwhelmingly populated, the bromo-product exists preferentially as the rotamer with *gauche* phenyl and t-butyl groups. No evidence for the rotamer with three *gauche* substituents is observed, in agreement with predictions from previous work.

THE electrophilic addition of hydrogen halides to simple olefins has not received a great deal of attention despite the synthetic importance of this reaction, though examples of both stereospecific *trans* and stereoselective *cis* addition are known. Thus addition of hydrogen halides to both 1,2-dimethylcyclohexene and 1,2-dimethylcyclopentene gives predominantly *trans*-addition products [2] and addition of deuterium halides to acenaphthylene, indene, and 1-phenylpropenes gives mainly *cis*-addition products.[3]

In the course of preparing some sterically hindered ethanes for coupling constant studies,[1] we investigated the addition of DBr to *trans*- (I) and *cis*- (II) β-t-butylstyrene. The severe steric requirements of the t-butyl group provide an extreme test for the ' faster rotation than collapse or rearrangement mechanism ' proposed [3c] a decade ago, on the basis of which the *cis* and *trans* pair of olefins are predicted to exhibit the same stereochemistry of addition. Furthermore, the presence of the t-butyl group considerably simplifies the n.m.r. spectra of the products and the interpretation of the addition–elimination sequence. The couplings and rotational preferences shown by these and other t-butyl-substituted ethanes permit further consideration of the factors which affect rotational energies in these compounds.

[1] R. J. Abraham and J. R. Monasterios, *J.C.S. Perkin I*, 1973, 1446.

RESULTS

Addition of DBr to either *trans*- (I) or *cis*- (II) β-t-butylstyrene in methylene chloride, at 0 °C, in the dark with hydroquinone present gives solely the polar reaction products *threo*- and *erythro*-1-bromo-3,3-dimethyl-1-phenylbutane, (III) and (IV) (Scheme 1).

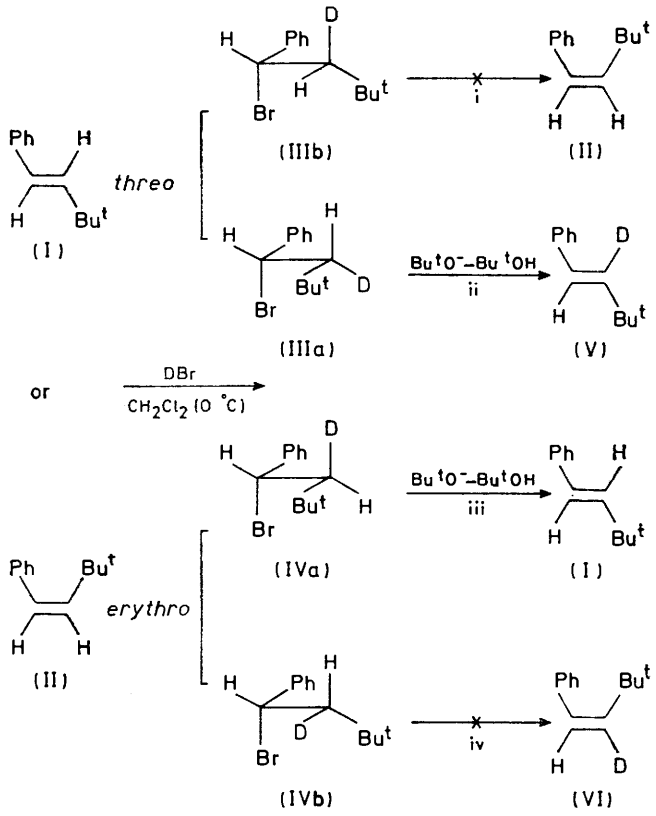
One of the more questionable assumptions in previous work [3c] is the assignment of *threo*- and *erythro*-configurations to the products from such DBr additions. This has usually been made on the basis of the subsequent elimination reaction with base (in our case sodium t-butoxide, since sodium methoxide in methanol gives rise to other substitution products) to give the deuteriated olefin. In our case no *cis*-olefin [(II) or (VI)] was found, and thus paths i and iv are eliminated (there is in fact essentially zero population of this particular rotamer present; see later). If we assume, therefore, that the elimination can occur only by path ii or iii, the ratio of aromatic to olefinic (or t-butyl to olefinic) proton signals in the n.m.r. spectrum of the *trans*-olefins (I) and (V) shows the stereochemistry of the reaction.

An independent and more direct estimate of the stereochemistry of the addition can be obtained from the n.m.r. spectrum of the addition products themselves [(III) and (IV)] which also identifies unambiguously the diastereotropic methylene protons of the non-deuteriated species. The proton spectrum of these protons in $PhCHBr{\cdot}CH_2Bu^t$

[2] G. S. Hammond and T. D. Nevitt, *J. Amer. Chem. Soc.*, (*a*) 1954, **76**, 4121; (*b*) 1960, **82**, 4323.

[3] M. J. S. Dewar and R. C. Fahey, *J. Amer. Chem. Soc.*, 1963, **85**, (*a*) p. 2245; (*b*) p. 2248; (*c*) p. 3645.

is shown in Figure 1 (lower trace) and is the AB part of an ABX spin system which may be analysed routinely. The



SCHEME 1

upper trace shows the same region for the products obtained from DBr addition to the *trans*-olefin (*threo* and *erythro*-PhCHBr·CHDBu^t) and the middle trace is the corresponding deuterium-decoupled spectrum. This gives immediately on integration the proportions of the two forms, but not their assignment.

However, the elimination reaction on this mixture gave the olefins (V) and (I) in almost the same ratio [(III) : (IV), 81 : 19; (V) : (I), 70 : 30]. This immediately provides an unambiguous assignment of the *threo*- and *erythro*-isomers (*threo* J_{HH} 9·0; *erythro* J_{HH} 5·0 Hz) and also confirms the general stereospecificity of the elimination reaction.*

The stereochemical results for the additions carried out with *trans*- and *cis*-β-t-butylstyrene are given in Table 1, which also includes the results [3c] for the corresponding methylstyrenes. Our results cannot be ascribed to isomerisation of the starting olefin, since in an incomplete reaction of DBr with a 50 : 50 mixture of olefins, the unchanged olefin showed no isomerisation. Secondary isomerisation of the product monobromides can also be ruled out, since solutions of different mixtures of *erythro*- and *threo*-monobromides in CH_2Cl_2, saturated with DBr, placed in n.m.r. tubes, and left for 96 h showed no isomerisation. It is also important to note that all the DBr additions were carried out in the dark. The results obtained using a vacuum line to degas the solutions by the freeze–pump–thaw technique were identical both with those of experiments in which nitrogen was bubbled through the solution, and with those where no special precautions were taken to remove oxygen from the reaction mixture. Saturated solutions of DBr and low concentrations (*ca.* 4 × 10^{-2}M) of olefin were used deliberately.[5]

* Observation of the $^2D[^1H]$ spectrum could also have given this information; this technique has been used recently in a similar situation.[4]

TABLE 1

Stereochemistry of the DBr addition to *cis*- and *trans*-PhCH:CHR (R = Me or Bu^t) [a]

	PhCH:CHR	*erythro* (IV)	*threo* (III)	*cis*-Adduct (%)
R = Bu^t	*cis–trans* [b]	60	40	
	trans	19	81	81
	cis [c]	67	33	67
R = Me [d]	*cis*			82
	trans			88

[a] In CH_2Cl_2 at 0 °C. [b] *cis* : *trans* ratio, 84 : 16. [c] Calculated from the other results. [d] Ref. 3c.

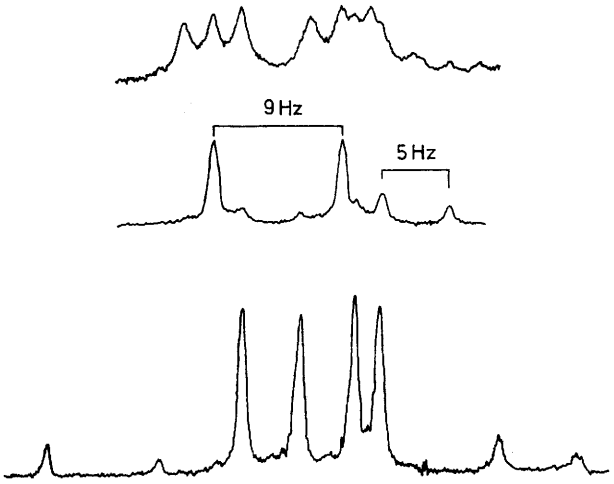


FIGURE 1 The 100 MHz ^1H n.m.r. spectra of the methylene proton region of PhCHBr·CH$_2$Bu^t and the β-Bu^t-styrene addition products

DISCUSSION

Mechanism of Deuterium Bromide Addition.—The results (Table 1) can be explained in terms of the mechanistic picture illustrated in Scheme 2. According to Dewar *et al.*,[3c] an initial equilibrium forms a deuterium halide–olefin complex. Steps 1a and b are rate-determining and give rise to the intimate ion pairs (VIIa—f). It is unlikely that collapse or rearrangement occurs *via* the intimate ion pair (VIIa) or (VIIf) because their concentration should be negligible in comparison with (VIIb—e), which are sterically far less crowded. Furthermore, it is also unlikely that either collapse, to give *cis*-product, occurs directly through

[4] C. H. Depuy, personal communication.

[5] D. J. Pasto, G. R. Meyer, and Sung-Song Kang, *J. Amer. Chem. Soc.*, 1969, **91**, 2163.

(VIIc) or (VIIe) or rearrangement, to give *trans*-adduct, occurs directly through (VIIb) or (VIId), since both processes would lead to products in which all bonds are eclipsed.[3c]

It is possible to demonstrate that ' the rate of interconversion of intimate ion pairs (VIIb—c) is not very fast compared with the rate of collapse (VIIb) or rearrangement (VIIc).' If this were not the case, then addition of DBr to both *cis*- and *trans*-β-alkylstyrene would exhibit the *same* stereochemistry of addition, irrespective of the starting olefin (see Scheme 1). Table 1 reveals that the addition of DBr to *trans*- and *cis*-β-t-butylstyrene gives rise to 81 and 67% *cis*-addition, respectively. These results confirm that the above proposition is correct. In the light of this conclusion it is possible to rationalise the results presented in Table 1.

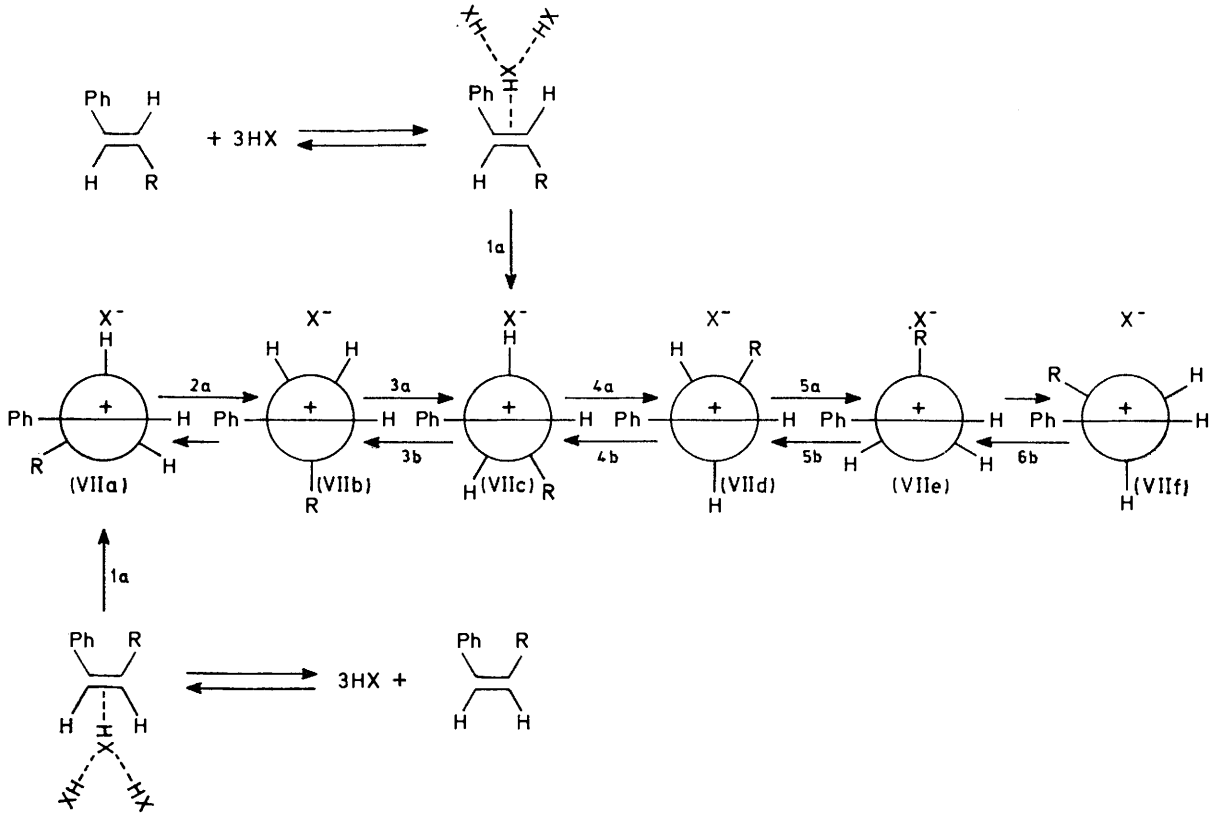
Let us first of all consider DBr addition to either *trans*- or *cis*-β-t-butylstyrene (R = Bu^t; Scheme 2). As far as the *cis*-addition is concerned, (VIId) is a far more reactive species than (VIIb). This can be easily understood if we consider that in the transition state leading to *cis*-adduct the stereochemistry of the reaction will be sterically controlled by the Ph–Bu^t interaction, rather than by the Bu^t–X$^-$ interaction. Addition to the *trans*-olefin occurs according to the sequence (*a*),

$$(\text{VIIc}) \rightleftharpoons (\text{VIId}) \rightleftharpoons (\text{VIIe}) \qquad (a)$$

and addition to the *cis*-olefin according to the sequence

$$(\text{VIIb}) \rightleftharpoons (\text{VIIc}) \rightleftharpoons (\text{VIId}) \rightleftharpoons (\text{VIIe}) \qquad (b)$$

(*b*). Nucleophile X$^-$ enjoys a longer time for rearrangement (which gives rise to *trans*-adduct) in process (*b*) than in (*a*), so the *cis*-olefin would exhibit a bigger preference for the *trans*-addition stereochemistry, as is found.

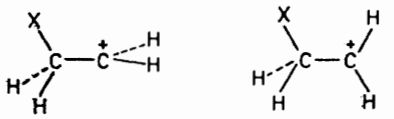


SCHEME 2

When R = Me (Scheme 2), (VIIb) will be both more stable and more reactive (toward *cis*-adduct formation) than the corresponding intimate ion pair with R = Bu^t. Furthermore, the barrier for (VIIc) $\rightleftharpoons$ (VIId) should be higher for R = Bu^t than for R = Me, as has been recently demonstrated by molecular orbital calculations carried out by Pople *et al.*[6] They found that the rotational barriers (B — A) for the free mono-β-substituted cations (VIIIA and B) are 2·52 and 3·73 kcal mol^{-1} for X = Me and Et, respectively. So for X = Bu^t this barrier is expected to be >3·73 kcal mol^{-1} and the interconversion (VIIc) $\rightleftharpoons$ (VIId) will be consequently less favoured. Thus, the ratio (*cis*-addition to *cis*-olefin) : (*cis*-addition to *trans*-olefin) will be bigger for R = Me than for R = Bu^t, as observed.

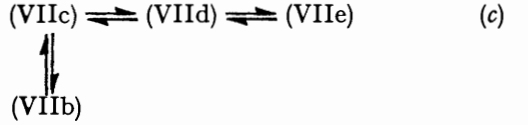
[6] L. Radom, J. A. Pople, and P. von R. Schleyer, *J. Amer. Chem. Soc.*, 1972, **94**, 5935.

It is interesting to compare the behaviour of the two *trans*-olefins (*i.e.* R = Bu^t or Me) towards addition of



(VIIIA) (VIIIB)

DBr. When R = Bu^t, addition occurs *via* sequence (*a*). For R = Me, addition occurs *via* sequence (*c*). Consequently, a higher percentage of *cis*-adduct is expected for the latter, as is found.



(VIIc) ⇌ (VIId) ⇌ (VIIe) (*c*)

(VIIb)

In the present discussion we have made the basic assumption that the reaction is third-order with respect to the deuterium bromide. This is consistent

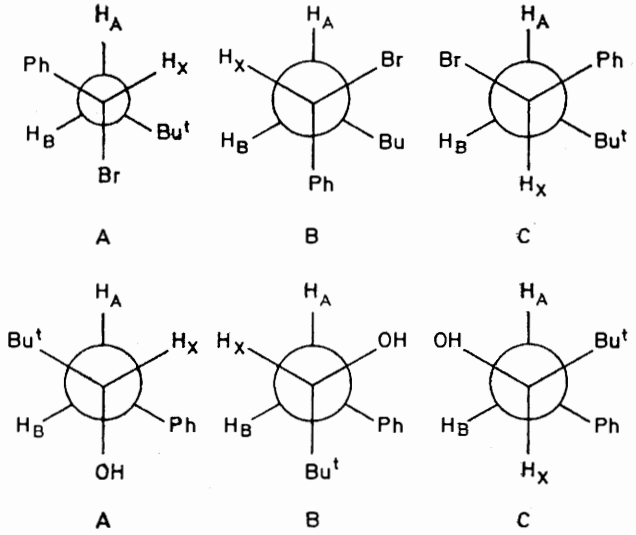


FIGURE 2 Rotamers of PhCHBr·CHBu^t and PhCH$_2$·CH(OH)Bu^t

with the kinetics of hydrogen bromide addition in non-polar solvents reported by Mayo and Savoy.[7]

Rotamer Populations.—We now consider the rotamer populations of the addition product PhCHBr·CH$_2$Bu^t and of two related compounds, PhCH$_2$·CH(OH)Bu^t and the corresponding acetate.

There are three non-equivalent rotamers for these compounds (Figure 2) for which the ^{1}H n.m.r. parameters are collected in Table 2. We will be mainly concerned with the $^3J_{HH}$ couplings, for which the observed value in any solvent is the weighted mean of the values for the distinct rotamers,

$$i.e. \qquad J_{obs} = \sum_{i=A,B,C} n_i J_i \qquad (1)$$

where $\sum n_i = 1$

The deuteriation studies, by identifying the *erythro*-(H_A = D) and *threo*-(H_B = D) compound, immediately make it possible to assign H_A and H_B in the parent compound; thus we can write, for the bromo-compound:

$$J_{AX} = 9{\cdot}01 = n_A J_A^{AX} + n_B J_B^{AX} + n_C J_C^{AX} \text{ and}$$

$$J_{BX} = 5{\cdot}0 = n_A J_A^{BX} + n_B J_B^{BX} + n_C J_C^{BX}$$

where $n_A + n_B + n_C = 1$

Exactly analogous equations hold for the hydroxy- and acetoxy-compounds. However, it is immediately obvious that these latter compounds exist virtually completely in one form, as the value of J_{BX} is very similar to that ($J_{ax,ax}$) found for cyclic compounds with the same C·CH$_2$·CH(OR)·C fragment (*trans*-cyclohexane-1,2-diol and diacetate, 11·0 Hz;[8] *trans*-4-t-butylcyclohexanol, 11·07 Hz[9]).* This would be expected to be rotamer A, and on this basis we have assigned H_A and H_B as shown in Table 2. The values

TABLE 2

Proton chemical shifts (δ) and couplings (Hz) in PhCHBr·CH$_2$Bu^t (III) and PhCH$_2$·CHXBu^t (X = OH or OAc)

	δ_A [a]	δ_B [a]	δ_X	J_{AB}	J_{AX}	J_{BX}
X = OH [b]	2·84	2·37	3·33	−13·4	2·2	10·6
X = OAc [b]	2·90	2·64	4·96	−13·8	2·7	10·8
(III) [c]	2·44	2·35	5·29	−14·3	9·0	5·0

[a] For assignment of A and B see Figure 2 and text. [b] Solvent $CDCl_3$. [c] Solvent $(CD_3)_2CO$ (in CCl_4 $\delta_A = \delta_B = 2{\cdot}35$, $\delta_X = 5{\cdot}07$).

of the couplings allow the rotamer populations of the bromo-compound to be obtained, as we may take one value of J_{trans} and one of J_{gauche} in these fragments without serious error. Using values of J_t 11·0 and J_g 3·0 Hz for the bromo-compound, derived from these, and correcting for the bromine electronegativity,[10] gives n_A 0·25, n_B 0·00, and n_C 0·75,

$$i.e. \qquad E_A - E_C = 0{\cdot}65; \; E_B - E_C > 2 \text{ kcal mol}^{-1}$$

The at first sight surprising conclusion that rotamer A is overwhelmingly populated for X = OH or OAc but that rotamer C is the most stable rotamer for X = Br can in fact be rationalised on the basis of the relative sizes of the substituents in acyclic and not

* This is of course not the case for J_{BX} and $J_{eq,ax}$ owing to the differing torsion angles in the acyclic and cyclic compounds.

[7] F. R. Mayo and M. G. Savoy, *J. Amer. Chem. Soc.*, 1947, **69**, 1339.

[8] R. U. Lemieux and J. W. Lown, *Canad. J. Chem.*, 1964, **42**, 893.

[9] F. A. L. Anet, *J. Amer. Chem. Soc.*, 1962, **84**, 1053.

[10] R. J. Abraham and G. Gatti, *J. Chem. Soc.* (*B*), 1969, 961.

cyclic compounds. For example the energy differences $E_g - E_t$ in a series of 1,2-disubstituted ethanes have been measured by several workers. For the pairs of substituents Bu^t, Ph; Bu^t, Br; and Ph,OH they are *ca.* 1·8, 1·5, and 0·3 kcal mol^{-1}, respectively.[10] By using these additively, $E_C - E_A$ is calculated to be *ca.* 1·5 kcal mol^{-1} for the hydroxy-compound but only 0·3 kcal mol^{-1} for the bromo-compound. In fact these rules predict that rotamer A is more stable than C for X = Br, which is not the case, but parameters obtained from disubstituted ethanes cannot be applied rigorously to polysubstituted ethanes owing to the differing molecular geometries. A good example of this was found in the analogous compounds PhCHX·CHXBu^t (X = Cl or Br), in which the rotamers with *trans*-hydrogen substituents were strongly disfavoured compared with the predicted energies.[1] This has an analogy with the well known tetrahalogenoethanes and it was suggested that if the trisubstituted ethanes behaved similarly to 1,1,2-trichloroethane, the rotamers with three *gauche* substituents would be of very high energy. This is certainly observed here, in that rotamer B has essentially zero population, and this has kinetic significance in that it could be a major reason for the absence of any *cis*-olefin in the elimination reaction.

EXPERIMENTAL

N.m.r. Measurements.—The n.m.r. spectra were obtained on Varian XL-100, HA-100, and A60 spectrometers. The average values from three calculated spectra (measured by the side band technique) were taken; r.m.s. errors were 0·05 Hz when averaged over the entire spectrum. Values for percent reaction quoted in Table 1 (those obtained from the n.m.r. spectra of *erythro*- and *threo*-compounds) were based on the integrated intensities of the AB part (deuterium-decoupled).

cis- *and* trans-β-*t-Butylstyrene.*—These olefins were prepared as previously described.[1] *trans*-β-t-Butylstyrene showed δ_{Bu^t} 1·13, δ_{ArH} 7·20, δ_A 3·75, δ_B 3·69 (J_{AB} 16·15 Hz); the *cis*-isomer showed δ_{Bu^t} 0·98, δ_{ArH} 7·17, δ_A 3·82, δ_B 3·32 (J_{AB} 12·58 Hz). Both olefins were measured as neat liquids.

Deuterium Bromide.—Deuterium bromide was prepared by slow addition over 30 min of deuterium oxide (10 ml) to phosphorus tribromide (20 ml). The reaction was surprisingly slow (rapid addition of D_2O causes violent reaction) and the gas was collected during 72 h in a solid CO_2–acetone trap as formed. The liquid was partially distilled twice (trap-to-trap) before use.

Addition of Deuterium (or Hydrogen) Bromide to cis- *and* trans-β-*t-Butylstyrene.*—In a typical reaction methylene chloride (10 ml) containing hydroquinone (0·02 g) was placed in a dry flask equipped with drying tube, gas inlet tube, and syringe cap. The flask was immersed in an ice-bath, light was excluded, and the solution was saturated with deuterium bromide. *cis*- or *trans*-β-t-Butylstyrene (0·121 g, $6·25 \times 10^{-4}$ mol) dissolved in CH_2Cl_2 (5 ml) was added. Deuterium bromide was passed into the mixture in a steady stream to maintain a saturated solution throughout the reaction. After 45 min the excess of deuterium bromide and CH_2Cl_2 was removed under vacuum. The n.m.r. spectrum revealed that the product was free of unchanged olefin and free-radical addition product. The product was stored in an n.m.r. tube at −70 °C. The relative peak heights for the CHD protons (deuterium-decoupled) in the *threo*- and *erythro*-products were 31 and 46, respectively, for the DBr addition to the 84 : 16 mixture of *cis*- and *trans*-olefin, and 97 and 23 for the addition to the *trans*-olefin.

Dehydrobromination of trans-1-*Bromo*-1-*phenyl*-2-*t-butyl*-[2-$^2H_1$]*propane.*—The samples obtained from addition of deuterium bromide were added to a 3—4 molar excess of 0·33M-sodium t-butoxide in t-butyl alcohol. The mixture was refluxed for about 5 h, then quenched in ice–water and extracted with pentane. The pentane layers were combined, washed with dilute hydrochloric acid and water, dried (Na_2SO_4), filtered, and evaporated, leaving a yellow oil. The n.m.r. spectrum of the oil showed the presence of *trans*-olefin (area of the Bu^t resonance, 43), pure *threo*-monobromide (area of Bu^t, 22), and PhCH·OBu^t·CHDBu^t (area of one Bu^t peak, 25). Pure *trans*-olefin was isolated by preparative g.l.c. (same experimental conditions as reported previously [1]). The relative areas for the aromatic and olefinic protons were 69 and 18, respectively.

Stability of Mixtures of erythro- *and* threo-1-*Bromo*-3,3-*dimethyl*-1-*phenylbutane.*—Solutions of different mixtures of *erythro*- and *threo*-monobromides in CH_2Cl_2, saturated with DBr, were placed in n.m.r. tubes. After 96 h no isomerisation was observed.

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