Carbonium-ion Rearrangements in the Addition of Bromine to Some Olefins

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The olefins $Ph_2ArC{\cdot}CR{=}CH_2$ (R = H, Me; Ar = Ph, p-$C_6H_4{\cdot}OMe$) have been treated with bromine in various solvents and their rates of reaction in carbon tetrachloride at 25° have been measured. The extent of rearrangement of the group Ar depends on the nature of this group and of R, and on the solvent. The mechanisms of the reactions are discussed.

THE skeletal migration of carbon during the electrophilic addition of halogens to olefins is of relatively rare occurrence, in contrast to the situation which obtains in other electrophilic reactions. For example, whereas t-butylethylene reacts with hydrogen chloride [1] to give *ca.* 60% of the rearranged adduct, $Me_2CCl{\cdot}CHMe_2$, no rearranged product has been detected from its reaction with bromine in methanol.[2] Rearrangement products have, however, been obtained from reactions of the halogens at olefinic bonds in systems which have an especially powerful propensity for rearrangement, such as norbornene.[3] The rearrangement of elements other than carbon is also well established. Thus, although the acetate group does not migrate during the addition of bromine to allyl acetate,[4] the reaction of bromine with allyl *p*-anisate gives 32% of 1,3-dibromoprop-2-yl *p*-anisate; [5] and the products of the addition of hypochlorous acid to allyl chloride [6, 7] and allyl bromide [8] include ones in which the halogen substituent has migrated.

The probable explanation of the absence of carbon rearrangements in additions to the simpler acyclic olefins follows from a consideration of the mechanism of addition of halogens. It was envisaged originally that the first step leads to a cyclic halonium ion (I; X = halogen). Evidence has since been adduced, however, that an asymmetric ion, represented for addition of a halogen X_2 to $RCH{=}CH_2$ by the structure (II), is formed initially; [7-10] this can then react with a nucleophile both directly, at its secondary carbon, and, *via* rearrangement to the asymmetric ion (III) or possibly the corresponding cyclic halonium ion, at its primary carbon atom. This mechanism accounts for the orientation and stereochemistry of the products, including those instances

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[1] G. G. Ecke, N. C. Cook, and F. C. Whitmore, *J. Amer. Chem. Soc.*, 1950, **72**, 1511.

[2] W. H. Puterbaugh and M. S. Newman, *J. Amer. Chem. Soc.*, 1957, **79**, 3469.

[3] H. Kwart and L. Kaplan, *J. Amer. Chem. Soc.*, 1954, **76**, 4072; J. D. Roberts, F. O. Johnson, and R. A. Carboni, *ibid.*, p. 5692; H. Kwart, *ibid.*, 1953, **75**, 5942.

[4] S. Winstein and L. Goodman, *J. Amer. Chem. Soc.*, 1954, **76**, 4368.

[5] J. H. C. Nayler, *J. Chem. Soc.*, 1959, 189.

[6] P. B. D. de la Mare and J. G. Pritchard, *J. Chem. Soc.*, 1954, 3910.

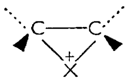
[7] P. B. D. de la Mare and J. G. Pritchard, *J. Chem. Soc.*, 1954, 3990.

[8] P. B. D. de la Mare, P. G. Naylor, and D. L. H. Williams, *J. Chem. Soc.*, 1962, 443.

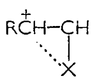
[9] P. B. D. de la Mare and A. Salama, *J. Chem. Soc.*, 1956, 3337.

[10] P. B. D. de la Mare and S. Galandauer, *J. Chem. Soc.*, 1958, 36.

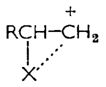
in which "abnormal" (anti-Markownikoff) products are formed (*e.g.*, the reactions of methanolic bromine with t-butylethylene to give 2-bromo-1-methoxy-3,3-dimethylbutane,[2] and of bromine and bromine chloride with cholesterol [11]).



(I)



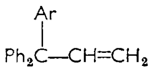
(II)



(III)

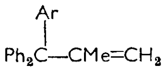
It appears likely, then, that, compared with the ion $R\overset{+}{C}H\text{-}CH_3$, the ion (II; X = halogen) is stabilised by neighbouring-group interaction so that the tendency towards rearrangement of a carbon group (*e.g.*, Me, when $R = Me_3C$) is reduced. Moreover, it has been shown that in the ion (II; X = Cl, $R = CH_2Cl$), formed in the addition of hypochlorous acid to allyl chloride, the entering halogen is sited more favourably for interaction with the carbonium-ion centre than is the substituent chlorine.[7]

These considerations indicate that a prerequisite for migration in an acyclic system is that the potential migrating group should be one of considerable migratory aptitude, certainly superior to that of methyl. We therefore chose for study the olefins [12] (IVa, b) and (Va, b). Since the interacting capacity of bromine in ions of the type (II) is greater than that of chlorine,[8, 13] the addition of bromine was chosen as providing the more critical circumstances in which to test for the possibility of aryl migration.



$Ph_2\overset{\displaystyle Ar}{\overset{|}{C}}\text{—}CH\text{=}CH_2$

(IV)



$Ph_2\overset{\displaystyle Ar}{\overset{|}{C}}\text{—}CMe\text{=}CH_2$

(V)

a; Ar = Ph b; Ar = $p\text{-}C_6H_4\cdot OMe$

RESULTS

Products of Reactions with Bromine.—(*a*) 3,3,3-*Triphenylpropene* (IVa). Treatment of the olefin with bromine in carbon tetrachloride at room temperature gave a product whose proton magnetic resonance (p.m.r.) spectrum was consistent with the presence of 2,3,3-triphenylallyl bromide (XIIa) and 1,2-dibromo-3,3,3-triphenylpropane (VI; R = Ph). Separation was achieved by boiling the mixture in methanol to convert the former component into the corresponding allyl methyl ether [14] which crystallised on cooling. The latter component was isolated from the filtrate by column chromatography and shown to have the structure (VI; R = Ph) as follows. Microanalyses were consistent with the formulation of the product as an adduct of the reactant and bromine. The p.m.r. spectrum (carbon tetrachloride) was consistent with the structure (VI; R = Ph) provided that the two protons at C(1) are non-equivalent. Synder [15] has shown that the corresponding protons in 1,2-dibromo-3,3-dimethylbutane (VI; R = Me) are non-equivalent and has determined the coupling constants for the ABC system formed by the protons at C(1) and C(2). In (VI; R = Ph) these protons form more nearly an AMX system, so that the coupling constants can be determined by measurement; the τ-values and coupling constants, together with those for (VI; R = Me) for comparison, are shown in the Table.

τ-Values and *J*(c./sec.) for solutions in carbon tetrachloride

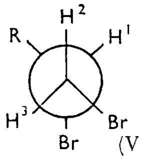
	$\tau_{H(1)}$	$\tau_{H(2)}$	$\tau_{H(3)}$	J_{12}	J_{13}	J_{23}
(VI; R = Ph) ...	4·29	5·97	7·16	0·9	9·7	11·7
(VI; R = Me) *	5·98	6·07	6·45	3·08	9·26	11·37

* τ-Values for (VI; R = Me) are calculated from the resonance frequencies relative to tetramethylsilane quoted by Snyder.[15]

The most stable conformer of (VI; R = Me) has been shown [16] to be (VII; $R = CMe_3$) and models show that the analogous structure (VII; $R = CPh_3$) should be the most stable conformer of (VI; R = Ph) since in the other two staggered conformers the bromine atom at C(2) interferes with the highly specific arrangements of the phenyl groups about C(3). H(1) occurs at lower field in (VII; $R = CPh_3$) compared with (VII; $R = CMe_3$) because of the deshielding effect of the triphenylmethyl group. H(3) occurs at higher field in (VII; $R = CPh_3$) than in (VII; $R = CMe_3$) evidently because, as a model shows, the proton lies in the shielding cone of one of the phenyl rings. Finally, confirmation that the dibromide is the 1,2-compound (VI; R = Ph) and not the skeletally rearranged 1,3-dibromo-compound (VIII) (which might be expected to have a similar p.m.r. spectrum) was derived from the mass spectrum which contained an intense line at *m*/*e* 243 (CPh_3 fragment), as well as lines due to parent ions at 428, 430, and 432 (*ca.* 1 : 2 : 1) and a moderately strong line at 270 (loss of a molecule of bromine).

$R_3C\cdot CHBr\cdot CH_2Br$

(VI)



(VII)

$Ph_2CBr\cdot CHPh\cdot CH_2Br$

(VIII)

The allylic bromide (XIIa) was synthesised independently and it was shown that the p.m.r. spectrum of the original crude product was fully accounted for by the presence of the allylic bromide (XIIa) and the dibromide (VI; R = Ph) in the proportions 1·15 : 1 (mean of three analyses).

Because of the low solubility of 3,3,3-triphenylpropene in methanol, the reaction of the olefin with bromine in the presence of methanol was carried out with carbon tetrachloride as co-solvent. The only detectable product (p.m.r. spectrum) was the methoxybromide (XIV; Ar = Ph) which was isolated in 50% yield and whose structure was confirmed as follows. The p.m.r. spectrum had an aromatic multiplet (15H) at τ 2·7—3·4 [main components: τ 2·7—3·0 (13H) and 3·1—3·4 (2H)], a distorted doublet of doublets (1H) centred at τ 5·70 (*J* = 2·4, *J'* = 11·6 c./sec.) (methine proton), a distorted doublet of doublets (1H) centred at τ 5·94 (*J* = 2·4, *J''* = 9·6 c./sec.) (one of the methylene protons), a 1 : 1 : 1 : 1 quartet (1H) centred

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[11] D. H. R. Barton, E. Miller, and H. T. Young, *J. Chem. Soc.*, 1951, 2598.

[12] R. O. C. Norman and C. B. Thomas, *J. Chem. Soc.* (*C*), 1967, 1115.

[13] S. Winstein and E. Grunwald, *J. Amer. Chem. Soc.*, 1948, **70**, 828.

[14] C. F. Koelsch, *J. Amer. Chem. Soc.*, 1932, **54**, 2045.

[15] E. I. Snyder, *J. Amer. Chem. Soc.*, 1966, **88**, 1155.

[16] M. Buza and E. I. Snyder, *J. Amer. Chem. Soc.*, 1966, **88**, 1161.

at τ 6·61 (J' = 11·6, J'' = 9·6 c./sec.) (the other methylene proton), and a singlet (3H) at τ 7·14 (OMe). The components of the aromatic multiplet at higher field (τ 3·1—3·4) are attributed to the *ortho*-protons of the phenyl group which has migrated (see below); the high-field τ-value of the methoxy-group is attributed to shielding by one of the phenyl rings. The mass spectrum showed no parent ion but contained peaks at *m/e* 268 (M − HBr − MeOH), 197 (Ph_2COMe), and 105 (PhCO).

Treatment of the olefin with bromine in a mixture of acetic acid and carbon tetrachloride gave 2,3,3-triphenylallyl bromide (XIIa) as the only detectable product (p.m.r. spectrum); the compound was isolated in 65% yield.

(*b*) 3-p-*Anisyl*-3,3-*diphenylpropene* (IVb). Reaction with bromine in carbon tetrachloride gave the allylic bromide (XIIb) as the only isolable product; it was formed in 85% yield, as estimated by gas chromatography of the reaction product, and was characterised by independent synthesis. The p.m.r spectrum of the crude product showed no resonance attributable to a dibromide.

Reaction in a mixture of methanol and carbon tetrachloride gave 2-*p*-anisyl-3,3-diphenylallyl bromide (XIIb) as the major product, together with a small quantity of the methoxybromide (XIV; Ar = *p*-OMe·C_6H_4) whose structure was confirmed as follows. Its p.m.r. spectrum had two aromatic singlets (total, 10H) at τ 2·62 and 2·72, a singlet (4H) at τ 3·33 (aromatic protons of the *p*-anisyl group), a multiplet (2H) at τ 5·6—6·1 which was partially resolved into two sets of doublets of doublets centred at τ 5·79 (J = 2·4, J' = 11·5 c./sec.) (methine proton) and τ 5·90 (J = 2·4, J'' = 9·8 c./sec.) (one of the methylene protons), a singlet (3H) at τ 6·23 (aromatic OMe), a 1 : 1 : 1 : 1 quartet (1H) centred at τ 6·67 (J' = 11·5, J'' = 9·8 c./sec.) (the other methylene proton), and a singlet (3H) at τ 7·13 (aliphatic OMe). That the four protons of the *p*-anisyl group appear as a singlet is consistent with the conclusion above that the resonances due to the *ortho*-protons of the 2-phenyl substituent in the methoxybromide (XIV; Ar = Ph) are at higher field than the remainder. The mass spectrum showed no parent ion but had peaks at *m/e* 378 and 380 (M − MeOH), 330 (M − HBr), 298 (M − MeOH − HBr), 197 (Ph_2COMe), and 105 (PhCO).

(*c*) 2-*Methyl*-3,3,3-*triphenylpropene* (Va). Kharasch *et al.* reported [17] that this olefin reacts with bromine to give a single monobromide, m. p. 146—148°, but they did not characterise the product nor give experimental conditions. We found that reaction in a mixture of acetic acid and carbon tetrachloride gives two isomeric monobromides. One was isolated pure by fractional crystallisation and characterised as the vinylic bromide (XVIIa) by its p.m.r. spectrum. The other, which could only be obtained impure by fractional crystallisation, was identified as the allylic bromide (XVIIIa) by its having identical p.m.r. and infrared spectra to those of the authentic material, synthesised independently. These two compounds have m. p. 210—213 and 125—127°, respectively, so that neither appears to be the monobromide previously reported.[17] The p.m.r. spectrum of the crude product showed that the isomeric bromides were formed in approximately equal proportions and there was no indication of the presence of a further product.

Treatment of the olefin (Va) with bromine in a mixture of methanol and carbon tetrachloride gave only one detectable product (p.m.r. spectrum) which was isolated in 63% yield and was characterised as the 1,3-methoxybromide (XXa) on the following grounds: the p.m.r. spectrum had two aromatic singlets (total 15H) at τ 2·60 and 2·77, a doublet (1H) centred at τ 5·65 (J = 9·8 c./sec.) (one of the methylene protons), a doublet (1H) centred at τ 6·34 (J = 9·8 c./sec.) (the other methylene proton), a singlet (3H) at τ 7·09 (OMe), and a singlet (3H) at τ 8·46 (Me); the mass spectrum showed no parent ion but contained peaks at *m/e* 282 (M − HBr − MeOH), 197 (Ph_2COMe), 182 (Ph_2CO), 118 (CH_2=CMePh), and 105 (PhCO). Reaction with bromine in carbon tetrachloride alone gave a mixture of at least three products, of which two were the vinylic bromide (XVIIa) and the allylic bromide (XVIIIa) and a third showed resonances in the p.m.r. spectrum which could be attributed to the unrearranged olefin dibromide (multiplet at τ 5·5—6·0, singlet at τ 7·70). Attempts to isolate this product were unsuccessful.

(*d*) 3-p-*Anisyl*-2-*methyl*-3,3-*diphenylpropene* (Vb). Treatment with bromine in acetic acid–carbon tetrachloride gave two monobromides. The p.m.r. spectrum of the crude product showed resonances corresponding to those of the vinylic bromide (XVIIb), identified by comparison with the p.m.r. spectrum of the vinylic bromide (XVIIa), and the allylic bromide (XVIIIb) which was synthesised independently. The two bromides were present in approximately equal amounts (p.m.r. spectrum), but could not be separated because they formed a eutectic mixture which was shown (p.m.r. spectrum) to consist of *ca.* 55% of the allylic compound and *ca.* 45% of the vinylic isomer.

Rates of Reaction with Bromine.—The kinetics for the reactions of the olefins (IVa, b) and (Va, b) with bromine in carbon tetrachloride were determined by following the decrease in the concentration of bromine spectrophotometrically. In each case, the kinetics were of the first order in each reactant until the reaction was at least 60% complete. The derived second-order rate constants, k_2 (l. mole^{-1} min.$^{-1}$), at 25° were: (IVa), 0·08; (IVb), 2·0; (Va), 0·48; (Vb) 24·5.

DISCUSSION

Reactions of the Triarylpropenes (IVa, b).—Both olefins gave rearranged products in each of the conditions we employed. Thus, whatever may be the nature of the interaction between the entering halogen and the positive carbon in the initial carbonium ion, comparable or more powerful stabilising influences may be invoked through interaction with a neighbouring aryl group. It also appears that the effect of the competition between skeletal rearrangement and 1,2-addition in these systems depends on both the migratory aptitude of the rearranging group and the nature of the solvent.

Treatment of the olefin (IVa) with bromine in carbon tetrachloride gave a mixture of the rearranged allylic bromide (XIIa) and the unrearranged dibromide (XIIIa), with slight predominance of the former. On the other hand, the olefin (IVb) gave only the rearranged product (XIIb). The probable reaction mechanism is shown in Scheme 1.

The much greater rate of reaction in carbon tetra-

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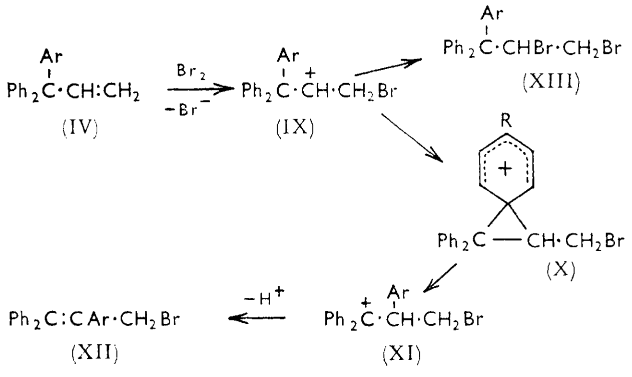
[17] M. S. Kharasch, A. C. Poshkus, A. Fono, and W. Nudenberg, *J. Org. Chem.*, 1951, **16**, 1458.

chloride of (IVb) than of (IVa) ($k_{\text{rel.}} = 25$) suggests that the uptake of the first bromine atom is assisted anchimerically by the neighbouring *p*-anisyl group; moreover, the anisyl-containing compound did not give

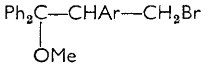


Scheme I

(a: Ar = Ph b: Ar = *p*-C_6H_4·OMe)

an unrearranged product such as (XIIIb) in detectable amount. We conclude that the carbonium ion (IXb) is by-passed, the initial reaction giving the bridged phenonium ion (X; R = OMe) and thence the rearranged carbonium ion (XIb) in which the charge is delocalised over two aromatic rings. In contrast, the formation of the dibromide (XIIIa) from the olefin (IVa) suggests that the carbonium ion (IXa) (possible interaction with bromine or phenyl not shown) is a discrete intermediate to which two reaction paths are available, namely, reaction with bromide ion and rearrangement.

Treatment of the olefin (IVa) with bromine in methanol and in acetic acid (each solvent containing some carbon tetrachloride to dissolve the olefin) gave only the rearranged products (XIV; Ar = Ph) and (XIIa), respectively. Since these solvents are both more polar and better solvating solvents than carbon tetrachloride alone, we should not expect a greater call on anchimeric assistance from a neighbouring phenyl group in these solvents than with carbon tetrachloride, so we presume that the carbonium ion (IXa) mediates in methanol and in acetic acid, as it does in carbon tetrachloride. The absence of 1,2-adducts then suggests that nucleophiles react less rapidly with the ion (IXa) in the more polar solvents and thereby allow more time for phenyl migration.



$$\underset{\text{OMe}}{Ph_2\overset{}{C}}\text{—CHAr—CH}_2\text{Br}$$

(XIV)

None of the allylic bromide (XIIa) was formed in methanol as solvent, showing that, in these weakly basic conditions, nucleophilic attack by the solvent at the carbonium-ion centre is preferred to the removal of a proton. It seems likely, then, that the 1,3-dibromide and the 1,3-bromoacetate corresponding to the methoxy-bromide (XIV; Ar = Ph) are formed in carbon tetrachloride and in acetic acid, respectively, but are unstable in the reaction conditions and decompose to the allylic bromide (XIIa), probably by the *E*1 mechanism through carbonium ion (XIa). This difference between the reactions in methanol and those in either carbon tetrachloride or acetic acid would arise from the greater leaving-group capacities of bromide and acetate than of methoxide.

As expected from the behaviour of the olefin (IVa), the reaction of (IVb) in methanol gave only rearranged products; in this case, however, the allylic bromide (XIIb) was obtained in addition to the methoxy-bromide (XIV; Ar = *p*-C_6H_4·OMe). It is possible that the former product arises from the latter through elimination of methoxide ion, anchimerically assisted by the neighbouring *p*-anisyl group.

Finally, whereas t-butylethylene reacts with bromine in methanol to give 44% of the terminal-methoxy-compound Me_3C·CHBr·CH_2OMe, *via* migration of bromine from the primary to the secondary carbon atom in the initial carbonium ion,[2] no product with this structural feature was detected from the reactions of the triarylpropenes (IVa, b) in methanol. We conclude that the carbonium-ion centre interacts sufficiently strongly with a neighbouring aryl group essentially to eliminate the possibility of bromine migration.

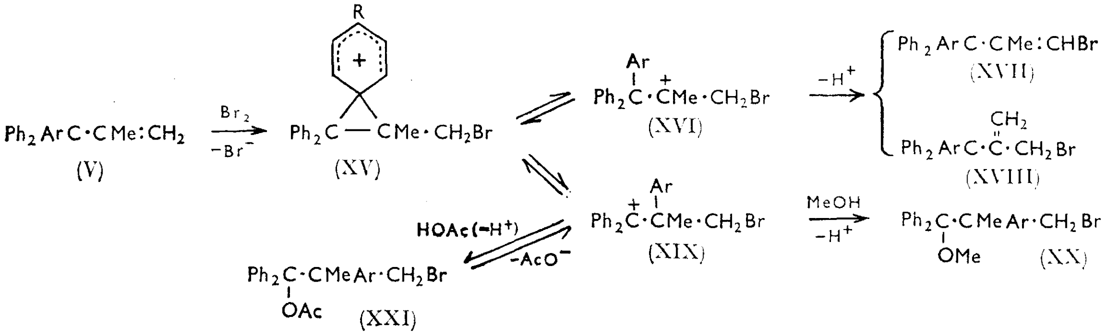
Reactions of the Methyltriarylpropenes (Va, b).—Treatment with bromine in acetic acid containing carbon tetrachloride to dissolve the olefin gave the unrearranged products (XVIIa, b) and (XVIIIa, b); on the other hand, treatment of the olefin (Va) in methanol containing carbon tetrachloride gave only the rearranged methoxy-bromide (XXa). In carbon tetrachloride, the relative rates of reaction of the olefins (Vb) and (Va) were 50 : 1. These results are consistent with the mechanism set out in Scheme 2.

As in the case of the triarylpropenes, the much greater rate of reaction of the anisyl-containing olefin (Vb) compared with (Va) indicates the occurrence of anchimeric assistance by the *p*-anisyl group, so that the rearranged carbonium ion (XIXb) is formed from the olefin through (XVb) rather than through (XVIb). We cannot necessarily assume this for the triphenyl-substituted compound, however, and it is possible that in this case the order of events leading to the rearranged carbonium ion is (Va) ⟶ (XVIa) ⟶ (XVa) ⟶ (XIXa).

The higher rate constants for the olefins (Va) and (Vb) compared, respectively, with (IVa) and (IVb) follow from the fact that the methyl substituents in (Va, b) provide stabilising influences in the transition states leading to the initially formed carbonium ions. We should expect, therefore, that the degree of participation of the *p*-anisyl group would be smaller for the reaction of (Vb) than of (IVb), yet $k_{\text{rel.}}$ is greater for the pair (Vb) and (Va) than for the pair (IVb) and (IVa). This may be because the transition states involving aryl-participation are sterically compressed so that the selectivity between the phenyl and *p*-anisyl groups is increased.

Evidence that the carbonium ions (XVI) and (XIX) equilibrate, probably through the phenonium ions

(XV), is derived from comparison of the products obtained in the presence of acetic acid and of methanol. Since reaction of (Va) in methanol gives the 1,3-methoxy-bromide (XXa) but no 1,2-product, we infer that (XIXa) is the major carbonium-ion component; this is in accord with the fact that the positive charge in this ion is delocalised over two aromatic rings. We should likewise expect that the acetate (XXIa) would be formed in the presence of acetic acid, whereas the unsaturated bromides (XVIIa) and (XVIIIa) are obtained. We conclude that the acetate is not stable in the reaction conditions and that loss of acetate ion, equilibration of (XIXa) and (XVIa), and elimination of a proton lead to the isolated products. The difference between reactions in acetic acid and in methanol would then be due to the greater capacity of acetate ion than of methoxide ion as a leaving group (cf. the discussion above of reactions of the triarylpropenes in methanol and in acetic acid).



Scheme 2

(a: Ar = Ph b: Ar = p-$C_6H_4\cdot OMe$)

The elimination of a proton from the β-chloro-substituted carbonium ion $Me_2\overset{+}{C}-CH_2Cl$ occurs more readily from a methyl group than from the chloromethyl group; thus, the allylic product, $CH_2=CMe\cdot CH_2Cl$, predominates over the vinylic product, $Me_2C=CHCl$.[9] Since the opposite would be expected on electronic grounds, it has been argued in this and related cases[18] that neighbouring-group interaction between the chlorine substituent and the carbonium-ion centre gives a geometric configuration which is unfavourable to proton-loss from the chloromethyl group. However, in the carbonium ions (XVa, b) interaction between the carbonium-ion centre should be at least as powerful with a β-aryl group as with the β-bromo-substituent [cf. the discussion of the reactions of the olefins (IVa, b) in methanol], so that the protons of the $-CH_2Br$ group are stereochemically more suited for elimination. It is therefore not surprising that the vinylic (XVIIa, b) and allylic products (XVIIIa, b) are formed in approximately equal amounts in the reactions of the olefins (Va, b). Evaluation of the factors which govern the relative ease of elimination from the methyl and bromomethyl groups is not at present possible; however, electronic effects due to the aryl groups seem unimportant, since the two olefins give similar ratios of the two products.

EXPERIMENTAL

Proton magnetic resonance spectra were measured in deuteriochloroform (unless stated otherwise) on a Perkin-Elmer R10 60 Mc./sec. spectrometer. Mass spectra were determined on an AEI MS9 spectrometer. Melting points were determined on a Kofler micro-stage and are uncorrected. Chromatography was on alumina (Spence type " H "). Light petroleum had b. p. 40—60°.

Materials.—The syntheses of 2-methyl-3,3,3-triphenylpropene, 3-*p*-anisyl-2-methyl-3,3-diphenylpropene, 3,3,3-triphenylpropene, and 3-*p*-anisyl-3,3-diphenylpropene are described elsewhere.[12] 2-*p*-Anisyl-1,1-diphenylpropene was prepared following Russell and Becker[19] and had m. p. 107—108° (lit.,[19] 103—104°) (Found: C, 87·9; H, 6·7. Calc. for $C_{22}H_{20}O$: C, 88·0; H, 6·7%).

2,3,3-*Triphenylallyl Bromide*.—The method was based on that of White and Norcross.[20] *N*-Bromosuccinimide (0·29 g.) and dibenzoyl peroxide (0·01 g.) were added to a solution of 1,1,2-triphenylpropene (0·36 g.) in carbon tetrachloride (10 ml.). After 2 hr. under reflux, the mixture was filtered to remove succinimide, the precipitate was washed with carbon tetrachloride, and the combined filtrate was shaken twice with aqueous sodium thiosulphate and with water and was dried ($MgSO_4$). Distillation of the solvent left a yellow solid which was recrystallised twice from ether to give 2,3,3-triphenylallyl bromide (0·28 g.; 61%) as a white powder, m. p. 125—127° (lit.,[21] 122°); p.m.r. spectrum: aromatic singlets (each 5H) at τ 2·55, 2·77, and 2·96, and singlet (2H) at τ 5·59 (CH_2).

2-p-*Anisyl*-3,3-*diphenylallyl Bromide*.—The method for the triphenyl analogue above was followed, with the olefin (1·9 g.), *N*-bromosuccinimide (1·2 g.), and dibenzoyl peroxide (0·05 g.) in carbon tetrachloride (40 ml.). The resulting pale yellow solid was recrystallised from ether to give 2-p-*anisyl*-3,3-*diphenylallyl bromide* (1·8 g.; 75%) as white crystals which melted (decomp.) at *ca.* 160° when heated rapidly but decomposed above *ca.* 130° with evolution of hydrogen bromide when heated slowly; p.m.r.

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[18] P. B. D. de la Mare, in " Molecular Rearrangements," ed. P. de Mayo, Part 1, Interscience, New York, 1963, p. 101.

[19] G. A. Russell and H.-D. Becker, *J. Amer. Chem. Soc.*, 1963, **85**, 3406.

[20] W. N. White and B. E. Norcross, *J. Amer. Chem. Soc.*, 1961, **83**, 3265.

[21] J. Meisenheimer and W. Schlichenmaier, *Annalen*, 1927, **456**, 126.

spectrum: aromatic multiplet (14H) at τ 2·5—3·35, singlet (2H) at τ 5·59 (CH_2), and singlet (3H) at τ 6·24 (OMe) (Found: C, 69·1; H, 5·1; Br, 21·1. $C_{22}H_{19}BrO$ requires C, 69·7; H, 5·05; Br, 21·1%). The decomposition product, m. p. 119—122° (from methanol), was identified as 2-*p*-anisyl-3-phenylindene by comparison (mixed m. p. and infrared and p.m.r. spectra) with the authentic material.[22]

3-p-*Anisyl*-2-*bromomethyl*-3,3-*diphenylpropene*.— 3-*p*-Anisyl-2-methyl-3,3-diphenylpropene (1·0 g.), *N*-bromosuccinimide (0·6 g.), and dibenzoyl peroxide (0·01 g.) in carbon tetrachloride (20 ml.) were heated under reflux for 2 hr. The filtrate was washed with aqueous sodium pyrosulphite and water and was dried ($MgSO_4$). The solvent was distilled off, leaving a yellow liquid which slowly solidified and was recrystallised from ethanol to give 3-p-*anisyl*-2-*bromomethyl*-3,3-*diphenylpropene* (0·9 g.; 72%) as white crystals, m. p. 135—136°; p.m.r. spectrum: aromatic multiplet (14H) at τ 2·7—3·3, singlets (each 1H) at τ 4·07 and 4·43 (vinyl protons), singlet (3H) at τ 6·24 (OMe), and singlet (2H) at τ 6·32 (CH_2) (Found: C, 70·8; H, 5·6; Br, 19·8. $C_{23}H_{21}BrO$ requires C, 70·2; H, 5·4; Br, 20·3%).

2-*Bromomethyl*-3,3,3-*triphenylpropene*.—This was prepared in the same way except that 2-methyl-3,3,3-triphenylpropene (0·28 g.) and *N*-bromosuccinimide (0·18 g.) were used. The product was recrystallised twice from ethanol to give 2-*bromomethyl*-3,3,3-*triphenylpropene* (0·17 g.; 48%) as white needles, m. p. 125—127°; p.m.r. spectrum: aromatic singlet (15H) at τ 2·73, singlets (each 1H) at τ 4·05 and 4·40 (vinyl protons), and singlet (2H) at τ 6·27 (CH_2) (Found: C, 72·6; H, 5·5; Br, 21·6. $C_{22}H_{19}Br$ requires C, 72·7; H, 5·3; Br, 22·0%).

Reaction of 3,3,3-*Triphenylpropene with Bromine*.—(i) *In carbon tetrachloride*. Solutions of 3,3,3-triphenylpropene (0·50 g.) in carbon tetrachloride (10 ml.) and bromine in carbon tetrachloride (8·1 ml., 0·229M) were mixed. After 48 hr. at room temperature in a stoppered bottle, the solvent was distilled off to leave a yellow liquid which slowly solidified. The p.m.r. spectrum showed resonances consistent with the presence of only 2,3,3-triphenylallyl bromide and 1,2-dibromo-3,3,3-triphenylpropane (see below), in the ratio 1·15 : 1 (mean value from three spectra which gave ratios 1·18, 1·14, and 1·12, respectively). The solid was boiled in methanol for a few minutes and the resulting yellow crystals (0·28 g.) were recrystallised twice from ethanol to give methyl 2,3,3-triphenylallyl ether as white crystals, m. p. 132—133° (lit.,[14] 131—132·5°); p.m.r. spectrum: aromatic singlets (each 5H) at τ 2·58, 2·74, and 2·92, singlet (2H) at τ 5·72 (CH_2), and singlet (3H) at τ 6·72 (OMe) (Found: C, 87·8; H, 6·6. Calc. for $C_{22}H_{20}O$: C, 88·0; H, 6·7%). The filtrate from the methanol solution was evaporated and the residual yellow liquid in light petroleum (b. p. 40—60°) containing 10% of ether was chromatographed to give, successively, 1,2-*dibromo*-3,3,3-*triphenylpropane* (0·16 g.) as white crystals, m. p. 140—142° (from methanol) (p.m.r. and mass spectra: see Results section) (Found: C, 58·55; H, 4·3; Br, 37·4. $C_{21}H_{18}Br_2$ requires C, 58·6; H, 4·2; Br, 37·2%); and an impure sample of methyl 2,3,3-triphenylallyl ether, identified by its p.m.r. and infrared spectra.

(ii) *In methanol–carbon tetrachloride*. A solution of bromine in methanol (4·8 ml.; 0·39M) was added to a solution of 3,3,3-triphenylpropene (0·5 g.) in a mixture of carbon tetrachloride (5 ml.) and methanol (10 ml.) contained in a stoppered bottle. After 16 hr. at room temperature the solvent was distilled off under reduced pressure to leave a yellow liquid which slowly solidified to give 1-*bromo*-3-*methoxy*-2,3,3-*triphenylpropane* (0·35 g.) as white crystals, m. p. 110—112° (from ethanol) (p.m.r. and mass spectra: see Results section) (Found: C, 69·8; H, 5·8; Br, 21·1. $C_{22}H_{21}BrO$ requires C, 69·3; H, 5·5; Br, 21·0%). The p.m.r. spectrum of the crude product showed no trace of other compounds.

(iii) *In acetic acid–carbon tetrachloride*. A solution of bromine in carbon tetrachloride (8 ml.; 0·28M) was added to 3,3,3-triphenylpropene (0·5 g.) in carbon tetrachloride (4 ml.) and acetic acid (20 ml.) in a stoppered bottle. After 16 hr. at room temperature, the solution was washed with dilute aqueous sodium carbonate and water and was dried ($MgSO_4$). Evaporation of the solvent left a yellow solid which was recrystallised from ether to give 2,3,3-triphenylallyl bromide (0·42 g.), m. p. and mixed m. p. 125—127°. The p.m.r. spectrum of the crude product showed no trace of other compounds.

Reaction of 3-p-*Anisyl*-3,3-*diphenylpropene with Bromine*.—(i) *In carbon tetrachloride*. The procedure for the triphenyl analogue was followed, with the olefin (0·50 g.) and a solution of bromine in carbon tetrachloride (7·3 ml., 0·229M). The p.m.r. spectrum of the crude product (a red gum) showed resonances only of 2-*p*-anisyl-3,3-diphenylallyl bromide, and this compound (0·26 g.; 41%) was isolated by crystallisation from ether (p.m.r. spectrum and melting characteristics identical with those of the authentic sample). Gas chromatography (silicone oil, 10%, on Celite; 245°) showed that the crude product contained 85% of the allyl bromide.

(ii) *In methanol–carbon tetrachloride*. A solution of bromine in methanol (3 ml.; 0·20M) was added to 3-*p*-anisyl-3,3-diphenylpropene (0·18 g.) in methanol (6 ml.) and carbon tetrachloride (3 ml.) in a stoppered bottle. After 16 hr. at room temperature, the solvent was distilled off under reduced pressure to leave a yellow gum. This was shaken with a small quantity of ether and the precipitate was recrystallised from ether to give 2-*p*-anisyl-3,3-diphenylallyl bromide (85 mg.) as white crystals, decomposing above 130°, whose infrared and p.m.r. spectra were identical with those of an authentic sample. Chromatography of the filtrate gave 2-p-*anisyl*-1-*bromo*-3-*methoxy*-3,3-*diphenylpropane* (19 mg.) as white crystals, m. p. 111—112·5° (from methanol) (p.m.r. and mass spectra: see Results section).

Reaction of 2-*Methyl*-3,3,3-*triphenylpropene with Bromine*.—(i) *In acetic acid–carbon tetrachloride*. A solution of bromine in carbon tetrachloride (25·2 ml.; 0·0638M) was added to a solution of 2-methyl-3,3,3-triphenylpropene (0·47 g.) in carbon tetrachloride (10 ml.) and acetic acid (30 ml.) in a stoppered bottle. When the bottle was opened after 24 hr. at room temperature, fumes of hydrogen bromide were liberated. Distillation of the solvent left a white solid whose p.m.r. spectrum was consistent with the presence, in approximately equal amounts, of the isomeric 1-bromo-2-methyl-3,3,3-triphenylpropene and 2-bromomethyl-3,3,3-triphenylpropene. After five recrystallisations from methanol, this solid gave 1-*bromo*-2-*methyl*-3,3,3-*triphenylpropene* (0·11 g.; 19%) as white needles, m. p. 210—213°; p.m.r. spectrum: aromatic singlet (15H) at τ 2·78, singlet (1H) at τ 3·69 (vinyl proton), and singlet (3H) at τ 8·30 (Me) (Found: C, 72·9; H, 5·3; Br, 22·1. $C_{22}H_{19}Br$ requires C, 72·7; H, 5·3; Br, 22·0%). The

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[22] R. O. C. Norman and C. B. Thomas, *J. Chem. Soc.* (*B*), 1967, following Paper.

combined filtrates from the first two recrystallisations were evaporated and the white solid was recrystallised twice from methanol to give impure 2-bromomethyl-3,3,3-triphenylpropene (0·05 g.; 9%) as white needles, m. p. 115—128°, whose p.m.r. and infrared spectra were identical with those of an authentic sample.

(ii) *In methanol–carbon tetrachloride.* A solution of bromine in carbon tetrachloride (7·6 ml., 0·23M) was added to 2-methyl-3,3,3-triphenylpropene (0·5 g.) in carbon tetrachloride (2 ml.) and methanol (20 ml.) in a stoppered bottle. The colour faded rapidly. After 16 hr. the solution was poured into water and the ether extract was dried ($MgSO_4$). The solvent was distilled off to leave a yellow solid which, after two recrystallisations from methanol, gave 1-*bromo*-3-*methoxy*-2-*methyl*-2,3,3-*triphenylpropane* (0·44 g.; 63%) as white crystals, m. p. 123—124·5° (p.m.r. and mass spectra: see Results section) (Found: C, 69·6; H, 6·1; Br, 20·4. $C_{23}H_{23}BrO$ requires C, 69·9; H, 5·9; Br, 20·2%). The p.m.r. spectrum of the crude product showed no trace of other compounds.

(iii) *In carbon tetrachloride.* A solution of bromine in carbon tetrachloride (8 ml.; 0·23M) was added to the olefin (0·5 g.) in carbon tetrachloride (8 ml.) in a stoppered bottle. After 4 days, the solvent was distilled off to leave a yellow semi-solid product (0·7 g.) whose p.m.r. spectrum showed it to contain 1-bromo-2-methyl-3,3,3-triphenylpropene and 2-bromomethyl-3,3,3-triphenylpropene. The presence of 1,2-dibromo-3,3,3-triphenylpropane was suggested by the occurrences of resonances in the p.m.r. spectrum at τ 5·6—6·0 (multiplet) and τ 7·70 (singlet), but attempts to isolate this compound, by fractional crystallisation and by chromatography on alumina, were unsuccessful.

Reaction of 3-p-*Anisyl*-2-*methyl*-3,3-*diphenylpropene with Bromine in Acetic Acid–Carbon Tetrachloride.*—The method for 2-methyl-3,3,3-triphenylpropene was followed, with 0·50 g. of the olefin. The p.m.r. spectrum of the resulting white solid was consistent with the presence, in approximately equal amounts, of the isomeric 3-*p*-anisyl-2-bromomethyl-3,3-diphenylpropene [resonances at τ 4·06 and 4·42 (vinyl protons), τ 6·22 (OMe), and τ 6·30 (CH_2)] and 3-*p*-anisyl-1-bromo-2-methyl-3,3-diphenylpropene [resonances at τ 3·72 (vinyl proton), τ 6·22 (OMe), and τ 8·34 (Me)]. Recrystallisation from methanol gave white crystals (0·53 g.; 87%), m. p. 130·5—131·5°, whose p.m.r. spectrum indicated it to be a eutectic mixture of the above two isomers of approximate content 55% (2-bromomethyl) and 45% (1-bromo-2-methyl) (Found: C, 69·5; H, 5·6; Br, 20·4. Calc. for $C_{23}H_{21}BrO$: C, 70·2; H, 5·4; Br, 20·3%).

Kinetics.—A solution of bromine in carbon tetrachloride (1·5 ml.; 0·019M) was added to the olefin in carbon tetrachloride (1·5 ml.; 0·019M) contained in the spectroscopic cell (path-length, 1 cm.). After being shaken, the cell was quickly transferred to the cell compartment of a Unicam SP 825 spectrophotometer maintained at 25° ± 0·1°. The optical density at 400 mμ was measured as a function of time; plots of the reciprocal of the optical density against time were linear. The derived rate constants were the mean of three experiments in each case and were reproducible to within ±2%.

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