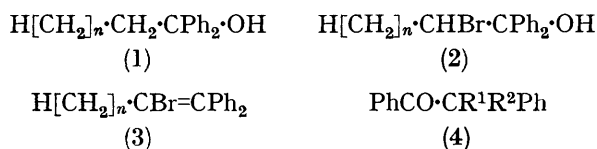# Reaction of Bromine with Phenyl-substituted Tertiary Alcohols

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The reaction between bromine and 1,1-diphenylalkan-1-ols is shown to proceed by dehydration to an alkene, followed in aqueous acetic acid by formation of a bromohydrin which may then rearrange to a ketone. A number of new bromohydrins and bromoalkenes have been prepared.

THE reaction of bromine with tertiary alcohols has sometimes been used as a preparative method for vicinal dibromides,[1] but there have been few investigations of its scope and pathway. In the case of the reaction between 1,1-diphenylpropan-1-ol and bromine in 80% acetic acid–water, Pansevich-Kolyada and Prilezhaev[2] were able to isolate a bromohydrin, 2-bromo-1,1-diphenylpropan-1-ol, which they assumed to react further either by dehydration to give a 2-bromoalkene or by reaction with hydrobromic acid to give a vicinal dibromide. Since this seemed inherently unlikely we have examined the reaction between bromine and a number of 1,1-diphenylalkan-1-ols (1; $n = 0$—10).

$$H[CH_2]_n\cdot CH_2\cdot CPh_2\cdot OH \qquad H[CH_2]_n\cdot CHBr\cdot CPh_2\cdot OH$$
$$(1) \qquad\qquad\qquad (2)$$

$$H[CH_2]_n\cdot CBr{=}CPh_2 \qquad\qquad PhCO\cdot CR^1R^2Ph$$
$$(3) \qquad\qquad\qquad (4)$$

The required alcohols were prepared by conventional Grignard reactions between phenylmagnesium bromide and esters of the appropriate acids. These alcohols have the reputation [3,4] of being easily dehydrated during work-up, but we were able to isolate them in good yield by decomposing the slurry of magnesium salts formed after pouring on ice by using ammoniacal ethylenediaminetetra-acetic acid, rather than the usual acidic reagents. Details of new alcohols prepared are given in Table 1.

TABLE 1

New 1,1-diphenylalkan-1-ols

	B.p. (°C) [pressure (mmHg)]	n_D^{20}	Reqd. (%) C	H	Found (%) C	H
1,1-Diphenylheptan-1-ol	165—166 [0·03] *	1·5508	85·0	9·0	85·2	8·9
1,1-Diphenyloctan-1-ol	172—173 [0·01]	1·5463	85·1	9·3	85·2	9·0
1,1-Diphenylnonan-1-ol	200—210 [0·20]	1·5410	85·1	9·5	84·8	9·2
1,1-Diphenyldecan-1-ol	192—194 [0·05]	1·5345	85·1	9·7	85·4	10·0
1,1-Diphenylundecan-1-ol	184—186 [0·02]	1·5328	85·1	9·9	85·0	9·9
1,1-Diphenyldodecan-1-ol	182—184 [0·07]	1·5315	85·1	10·1	85·4	9·8

* Lit.,[5] 200—201° at 11 mmHg.

When the alcohols were dissolved in 4 : 1 acetic acid–water and heated to 70—80 °C, and bromine was added

slowly we were able to isolate the bromohydrin in only two cases. 1,1-Diphenylpropan-1-ol (1; $n = 1$) gave 2-bromo-1,1-diphenylpropan-1-ol (2; $n = 1$), as previously reported,[2] and 1,1-diphenylheptan-1-ol (2; $n = 5$) gave a mixture of the corresponding bromohydrin (2; $n = 5$) and 2-bromohept-1-ene (3; $n = 5$). In other cases the product isolated was the bromoalkene, as indeed was the case with the diphenyl-propanol and -heptanol when the bromine was added rapidly. Since most of the bromohydrins had not been prepared previously we sought suitable conditions for their formation, and found that they could be prepared in good yield by dissolving the 1,1-diphenylalkan-1-ol with potassium bromide and bromine in 80% v/v acetic acid–water, and leaving the mixture at room temperature for 48—72 h. The bromohydrin was then precipitated with water. The same reaction was observed when the solvent was t-butyl alcohol, containing water and hydrochloric acid. Details are given in Table 2. All the compounds showed the expected features in their i.r. and n.m.r. spectra, notably a resonance (triplet except for 2-bromo-1,1-diphenylethanol) close to τ 4·9 for the proton on C-2. In some cases the structure was also proved by conversion into an epoxide with potassium hydroxide in t-butyl alcohol.

We observed during the reactions at 70—80 °C that after a little bromine had been added the mixture usually became turbid, then clearer after more bromine had been added. By stopping the reaction at the onset of turbidity (when the molecular ratio of added bromine to alcohol was about 1 : 30) we were able to isolate in good yield the alkene expected from dehydration of the alcohol. Although it has been assumed [6] that bromine reacts with tertiary alcohols by catalysing dehydration followed by addition we know of only one other case [7] in which the dehydration product has been isolated. Moreover, addition of bromine in carbon tetrachloride to a solution of the alcohol in carbon tetrachloride to the onset of turbidity also led to the formation, in good yield, of the alkene. Control experiments in which the alcohol was omitted showed that under the conditions we used (open vessels) much of the bromine evaporated over the time span of the experiment, and the quantity of bromine ion left in the solution never exceeded 0·5% of the quantity of alcohol.

It seemed likely that the subsequent transformation (formation of a vicinal dibromide or a bromoalkene

[1] E. A. Braude and E. A. Evans, J. Chem. Soc., 1955, 3331.
[2] V. I. Pansevich-Kolyada and N. A. Prilezhaev, J. Gen. Chem. (U.S.S.R.), 1951, 21, 571 (Eng. trans.).
[3] A. Jung and M. Brini, Bull. Soc. chim. France, 1964, 693.
[4] F. J. Kakis, D. Brase, and A. Oshima, J. Org. Chem., 1971, 36, 4117.
[5] A. Klages and S. Heilmann, Ber., 1904, 37, 1447.
[6] L. J. Andrews and R. M. Keefer, J. Amer. Chem. Soc., 1953, 75, 3557.
[7] E. M. Arnett and G. B. Klingensmith, J. Amer. Chem. Soc., 1965, 87, 1023.

derived therefrom by dehydrobromination, or formation of a bromohydrin) was a secondary reaction of the alkene. This was shown to be so by treatment of the preformed alkenes in 80% acetic acid–water with potassium bromide and bromine in the same solvent at room temperature at 75 °C. We were unable to find any evidence for the presence of acetates to any important extent, although the acetate ion is a good nucleophile.

In some cases we added the bromine to a solution of the alcohol in 80% acetic acid–water at reflux temperature. In these cases the product isolated was, except in the case of 1,1-diphenylethanol, a substituted deoxybenzoin (4). Results are given in Table 4. We attribute this to a semipinacolic reaction of the bromohydrin, similar to the cases reported by other workers.[4,8a,b] In confirmation, refluxing of the bromohydrins in 80% acetic acid–water also led to formation of the deoxybenzoins, as did treatment of the bromohydrins with silver nitrate solution. Kakis[4] et al. have recently suggested a method for conversion of certain alkenes into ketones by a similar route. However the Kakis method involves dehydration of the alcohol to an alkene, followed by bromination at low temperature, followed by treatment with methanolic silver nitrate solution containing a little water. Our method of merely refluxing a solution of the alcohol in aqueous acetic acid and adding bromine is shorter, although the essential steps appear to be the same, namely ionisation of the bromohydrin $RCHBr \cdot CPh_2 \cdot OH$, to a carbonium ion $RCH^+ \cdot CPh_2 \cdot OH$, followed by a pinacolic rearrangement to form, eventually, $RCHPh \cdot COPh$. In support of this we cite two pieces of evidence: (i) 1,1-diphenylethanol, which would have to ionise to form a primary carbonium ion, could not be made to rearrange under these conditions; (ii) 2-methyl-1,1-diphenylpropan-1-ol, which would form the bromohydrin $Me_2CBr \cdot CPh \cdot OH$, rearranged even in the cold to $PhCMe_2COPh$, because the carbonium ion to be formed is tertiary.

The reaction pathways can then be summarised as in the Scheme. Andrews and Keefer[6] have investigated

SCHEME
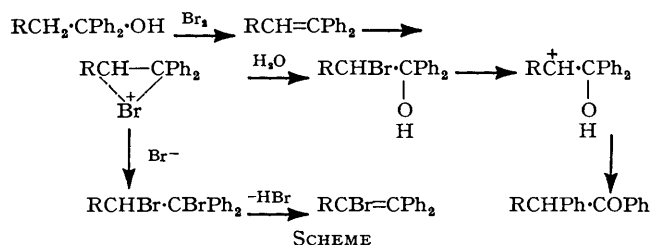
the kinetics of the reaction between t-amyl alcohol and bromine, and have reported that comparison of results for methods in which the concentration of bromine was followed iodometrically with those for methods in which it was followed spectrophotometrically shows a reducible intermediate to accumulate during the reaction. We carried out a few experiments to try to follow the

[8] (a) J. F. Lane and D. R. Walters, J. Amer. Chem. Soc., 1951, 73, 4234; (b) Y. Pocker, Chem. and Ind., 1959, 332.

kinetics of reaction of our alcohols with bromine by iodometric methods, but were frustrated by a tendency of the reaction to show the features of a damped oscillation.

EXPERIMENTAL

1,1-Diphenylalkan-1-ols.—The tertiary alcohols were prepared by Grignard reactions between phenylmagnesium bromide and appropriate ethyl or methyl esters. Work-up was accomplished by pouring the product on crushed ice, followed by pouring the slurry of ice, magnesium salts, and ether into ammoniacal ethylenediaminetetra-acetic acid. The magnesium salts were thus removed as a complex, and the alcohol dissolved in the ether forming a yellow solution. After drying ($MgSO_4$ or Na_2CO_3) the ether was removed and the alcohols could be distilled under reduced pressure or recrystallised from ethyl acetate; yields 65—85%.

2-Bromo-1,1-diphenylalkan-1-ols.—2-Bromo-1,1-diphenylpropan-1-ol was prepared by the method of Pansevich-Kolyada and Prilezhayev.[2] This method gave 2-bromo-substitution only for 1,1-diphenylpropan-1-ol and 1,1-diphenylheptan-1-ol. In the latter case bromoalkene was also formed. For bromination with tribromide ion the details given for 2-bromo-1,1-diphenylheptan-1-ol are typical.

TABLE 2

Products of reactions of 1,1-diphenylalkan-1-ols with tribromide ion [a]

Product (2)	M.p. (°C)	Calc. (%) C	H	Br	Found (%) C	H	Br
n = 0	54·5						
n = 1	57·5—58						
n = 2 [b]	47·5	63·0	5·6	26·2	63·0	5·6	26·1
n = 3 [b]	48—50	63·95	6·0	25·0	63·9	6·0	24·7
n = 4 [b]	50—51	64·9	6·4	24·0	65·2	6·1	24·1
n = 5 [b]	77·5—78	65·7	6·7	23·0	65·9	6·5	23·2
n = 6 [b]	60·5—61·5	66·5	7·0	22·1	66·8	6·9	22·1
n = 7 [b]	54—55	67·2	7·25	21·3	67·2	7·2	21·4
n = 8 [b]	45—46	67·8	7·5	20·5	68·1	7·5	20·2
n = 9 [b]	65—66	68·5	7·7	19·8	68·1	7·4	19·6
n = 10 [b]	50—51	69·05	8·8	19·1	69·4	8·3	19·2

[a] Yields 75—91%. [b] New compound.

TABLE 3

New 2-bromo-1,1-diphenylalkenes

	n_D^{20}	Calc. (%) C	H	Br	Found (%) C	H	Br
2-Bromo-1,1-diphenylbut-1-ene [a]	1·6090	66·9	5·3	27·8	67·2	5·4	28·1
2-Bromo-1,1-diphenylhept-1-ene [b]	1·5820	69·3	6·44	24·3	69·0	6·6	24·5
2-Bromo-1,1-diphenyloct-1-ene [c]	1·5760	70·0	6·8	23·3	70·4	6·5	23·7

[a] L. Luecke and E. Jassmann give b.p. 128—130° at 0·4 mmHg [E.G.P. 63,372 (Chem. Abs., 1969, 70, 77,560)]. [b] Klages and Heilmann [5] give m.p. 74° but no analytical data. We believe their product was 2-bromo-1,1-diphenylheptan-1-ol, m.p. 77°. [c] B.p. 174° at 0·05 mmHg.

1,1-Diphenylheptan-1-ol (2·684 g) was dissolved in 80% v/v acetic acid–water (50 ml). A solution of potassium bromide (5 g) and bromine (0·55 ml, ca. 1·6 g) dissolved in the same solvent (250 ml) was added and the mixture was set aside for 48—72 h until the yellow colour had disappeared. On addition of an excess of water the bromohydrin was precipitated and could be purified by crystallis-

ation from ethanol, ethanol–water, propan-2-ol–water, or t-butyl alcohol–water.

2,2-Dibromo-1,1-diphenylethanol was prepared by adding bromine (2 ml) dropwise to a solution of 1,1-diphenylethanol (5 g) in 80% acetic acid–water (100 ml) at 75° with stirring. When the yellow colour of the bromine persisted the contents of the flask were cooled, an excess of water was

Dehydration of Alcohols in the Presence of Bromine.—Details given for 1,1-diphenylhexan-1-ol are typical. The alcohol (5 g) was dissolved in acetic acid–water (4 : 1 v/v; 100 ml) and heated to 70—80° with stirring, and bromine was added very slowly. Turbidity set in after 0·02 ml had been added. The mixture was then quenched with an excess of water and left overnight. The oil was separated

TABLE 4

Preparation of substituted deoxybenzoins (4) from alcohols

Alcohol (1)	Ketone (4) R¹	R²	M.p. (°C)	Lit. m.p. (°C)	Calc. (%) C	H	Found (%) C	H	Oxine m.p. (°C)	Lit. oxine m.p. (°C)
n = 2	Et	H	54—55	58 [a]						
n = 4	Me[CH₂]₃	H	61—61·5	57 [b]	85·7	8·0	85·3	7·9		
n = 5	Me[CH₂]₄	H	41·5—42	38 [b]	85·6	8·35	85·6	8·2		
n = 6	Me[CH₂]₅	H	40—41	59 [c]	85·6	8·64	85·8	8·3	98—100	89
n = 7	Me[CH₂]₆	H	51—52		85·6	8·94	85·5	8·8	85—87	
n = 8	Me[CH₂]₇	H	54·5—55	61,[c] 56·5—57 [d]	85·6	9·15	85·6	8·9	98—100	101 [c]
n = 9	Me[CH₂]₈	H	51—53							
n = 10	Me[CH₂]₉	H	50—51		85·6	9·62	85·8	9·5		
Me₂CH·CPh₂·OH	Me	Me	50	46—47 [e]					195	192—193

[a] V. Meyer and L. Oelkers, *Ber.*, 1888, **21**, 1295. [b] N. P. Buu-Hoï, Hiong-Ki-Wi, A. Lacassagne, and J. Lecocq., *Compt. rend.*, 1944, **219**, 589. [c] E. Bischoff, *Ber.*, 1889, **22**, 346. [d] M. Fétizon, F. J. Kakis, and V. Ignatiou-Ragoussis, *J. Org. Chem.*, 1973, **38**, 1732. [e] Mme. Ramart-Lucas and M. E. Salmon-Legganeur, *Bull. Soc. chim. France*, 1929, **45**[4], 730

added, and the aqueous layer was decanted. The remaining oil was washed with aqueous solutions of sodium sulphite and sodium carbonate with continuous stirring. The solid was then filtered off and recrystallised from ethanol; m.p. 101—102° (Found: C, 47·1; H, 3·25; Br, 43·8. C₁₄H₁₂Br₂O requires C, 47·3; H, 3·1; Br, 45·0%).

The bromoalkenes were prepared by adding 1 mol equiv. of bromine to the alcohol in 80% acetic acid–water at 70 °C rapidly, followed by separation, drying, and distillation under reduced pressure.

(dissolved in ether if necessary), washed with sodium sulphite solution, then water, then dried (Na₂SO₄) and distilled under reduced pressure to yield 1,1-diphenylhex-1-ene.