Photochemical Bromination of Simple Arenes

Roger Bolton,* Muhammad Iqbal Bhangar, and Gareth H. Williams
Department of Chemistry, Royal Holloway and Bedford Colleges, Egham Hill, Egham, Surrey TW20 0EX

Photochemical bromination of benzene, fluorobenzene, chlorobenzene, t-butylbenzene, α,α,α-trifluorotoluene, and (in tetrachloromethane) biphenyl and naphthalene gives substitution products and adducts such as 1,2,3,4,5,6-hexabromocyclohexane (**1**). The decomposition of (**1**) and of the analogous chlorobenzene adduct (**3**) under photochemical conditions gives the parent arene, the monobrominated halogenobenzene, and bromine which may be scavenged by toluene to give benzyl bromide or by benzene to give bromobenzene and dibromobenzenes. Addition is a kinetically controlled process, so that the mechanism of formation of these aryl bromides must be largely through the reversible formation of these adducts. This is consistent with the unusual orientation of apparent attack by bromine upon the arene substrates, since the relative amounts of the isomeric aryl bromides is a consequence of the relative stabilities and ease of elimination of HBr and Br_2 from a family of adducts.

The range of isomer distribution found within the reaction of each arene with bromine is consistent with two competing processes involved in the formation of the aryl bromides; one of these might be the direct homolytic substitution by bromine atoms upon the arene.

Bromination of aromatic systems under heterolytic conditions is commonly associated with substitution in the ring;[1,2] under homolytic conditions side-chain substitution[3] or addition to the ring[4] is usual. The report[5] that bromobenzene is a minor product of the photochemical bromination of benzene implies that aromatic substitution by bromine might also proceed by a homolytic mechanism. After this work had been begun, Gouverneur and Soumillion[6] reported the orientation of bromine substitution of some mono- and di-halogenobenzenes under a range of conditions, some of which clearly encouraged homolytic mechanisms of reaction. Under such conditions in which free-radical processes prevailed, the orientation of substitution of the mono-halogenobenzenes appears to favour the *meta*-isomer, particularly in the reaction of chlorobenzene; this preponderance was not expected by reference either to heterolytic mechanisms or to common experience in other homolytic substitution processes such as arylation.[7]

We now report a study of the course of the photochemical bromination of benzene and of a number of its simple derivatives.

Discussion

Most of the photochemical studies used solutions of bromine in the liquid aromatic substrate, or in solutions of the aromatic compound in tetrachloromethane. A slow stream of nitrogen was maintained during the photolysis, and the effluent gas was passed through a water trap. At the end of the reaction (usually 16 h) unchanged bromine and evolved hydrogen bromide were estimated by conventional titrimetric methods. Under such conditions, benzene at 25 °C gave 1,2,3,4,5,6-hexabromocyclohexane (**1**), which accounted for 70% of the initial amount of bromine [equation (1)]. Bromobenzene [5% based on initial amount of bromine; equation (2)] and dibromobenzenes (0.1%)

$$C_6H_6 + 3Br_2 \longrightarrow C_6H_6Br_6 \quad (1)$$

$$C_6H_6 + Br_2 \longrightarrow C_6H_5Br + HBr \quad (2)$$

were the only aryl halides formed, together with hydrogen bromide [8%; equation (2)]; 10% of the bromine used was recovered. At 55 °C, somwhat less (**1**) was formed (equivalent to 40% of the halogen added initially), with proportionately more bromobenzene (15%), dibromobenzenes (19.6%), tribromobenzenes (1.8%), and hydrogen bromide (34%); the same amount of bromine remained unchanged.

Table 1. Products of photochemical bromination of aromatic compounds

Arene	*t*/h	*T*/°C	Conversion[a]	Products (mol %/mol Br_2 initially)
PhH	16	25	90	HBr (8); $C_6H_6Br_6$ (**1**) (23); C_6H_5Br (5); $C_6H_4Br_2$ (0.1)
PhH	16	55	90	HBr (34); $C_6H_6Br_6$ (**1**) (13); C_6H_5Br (15); *o*-$C_6H_4Br_2$ (1.8); (*m*- + *p*-)$C_6H_4Br_2$ (8)
PhF	16	25	40	HBr (35); *o*-FC_6H_4Br (12.3); *m*-FC_6H_4Br (2.5); *p*-FC_6H_4Br (26)
PhCl	16	25	51	HBr (41); *o*-ClC_6H_4Br (6.4); *m*-ClC_6H_4Br (27); *p*-ClC_6H_4Br (8.6)[b]
$PhCF_3$[c]	16	25	24	HBr (15.6); *o*-$CF_3C_6H_4Br$ (0.6); *m*-$CF_3C_6H_4Br$ (16); *p*-$CF_3C_6H_4Br$ (7)
$PhCMe_3$	20	25	60	HBr (48); *o*-$Me_3CC_6H_4Br$ (2.6); *m*-$Me_3CC_6H_4Br$ (34.8); *p*-$Me_3CC_6H_4Br$ (13.4)[d]

[a] Bromine consumed. [b] $C_6H_5ClBr_6$ (1.5 mol %) also isolated. [c] 83 g in 500 cm^3 of tetrachloromethane. [d] *m*-$C_6H_4(CMe_3)_2$, *ca.* 30 mol % based upon bromine initially present, was identified.

The corresponding reactions of fluorobenzene, chlorobenzene, α,α,α-trifluorotoluene, and t-butylbenzene gave the results shown in Table 1. The distribution of the isomeric bromofluorobenzenes and bromochlorobenzenes agreed with those found earlier[6] and the orientation of the dibromobenzenes formed by the further attack of benzene agreed with that found[6] for the homolytic bromination of bromobenzene. Some electrophilic character of the attacking reagent could be adduced from the preponderance of *m*-bromo-α,α,α-trifluorotoluene and of *p*-bromo-t-butylbenzene from $PhCF_3$ and $PhCMe_3$ respectively, but the great extent to which *meta*-attack seemed favoured in the halogenobenzenes suggested some other factors as well as electronic effects.

The formation of bromobenzene and dibromobenzenes at the expense of (1) in the photochemical bromination of benzene suggests two competing processes, but the increase in the

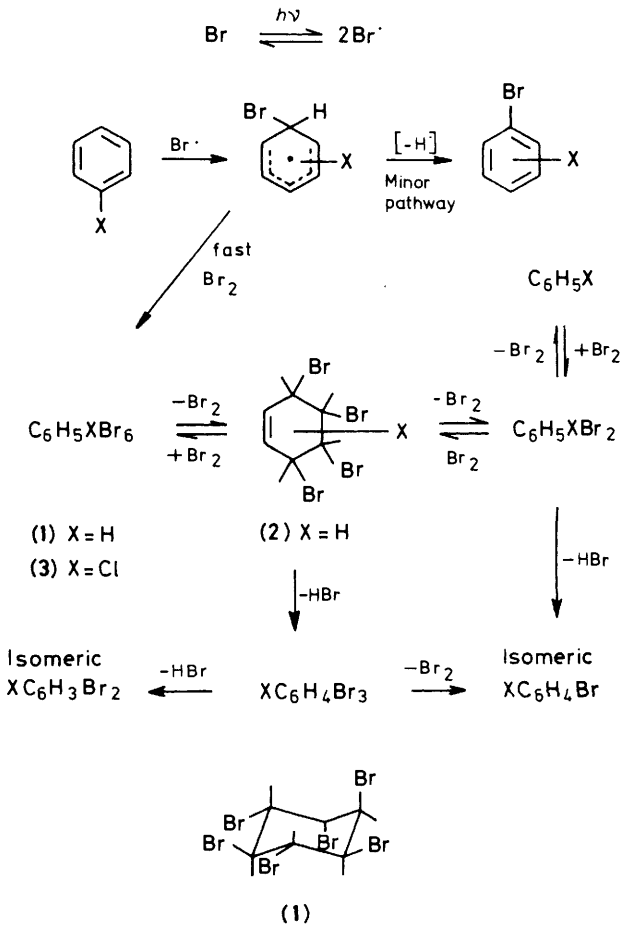
Table 2. Photolysis products of (**1**) and (**3**), $C_6H_5XBr_6$ (55 °C; 16 h)

Solvent	X	Moles adduct consumed	Products (mmol)
PhH	H	7.8×10^{-3}	HBr (20); C_6H_5Br (9); $C_6H_4Br_2$ (5.9)[a]
PhMe	H	5.3×10^{-3}	HBr (12); C_6H_5Br (1.3); $C_6H_4Br_2$ (0.8);[b] $C_6H_5CH_2Br$ (8); $(C_6H_5CH_2)_2$ (0.3)
CCl_4	H	2.1×10^{-3}	HBr (3); Br_2 (2); C_6H_5Br (1.2); $C_6H_4Br_2$ (0.4)
Cyclohexene	H	1.8×10^{-3}	HBr (0.08); C_6H_5Br (0.2); $C_6H_9Br + C_6H_{10}Br_2$ (<0.2)
PhH	Cl	6.2×10^{-3}	HBr (12); C_6H_5Cl (4.0); C_6H_5Br (3.8); $C_6H_4Br_2$ (2.0); C_6H_4ClBr (2.5)[c]
PhMe	Cl	8.4×10^{-3}	HBr (18); C_6H_5Cl (1.0); $C_6H_5CH_2Br$ (17); $(C_6H_5CH_2)_2$ (2.0); C_6H_4BrCl (5.1)

[a] *o*-/(*m*- + *p*-), 20/80. [b] *o*-/(*m*- + *p*-), 19/81. [c] $C_6H_4Br_2$ isomer distribution, *o*-(*m*- + *p*-), 20/80; C_6H_4BrCl isomer distribution shown in text.

relative ratio of dibromobenzenes and bromobenzene which occurs at higher temperatures suggests that there is more than one mechanism by which the aryl bromides are formed; it is improbable, on statistical grounds, that the dibromobenzenes arise solely from the further bromination of bromobenzene, itself in dilute solution in benzene. The decomposition of (**1**) must take place by such a mechanism; in other words, (**1**) is the kinetically controlled major product, whereas the aryl bromides are the thermodynamically controlled products. Certainly the addition of the last molecule of halogen to form (**1**) is reversible[8] and we have shown that, under photolysis conditions, (**1**) acts as a source of bromine towards toluene and its derivatives.[9] This decomposition of (**1**) occurs more quickly in toluene than in benzene, tetrachloromethane, or cyclohexene (Table 2), and it is induced by added peroxides, such as bis-(*p*-chlorobenzoyl) peroxide, which also gives the corresponding aryl bromide (*i.e.* *p*-bromochlorobenzene); it is not induced by heat alone. Bromine may be abstracted directly from (**1**), or may be in rapid equilibrium with the tetrabromocyclohexene (**2**). In benzene, (**1**) decomposes photolytically to give bromobenzene, the isomeric dibromobenzenes, and small amounts of tribromobenzenes. The corresponding decomposition of (**1**) in toluene gives much less of these aryl bromides, but the ratio of them, and the isomer distribution of the dibromobenzenes, are similar. Apparently toluene scavenges the halogen very effectively. In tetrachloromethane and, surprisingly, in cyclohexene, (**1**) decomposes only slowly to give mono- and di-bromobenzenes; in the second case, small amounts of 1,2-dibromocyclohexane and 3-bromocyclohexene were also found.

Analogues of (**1**) have been reported[10] from the photochemical bromination of both fluorobenzene and chlorobenzene; we were only able to prepare 1-chloro-1,2,3,4,5,6-hexabromocyclohexane (**3**). This decomposed upon irradiation in toluene to give, as expected, much benzyl bromide and also a mixture of bromochlorobenzenes whose isomer distribution (*o*-, 8%; *m*-, 78%; *p*-, 14%) resembled that found in the photochemical bromination of chlorobenzene (*o*-, 15%; *m*-, 65%, *p*-, 20%). In benzene, (**3**) gave these bromochlorobenzenes (*o*-, 12%; *m*-, 73%; *p*-, 15%) and both bromobenzene and the isomeric dibromobenzenes (*o*-, 20%; *m*- + *p*-, 80%); most significantly, chlorobenzene was also a product. This set of experiments suggested that the photolysis of the hexabromo-adduct $C_6H_5XBr_6$ gave both C_6H_5X and the mono-substitution



Scheme. Possible route to photochemical formation of substitution products from the attack of bromine upon arenes

product(s) BrC_6H_4X, so that the mono- and di-bromobenzenes formed in the halogenation of benzene probably arose from a rapid formation of the corresponding adduct (**1**) and its subsequent decomposition. The range of isomer distributions of the bromochlorobenzenes formed by the photolysis of (**3**) or found in the photolytic bromination of chlorobenzene itself suggests that there is more than one route to these substitution products, however; the reported[6] range of isomer distributions in the bromination of various halogenobenzenes is consistent with this.

The Scheme shows a plausible mechanism which is consistent with these experimental observations; it is also likely to operate in the bromination of t-butylbenzene and of α,α,α-trifluorotoluene, in both of which the yield of hydrogen bromide matches the yield of bromo-arenes but the amount of bromine consumed is greater than these. The formation of aryl halides by this photolysis of adducts explains the anomalous apparent substitution patterns, since the orientation of the substitution product does not reflect a selection between available sites of attack but rather a selection between a number of ways of eliminating HX or X_2 from an adduct in a sequence which ultimately produces the most stable product. The complexities of energetic and steric considerations which govern the orientation of addition of halogen to benzene under such conditions are well documented[11] and the corresponding elimination processes are presumably no more simple.

In t-butylbenzene a quite unexpected product was found; it was finally shown to be *m*-di-t-butylbenzene. In contrast with the other aryl bromides, both *m*- and *p*-bromo-t-butylbenzene

Table 3. Products of photochemical bromination of biphenyl (0.10 mol of Br_2; 50 °C)

$[C_{12}H_{10}]$/M	t/h	Solvent	% Conversion[a]	Products (mol %/mol Br_2 initially)
0.2	20	CCl_4	24	HBr (16); *o*-BrC_6H_4Ph (3.5); *m*-BrC_6H_4Ph (3.9); *p*-BrC_6H_4Ph (7.1)
1.0	20	CCl_4	63	HBr (31); *o*-BrC_6H_4Ph (6.9); *m*-BrC_6H_4Ph (8.4); *p*-BrC_6H_4Ph (14.7)
2.0	20	CCl_4	70	HBr (35); *o*-BrC_6H_4Ph (9.2); *m*-BrC_6H_4Ph (8.0); *p*-BrC_6H_4Ph (20.9)
0.2	20	PhH	70	HBr (40); *o*-BrC_6H_4Ph (0.96); *m*-BrC_6H_4Ph (0.27); *p*-BrC_6H_4Ph (1.7); C_6H_5Br (16); *o*-$C_6H_4Br_2$ (1.51); *m*- + *p*-$C_6H_4Br_2$ (7.0)
1.0	18	PhH	94	HBr (45); *o*-BrC_6H_4Ph (4.1); *m*-BrC_6H_4Ph (1.3); *p*-BrC_6H_4Ph (7.5); C_6H_5Br (16); *o*-$C_6H_4Br_2$ (1.6); *m*- + *p*-$C_6H_4Br_2$ (6.7)
2.0	20	PhH	98	HBr (60); *o*-BrC_6H_4Ph (6.9); *m*-BrC_6H_4Ph (4.2); *p*-BrC_6H_4Ph (16); C_6H_5Br (14); *o*-$C_6H_4Br_2$ (1.2); *m*- + *p*-$C_6H_4Br_2$ (5.6)
2.0	18	PhBr	60	HBr (42); *o*-BrC_6H_4Ph (9.6); *m*- + *p*-BrC_6H_4Ph (30.4); *O*-$C_6H_4Br_2$ (1); *m*- + *p*-$C_6H_4Br_2$ (2.8)

[a] Bromine consumed.

individually underwent ready photolysis to give *m*-di-t-butylbenzene, bromine, and bromobenzene. An equimolar mixture of these two bromo-t-butylbenzenes gave a mixture containing a preponderance of the *meta*-isomer (*m*-/*p*- 70/30); about 40% of the *p*-bromo-t-butylbenzene had been destroyed in 16 h. The formation of bromobenzene suggests that brominolysis of the t-butyl group occurred, and the formation of di-t-butylbenzene points to the ready occurrence of a Friedel–Crafts reaction similar to that seen in the rearrangement of *o*-bromo-t-butylbenzene, which gave a mixture of the *meta*- and *para*-isomers (*m*-/*p*- 70/30) in the presence of aluminium halide.[12] Under our reaction conditions, hydrogen bromide might act as the Lewis acid catalyst. The *m*-dialkylbenzene is the most thermodynamically stable isomer, and this presumably accounts for its sole production.

The photochemical bromination of biphenyl and of naphthalene was carried out in tetrachloromethane solution. The uptake of bromine by naphthalene was rapid, and after 8 h 80% of the bromine had been consumed to give hydrogen bromide (40%) and 1-bromonaphthalene (35%); none of the 2-isomer was detected. 1,2,3,4-Tetrabromo-1,2,3,4-tetrahydronaphthalene was formed as well; it was unstable to heat as well as to light, and so the mechanism by which it gave 1-bromonaphthalene, 1,4-dibromonaphthalene, and benzyl bromide upon irradiation in toluene solution was uncertain beyond the homolytic side-chain substitution.

The photochemical bromination of biphenyl occurred less readily than that of naphthalene. In tetrachloromethane each of the three isomeric monobromobiphenyls was formed. Although 4-bromobiphenyl gave no benzyl bromide when its solution in toluene was boiled with a little benzoyl peroxide, the crude reaction mixture did so; peroxide was essential for this reaction. Adducts were also shown to be present by their sensitivity towards base and silver ions; a mechanism of formation of the aryl bromides by the decomposition of such adducts, as in the Scheme is therefore possible. In benzene solutions of biphenyl, however, both arenes gave mono- and di-bromo-derivatives (Table 3). In tetrachloromethane the isomer distribution of the monobromobiphenyls did not seem to be affected by changes in the initial concentration of biphenyl, but in benzene there seems to be evidence that *ortho*-attack is preferred over *meta*-attack at lower biphenyl concentrations. In bromobenzene, however, the isomer distribution is the same as that in tetrachloromethane.

This behaviour might be ascribed to the formation of complexes between the various components of the reaction mixture, as has been suggested[13] in the bromination of toluene in the presence of naphthalene; this deduction is not justified here. In tetrachloromethane and in bromobenzene about half the bromine consumed appears as hydrogen bromide, and there is good agreement between the yields of aryl bromides and of hydrogen bromide. In benzene solution, much of the halogen is consumed by the solvent; only small amounts of the isomeric bromobiphenyls are formed at low initial concentrations of this arene, and the differences in the observed isomer distribution under these conditions might arise solely from experimental difficulties in the separation and analysis of the biaryl fraction. This reservation is particularly necessary because we have not been able to separate clearly two possible mechanisms of formation of the aryl bromides, for while it is certain that these products may arise from photolysis of the polybromo-adducts we are not sure whether direct homolytic substitution of hydrogen by bromine may occur in our system.

Experimental

AnalaR bromine and analytical reagent grade solvents were used after distillation. Biphenyl and naphthalene were commercial samples which were purified by recrystallisation from ethanol. The physical constants of these materials agreed well with reported values. Authentic samples of bromo-arenes were usually commercially available; the bromobiphenyls were prepared from the appropriate bromoaniline, benzene, and pentyl nitrite.[14]

m-Bromo-t-butylbenzene (74%, b.p. 88—94 °C at 20 mmHg) was obtained from t-butylbenzene *via* *p*-nitro-t-butylbenzene (33%), *p*-t-butylaniline (81%), *p*-t-butylacetanilide (70%), 2-bromo-4-t-butylacetanilide (78%), 2-bromo-4-t-butylaniline (80%), and finally diazotisation and treatment with hypophosphorus acid.[15] *p*-Bromo-t-butylbenzene (70%, b.p. 80—82 °C at 2 mmHg) was obtained directly from t-butylbenzene.[16] *m*-Di-t-butylbenzene [δ_H (90 MHz; $CDCl_3$) 1.22 (18 H, s) and 7.13—7.35 (4 H, m)] was prepared by the copper-catalysed decarboxylation of 3,5-di-t-butylbenzoic acid, itself prepared by the oxidation ($KMnO_4$–pyridine) of 3,5-di-t-butyltoluene.[17] It was identical with material isolated by preparative g.l.c. (Apiezon) of the product of photochemical bromination of t-butylbenzene. 1,2,3,4,5,6-Hexabromocyclohexane (**1**) was prepared in 86% yield by the prolonged exposure of a solution of bromine (16 cm^3; 50 g) in benzene (100 cm^3) to sunlight; successive crops were removed by filtration and were recrystallised from toluene to give white cubes, m.p. 216—218 °C (lit.,[18] 212 °C). The yield was greatly decreased by using stronger light sources. With chlorobenzene, (**3**) was similarly prepared [60%; m.p. 125 °C (from ethanol), lit.,[10] 126 °C]. 1,2,3,4-*Tetrabromo*-1,2,3,4-*tetrahydronaphthalene* (Found: C, 26.8; H, 1.7. $C_{10}H_8Br_4$ requires C, 26.8; H, 1.8%) was obtained by the gradual addition of bromine (32 g, 0.20 mol) during 3 h to

a solution of naphthalene (12.8 g, 0.10 mol) in tetrachloromethane (500 cm^3) in the photochemical reactor. After 16 h irradiation and the removal of unchanged halogen and excess of solvent by evaporation under reduced pressure, the pure material was isolated by three crystallisations from chloroform (23% yield).

All photochemical studies used a Hanovia reactor (1 l) containing a 100 W medium-pressure mercury lamp which was water-cooled. The reacting solution was in a concentric jacket, the outside of which was wrapped in aluminium foil. The whole reactor was then immersed in an oil thermostat. A slow stream of nitrogen passed over the reaction mixture and through a water scrubber while the irradiation took place. At the end of the reaction, free bromine was estimated titrimetrically (KI–$Na_2S_2O_3$) and the hydrogen bromide was washed from the organic layer, added to the contents of the water scrubber, and the combined solution estimated for bromide ion by titration with silver nitrate.

The dried organic layer was then concentrated by distillation under reduced pressure (biphenyl, naphthalene) or by careful fractional distillation (all other substrates). The residue was analysed by g.l.c. [Pye Unicam 204; PEGA or OV-1 columns generally useful; FFAP (1%) or SE-30P (1%) columns for bromobiphenyls; AP-15C column for bromo-t-butylbenzenes]. Steam-distillation was used as a check when the adducts were known to be stable to this temperature; no products were formed as a result of the pyrolysis of adducts on the g.l.c. column, except for adducts from naphthalene, which were thermally unstable. Both methods of extraction gave the same g.l.c. analyses; in solutions containing (**1**), this adduct could be removed almost completely from concentrated mixtures by treatment with light petroleum.

Independent checks of the g.l.c. analyses were possible using ^1H n.m.r. (bromo-t-butylbenzenes) and ^{19}F n.m.r. spectroscopy (bromofluorobenzenes) using a JEOL FX90-Q instrument.

References

1 P. B. D. de la Mare and J. H. Ridd, 'Aromatic Substitution—Nitration and Halogenation,' Academic Press, New York, 1959; R. O. C. Norman and R. Taylor, 'Electrophilic Substitution in Benzenoid Compounds,' Elsevier, Amsterdam, 1965.
2 *Cf.* P. B. D. de la Mare, 'Electrophilic Halogenation,' Cambridge University Press, Cambridge, 1976, pp. 155—158, 209—212; P. B. D. de la Mare and R. Bolton, 'Electrophilic Additions to Unsaturated Systems,' 2nd edn., Elsevier, Amsterdam, 1982, pp. 346—353.
3 M. S. Kharasch and M. G. Berkman, *J. Org. Chem.*, 1941, **6**, 810.
4 M. Poutsma, *J. Am. Chem. Soc.*, 1965, **87**, 2161, 2172; *J. Org. Chem.*, 1966, **31**, 4167.
5 W. Meidinger, *Z. Phys. Chem.*, 1929, **B5**, 29; E. Rabinowitsch, *ibid.*, 1932, **B19**, 190.
6 P. Gouverneur and L. Soumillion, *Tetrahedron Lett.*, 1976, 133.
7 D. H. Hey, *Adv. Free Radical Chem.*, 1967, **2**, 47.
8 A. J. Kolka and H. D. Orloff, U.S.P. 2 920 110 (*Chem. Abstr.*, 1960, **54**, 109 955e); U.S.P. 2 988 574 (*Chem. Abstr.*, 1962, **56**, 10 040a).
9 M. M. Aly, R. Bolton, and G. H. Williams, *J. Chem. Res. (S)*, 1983, 24.
10 T. van der Linden, *Recl. Trav. Chim. Pays-Bas*, 1936, **55**, 282, 287, 288.
11 H. D. Orloff and A. J. Kolka, *J. Am. Chem. Soc.*, 1954, **76**, 5484; H. D. Orloff, A. J. Kolka, G. Calingaert, M. E. Griffing, and E. R. Kerr, *ibid.*, 1953, **75**, 4243; H. D. Orloff, *Chem. Rev.*, 1954, **54**, 388.
12 G. A. Olah, J. C. Lapierre, and U. H. Schreier, *J. Org. Chem.*, 1966, **31**, 1268.
13 F. R. Mayo and W. A. Hardy, *J. Am. Chem. Soc.*, 1952, **74**, 911.
14 Huang Shu, *Acta Chim. Sinica*, 1959, **25**, 171; J. I. G. Cadogan, *J. Chem. Soc.*, 1962, 4257.
15 C. S. Marvel, H. W. Johnston, J. W. Meier, T. W. Mastin, J. Whitson, and C. M. Himel, *J. Am. Chem. Soc.*, 1944, **66**, 914; B. W. Larner and A. T. Peters, *J. Chem. Soc.*, 1952, 680.
16 D. A. Shirley, 'Preparation of Organic Intermediates,' Chapman and Hall, London, 1951, p. 42.
17 J. Geuze, C. Ruinard, J. Soeterbroek, P. E. Verkade, and B. M. Wepster, *Recl. Trav. Chim. Pays-Bas*, 1956, **75**, 301; M. J. Schlatter, U.S.P. 2635114 (*Chem. Abstr.*, 1954, **48**, 7059).
18 R. Cornubert and A. Rio, *Bull. Soc. Chim. Fr.*, 1955, **22**, 60.

Received 1*st August* 1983; *Paper* 3/1330