The Reactions of t-Butyl Peroxide with Toluene Derivatives

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The reactions of t-butyl peroxide with toluene derivatives, containing chloro-, bromo-, cyano-, methyl-, and phenyl-substituents in the alkyl side chain and *p*-halogeno-substituents in the nucleus, give variable yields of the corresponding dehydro-dimers. Good yields are obtained with the *p*-halogeno-substituted cumenes, benzyl cyanide, *p*-chlorobenzyl cyanide, benzylidene dichloride, and *p*-bromoethylbenzene. α-Chloroethylbenzene, benzyl bromide, benzyl chloride, *p*-chlorobenzyl chloride, and *p*-tolunitrile give moderate to low yields of the expected dimers. However, *p*-bromobenzyl bromide, α-bromoethylbenzene, α-bromophenylacetonitrile, and diphenylbromomethane fail to dimerise in the expected manner. The available evidence in the case of diphenylchloromethane suggests that both hydrogen and chlorine are abstracted, giving rise to a variety of mixed products.

FREE methyl radicals, liberated by thermolysis of acetyl peroxide, have long been known to abstract hydrogen atoms from the carbon atom adjacent to the unsaturated group in substances such as alkylbenzenes, ketones, acids, and esters.[1] More recently, similar behaviour has also been observed with t-butyl peroxide in its reactions with compounds containing the ArCH: nucleus.[2-4] This selectivity has been attributed to the effectiveness with which the t-butyloxy-radical can function as a dehydrogenating agent, when it is released from the thermal decomposition of t-butyl peroxide in a solvent. It has been established [3,4] that the course followed by these homolytic reactions with t-butyl peroxide is largely determined by the relative stability of the secondary radical produced by hydrogen abstraction, provided polar-orienting and steric effects are absent. Thus resonance-stabilised benzyl-type radicals tend to dimerise whilst less stable intermediates show a marked preference for disproportionation (when possible). Radicals of intermediate stability may undergo both processes concurrently.

When free-radical dimerisation is the favoured reaction, a convenient synthetic route becomes available whereby the preparation of certain stereochemically interesting compounds may be accomplished. We here describe the preparation and some attempted syntheses by this method of a variety of compounds of the type $(R^1R^2R^3C)_2$ derived from the radical $R^1R^2R^3C^{\cdot}$. Since physical methods, such as dielectric measurements, appear likely to provide significant information on the conformation and rotational isomerism of those compounds, work along these lines has also been initiated.

The details of the reactions examined are summarised in the Table. The results show a number of interesting

[1] M. S. Kharasch, H. C. McBay, and W. H. Urry, *J. Org. Chem.*, 1945, **10**, (*a*) 393; (*b*) 401; (*c*) M. S. Kharasch, E. V. Jensen, and W. H. Urry, *J. Org. Chem.*, 1945, **10**, 386; (*d*) M. S. Kharasch and M. T. Gladstone, *J. Amer. Chem. Soc.*, 1943, **65**, 15; (*e*) M. S. Kharasch, H. C. McBay, and W. H. Urry, *J. Amer. Chem. Soc.*, 1948, **70**, 1269.

[2] (*a*) J. H. Raley, F. F. Rust, and W. E. Vaughan, *J. Amer. Chem. Soc.*, 1948, **70**, 88; (*b*) F. F. Rust, F. H. Seubold, and W. E. Vaughan, *J. Amer. Chem. Soc.*, 1948, **70**, 95.

[3] E. H. Farmer and C. G. Moore, *J. Chem. Soc.*, 1951, 131.

[4] R. L. Huang and K. T. Lee, *J. Chem. Soc.*, (*a*) 1954, 2570; (*b*) 1955, 4229; (*c*) R. L. Huang and S. S. Si-Hoe in 'Vistas in Free-Radical Chemistry,' ed. W. A. Waters, Pergamon Press, London, 1959, p. 242; (*d*) R. L. Huang and H. H. Lee, *J. Chem. Soc.*, 1964, 2500.

features and may be roughly but conveniently classified into three groups according to the amount of expected dimer isolated. In the first place, appreciable yields of dimer were obtained with the *p*-halogeno-substituted cumenes, *p*-bromoethylbenzene, benzyl cyanide, *p*-chlorobenzyl cyanide, and benzylidene dichloride. It is clear from the nature of the dimeric products that dehydrogenation occurs at the side chain α-carbon atom, giving stabilised benzyl-type radicals which react further by coupling with each other. In all these cases, dimerisation was a major reaction and appeared to be facilitated by the presence of electronegative substituents in the *p*-position in the aromatic ring and/or at the α-carbon atom in the side chain. This is in harmony with Ingold's theory [5] and accords well with recent u.v. measurements on substituted benzyl radicals [6] and with some pyrolytic studies on bond strengths in substituted benzyl bromides,[7] which show that nitro-, cyano-, bromo-, and chloro-substituents in the *p*-position increase the resonance stabilisation of benzyl radicals. The cyano-group in particular, when substituted at the α-carbon atom, may be expected to enhance radical stability through resonance with the benzyl-type free-radical framework.

Summary of results

Substrate	t-Butyl peroxide g.	t-Butyl peroxide moles	Time hr.	Temp.	Yield of dimer g.	Yield of dimer moles
p-Fluorocumene	100·0	0·72	62·8	0·43	72	135—140°	15·0	0·055
p-Chlorocumene	75·0	0·48	43·2	0·29	48	138—143	11·0	0·036
p-Bromocumene	99·5	0·50	36·5	0·25	72	138—143	20·0	0·05
p-Chlorobenzyl cyanide	152·0	1·00	73·0	0·50	48	138—143	40·0	0·13
p-Bromoethylbenzene	185·0	1·00	58·4	0·40	72	120—125	20·0	0·054
Benzyl cyanide [a]	113·0	0·96	87·0	0·60	48	125—130	35·0	0·15
Benzylidene dichloride [a]	161·2	1·00	73·6	0·50	72	125—130	35·0	0·11
α-Chloroethylbenzene	140·5	1·00	73·0	0·50	48	130—135	5·0	0·018
Benzyl chloride [a]	127·0	1·00	73·0	0·50	48	140—145	9·2	0·036
p-Chlorobenzyl chloride	128·8	0·80	43·8	0·40	48	130—135	12·5	0·04
Diphenylchloromethane [b]	61·5	0·30	21·9	0·15	48	120—125		
p-Tolunitrile	70·0	0·60	10·0	0·07	30	125—130	3·0	0·013
α-Bromoethylbenzene	185·0	1·00	73·0	0·50	48	135—140		
α-Bromophenylacetonitrile	49·0	0·25	17·5	0·12	62	115—120		
Benzyl bromide	135·5	0·79	68·7	0·47	48	135—140	1·5	0·004
p-Bromobenzyl bromide	150·0	0·60	43·8	0·30	48	130—135		
Diphenylbromomethane	147·6	0·58	29·2	0·20	48	125—130		

[a] During the course of this work, it was found that these compounds had previously been studied in a similar way (K. Schwetlick, J. Jentzsch, R. Karl, and D. Wolter, *J. prakt. Chem.*, 1964, **25**, 1, 95). [b] The yield of dimer is not included in this Table as a mixture of products was obtained which could not be purified easily.

Of the five compounds placed in the second group (moderate to low yields), α-chloroethylbenzene gave the expected dimer in modest yield, but attempts to separate the *meso* and racemic modifications of the dimeric product proved unsuccessful, as the solubilities of the two forms were approximately the same in all the common solvents tested.

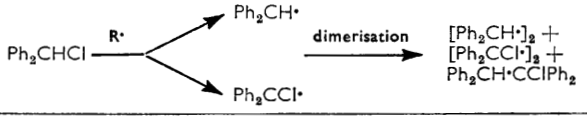
Similarly, benzyl and *p*-chlorobenzyl chloride gave the expected dimeric products in comparatively poor yields mainly as the *meso*-isomer, although the racemic form might have been expected from statistical considerations to be produced in a 1 : 1 ratio. The preferential formation of one stereoisomer by free-radical dimerisation has previously been noted in the reactions with dimethyl succinate,[1b] *p*-methoxyphenylacetic acid,[4b] and ethyl β-phenylpropionate,[8] and is explicable in terms of the difference in free energies of the diastereoisomers concerned. Eliel [9] has advanced the theory that provided the interactions between substituent groups of different sizes in a polysubstituted ethane molecule are purely steric in origin, *meso*-forms are generally more stable than (±)-pairs. Thus in the stilbene dichlorides discussed above, the gauche interactions in the *meso*-form in its most stable, *i.e.*, *anti*, conformation are 2 Ar–Cl + 2 Ar–H + 2 H–Cl whereas in the most favoured staggered conformation for the diastereoisomer, they are 2 Ar–Cl + 2 Ar–H + H–H + Cl–Cl. Assuming the validity of the general principle that the crossed terms describing steric repulsions are smaller than the sum of the like terms, *i.e.*, 2 H–Cl < (H–H + Cl–Cl), the *meso*-form may therefore be predicted to be more stable than the (±). Our results for the benzyl chlorides appear to substantiate this prediction as does the fact that our experiments with benzyl cyanide and *p*-chlorobenzyl cyanide yielded 1,2-dicyano-1,2-diphenylethane and 1,2-dicyano-1,2-di-*p*-chlorophenylethane in the ratios [*meso* to (±)] 97 : 3 and 98 : 2, respectively.

Johnston and Williams [10] showed that the reaction between t-butyl peroxide and *p*-chloro-, *p*-bromo-, and *p*-iodo-toluene proceeded smoothly at 110° with low yields of dimer but with minimum contamination by

[5] C. K. Ingold, *Trans. Faraday Soc.*, 1934, **30**, 52.
[6] J. E. Hodgkins and E. D. Megarity, *J. Amer. Chem. Soc.*, 1965, **87**, 5322.
[7] (*a*) M. Szwarc, *J. Chem. Phys.*, 1948, **16**, 128; (*b*) M. Szwarc and J. S. Roberts, *J. Chem. Phys.*, 1948, **16**, 609; (*c*) C. H. Leigh, A. H. Sehon, and M. Szwarc, *Proc. Roy. Soc.*, 1951, **209***A*, 97.
[8] R. L. Huang and S. Singh, *J. Chem. Soc.*, 1958, 891.
[9] E. L. Eliel, 'Stereochemistry of Carbon Compounds,' McGraw-Hill, New York, 1962, p. 138.
[10] K. M. Johnston and G. H. Williams, *J. Chem. Soc.*, 1960, 1168.

trimers and higher polymeric material if the molar peroxide : substrate ratio was kept low. The reaction with *p*-tolunitrile reported in this work, carried out under similar conditions, gave a reasonably pure dimeric product.

In contrast to the reactions discussed so far, diphenylchloromethane gave somewhat unexpected results. The variable melting point of the first crop of solid product isolated from the reaction mixture indicated, after repeated recrystallisations, that it still contained more than one chemical species and that, moreover, these could not be separated by simple recrystallisation. A small portion was then subjected to column chromatography which yielded a first fraction with m. p. 172—179°, a last fraction with m. p. 204—209°, and several intermediate fractions whose melting points steadily increased in the range between. Since 1,1,2,2-tetraphenylethane (m. p. 210—211°) was suspected to be a possible by-product in addition to the expected dimer, 1,2-dichloro-1,1,2,2-tetraphenylethane (m. p. 182—183°), the i.r. spectra of authentic samples of these two substances, including a mixed sample, were taken. The spectra obtained as mulls in Nujol showed in the range 800—690 cm.$^{-1}$ strong bands at 700 and 753 cm.$^{-1}$, clearly arising from the aromatic C–H out-of-plane deformation vibrations; and a medium band at 730 cm.$^{-1}$ due to the C–Cl stretching vibration (absent in tetraphenylethane). In carbon tetrachloride as solvent, apart from several strong bands characteristic of phenyl ring absorption common to both compounds, additional weak bands were observed in the case of tetraphenylethane at 2900 and 1370 cm.$^{-1}$ attributable to the aliphatic C–H stretching and deformation vibrations, respectively. On comparison, the spectra of the chromatographed fractions showed all the characteristic bands found in dichlorotetraphenylethane and tetraphenylethane (though in diminished intensity for the weak bands) and a few additional bands that could conceivably arise from the presence of a third substance, namely $Ph_2CH{\cdot}CClPh_2$. Such a compound would exhibit vibrational bands forbidden by the selection rules in the symmetrical compounds and still show the characteristic C–Cl and aliphatic C–H vibrational bands. Moreover, its presence in appreciable amounts would aggravate the difficulties of separating the two components dichlorotetraphenylethane and tetraphenylethane of similar solubility and also be largely responsible for the depression of melting point observed in the first and last chromatographed fractions. The available chemical and physical evidence indicates therefore that dichlorotetraphenyl-, tetraphenyl-, and probably also chlorotetraphenyl-ethane are present as major solid products and must have been formed by the following sequence of reactions:



[11] M. S. Kharasch, E. V. Jensen, and W. H. Urry, *J. Amer. Chem. Soc.*, 1947, **69**, 1100.

The production of $Ph_2CH{\cdot}$ radicals can readily be explained by postulating that the chlorine atom of the substrate is attacked by the methyl radicals derived from disproportionation of the t-butyloxy-radical. That methyl radicals are capable of abstracting chlorine atoms has previously been demonstrated [11] in the acetyl peroxide-initiated additions of carbon tetrachloride to olefins in which $Me{\cdot}$ attacks CCl_4 initially to give $CCl_3{\cdot}$, which then triggers off a series of reactions. It has also been shown [11] that although chlorine abstraction occurs with carbon tetrachloride, hydrogen is removed when chloroform is used. In the present case, the presence of two phenyl groups appears to increase the susceptibility of the chlorine atom to attack by methyl radicals. The foregoing conclusions are further substantiated by the isolation from the mother-liquor of further amounts of a pure crystalline polymer which elemental analysis suggests to be 1-chloro-1,1,2,2,3,3,4,4-octaphenylbutane. This compound, containing only one chlorine atom, could only have been formed as a result of further attack by the primary radicals on the dimeric products if chlorine abstraction had occurred at some stage in the reaction.

The third group of reactants consists of bromine-substituted compounds, all of which gave anomalous results. Although some stilbene dibromide was isolated from the reaction with benzyl bromide, a second component, possibly stilbene, containing a phenyl conjugated double bond as shown by i.r. spectroscopy, was detected. Evolution of hydrogen bromide was also observed, due possibly to the following process:

$$PhCHBr{\cdot}CHBrPh \xrightarrow{t\text{-}BuO\cdot} PhCHBr{\cdot}CBrPh \longrightarrow PhCH{:}CBrPh + Br{\cdot}$$

whence $Br{\cdot}$ abstracts H from another molecule of the toluene derivative to give hydrogen bromide.

Extensive decomposition occurred in the reactions with the other bromine-bearing compounds giving intractable tarry reaction mixtures. Only in the case of α-bromophenylacetonitrile was a solid isolated from the reaction mixture which later proved to be ammonium bromide. The presence of this compound can be explained by assuming that cleavage of the C–Br, C≡N, and C–H bonds in the parent compound occurred, although the details of the possible mechanism are not obvious. Since bromine atoms are known to be more labile than either chlorine or hydrogen atoms attached to carbon, the smaller energy of dissociation involved in homolytic scissions of the C–Br bond in comparison with C–Cl and C–H bonds may have some bearing on these cases. Steric effects may also be important.

EXPERIMENTAL

With the exception of α-bromophenylacetonitrile, all the substrates used were purified commercial samples. α-Bromophenylacetonitrile was prepared according to Robb and Schultz's method; [12] 1,2-dichloro-1,1,2,2-tetraphenyl-

[12] C. M. Robb and E. M. Schultz, *Org. Synth.*, Coll. Vol. III, 1955, p. 347.

ethane and 1,1,2,2-tetraphenylethane as described by Johnson *et al.*[13] and Johnston and Williams, [10] respectively. When diastereoisomers exist, the less soluble, higher melting isomer is tentatively assigned the *meso*, and the more soluble, lower melting isomer, the racemic (±) configuration. Infrared spectra were obtained with a Perkin-Elmer model 137 instrument.

Reactions with t-Butyl Peroxide.—General procedure. The substrate and the t-butyl peroxide were heated for a given length of time in an atmosphere of dry nitrogen at temperatures between 115 and 145°. The experimental conditions together with other details are summarised in the Table. Any solid which separated on cooling was filtered off. Volatile products (t-butanol, acetone, unchanged peroxide, and unchanged substrate) were then removed under reduced pressure and the residue worked up by standard methods.

p-*Fluorocumene*. The commercial product (100·0 g.) gave on reaction with t-butyl peroxide (62·8 g.) a yellow solution which, after removal of volatile products, deposited yellowish-white crystals (15·0 g.) on cooling and some resinous material (18·0 g.). Recrystallisation from ethanol gave 2,3-*dimethyl*-2,3-*di*-p-*fluorophenylbutane* as colourless prisms, m. p. 124·5—125° (Found: C, 79·2; H, 7·6; F, 14·6. $C_{18}H_{20}F_2$ requires C, 78·85; H, 7·3; F, 13·9%).

p-*Chlorocumene*. p-Chlorocumene (75·0 g.) and the peroxide (43·2 g.) reacted to give a yellow solution from which a yellowish white solid (7·0 g.) separated on standing. A further crop (4·0 g.) was obtained after volatile by-products, unchanged peroxide, and excess substrate were removed by distillation. Recrystallisation from ethanol gave 2,3-dimethyl-2,3-di-*p*-chlorophenylbutane in the form of colourless needles, m. p. 170—171° (lit.,[14] 171°) (Found: C, 70·5; H, 6·6; Cl, 23·3. Calc. for $C_{18}H_{20}Cl_2$: C, 70·35; H, 6·5; Cl, 23·1%). A high-boiling residue (22·0 g.) was also formed.

p-*Bromocumene*. *p*-Bromocumene (99·5 g.) gave on reaction with the peroxide (36·5 g.) a pale yellow solution from which a white solid (18·5 g.) separated. A further 1·5 g. of a pale yellowish white solid contaminated with a dirty yellow-green polymeric substance were recovered on working up the solution. The white solid, identified as 2,3-*dimethyl*-2,3-*di*-p-*bromophenylbutane*, was recrystallised as colourless plates from ethanol, m. p. 174—174·5° (Found: C, 54·85; H, 5·2; Br, 40·2. $C_{18}H_{20}Br_2$ requires C, 54·5; H, 5·05; Br, 40·45%). Some high-boiling material (20·0 g.) was also formed.

p-*Bromoethylbenzene*. *p*-Bromoethylbenzene (185·0 g.) gave on reaction with peroxide (58·4 g.) a yellow solution. After removal of low-boiling products in the usual way, a pale yellowish-white solid (19·0 g.) was obtained leaving behind a dirty green filtrate. The solid on recrystallisation from ethanol consisted almost entirely of *meso*-2,3-di-*p*-bromophenylbutane, colourless needles, m. p. 160—161° (lit.,[15] 160—161°) (Found: C, 52·25; H, 4·4; Br, 43·05. Calc. for $C_{16}H_{16}Br_2$: C, 52·15; H, 4·35; Br, 43·5%).

On further working up, the filtrate yielded a viscous yellow-brown residue (12·0 g.). Some needles (*meso*-form) were obtained from this on extraction with boiling ethanol, together with a yellow oil which was fractionated (bulb distillation *in vacuo*) to give some low-boiling fractions and a high-boiling light yellow oil, b. p. 158—165°/0·02 mm. (lit.,[15] 166—171/0·3 mm.). On chilling this yellow oil, white crystals were obtained. Recrystallisation from ethanol gave colourless needles, m. p. 63—66°, identified as the racemic 2,3-di-*p*-bromophenylbutane, hitherto unreported as a solid (Found: C, 52·4; H, 4·55; Br, 42·6. Calc. for $C_{16}H_{16}Br_2$: C, 52·15; H, 4·35; Br, 43·5%).

Benzyl cyanide. Benzyl cyanide (113·0 g.) gave on reaction with the peroxide (87·0 g.) a white flaky solid (30·0 g.) which was filtered off. Stepwise distillation of the mother-liquor gave two further crops of solid product, 5·0 g. of a white solid and 2·0 g. of a buff coloured solid [mainly (±)-1,2-dicyano-1,2-diphenylethane] and finally 12·0 g. of a resinous material. From the white solids, the less soluble *meso*-1,2-dicyano-1,2-diphenylethane (30·0 g.) was obtained with methanol, and recrystallised from ethanol, m. p. 239—240° (lit.,[16] 239—240°). The more soluble racemic form was isolated by fractional crystallisation from methanol or by chromatographing on activated alumina using benzene as eluent, to give colourless plates (1·0 g.), (from methanol), m. p. 160° (lit.,[16] 160°).

p-*Chlorobenzyl cyanide*. On cooling the reaction mixture obtained by heating p-chlorobenzyl cyanide (152·0 g.) and the peroxide (73·0 g.), an orange solid (40·0 g.) separated, and was filtered off. Recrystallisation from ethanol gave *meso*-1,2-dicyano-1,2-di-*p*-chlorophenylethane, as colourless needles, m. p. 234—235° (lit.,[17] 234—236°) (Found: C, 63·8; H, 3·4; Cl, 23·9; N, 8·9. Calc. for $C_{16}H_{10}Cl_2N_2$: C, 63·75; H, 3·3; Cl, 23·6; N, 9·3%). The mother-liquor was distilled to remove volatile products and unchanged substrate, giving a semi-solid viscous crimson-red mixture. On filtration and recrystallisation from ethanol, the racemic 1,2-dicyano-1,2-di-*p*-chlorophenylethane (1·0 g.) was obtained, m. p. 191·5—192° (Found: C, 64·15; H, 3·1; Cl, 23·35; N, 9·3). A high-boiling residue (*ca.* 12 g.) was also formed.

Benzylidene dichloride. 1,1,2,2-Tetrachloro-1,2-diphenylethane (35 g.), m. p. 162—162·5° (from ethanol) (lit.,[13] 161—162°) was obtained from benzylidene dichloride (161·2 g.), and peroxide (73·6 g.). No other solid product was isolated apart from 30·0 g. of high-boiling residue.

Benzyl chloride. The reaction mixture from benzyl chloride (127·0 g.) and peroxide (73·0 g.) gave of stilbene dichloride (9·2 g.) mainly in the *meso*-modification, m. p. 191—192° (lit.,[18] 193—194°), with traces of the racemic form, m. p. 93—94° (lit.,[18] 92—94°). Substantial amounts of resinous material were also formed (*ca.* 23·0 g.).

p-*Chlorobenzyl chloride*. Similarly, *p*-chlorobenzyl chloride (128·8 g.) and the peroxide (43·8 g.) gave the *p*-substituted stilbene dichloride (12·5 g.) as the *meso*-isomer, m. p. 221—221·5° (from acetic acid) (lit.,[19] 227—228°) (Found: C, 52·9; H, 3·3; Cl, 44·5. Calc. for $C_{14}H_{10}Cl_4$: C, 52·5; H, 3·1; Cl, 44·4%). Distillation of volatile by-products left a resinous residue (30·0 g.).

α-*Chloroethylbenzene*. After removal of volatile fractions, the reaction mixture from this substance (140·5 g.) and the peroxide (73·0 g.) deposited an orange yellow solid (5·0 g.) and finally a viscous brownish tarry substance. The solid

[13] L. V. Johnson, F. Smith, M. Stacey, and J. C. Tatlow, *J. Chem. Soc.*, 1952, 4710.
[14] K. Ziegler, W. Deparade, and H. Kühlhorn, *Annalen*, 1950, **567**, 151.
[15] H. J. Barber, R. Slack, and A. M. Woolman, *J. Chem. Soc.*, 1943, 99.
[16] L. Chalanay and E. Knoevenagel, *Ber.*, 1892, **25**, 289.
[17] R. B. Davis, *J. Amer. Chem. Soc.*, 1958, **80**, 1752.
[18] S. Winstein and D. Seymour, *J. Amer. Chem. Soc.*, 1946, **68**, 119.
[19] E. E. Fleck, *J. Org. Chem.*, 1947, **12**, 708.

on repeated recrystallisation from methanol and ethanol gave diamond shaped plates, m. p. 160—170° (mixture of *meso* and racemic modifications, not separable by solvents) (lit.,[20] 160—170°) (Found: C, 68·9; H, 5·95; Cl, 24·9; Calc. for $C_{16}H_{16}Cl_2$: C, 68·8; H, 5·75; Cl, 25·45%).

The tarry substance (20·0 g.) was adsorbed on alumina and eluted with light petroleum (b. p. 56—70°) from which a colourless solid, m. p. 160—170°, was extracted.

p-*Tolunitrile*. The product from *p*-tolunitrile (70·0 g.) and the peroxide (10·0 g.) was 1,2-di-*p*-cyanophenylethane, m. p. 201—202° (from benzene–ethanol) (lit.,[21] 198°) (Found: C, 82·4; H, 5·4; N, 11·9. Calc. for $C_{16}H_{12}N_2$: C, 82·75; H, 5·15; N, 12·05%). Some high-boiling polymeric material was also formed (8·0 g.).

Diphenylchloromethane. Diphenylchloromethane (61·5 g.) and the peroxide (21·9 g.) were heated for 48 hr. at 120—125° under nitrogen. On cooling, the solid which separated was filtered off and recrystallised from ethanol (10·0 g.). However, in spite of repeated recrystallisation, the m. p. of this product remained consistently about 10—20° higher than the expected melting point (182—183°) of 1,2-dichloro-1,1,2,2-tetraphenylethane. A small portion (0·98 g.) was then adsorbed on alumina and eluted with light petroleum–benzene (9 : 1) giving the following fractions: (*a*) m. p. 172—179°, (0·055 g.); (*b*) m. p. 180—186°, (0·051 g.); (*c*) m. p. 182—192°, (0·18 g.); (*d*) m. p. 188—200° (0·16 g.); (*e*) m. p. 197—207° (0·10 g.); (*f*) m. p. 204—213° (0·05 g.); (*g*) m. p. 208—214° (0·04 g.); (*h*) m. p. 205—213° (0·02 g.); (*i*) m. p. 204—209° (0·008 g.). The i.r. spectra of these fractions were recorded and compared with those of pure samples of 1,2-dichloro-1,1,2,2-tetraphenylethane and 1,1,2,2-tetraphenylethane as described. On prolonged standing, the mother-liquor deposited another crop of crystals (*ca.* 5 g.). Purification by adsorption on alumina produced a sample with m. p. 107—108°, probably 1-*chloro*-1,1,2,2,3,3,4,4-*octaphenylbutane* (Found: C, 88·5; H, 6·15; Cl, 6·05%; *M*, 700. $C_{52}H_{41}Cl$ requires C, 89·1; H, 5·85; Cl, 5·05%; *M*, 700). About 10 g. of a resinous material was also formed.

α-*Bromoethylbenzene*. Removal of volatile products from the reaction mixture gave an intractable tarry residue.

α-*Bromophenylacetonitrile*. The reaction afforded a very viscous brownish-black liquid which partially solidified on chilling. On extraction with acetone, a white solid, m. p. > 300°, insoluble in benzene, but soluble in ethanol and water, was obtained (Found: H, 4·05; Br, 79·4; N, 14·9. Calc. for NH_4Br: H, 4·1; Br, 81·6; N, 14·3%). The white solid gave ammonia on heating with sodium hydroxide and a positive test with silver nitrate. The chemical evidence suggests therefore that it is ammonium bromide.

Benzyl bromide. Some of the solid (1·5 g.) obtained from the reaction of benzyl bromide (135·5 g.) and the peroxide (68·7 g.) was chromatographed on alumina with light petroleum as eluent. Traces of a substance melting at 120—122° was isolated in addition to stilbene dibromide. This, together with its i.r. spectrum (conjugated C:C medium bands at 1580 and 1620 $cm.^{-1}$) suggests that it is probably stilbene (lit.,[22] m. p. 124°).

Diphenylbromomethane. Distillation of the reaction mixture under reduced pressure afforded only low boiling products and excess of substrate (b. p. 68—70°/2·0 mm) and a very high boiling intractable tarry residue.

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[20] S. Goldschmidt and B. Acksteiner, *Chem. Ber.*, 1958, **91**, 502.
[21] P. Kattwinkel and R. Wolffenstein, *Ber.*, 1901, **34**, 2423.
[22] R. L. Shriner and A. Berger, *Org. Synth.*, Coll. Vol. III, p. 786.