Some 1 : 1-*Diphenylpropyl and* 9-*Phenyl*-9-*fluorenyl Peroxides.*

By M. Bassey, E. Buncel, and A. G. Davies.

[Reprint Order No. 6229.]

By reactions which involve the intermediate formation of 1 : 1-diphenylpropyl or 9-phenyl-9-fluorenyl carbonium ions, the corresponding alcohols have been converted successively into the alkyl hydroperoxides and dialkyl peroxides. The xanthhydryl or triphenylmethyl derivatives of the hydroperoxides have been prepared, and the carbonium ions which are formed by ionisation of the alcohols or peroxides have been characterised by the formation of 1 : 1-diphenylpropyl and 9-phenyl-9-fluorenyl *p*-tolyl sulphone.

1 : 1-Diphenylpropyl hydroperoxide and di-(9-phenyl-9-fluorenyl) peroxide have been prepared by other workers by homolytic autoxidation reactions. These two alkyl groups powerfully release electrons and it would be expected that such compounds could also be prepared from the corresponding alcohols by reactions involving unimolecular alkyl–oxygen heterolysis (Davies, Foster, and White, *J.*, 1953, 1541; 1954, 2200; Davies, Foster, and Nery, *J.*, 1954, 2204). A study of some 1 : 1-diphenylpropyl and 9-phenyl-9-fluorenyl peroxides by these reactions has now confirmed the structures assigned to them.

1 : 1-Diphenylpropanol reacts with concentrated hydrogen peroxide in the presence of a trace of acid to form 1 : 1-diphenylpropyl hydroperoxide which, in formic acid solution, disproportionates into hydrogen peroxide and bis-1 : 1-diphenylpropyl peroxide. As a derivative diagnostic of the 1 : 1-diphenylpropyl cation, 1 : 1-diphenylpropyl *p*-tolyl sulphone has been obtained by the reaction of the alcohol with sodium toluene-*p*-sulphinate in 90% formic acid. The hydroperoxide has been characterised by its alkylation with triphenylmethanol and with xanthhydrol to form the corresponding unsymmetrical peroxides.

9-Phenylfluoren-9-ol with a m. p. between 107° and 109° has been prepared by a variety of reactions (for references, see Elsevier's " Encyclopaedia of Organic Chemistry," 1946, Vol. XIII, p. 64), but from the reaction between phenylmagnesium bromide and fluorenone Arcus and Coombs (*J.*, 1954, 3977) isolated the alcohol with m. p. 85° and concluded that the compound was dimorphic. By the same method we obtained the alcohol, m. p. 84°; it formed a 1 : 1 compound with dioxan, which at 100°/1 mm. lost dioxan and water forming di-(9-phenyl-9-fluorenyl) ether.

9-Phenylfluoren-9-ol reacts with hydrogen peroxide to form the hydroperoxide which in acetic–sulphuric acid disproportionates, or is alkylated by more of the alcohol, yielding di-(9-phenyl-9-fluorenyl) peroxide, m. p. 193°. Other workers (for references, see *op. cit.*, p. 74) have reported melting points of 193° and 204°. We have confirmed the structure of the peroxide by converting it into 9-phenyl-9-fluorenyl *p*-tolyl sulphone, identical with the product obtained from the similar reaction of 9-phenylfluoren-9-ol. The hydroperoxide has also been characterised by the preparation of 9-phenyl-9-fluorenyl xanthhydryl peroxide.

Experimental

1 : 1-*Diphenylpropanol.*—The Grignard reaction between phenylmagnesium bromide and propiophenone gave crude 1 : 1-diphenylpropanol, m. p. 90—94°, in 75% yield. Several recrystallisations from light petroleum gave the pure alcohol, m. p. 94—95°. Hell and Bauer (*Ber.*, 1903, **37**, 231) and Tolopko and Jurgjenko (*Doklady Akad. Nauk S.S.S.R.*, 1954, **94**, 207) report m. p. 94—95° for the compound obtained from ethylmagnesium iodide and benzophenone, but no yields. We found that this reaction gave only 7—11% of the alcohol, together with a large amount of the olefin, m. p. 47·5°. A solution of the alcohol (1·15 g.) in 90% formic acid (30 c.c.) was kept overnight, then poured on ice, and the solid which separated was recrystallised from light petroleum, yielding 1 : 1-diphenylprop-1-ene (0·85 g.), m. p. 47·5°, undepressed on mixture with the olefin obtained from the above Grignard reaction (Found : C, 92·5; H, 7·4. Calc. for $C_{15}H_{14}$: C, 92·7; H, 7·3%).

1 : 1-*Diphenylpropyl Hydroperoxide.*—A solution of 1 : 1-diphenylpropanol (1·0 g.) in the minimum of ether was shaken for 5 hr. with 90% hydrogen peroxide (5 c.c.) containing concentrated sulphuric acid (0·02 c.c.). The product was diluted with water, and the ethereal layer

separated and washed with aqueous sodium hydrogen carbonate and with water. Removal of the ether gave an oil with a slight phenolic odour. The oil solidified when washed with water, yielding 1 : 1-diphenylpropyl hydroperoxide (1·22 g.), m. p. 79·0—79·5° (from light petroleum) (Found : C, 78·6; H, 7·1. Calc. for $C_{15}H_{16}O_2$: C, 78·9; H, 7·1%). Ziegler and Herte (*Annalen*, 1942, **551**, 206), and Tolopko and Jurgjenko (*loc. cit.*), report m. p. 81—82° and 80° respectively.

Bis-1 : 1-*diphenylpropyl Peroxide.*—1 : 1-Diphenylpropyl hydroperoxide (0·56 g.) was suspended in 90% formic acid (30 c.c.). Next day the precipitate was filtered off and recrystallised twice from light petroleum, yielding *di*-(1 : 1-*diphenylpropyl*) *peroxide* (76 mg.), m. p. 140—140·5° (Found : C, 85·0; H, 7·3. $C_{30}H_{30}O_2$ requires C, 85·0; H, 7·0%).

1 : 1-*Diphenylpropyl Xanthhydryl Peroxide.*—The hydroperoxide (0·53 g.), in chloroform (9 c.c.), was added to xanthhydrol (0·44 g.) in acetic acid (20 c.c.). Next day the solution was poured on ice, yielding 1 : 1-*diphenylpropyl xanthhydryl peroxide*, m. p. 86—87° (from light petroleum) (Found : C, 81·9; H, 5·7. $C_{28}H_{24}O_3$ requires C, 82·3; H, 5·9%).

1 : 1-*Diphenylpropyl Triphenylmethyl Peroxide.*—A mixture of the hydroperoxide (0·47 g.) in chloroform (8 c.c.), and triphenylmethanol (0·62 g.) in acetic acid (10 c.c.) containing sulphuric acid (1·0 c.c.), similarly yielded 1 : 1-*diphenylpropyl triphenylmethyl peroxide* (0·3 g.; from light petroleum), m. p. (rapid heating) 151—160°, (slow heating) 150—152° (Found : C, 86·4; H, 6·4. $C_{34}H_{30}O_2$ requires C, 86·8; H, 6·4%).

1 : 1-*Diphenylpropyl* p-*Tolyl Sulphone.*—A suspension of the alcohol (1·49 g.) in a solution of sodium toluene-p-sulphinate (1·27 g.) in 90% formic acid (30 c.c.) was kept for 1 day, then poured on ice, yielding 1 : 1-*diphenylpropyl* p-*tolyl sulphone*, m. p. 118·5° (Found : C, 75·4; H, 6·5; S, 9·3, 9·4. $C_{22}H_{22}O_2S$ requires C, 75·4; H, 6·3; S, 9·2%). An attempt to prepare the same derivative under similar conditions from the hydroperoxide gave only 1 : 1-diphenylprop-1-ene.

9-*Phenylfluoren*-9-*ol.*—The alcohol was prepared (Ullmann and von Wurstemberger, *Ber.*, 1904, **37**, 73) from phenylmagnesium bromide and fluorenone. The complex formed was decomposed with ammonium chloride, giving the crude alcohol in 80% yield. Recrystallisation from ether–light petroleum gave rhombs, m. p. 75°, which lost solvent and attained constant weight during 30 min. at 120°. The resulting colourless melt solidified on cooling, to yield 9-phenylfluoren-9-ol, m. p. 84° (Found : C, 88·3; H, 5·6. Calc. for $C_{19}H_{14}O$: C, 88·4; H, 5·45%). Recrystallisation from dioxan yielded a complex, m. p. 104°, containing approx. 1 mol. of dioxan of solvation (Found, after some days in air : C, 81·2; H, 6·2. Calc. for $C_{19}H_{14}O,C_4H_8O_2$: C, 79·8; H, 6·4%). An attempt to remove the solvent from a freshly prepared specimen at 100°/0·1 mm. gave a change in weight corresponding to a loss of 1 mol. of dioxan and ½ mol. of water, and yielded di-(9-phenyl-9-fluorenyl) ether, m. p. 235—236° (Found : loss, 28·1. Calc. : loss, 28·0 %). Gomberg (*J. Amer. Chem. Soc.*, 1913, **35**, 200) reports m. p. 232—233° for the ether.

9-*Phenyl*-9-*fluorenyl Hydroperoxide.*—A solution of 9-phenylfluoren-9-ol (2·0 g.) in ether was stirred for 5 hr. with 90% hydrogen peroxide (5 c.c.) containing sulphuric acid (0·10 c.c.). The ethereal layer yielded crude 9-*phenyl*-9-*fluorenyl hydroperoxide* (2·0 g., 94%) which was precipitated from acetic acid by water, then having m. p. 53—55° (Found : C, 83·5; H, 5·7. $C_{19}H_{14}O_2$ requires C, 83·2; H, 5·1%).

Di-(9-*phenyl*-9-*fluorenyl*) *Peroxide.*—(i) *By alkylation of the hydroperoxide with the alcohol.* The alcohol (0·47 g.) in acetic acid containing sulphuric acid (0·10 c.c.) was added to a solution of the hydroperoxide (0·51 g.) in ether. Next day the solid which had separated (0·23 g.) was filtered off and recrystallised from benzene, yielding the solvated peroxide. The benzene was removed during 2 hr. at 100°/1 mm., leaving the pure peroxide, m. p. 193° (decomp.) (Found : C, 88·4; H, 5·45. Calc. for $C_{38}H_{26}O_2$: C, 88·7; H, 5·1%).

(ii) *By dismutation of the hydroperoxide.* A solution of the hydroperoxide in acetic acid containing sulphuric acid, after 10 min. at 50°, was poured over crushed ice, yielding the peroxide, m. p. and mixed m. p. 193° (decomp.). The peroxide was also obtained from a similar reaction in aqueous acetic acid in the absence of added sulphuric acid, but the hydroperoxide was recovered from absolute acetic acid.

9-*Phenyl*-9-*fluorenyl Xanthhydryl Peroxide.*—A solution of the hydroperoxide (0·27 g.) and xanthhydrol (0·17 g.) in acetic acid, after 16 hr., yielded 9-*phenyl*-9-*fluorenyl xanthhydryl peroxide* as prisms (from light petroleum; 0·38 g.), m. p. 123° (Found : C, 84·2; H, 5·0. $C_{32}H_{22}O_3$ requires C, 84·5; H, 4·9%).

9-*Phenyl*-9-*fluorenyl* p-*Tolyl Sulphone.*—(i) *From the alcohol.* Addition of 9-phenylfluoren-9-ol (0·50 g.) in acetic acid (5 c.c.) to sodium toluene-*p*-sulphinate (0·34 g.) in acetic acid (5 c.c.) containing sulphuric acid (0·05 c.c.) gave an immediate precipitate. Next day this solid (0·31 g.) was recrystallised from ethanol, yielding 9-*phenyl*-9-*fluorenyl* p-*tolyl sulphone*, m. p. 208—209° (decomp.) (Found: C, 78·9; H, 5·3; S 7·9. $C_{26}H_{20}O_2S$ requires C, 78·8; H, 5·1; S, 8·1%).

(ii) *From the peroxide.* By a similar procedure di-(9-phenyl-9-fluorenyl) peroxide yielded the same sulphone, m. p. and mixed m. p. 208—209° (decomp.).

Grateful acknowledgment is made to Messrs. Laporte Chemicals Limited for the gift of 90% hydrogen peroxide, and to the Society of Chemical Industry for the award of the John Gray Jubilee Scholarship (to M. B.).

WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES,
UNIVERSITY COLLEGE, LONDON, W.C.1.

[*Received, March 12th*, 1955.]