1035. *Organic Peroxides. Part VI.*[1] *The Decomposition of* p-*Nitrophenyldiphenylmethyl Peroxides.*

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Thermal decomposition of t-butyl *p*-nitrophenyldiphenylmethyl peroxide in *p*-xylene and of bis-(*p*-nitrophenyldiphenylmethyl) peroxide in bromobenzene gives benzophenone, *p*-nitrophenol, *p*-nitrobenzophenone, and phenol. No evidence for the formation of free *p*-nitrophenyldiphenylmethoxy-radicals was obtained.

Kharasch, Poshkus, Fono, and Nudenberg,[2] in a study of the thermal decomposition of t-butyl triarylmethyl peroxides (I) in cumene, concluded that triarylmethoxy-radicals

[1] Part V, Cadogan, Hey, and Sanderson, *J.*, 1961, 3879.
[2] Kharasch, Poshkus, Fono, and Nudenberg, *J. Org. Chem.*, 1951, **16**, 1458.

(II) were first formed and then rearranged, as described by Wieland,[3] to give aryloxydiphenylmethyl radicals (III; Ar = *p*-$CH_3 \cdot C_6H_4$, α-$C_{10}H_7$, *p*-Ph·C_6H_4), which eventually formed the dimer (IV). Subsequent reaction of the latter with α-cumyl radicals is then claimed to give the ether (V).

p-Nitrophenyldiphenylmethyl t-butyl peroxide (I; Ar = *p*-$NO_2 \cdot C_6H_4$) behaved differently and only benzophenone and *p*-nitrophenol were isolated. This anomalous

$ArCPh_2 \cdot O \cdot O \cdot CMe_3$ (I)

$ArCPh_2 \cdot O \cdot$ (II)

$Ph_2\dot{C} \cdot OAr$ (III)

$Ph_2C(OAr) \cdot Ph_2C(OAr)$ (IV)

$Ph_2C(OAr) \cdot Ph \cdot CMe_2$ (V)

$Ar \cdot CPh_2 \cdot O \cdot O \cdot CPh_2 \cdot Ar$ (VI)

reaction has been reinvestigated because a possible mode of decomposition, apparently ignored by Kharasch and his co-workers,[2] could involve the *p*-nitrophenyldiphenylmethoxy-radical, which in turn could give benzophenone and a *p*-nitrophenyl radical, and/or *p*-nitrobenzophenone and a phenyl radical.

In theory *p*-nitrophenyldiphenylmethyl t-butyl peroxide (I; Ar = *p*-$NO_2 \cdot C_6H_4$) on decomposition can produce two different alkoxy-radicals. In an attempt to overcome this complication the hitherto unknown bis-(*p*-nitrophenyldiphenylmethyl) peroxide

$$(VI) \rightarrow Ph_2CO + ArO \cdot CPh_2Ar \quad (VII)$$
$$(VI) \rightarrow ArCOPh + PhO \cdot CPh_2Ar \quad (VIII)$$

(VI; Ar = *p*-$NO_2 \cdot C_6H_4$), which on decomposition might be expected to produce two *p*-nitrophenyldiphenylmethoxy-radicals, has been prepared and allowed to decompose in bromobenzene at 115°. No free-radical arylation of the solvent was detected but *p*-nitrophenol (0·32 mole/mole of peroxide), benzophenone (0·35), phenol (0·04), and *p*-nitrobenzophenone (0·02), were isolated. The correspondence between the yields of phenol and ketone implies that their formation by rearrangement of a single *p*-nitrophenyldiphenylmethoxy-radical, if indeed it is formed, does not occur, since there is insufficient oxygen in the radical. It appears more likely that these products may be formed by way of the ethers (VII) and (VIII), although no direct evidence on the point is available. The hydrogen needed for phenol and *p*-nitrophenol formation does not arise from the solvent, for this would have given rise to dibromobiphenyls. No product derived from a Wieland rearrangement was detected.

In view of these results the decomposition of t-butyl *p*-nitrophenyldiphenylmethyl peroxide (I; Ar = *p*-$NO_2 \cdot C_6H_4$), was reinvestigated. *p*-Xylene, rather than cumene, was used as the solvent because the formation of aryl radicals is more easily detected in this case, there being only one product of substitution. Again, no arylation occurred and *p*-nitrophenol (0·59 moles/mole peroxide), benzophenone (0·44), phenol (0·13), and *p*-nitrobenzophenone (0·12) were formed. Kharasch *et al.*[2] did not report the formation of phenol and *p*-nitrobenzophenone. On the other hand, Bartlett and Cotman[4] reported that thermal decomposition of the related *p*-nitrophenyldiphenylmethyl hydroperoxide gave *p*-nitrophenol, phenol, and *p*-nitrophenyldiphenylmethanol but no benzophenone, and concluded that radicals were intermediates in the reaction. We have no evidence in favour of a homolytic mechanism for the decomposition of the peroxides described in this paper.

Experimental

Preparation of Compounds.—*p*-Nitrobenzophenone, m. p. 137—139°, prepared by Schroeter's method,[5] was converted into *p*-nitrophenylphenyldichloromethane, yellow crystals, m. p.

[3] Wieland, *Ber.*, 1911, **44**, 2550.
[4] Bartlett and Cotman, *J. Amer. Chem. Soc.*, 1950, **72**, 3095.
[5] Schroeter, *Ber.*, 1909, **42**, 3356.

55—57°, from light petroleum (b. p. 40—60°), as described by Baeyer and Villiger,[6] who reported m. p. 56—57°. Treatment of the dichloride with benzene and aluminium chloride and subsequent recrystallisation of the product from light petroleum (b. p. 100—120°) gave *p*-nitrophenyldiphenylmethyl chloride, m. p. 90—93°. Baeyer and Villiger [6] reported m. p. 92—93°. The following method of conversion of the above chloride into the corresponding carbinol was found to be more convenient than those of Baeyer and Villiger [6] and of Bartlett and Cotman.[4] The crude chloride (80 g.) in ethanol (200 ml.) was boiled under reflux with potassium hydroxide (16·5 g.) in ethanol (100 ml.) for 30 min. Water (200 ml.) was added to the cooled solution to precipitate *ethyl* p-*nitrophenyldiphenylmethyl ether*, which crystallised from aqueous methanol as pale yellow crystals (45 g.), m. p. 105—107° (Found: C, 75·8; H, 5·5. $C_{21}H_{19}NO_3$ requires C, 75·7; H, 5·7%). The ether (20 g.) in acetic acid (200 ml.) was treated with perchloric acid (70%; 70 ml.). Water (100 ml.) was added to precipitate *p*-nitrophenyldiphenylmethanol, which on recrystallisation from light petroleum (b. p. 100—120°) had m. p. 98·5—100°. Bartlett and Cotman [4] reported m. p. 97—98°. Bis-(*p*-nitrophenyldiphenylmethyl) peroxide was prepared by stirring the carbinol (8 g.) in ether (30 ml.) with sulphuric acid (*d* 1·8; 0·15 ml.) and hydrogen peroxide (86% w/w; 15 ml.) for 24 hr. Special precautions against explosion were taken.* Water (50 ml.) was added and the mixture was separated and washed with ether. The ether solution was washed with alkali and dried (Na_2SO_4). Evaporation of the solution left crude *p*-nitrophenyldiphenylmethyl hydroperoxide (8·6 g.; 90% hydroperoxide content [7]) as a yellow viscous liquid, which slowly (7 days) solidified. The crude hydroperoxide (4 g.) and *p*-nitrophenyldiphenylmethanol (4 g.) in acetic acid (20 ml.) were treated with sulphuric acid (*d* 1·8; 0·2 ml.) in acetic acid (10 ml.) at 80° for 1 hr. Filtration of the hot mixture and recrystallisation of the residue from chloroform–ethanol gave *bis-*(p-*nitrophenyldiphenylmethyl*) *peroxide* (1·7 g.), m. p. 182° (decomp.) (Found: C, 74·4; H, 4·7; N, 4·6. $C_{38}H_{28}N_2O_6$ requires C, 75·0; H, 4·6; N, 4·6%). The acetic acid filtrate deposited *p*-nitrobenzophenone (1·7 g.), m. p. and mixed m. p. 136—137°.

p-Nitrophenyldiphenylmethyl t-butyl peroxide crystallised as yellow needles, m. p. 123—124°, from chloroform–ethanol. Kharasch *et al.*[2] reported m. p. 119°.

Decomposition of Bis-(p-*nitrophenyldiphenylmethyl*) *Peroxide in Bromobenzene.*—The peroxide (2·504 g.) in bromobenzene (150 ml.) was kept under nitrogen at 115° for 3 days. After removal of the solvent the residue was distilled (0·1 mm.) to give the following fractions: (*a*) a colourless oil (0·015 g.; b. p. <100°), (*b*) a pale yellow oil (0·456 g.; b. p. 100—120°), and left a residue (*c*) (1·972 g.; b. p. >180°). The infrared spectrum of fraction (*a*) indicated the presence of benzophenone and phenol only. A portion (0·331 g.) of fraction (*b*) on chromatography on alumina gave benzophenone (0·189 g.), m. p. and mixed m. p. 45—47° and *p*-nitrobenzophenone (0·008 g.), identified by its infrared spectrum. Elution with methanol gave sodium *p*-nitrophenoxide (0·036 g.), identified by its infrared spectrum, formed by interaction of *p*-nitrophenol with alkali present in the alumina. Chromatography of the residue from the distillation, and examination of the spectra of the eluted fractions, indicated the presence of many unidentified products. Only one fraction (elution with benzene) appeared to be homogeneous and gave a yellow solid (0·099 g.), which after recrystallisation from ethanol had m. p. 205—210° (Found: C, 68·2; H, 4·4%). The infrared spectrum indicated the presence of the aryl-alkyl ether linkage (8·05—8·3μ; 9·9μ) and the nitro-group.

Decomposition of p-*Nitrophenyldiphenylmethyl t-Butyl Peroxide in* p-*Xylene.*—The peroxide (4·000 g.) in *p*-xylene was kept under nitrogen at 115° for 3 days. Extraction with 4N-sodium hydroxide gave impure *p*-nitrophenol (0·403 g.), which on recrystallisation from toluene had m. p. and mixed m. p. 112—114°. The infrared spectrum of the impure product showed no evidence of the presence of phenol. After removal of *p*-xylene the residue was distilled at 0·1 mm. to give the following fractions: (*a*) a yellow liquid (0·134 g.; b. p. 42°), (*b*) a mixture of a colourless solid and orange oil (2·754 g.; b. p. 90—212°), and a black residue (0·782 g.; b. p. >250°). Fraction (*a*) was shown to be phenol (benzoate, m. p. and mixed m. p. 69—71°). Fraction (*b*) (1·130 g.) on chromatography on alumina gave only sodium *p*-nitrophenoxide (0·22 g.) and *p*-nitrobenzophenone (0·12 g.), m. p. and mixed m. p. 136—139°, and impure

* It should be noted that mixtures containing organic material and hydrogen peroxide of this strength sometimes result in explosion (see Criegee and Dietrich, *Annalen*, 1948, **560**, 135), although some twenty experiments of the type described above were carried out without incident.

[6] Baeyer and Villiger, *Ber.*, 1904, **37**, 597.
[7] Davies, Foster, and White, *J.*, 1953, 1541.

benzophenone (0·401 g.) as identified products. The presence of benzophenone was confirmed by its conversion into the 2,4-dinitrophenylhydrazone, m. p. and mixed m. p. 236—238°, and by its infrared spectrum. The impurities present in the benzophenone fraction were isolated by fractional crystallisation. With ethanol a trace of a nitro-compound, m. p. 161·5—162·5° (Found: C, 77·5; H, 5·6; N, 4·7%), was obtained, while light petroleum (b. p. 40—60°) gave a colourless crystalline compound, m. p. 50—51°, which depressed the m. p. of benzophenone (Found: C, 87·0; H, 6·5%).

The authors acknowledge the gift of 86% hydrogen peroxide from Messrs. Laporte Chemicals Ltd., Luton. This work was carried out during the tenure (by W. A. S.) of a Peter Spence Fellowship.

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[*Received, June 6th,* 1961.]