255. *Decomposition Reactions of Heterocyclic Diacyl Peroxides. Part IV.*[1] *Nicotinoyl Peroxide.*

By (the late) M. C. Ford and Donald Mackay.

Decomposition of nicotinoyl peroxide generates 3-pyridyl radicals, which attack aromatic solvents to give 3-arylpyridines.

It was expected that nicotinoyl peroxide would provide a contrast with the peroxides previously examined, and would resemble an aroyl peroxide in its decompositions.

The great ease with which nicotinoyl chloride is hydrolysed makes the preparation of the peroxide difficult: Milas and Panagiotakos[2] obtained it, in low yield, by addition of the ethereal acid chloride to aqueous sodium peroxide; a more easily purified product was obtained by treatment of an ethereal mixture of the acid chloride and pyridine, at −70°, with ethereal hydrogen peroxide.

---

* Yields are calculated on the equation: $(R{\cdot}CO_2)_2 + ArH \longrightarrow ArR + CO_2 + R{\cdot}CO_2H$.

[1] Part II, *J.*, 1957, 4620; Part III, preceding paper.

[2] Milas and Panagiotakos, *J. Amer. Chem. Soc.*, 1940, **62**, 1878.

Decomposition of the peroxide in aromatic solvents gave 3-arylpyridines: 3-phenylpyridine (55% *) was formed in benzene, 3-tolylpyridines (36%) in toluene, 3-nitrophenylpyridines (70%) in nitrobenzene, and 3-bromophenylpyridines, in low yield, in bromobenzene. The mixture of nitrophenylpyridines consisted chiefly of the 3-*o*-isomer, along with smaller amounts of the 3-*p*-isomer: both were obtained pure. Oxidative degradation showed that the tolylpyridine mixture likewise contained 3-*o*- and 3-*p*-isomers. The 3-*m*-isomers were almost certainly produced, but in neither case was their presence in the mixture definitely established.

Aryl nicotinates were probably also formed, though in very small amount (cf. Parts II and III), for the crude arylpyridine fractions gave only traces of phenolic material when boiled with acid or alkali. In solvents lacking side-chain hydrogen traces of pyridine were produced, but in toluene a larger amount was formed, and, in addition to the tolylpyridines, dibenzyl was isolated. The proportion of side-chain attack (for which 3-pyridyl radicals were evidently responsible) appeared to be rather high: the mixture of dibenzyl and diaryls obtained by decomposition of benzoyl peroxide in toluene contains 13% by weight of dibenzyl,[3] corresponding to a molar ratio (dibenzyl : diaryls) of 0·14; with nicotinoyl peroxide the molar ratio was *ca.* 0·2.

EXPERIMENTAL

Nicotinoyl Peroxide.—Moisture was rigidly excluded throughout. Dropwise addition of thionyl chloride (108 ml., 3 mol.) to dry sodium nicotinate (73 g.) at room temperature caused an exothermic reaction. The mixture was heated under reflux for 1 hr. at 100°, the excess of thionyl chloride was removed, and the nicotinoyl chloride (64 g., 90%) slowly distilled at *ca.* 10 mm. (free flame) from the sodium chloride. Redistillation under dry nitrogen gave a colourless liquid, b. p. 90°/13 mm. (lit.,[4] 85°/12 mm.).

Pyridine (2·9 ml., 1 mol.) was added to the acid chloride (5 g.) in dry ether (50 ml.); the mixture was set aside for 5 min. and then cooled to −70°: freshly prepared 1·5N-ethereal hydrogen peroxide (dried over $CaSO_4$; 50 ml.) was added dropwise, with stirring, and the mixture then allowed to warm to room temperature and filtered. The filtrate was washed sparingly with 2N-potassium hydrogen carbonate and water, and dried ($MgSO_4$), the ether was removed, and the residue (1·5 g.) washed with light petroleum (b. p. 30—40°). Several preparations were carried out and the product was accumulated and stirred with cold benzene : nicotinic acid was filtered off. Addition of light petroleum to the filtrate first precipitated traces of the acid, and then the peroxide (15—20%), prisms, m. p. 92° (lit.,[2] 88—89°) [Found: equiv. (iodometric in 2N-sulphuric acid), 118. Calc. for $C_{12}H_8O_4N_2$: equiv., 122]; the purity (97%) was increased to 99% by a further recrystallisation (lit.,[2] purity 93—98·5%).

Decomposition in Aromatic Solvents.—The reaction mixtures were worked up as follows. The solvent was removed, through a column, at a suitable pressure (cold-trap) and the appropriate cut was combined with the trap-condensate and the whole extracted with 2N-sulphuric acid; the extract was basified and distilled: pyridine in the distillate was characterised as the picrate and determined as dipyridinecopper(II) thiocyanate. Nicotinic acid crystallised from the concentrate, and was completely removed by treatment of the mother-liquor with ether–light petroleum; recrystallisation gave the pure acid. The residual non-acidic material was treated as described.

Benzene. A solution of the peroxide (8·13 g.) in benzene (813 ml.) was refluxed for 48 hr.: carbon dioxide (1·3 moles per mole of peroxide), pyridine (100 mg.), nicotinic acid (1·4 g.), and an oil (3·74 g.), b. p. <70°/0·01 mm., which was substantially 3-phenylpyridine, were produced. A portion of the oil (0·65 g.) was refluxed with 2N-sodium hydroxide, giving phenol (9 mg.) (*s*-tribromophenol, m. p. 91·5°), recovered (0·63 g.), and treated with a slight excess of methanolic picric acid: recrystallisation of the precipitate from acetone–methanol gave 3-phenylpyridine picrate (1·2 g.), m. p. and mixed m. p. 159—160° (Found: C, 53·2; H, 3·3; N, 14·4. Calc. for $C_{17}H_{12}O_7N_4$: C, 53·1; H, 3·1; N, 14·6%), from which pure 3-phenylpyridine was liberated as a colourless oil, b. p. 98—102°/0·7 mm. The *picrolonate* formed orange-yellow plates, m. p. 208°

---

[3] Hey, Pengilly, and Williams, *J.*, 1956, 1461.

[4] Meyer and Graf, *Ber.*, 1928, **61**, 2205.

(decomp.), from acetone–methanol (Found: C, 59·9; H, 4·1; N, 16·4. $C_{21}H_{17}O_5N_5$ requires C, 60·1; H, 4·1; N, 16·7%).

Nitrobenzene. Decomposition of the peroxide (5·2 g.) in nitrobenzene (520 ml.) at 85—90° for 24 hr. gave carbon dioxide (0·62 mol.), pyridine (20 mg.), nicotinic acid (2·6 g.) and non-acidic material which on trituration with ether furnished 3-*p*-nitrophenylpyridine, obtained as cream-coloured needles (0·47 g.), m. p. 148° (lit.,[5] 148—149°), after recrystallisation (twice) from methanol (Found: C, 66·0; H, 4·2; N, 13·8. Calc. for $C_{11}H_8O_2N_2$: C, 66·0; H, 4·0; N, 14·0%); the picrate crystallised from acetone–methanol as yellow prisms, m. p. 218—219° (decomp.) (lit.,[6] 220°) (Found: N, 16·2. Calc. for $C_{17}H_{11}O_9N_5$: N, 16·3%). The ethereal mother-liquor was evaporated and distilled: removal of traces of the 3-*p*-isomer from the distillate (b. p. 120—140°/0·01 mm.) gave a pale yellow oil (A) (2·5 g.).

Chromatography of the oil A (0·46 g.) on basic alumina from ether–light petroleum (1 : 2) solution gave mainly oily 3-*o*-nitrophenylpyridine (Found: C, 66·0; H, 4·1%); the picrate formed yellow needles, m. p. 182—183° (lit.,[6] 182—183°), after a single recrystallisation from acetone–methanol (Found: N, 16·0%). The oil A (1·6 g.) was recovered almost quantitatively after 2 hr. in refluxing 30% sulphuric acid, only traces of nitrophenols being produced. Quaternisation of the recovered material with methyl sulphate followed by treatment of the product in turn with 2N-sodium hydroxide and boiling aqueous permanganate yielded a mixture of nitrobenzoic acids (0·18 g.): fractional crystallisation from water gave the pure *o*-isomer, m. p. and mixed m. p. 144—145°, after recrystallisation from toluene; no *m*-isomer could be isolated.

Toluene. Decomposition of the peroxide (6·93 g.) in toluene (710 ml.) under nitrogen at 70—75° for 70 hr. gave carbon dioxide (1·0 mol.), pyridine (1·0 g.), nicotinic acid (2·3 g.), and non-acidic material. The latter was separated into a neutral fraction, which was chromatographed on alumina from light petroleum (b. p. 30—40°) solution, giving dibenzyl (0·42 g., 2·3 mmoles), m. p. and mixed m. p. 51—52° (methanol), and a basic fraction (2·3 g.), which was refluxed with 5N-sodium hydroxide (giving 17 mg. of phenolic material), recovered (2·1 g.), and heated with a slight excess of methanolic picric acid: a mixture of 3-tolylpyridine picrates (4·1 g., 10·3 mmoles), m. p. 152—156° (Found: C, 54·1; H, 3·7; N, 13·8. Calc. for $C_{18}H_{14}O_7N_4$: C, 54·3; H, 3·5; N, 14·1%), resulted, from which the mixed 3-tolylpyridines (1·5 g.), b. p. 100—110°/1·0 mm., were liberated. A portion gave a mixture of picrolonates, m. p. 163—165° (decomp.) (Found: N, 16·0. Calc. for $C_{22}H_{19}O_5N_5$: N, 16·2%), which, like that of the picrates, was not amenable to fractional crystallisation. Another portion, on quaternisation (methyl iodide) and oxidation, gave phthalic acid (anhydride, m. p. 128°) and terephthalic acid, subl. >300°; no *iso*phthalic acid could be isolated.

Bromobenzene. Decomposition of the peroxide (2·2 g.) in bromobenzene (220 ml.) at 80—85° for 20 hr. gave a trace of pyridine, nicotinic acid, and an oil, which was refluxed with 30% sulphuric acid (giving 12 mg. of phenolic material), recovered, and treated with methanolic picric acid: a mixture of 3-bromophenylpyridine picrates (0·16 g.), m. p. 174—180°, resulted (Found: C, 43·8; H, 2·6; Br, 17·4. Calc. for $C_{17}H_{11}O_7N_4Br$: C, 44·0; H, 2·4; Br, 17·3%).

An authentic specimen of 3-phenylpyridine picrate was kindly supplied by Professor D. H. Hey, F.R.S. One of us (D. M.) thanks the Carnegie Trust for the Universities of Scotland for a scholarship and the Murdo Macaulay Trust for a grant. Microanalyses are by Miss D. A. Thomson.

THE UNIVERSITY, OLD ABERDEEN.

[*Received, August 9th,* 1957.]

---

[5] Forsyth and Pyman, *J.*, 1926, 2912.

[6] Haworth, Heilbron, and Hey, *J.*, 1940, 349.