

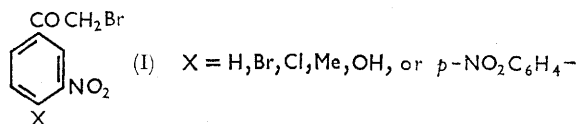
3-Nitro-substituted Phenacyl Bromides

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3-Nitrophenacyl bromides of 4-bromo-, 4-chloro-, 4-methyl-, and 4-hydroxy-acetophenones are obtained in excellent yield by the nitration of the corresponding phenacyl bromides in fuming nitric acid (*d*, 1.42) at 5°. Nitration of 4-phenylphenacyl bromide yields 3-nitro-4-(4-nitrophenyl)phenacyl bromide. The identity of these products has been established by inverse substitution with acidified potassium iodide solution.

BARKENBUS and Clements¹ obtained a mixture of 3-nitro- and 2-(4-)nitro-phenacyl bromides in the ratio of 7 : 3, by the direct nitration of phenacyl bromide with a mixture of nitric and sulphuric acids. We have made several unsuccessful attempts to separate the 3-nitro-phenacyl bromide (I; X = H) from its 2-(4-) nitro-isomer by repeated fractional crystallization.

This paper describes the successful preparation of 3-nitrophenacyl bromide (80%) by the nitration of phenacyl bromide² with fuming nitric acid (*d*, 1.42) at *ca.* 5°. The identity of the product was established by a mixed m.p. with a specimen of authentic material prepared by a different route,³ the identity of the compound was confirmed by treatment with acidified potassium iodide to give 3-nitroacetophenone.⁴ Similarly, 4-bromo-⁵, 4-chloro-⁵, 4-methyl-⁶, and 4-hydroxy-⁷ phenacyl bromides give the corresponding 3-nitro-substituted phenacyl bromides (I).



The nitration of 4-phenylphenacyl bromide⁸ requires some comment. Attempts to prepare 3-nitro-4-phenylphenacyl bromide under similar conditions gives 3-nitro-4-(4-nitrophenyl)phenacyl bromide as the chief product, the identity of which was proved by inverse substitution with acidified potassium iodide solution to give the known 3-nitro-4-(4-nitrophenyl)acetophenone.⁹ This difficulty of nitration in the case of 4-phenylacetophenone was also reported by earlier workers.^{9,10}

EXPERIMENTAL

M.p.'s were determined with a Kofler hot-stage apparatus and are uncorrected.

Nitration of Phenacyl Bromide (I; X = H).—Phenacyl

¹ C. Barkenbus and J. P. Clements, *J. Amer. Chem. Soc.*, 1934, **56**, 1369.

² R. M. Cowper and L. H. Davidson, *Org. Synth.*, 1959, Coll. Vol. II, 480.

³ D. L. Brebner and L. C. King, *J. Amer. Chem. Soc.*, 1953, **75**, 2330.

⁴ B. B. Corson and R. K. Hazen, *Org. Synth.*, 1959, Coll. Vol. II, 434.

⁵ W. Lee Judefind and E. E. Reid, *J. Amer. Chem. Soc.*, 1920, **42**, 1043.

⁶ J. Wegmann and H. Dahn, *Helv. Chim. Acta*, 1946, **29**, 101.

bromide (0.99 g., 0.005 mole) was added portionwise to fuming nitric acid (10 ml.; *d*, 1.42) cooled in an ice-bath; the rate of addition was such that the temperature did not exceed 5°. The reaction mixture was left in the ice-bath for *ca.* 1 hr. and was decomposed upon being poured on crushed ice (100 g.). The product was filtered off and washed with water (200 ml.). Recrystallisation from ethanol gave 3-nitrophenacyl bromide, as a pale yellow crystalline product (0.95 g., 80%), m.p. 94—95°.

The details of the other 3-nitrophenacyl bromides which were prepared are given in the Table.

3-Nitrophenacyl bromides

Phenacyl bromides	Yield (%)	M.p.	Formula	Br Analysis	
				Found (%)	Calc. (%)
3-NO ₂	80	94—95° *	C ₈ H ₇ BrNO ₃	32.6	32.8
3-NO ₂ , 4-Br...	75	94° *	C ₈ H ₆ Br ₂ NO ₃	49.4	49.5
3-NO ₂ , 4-Cl ...	80	84—85° †	C ₈ H ₆ BrClNO ₃	41.3 ‡	41.5 ‡
3-NO ₂ , 4-Me	65	57° †	C ₉ H ₈ BrNO ₃	31.2	31.0
3-NO ₂ , 4-OH	70	98—99° *	C ₈ H ₆ BrNO ₄	30.6	30.8
3-NO ₂ , 4-(<i>p</i> -O ₂ N(C ₆ H ₄))	80	142° *	C ₁₄ H ₉ BrN ₂ O ₅	21.8	21.9

* Undepressed on admixture with an authentic sample (ref. 12).

† Pale yellow. ‡ Colourless. † Br + Cl.

Reaction with Potassium Iodide.—3-Nitrophenacyl bromide (0.5 g., 0.002 mole) was dissolved in alcohol (15 ml.) and to this, aqueous potassium iodide (10%; 5 ml.) and dilute sulphuric acid (10 ml.) were added; the mixture was warmed to 60—70°. The liberated iodine was destroyed with an excess of sodium thiosulphate solution and the product was extracted with ether (3 × 30 ml.). The ether was removed to give 3-nitroacetophenone (0.25 g., 75%) m.p. 76—78°, 2,4-dinitrophenylhydrazone, m.p. and mixed m.p. 232—233°.^{4,11}

Other nitrophenacyl bromides behaved similarly.^{9,10,12}

The authors thank Professor W. U. Malik, Head of the Chemistry Department, for providing research facilities, the U.G.C. for a grant for chemicals, and the C.S.I.R. (New Delhi) for a junior research fellowship (held by P.P.S.).

[8/1019 Received, July 18th, 1968]

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⁸ N. L. Drake and J. Bronitsky, *J. Amer. Chem. Soc.*, 1930, **52**, 3715.

⁹ Ng. Ph. Buu-Hoi and D. Lavit, *Bull. Soc. chim. France*, 1958, 1408.

¹⁰ C. Runti, *Ann. Chim. (Italy)*, 1954, **44**, 489.

¹¹ G. Dana Johnson, *J. Amer. Chem. Soc.*, 1951, **73**, 5888.

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