# Reactions of Substituted Phenacyl Bromides with Various Bases. o- and p-Nitrophenacyl Bromide. I

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The products obtained from the reaction of o- and p-nitrophenacyl bromide with various bases is described.

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In a previous paper [2], we reported the formation of a bis-epoxide from the attack of sodium methoxide on either 4-oxo-2,3-epoxy-2,4-bis-(o-nitrophenyl)-1-bromobutane, (2), or the para isomer 8. Both 1 and 8 were obtained from the reaction of o- or p-nitrophenacyl bromide with sodium methoxide in methanol. We have now looked further at the reactions of the o- and p-nitrophenacyl bromides with different bases. Although a considerable amount of work has been done with reactions of various phenacyl halides [3-11], the product(s) obtained seemingly depend upon the base used as well as the solvent for the reaction media with no apparent correlation.

In this study we have looked at the reactions of o-nitrophenacyl bromide (1) and p-nitrophenacyl bromide (6), with sodium methoxide, potassium hydroxide, potassium carbonate, potassium cyanide and sodium acetate in methanol.

When 1 was treated with either sodium methoxide or potassium carbonate both the keto-epoxide 2 and 1-meth-

oxy-1,2,3,4-diepoxy-1,3-bis(o-nitrophenyl)butane (3) were obtained. When 1 was treated with potassium hydroxide only 2 was obtained. However, when 1 was treated with potassium cyanide 2,3-epoxy-2-(o-nitrophenyl)propanenitrile (4) was the product and when sodium acetate was the base, o-nitrophenacyl acetate (5) was obtained.

For the reactions involving p-nitrophenacyl bromide (6) with sodium methoxide, potassium hydroxide and potassium carbonate only 1-methoxy-1,2,3,4-diepoxy-1,3-bis(p-nitrophenyl)butane (7) was obtained. 4-Oxo-2,3-epoxy-2,4-bis(p-nitrophenyl)-1-bromobutane (8) is the product when 6 was treated with either potassium cyanide or sodium acetate.

#### EXPERIMENTAL

Melting points were determined with a Mel-Temp capillary melting point apparatus previously calibrated. The ir spectra were recorded with a Perkin-Elmer Model 567 spectrophotometer. Chemical shifts are reported in  $\delta$  units. Elemental analyses were performed by Midwest Microlab, Ltd., Indianapolis, Indiana.

# 2,3-Epoxy-2-(o-nitrophenyl)propanenitrile (4).

A solution of potassium cyanide (0.91 g, 13 mmoles) in 40 ml of methanol was added dropwise with stirring to a slurry of o-nitrophenacyl bromide (3.07 g, 13 mmoles) in 50 ml of methanol at ambient temperature. After one hour the orange solution was poured over 400 g of ice and a pale yellow solid was collected by filtration. Recrystallization from benzene afforded 1.33 g (54%) of colorless crystals, mp 101-102°; ir (potassium bromide): 2250 (CN, very weak), 1515 and 1335 (ArNO<sub>2</sub>), 1240 and 850 cm<sup>-1</sup> (epoxy); pmr (deuteriochloroform):  $\delta = 7.2$ -8.2 (m, 4, aromatic H), 3.7 (d, J = 6 cps, 1 epoxy H), 3.1 (d, J = 6 cps, 1 epoxy H). Anal. Calcd. for  $C_0H_6N_2O_3$ : C, 56.80; H, 3.16; N, 14.62. Found: C,

### o-Nitrophenacyl Acetate (5).

56.63; H, 3.34; N, 14.49.

To a stirred solution of 1 (5.0 g, 20.5 mmoles) in 40 ml of methanol was added sodium acetate (1.6 g, 20.5 mmoles) in one portion. After four hours at ambient temperature, the reaction mixture was heated to reflux for four hours, cooled, and poured over crushed ice which on melting yielded a milky white solution with orange oily droplets interspersed throughout.

The solution was extracted  $4 \times 100$  ml portions of ether, the ethereal solutions were combined and dried over anhydrous sodium sulfate. After evaporation of the ether a light yellow oil was obtained. The oil (0.63 g) was combined with about 2.0 g of silica gel to a height of 9 inches. About 10 ml of benzene was added to fix the components to the silica gel and

the pure compound was eluted with ethyl acetate. Evaporation of the solvent afforded 0.44 g of a light yellow oil (44%); ir (potassium bromide): 1755 (ester C=0), 1730 (ketone C=0), 1535 and 1350 (ArNO<sub>2</sub>), 1220 cm<sup>-1</sup> (ester C-O); pmr (deuteriochloroform):  $\delta = 8.4-8.2$  (m, 1 aromatic H), 7.9-7.4 (m, 3 aromatic H), 5.1 (s, 2 methylene H), 2.0 (s, 3 methyl H).

Anal. Calcd. for C<sub>10</sub>H<sub>9</sub>NO<sub>5</sub>: C, 53.81; H, 4.06; N, 6.28. Found: C, 53.53; H, 4.14; N, 6.20.

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## REFERENCES AND NOTES

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