

Nitration of Diethyl Homophthalate

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Nitration of diethyl homophthalate gives diethyl 4-nitrohomophthalate and ethyl 2-carboxy-4-nitrophenylacetate.

D'COSTA and Nadkarny¹ reported that when phthalide was nitrated with potassium nitrate sulfuric acid, nitration took place at the benzylic position. As the phenyl nucleus is deactivated by the presence of the carbonyl group, nitration at the benzylic position is likely. We were interested to investigate the nitration of a system where the aromatic ring is deactivated and an electron withdrawing group is attached to the benzylic position. Such a system is offered by diethyl homophthalate. Our findings on the nitration of diethyl homophthalate are presented in this paper.

Nitration of diethyl homophthalate in conc. sulfuric acid with potassium nitrate at room temperature gave a mixture of a neutral and an acidic material in nearly equal proportions. The neutral matter gave the following signals in NMR spectrum (in CCl₄, TMS internal standard): δ 1.07-1.53 (6H, irregular sextet, 2 CH₃), 4.00-4.50 (6H, multiplet, 2-CO₂CH₂- and ArCH₂), 7.40 (1H, d, J=8 Hz, H_c), 8.17 (1H, d, J=8 and 2Hz, H_b) and 8.80 (1H, d, J=2 Hz, H_a). The low field signal of one (H_a) of the aromatic protons can only be explained if NO₂ group is placed at position 4 in the phenyl nucleus. This proton (H_a) is much deshielded by the reinforced electron withdrawing and diamagnetic anisotropic effects of the nitro and carboxy groups, both being at *ortho* position to this proton. The NMR spectrum of this compound is compatible with the structure (I). This structure (I) of the compound is corroborated by its hydrolysis and degradative

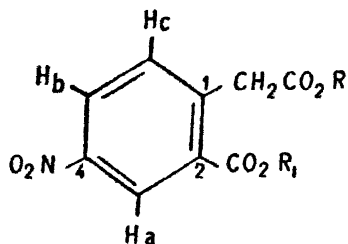
experiments. The nitro ester (I) on acid hydrolysis afforded 4-nitrohomophthalic acid (II) m. p. 221° (lit² m. p. 220°) and the latter on oxidation with alkaline permanganate yielded 4-nitrophthalic acid (m. p. and mixed m.p. 165°).

The acidic material had the equivalent weight corresponding to a mononitrohomophthalic acid ester. The splitting pattern of the aromatic protons in its NMR spectrum suggested it to be an acid ester corresponding to 4-nitrohomophthalic acid (II). It gave signals at δ 1.40 (3H, t, -CO₂CH₂CH₃), 4.12 (2H, s ArCH₂), 4.38 (2H, q, -CO₂CH₂CH₃), 7.35 (1H, d, J=8Hz, H_c), 8.28 (1H, dd, J=8, 2Hz, H_b), 8.77 (1H, s, COOH) and 8.80 (1H, d, J=2Hz, H_a). This acid ester on hydrolysis afforded an acid identical with the acid (II) obtained by hydrolysis of the diester (I). So it is evident that this acid ester is produced by the hydrolysis of the neutral ester (I) during nitration. One of the two structures (III) and (IV) could be assigned to it. Structure (III) is more probable due to the following considerations: (a) In the strongly acidic medium as in conc. sulfuric acid A_{AC}² mechanism for hydrolysis is likely to be operative and it is known that A_{AC}² mechanism is accelerated by electron attracting groups³. In the diester (I) the nitrophenyl group (electron attractor) will facilitate the formation of positively charged C-O at the benzylic position preferentially, hence it is the carboxy group attached to the benzene ring that undergoes hydrolysis first. (b) Phenylacetic acid gives the signal of the acidic proton at δ 11.95⁴. Had the acid ester the structure (IV), the chemical shift of the acidic proton would be more than that (8.77) observed.

An authentic sample of the acid ester (III) was prepared starting from 4-nitrohomophthalic acid (II). The diacid (II) was converted to its anhydride and the latter on refluxing with dry ethanol gave the acid ester (III). The acid ester obtained by nitration of diethyl homophthalate was found to be identical with this authentic sample of ethyl 2-carboxy-4-nitrophenylacetate (III).

Experimental

Diethyl homophthalate: Homophthalic acid was prepared from indene following a literature procedure⁵. A mixture of homophthalic acid (20 g), superdry ethanol



- I, R = R₁ = C₂H₅
 II, R = R₁ = H
 III, R = C₂H₅, R₁ = H
 IV, R = H, R₁ = C₂H₅

(40 ml) and dry benzene (60 ml) was refluxed in a 250 ml Dean Stark apparatus. After usual work up *diethyl homophthalate* (19 g) b. p. $160^{\circ}/5$ mm was obtained.

Nitration of diethyl homophthalate: Diethyl homophthalate (7 g) was dissolved in well cooled conc. sulfuric acid (20 ml). The solution was stirred magnetically and potassium nitrate (12 g) was added in portions to it at room temp. After 2 hr. the reaction mixture was poured over ice and the organic matter extracted with ether. The ethereal extract was thoroughly washed with a saturated solution of sodium bicarbonate.

The ethereal extract was dried (Na_2SO_4), solvent removed and the residue distilled to afford *diethyl 4-nitrohomophthalate* (I, 4 g) b.p. $200^{\circ}/5$ mm.

The combined washings that assumed red coloration were acidified with conc. hydrochloric acid when solid separated out. It was filtered and recrystallised from chloroform; greyish crystals of *ethyl 2-carboxy-4-nitrophenylacetate* (III, 3 g) m. p. $140-41^{\circ}$ were obtained.

4-Nitrohomophthalic acid (II): The diester (I, 1.2 g) was hydrolysed by refluxing it with 40% sulfuric acid (10 ml) for 16 hrs. *4-Nitrohomophthalic acid* (II, 1.0 g), m. p. 221° (CHCl_3) was obtained. The same acid was also obtained by hydrolysis of the acid ester (III).

4-Nitrophthalic acid: A mixture of 4-nitrohomophthalic acid (II, 0.5 g), potassium permanganate (1.5 g) and potassium hydroxide solution (10 ml, 30%) was refluxed for 12 hr. Then it was filtered and the filtrate on acidification yielded *4-nitrophthalic acid* (0.1 g), m. p. 165° (water). An authentic sample of *4-nitrophthalic acid* was prepared by nitrating phthalic anhydride⁶.

Ethyl 2-carboxy-4-nitrophenylacetate (III): 4-Nitrohomophthalic acid (II, 0.7 g) was refluxed with acetic anhydride for 4 hrs. The resulting crude anhydride m.p. 151° without further purification was refluxed with dry ethanol (10 ml) for 3 hr. The solution was concentrated and cooled. *Ethyl 2-carboxy-4-nitrophenylacetate* (0.4 g) m. p. 140° (CHCl_3) could be collected.

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