[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ANTIOCH COLLEGE]

THE NITRATION OF BENZHYDROL AND DIPHENYLBROMOMETHANE

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The literature appears to contain no reference to the nitration of either benzhydrol or diphenylbromomethane. However, the somewhat unexpected results obtained (1) on nitrating diphenylacetic acid, coupled with a desire to explore alternate routes to the preparation of 4,4′-dinitrodiphenylacetic acid, led us to make the present study.

Benzhydrol was nitrated at 30° with an excess of white fuming nitric acid. The crude product melted over a wide range, but on fractional crystallization from ethanol or glacial acetic acid there finally was obtained a small yield of 4,4′-dinitrobenzhydryl nitrate[2] as white needles, m.p. 160.5–162°. The structure of this product was proved by elemental analysis and by oxidation to the known 4,4′-dinitrobenzophenone. Also, an infrared spectrum of the nitration product showed no OH band.

It was hoped that hydrolysis of this nitrate ester under mildly reducing conditions would permit the isolation of 4,4′-dinitrobenzhydrol.[3] However, hydrolysis in aqueous ethanol containing sodium sulfide produced 4,4′-dinitrobenzophenone in 55% yield as the only product isolated.

In a search for other products formed in the nitration of benzhydrol the crude nitrated product from a separate nitration was subjected to a very tedious fractional crystallization from glacial acetic acid, ethanol, dioxane, and benzene in the order named. In this way a small amount of 3,4′-dinitrobenzophenone was obtained. The nature of this unexpected product was suggested first by its infrared spectrum and was confirmed by elemental analysis and mixture m.p. with authentic 3,4′-dinitrobenzophenone. No 4,4′-dinitrobenzhydryl nitrate was isolated from this nitration.

The small amount of the two products obtained from nitrating benzhydrol makes it impossible to state whether either is the main product, particularly since the two products were obtained from separate nitrations. Similarly it seems unwise to postulate a mechanism for the reaction. Nevertheless, it is worth noting that nitration of diphenylacetic acid unexpectedly produced the 3,4′-dinitro derivative as the only product isolated (1).

Diphenylbromomethane, nitrated as in the case of benzhydrol, produced a gummy crude product melting over a wide range. Several crystallizations (less tedious than in the case of nitrated benzhydrol) from acetic acid finally produced

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[1] Kindly refer communications to this author.

[2] Recently it has been reported (2) that nitration of phenyltrichloromethylcarbinol with fuming nitric acid produced (4-nitrophenyl)trichloromethylcarbinol nitrate.

[3] While this work was in progress, the preparation of 4,4′-dinitrobenzhydrol by reduction of the corresponding ketone with aluminum isopropoxide was reported (3).

a low yield of white needles, m.p. 160.3–161.3°, shown to be 4,4′-dinitrobenzhydryl nitrate by the method of mixture m.p. Thus, the reactive bromine atom did not survive the nitration.[4]

The nitration of diphenylacetonitrile also was attempted using the same conditions as above. However, up to the present no crystalline product has been obtained.

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EXPERIMENTAL[5]

Nitration of benzhydrol. (*a*) *4,4′-Dinitrobenzhydryl nitrate.* To 100 ml. of white fuming nitric acid (*sp. gr.* 1.5) held at 28–30° 10 g. (0.054 mole) of benzhydrol (5) was added portionwise during 30 minutes and with stirring. The dark red solution was allowed to stand 5 hours and then was poured into 150 g. of chopped ice. Water was added and the cooled mixture filtered to yield 11.2 g. of crude yellowish product, m.p. *ca.* 80–125°. After four recrystallizations (two with charcoal) from glacial acetic acid there was obtained 1.6 g. (9.4%) of fairly pure 4,4′-dinitrobenzhydryl nitrate, m.p. 156–160°. As the product became purer, proportionately more acetic acid was required for the recrystallization. The analytical sample, m.p. 160.5–162°, was prepared by an additional crystallization from a large volume of ethanol. Another recrystallization from acetic acid did not alter the m.p.

Anal. Calc'd for $C_{13}H_9N_3O_7$: C, 48.91; H, 2.84; N, 13.17.

Found: C, 49.60; 49.40; H, 2.96, 2.79; N, 13.18, 13.21.

A mixture m.p. with authentic 3,3′-dinitrobenzophenone (6) (m.p. 156–157°) showed a large depression. An infrared spectrum of this nitrate ester showed no OH band.

In another preparation performed as before the crude product was washed with small amounts of methanol and recrystallized twice from ethanol (charcoal) and three times from acetic acid.

(*b*) *3,4′-Dinitrobenzophenone.* The crude product from the nitration of 50 g. of benzhydrol was recrystallized four times (twice with charcoal) from acetic acid and twice from large volumes of ethanol to yield 12 g. of fine needles, m.p. 132–155°. Two recrystallizations from 75 and 10 ml., respectively, of boiling dioxane then gave 1.29 g. of solid, m.p. 167–171.5°. A final recrystallization from 60 ml. of boiling benzene afforded 0.79 g. of pure 3,4′-dinitrobenzophenone, m.p. 171.7–173.7°; a mixture m.p. with authentic 3,4′-dinitrobenzophenone (1) showed no depression. Further recrystallization from benzene did not alter the m.p.

The first clue to the identity of this compound came from its infrared spectrum (Nujol mull), which showed bands at 1672 cm.$^{-1}$ (diaryl ketone), 1522 cm.$^{-1}$ (asymmetrical N—O stretching), 1347 cm.$^{-1}$ (symmetrical N—O stretching), 850 cm.$^{-1}$ (C—N stretching), 819 cm.$^{-1}$ (*p*-substitution), and 780 cm.$^{-1}$ (*m*-substitution).

4,4′-Dinitrobenzophenone. (*a*) *From oxidation of 4,4′-dinitrobenzhydryl nitrate.* A solution of 100 mg. (0.313 mmol.) of nitrate ester and 200 mg. (2.0 mmoles) of chromic anhydride in 10 ml. of acetic acid was refluxed for nine hours and then poured into 150 ml. of cold water. Scratching caused the separation of 61 mg. (72%) of white solid, m.p. 192–193°.

(b) *From hydrolysis of 4,4′-dinitrobenzhydryl nitrate.* This hydrolysis was performed in general accordance with Schmidt's directions (7) for hydrolyzing pentaerythritol tetrani-

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[4] During the course of this work bromobis(*p*-nitrophenyl)methane was prepared, apparently for the first time, in 44.8% yield by brominating 4,4′-dinitrodiphenylmethane with 1,3-dibromo-5,5-dimethylhydantoin (4).

[5] All m.p.'s are corrected. All combustion analyses were performed by the Clark Microanalytical Laboratory, Urbana, Illinois.

trate to pentaerythritol. To 0.40 g. (0.0017 mole) of sodium sulfide nonahydrate in 15 ml. of water and 35 ml. of ethanol at 70–80° 0.50 g. (0.0016 mole) of 4,4′-dinitrobenzhydryl nitrate was added portionwise over 30 minutes. The first addition produced a dark red color. After 1.5 hours of refluxing 0.07 g. of light orange crystals, m.p. 189–190°, was removed by filtration of the hot mixture. The filtrate on cooling deposited an additional 0.17 g. of crystals, m.p. 187.5–190°. The combined solids (0.24 g., 55%) were recrystallized twice from ethanol to produce the analytical sample as colorless, sulfur-free needles, m.p. 190.7–191.6°.

Anal. Calc'd for $C_{13}H_8N_2O_5$: C, 57.36; H, 2.96; N, 10.29.

Found: C, 57.47; H, 3.23; N, 10.52.

Neither the ketone from (a) nor (b) depressed the m.p. of authentic 4,4′-dinitrobenzophenone (1).

Nitration of diphenylbromomethane. Over one hour 19.5 g. (0.0789 mole) of diphenylbromomethane (8), b.p. 175–179° at 22 mm., was added in small portions to 130 ml. of well-stirred white fuming nitric acid held at 25°. The dark red-brown solution was stirred for another 15 minutes and then poured with stirring into 100 g. of cracked ice. The resulting orange gum was washed with a total of about 1 liter of hot water. Two recrystallizations (one with charcoal) from acetic acid afforded 2.40 g. (9.5%) of white crystals, m.p. 156–158°. Two more recrystallizations from the same solvent (the second did not alter the m.p.) produced the analytical sample of 4,4′-dinitrobenzhydryl nitrate as white, bromine-free needles, m.p. 160.3–161.3°; a mixture m.p. with the sample prepared from benzhydrol showed no depression.

Anal. Calc'd for $C_{13}H_9N_3O_7$: N, 13.17. Found: N, 13.10.

SUMMARY

Nitration of benzhydrol has produced 4,4′-dinitrobenzhydryl nitrate and 3,4′-dinitrobenzophenone, both in low yield. The former also was obtained in low yield by nitrating diphenylbromomethane.

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