p-Nitrobenzoic Acid by Nitration and Oxidation of Phenylalkanes[1]

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Dinitration of bibenzyl was performed quantitatively. The product mixture contains 63% para-substituted rings. Dinitration of 1,2-diphenylpropane gives about 75% para-substituted rings. Mononitration of the rings in polystyrene is readily accomplished with mixed acid in methylene chloride solution; when the degree of nitration reaches about 0.99, the mono-nitro polymer precipitates and is protected from dinitration. The rings are about 90% para-substituted. Nitric acid oxidation of mixed dinitrobibenzyls yielded 44% of pure p-nitrobenzoic acid. Mixed dinitrodiphenylpropanes yielded 41% of pure p-nitrobenzoic acid. Nitropolystyrene gave 88% p-nitrobenzoic acid when oxidized to 70–80% conversion; unoxidized material may be recycled. Oxidation to higher conversions caused destruction of some of the product.

p-Nitrobenzoic acid is prepared commercially by oxidation of p-nitrotoluene. However, the nitration of toluene gives only about 35% (isolated) of the useful para isomer. Thus two-thirds of the nitration product does not find a ready market. One possible approach to reducing the amount of unwanted ortho isomer is nitration of higher alkylbenzenes in which increasing steric hindrance at the ortho position favors the production of para isomer. Thus in the series methyl-, ethyl-, isopropyl-, and tert-butylbenzene, the respective amounts of para-nitro isomer are 40, 48, 62, and 80%. However, the added carbon atom(s) providing isomer control must be subsequently "burned off" in the oxidation of alkyl to carboxyl.

We considered other hydrocarbons possessing enhanced hindrance to ortho substitution but with minimal added side-chain carbon substitution. The series 1,2-diphenylethane (bibenzyl), 1,2-diphenylpropane, and 1,3,5 . . . polyphenylalkane (polystyrene) was well suited for contrasting the effects of added hindrance and added "excess" carbon. ("Excess carbon" is the number of sidechain carbons to be oxidized less the number of carboxyl groups to be produced; in this series this number is 0, 0.5, and 1.0 atom per mol of PNBA.)

Bibenzyl. Nitration of bibenzyl has been reported by numerous authors, but numerical yields are rare, experimental details are scanty, and the formation of many isomers is barely noted. Only the 4,4' isomer has been isolated from the nitration; Tsekhanski (1958) obtained it in 31% yield, about our experience; Rinkenbach and Aaronson's claim (1930) of 95% is completely erroneous. Onopchenko and Schulz (1976b) did not report yields of nitrobibenzyls, but oxidized the crude nitration product directly to nitrobenzoic acids.

We examined the dinitration of bibenzyl. With nitric acid alone or with premixed nitric–sulfuric acids, considerable trinitration was noted before the mono-nitro compounds had disappeared. The problem was solved by nitrating near room temperature with 90% nitric acid (3 mol/mol of bibenzyl), then adding sulfuric acid (100 mL/mol) slowly at the same temperature. Only traces of trinitro compounds were formed, while mono-nitro was reduced to about 0.5%. The yield of the mixed dinitrobibenzyls was quantitative. Gas chromatography resolved the mixture of the six possible isomers which were identified by comparing their retention times with those of the authentic isomers independently synthesized. The isomer composition is given in Table I.

Thus the mixture is potentially convertible to 63% p-nitrobenzoic acid by oxidation. Leppert (1876) oxidized dinitrobibenzyl with dichromate–sulfuric acid mixture, but no

yield was given. Onopchenko and Schulz (1976b) oxidized the mixture with dilute nitric acid at 180–185 °C to obtain 71–79% of mixed nitrobenzoic acids containing 86–78% p-nitrobenzoic acid, that is 61% (on bibenzyl) of the desired isomer. We found that pure 4,4'-DNBB furnished 83% of PNBA when heated for 6 h at 180 °C with 6 mol of dilute nitric acid, the same yield as obtained from p-nitrotoluene under these oxidation conditions. The crude DNBB mixture yielded 44% of pure PNBA based on bibenzyl.

Now bibenzyl may be prepared by a Friedel–Crafts alkylation of benzene with 1,2-dichloroethane in 82% yield (Yura and Hashimoto, 1944; Van Schaack, 1944). Thus the overall yield of PNBA from benzene is about 40%, superior to the 28% available from toluene.

1,2-Diphenylpropane. This hydrocarbon is available from benzene and either propylene dichloride, allyl chloride, or propylene oxide (Simons and Archer, 1939; Calcott et al., 1939; Smith and Natelson, 1931; Dolgov and Larin, 1950). We noted that its nitration by the procedure successfully employed with bibenzyl gave significant quantities of trinitro derivative before dinitration was complete. GC analysis suggested that the anticipated increase in para substitution had occurred in the ring closer to the lateral methyl group. Of the nine possible dinitro isomers, six were observed in the chromatograms. Extrapolating from the established fact that in nitrobibenzyls, retention times increase going from 2- to 3- to 4-nitro, structures were assigned to the major peaks. Apparently about 75% of the rings were para-substituted, in line with expectation.

Pure 4,4'-dinitrodiphenylpropane isolated from the crude product yielded 76% p-nitrobenzoic acid by nitric acid oxidation, compared to the 82% obtained from pure 4,4'-dinitrobibenzyl. The crude mixed dinitrodiphenylpropanes yielded 41% of the desired acid. Oxidation of a branched side-chain is clearly more difficult than oxidation of a straight chain.

1,2,3-Triphenylpropane was a candidate for nitration, but the unattractive yield in its possible syntheses (Furukawa and Oda, 1955) deterred that study.

Polystyrene. Nitration studies in the past emphasized the preparation of dinitropolystyrene as an ingredient of explosives (Zenftman, 1959; Langhans, 1953; Matlack and Breslow, 1960; Pujo et al., 1953; Namba et al., 1958). Onopchenko and Schulz (1976a) used 90% nitric acid in great excess (20 mol) at room temperature to prepare an uncharacterized product which, on oxidation, yielded 67% p-nitrobenzoic acid. The large excess of nitric acid was required to maintain the viscosity in the stirrable range.

Polystyrene is readily soluble in dichloromethane. We observed that it was readily nitrated in this medium using only

Table I. Product Distribution in Crude Dinitrobibenzyl Mixture [a,b]

Compound	%	Compound	%
2-NO$_2$BB	Trace	2,4'-DNBB	33.6
4-NO$_2$BB	0.5	3,3'-DNBB	Trace
2,2'-DNBB	12.7	3,4'-DNBB	8.6
2,3'-DNBB	3.0	4,4'-DNBB	41.7

[a] Corrected for instrument response using reference compounds. The pure 2,3'- and 3,3'-DNBB were not available. [b] BB = bibenzyl; DNBB = dinitrobibenzyl.

Table II. Properties of Nitrobibenzyls Used for Reference

Compound	Mp, °C
2-NO$_2$	63.0–64.5[a]
4-NO$_2$	69–70[b]
2,2'-(NO$_2$)$_2$	121–122[c]
2,4'-(NO$_2$)$_2$	92–93[d]
3,4'-(NO$_2$)$_2$	129–131[e]
4,4'-(NO$_2$)$_2$	180–181[f]

[a] Anal. Calcd for $C_{14}H_{13}NO_2$: C, 74.0; H, 5.8; N, 6.1. Found: C, 74.1; H, 5.8; N, 5.9. [b] Kursanov and Kichkina (1935) gave mp 70–71 °C. [c] Schindler and Häfliger (1956) gave mp 123 °C. [d] Stelling and Fittig (1866) reported a product, mp 74–75 °C, which must be contaminated with isomers. Our product was purified chromatographically. [e] Anal. Calcd for $C_{14}H_{12}N_2O_4$: C, 61.9; H, 4.4; N, 10.3. Found: C, 62.0; H, 4.3; N, 10.3. [f] Rinkenbach and Aaronson (1930) and House (1963) report mp 179–180 °C.

4 mol of 90% nitric acid. As the degree of nitration approached 0.99 nitro group per ring, the polymer precipitated abruptly from solution. This observation formed the basis for a "dead-stop" technique for avoiding dinitration; dinitrobenzoic acid in the p-nitrobenzoic acid greatly complicates purification of the latter. Further study of nitric–sulfuric acid mixtures permitted nitration of polystyrene in methylene chloride with only 2 mol of nitric acid in 5 min to degree of nitration 0.99.

Examination of the nitropolystyrene by NMR suggested that about 90% of the nitro groups were para to the side-chain. This value was confirmed by oxidation. However, oxidation to 100% conversion (6 h at 180 °C) caused up to 20% loss of the p-nitrobenzoic acid. Optimum results were obtained by oxidizing for 1 h at 180 °C, to about 75% conversion. In several experiments, 88% yield of good-quality p-nitrobenzoic acid was obtained in two steps from polystyrene.

Experimental Section

Nitration of Bibenzyl. Nitric acid (90%), 69.5 mL, 1.5 mol was added during 50 min to 91.0 g, 0.50 mol of bibenzyl with ice cooling to maintain the temperature near 25 °C. The initial black color changed to yellow. When the ice bath was removed, the temperature rose slowly to 43 °C; it was held there with gentle cooling until the exothermic reaction was spent. Then 50 mL of 96% sulfuric acid was added slowly, with cooling to hold the temperature at 25–40 °C. Near the end of the addition, the product agglomerated and impeded stirring. When the exothermic reaction was finished, the spent acid was removed by filtration, and the lumpy product was washed acid-free with water, most conveniently in a blender. The yield of crude dry dinitrobibenzyl was quantitative. Different ratios of nitric and sulfuric acids were not studied.

One such crude product was crystallized from 800 mL of benzene to give 33% of nearly pure 4,4'-dinitrobibenzyl. The filtrate was roughly fractionally distilled *rapidly,* collecting fractions with a "cow" receiver. Considerable tar was formed during this distillation. Chromatography of the fractions on neutral alumina (Woelm), using benzene–hexane for elution, permitted isolation of pure 2,4'-dinitrobibenzyl.

3,4'-Dinitrobibenzyl was prepared by condensing m-nitrobenzaldehyde with p-nitrophenylacetic acid according to the general procedure of Harrison and Wood (1926), and reducing selectively *only the double bond* of the resulting dinitrostilbene in benzene over chlorotris(triphenylphosphine)rhodium(I) at 60–80 °C, 4 atm of H$_2$, following the basic method of Harmon et al. (1969).

2,2'-Dinitrobibenzyl was prepared by base-catalyzed coupling of o-nitrotoluene in the presence of ethyl formate, an adaptation of the procedure of Schindler and Häfliger (1956). The 4,4'-isomer was conveniently prepared by base-catalyzed oxidation of p-nitrotoluene according to House (1963). However, an attempted crossed coupling between o- and p-nitrotoluene by House's procedure failed to give useful amounts of the 2,4'-dinitrobibenzyl. The o- and p-nitrobibenzyls were prepared by nitration with one mole of nitric

acid, followed by distillation and crystallization; the nitration mixtures contained both unreacted bibenzyl and dinitro compounds, despite the limited amount of nitric acid.

Gas chromatographic analysis of nitrobibenzyl mixtures was performed on a 2-m column packed with 20% SE-30 silicone gum rubber on 60–80 mesh Chromosorb W AW-DMCS at 200 °C. Most of the isomers were readily resolved. With the reference compounds described, "response factors" could be determined for all of the major components. For the minor compounds which lacked reference samples, the response factors were set equal to the average values obtained for the other isomers. Typical results are given in Table I.

Nitration of 1,2-Diphenylpropane. The hydrocarbon was prepared in 62% yield from benzene and propylene dichloride by Yura and Hashimoto's (1944) procedure for bibenzyl; bp 90–91 °C (2 Torr), n^{25}D 1.5563–1.5570, with only trace impurities visible in the GC scan. The nitration was run by the method described for bibenzyl, and the product was examined by GC. The best products still contained 1–2% each of mono- and trinitro derivatives. The 4,4'-dinitroisomer (about 10% of the crude product) could be obtained by chilling a methanol or ethyl acetate solution of the crude product to −20 °C, and further recrystallization from methanol; mp 91.5–92.0 °C.

Anal. Calcd for $C_{15}H_{14}N_2O_4$: C, 63.0; H, 4.93; N, 10.12. Found: C, 63.0; H, 4.95; N, 9.99.

Its structure was demonstrated by nitric acid oxidation (see below) to 76% of p-nitrobenzoic acid.

Nine isomers are possible, of which only one was available. By assigning structures to peaks based upon increasing retention times in the series 2, 3, and 4 nitro, we estimate that about 75% of the rings had a para-nitro group.

Nitration of Polystyrene. In nitrations in 90% nitric acid, about 20 parts (w/w) of acid were required to give a mixture stirrable at 30–50 °C. About the same quantity of mixed acid was required. In both cases, the product must be isolated by drowning in water, so recovery of the excess acid was impractical. More conveniently and practically, polystyrene (150 g) was dissolved in methylene chloride (1 L); foam polystyrene and low molecular weight polymers dissolve faster than denser material or high molecular weight polymers. The solution was filtered, diluted to about 10% solids, and treated with 4.0 mol (per ring) of 90–95% nitric acid in 5 min. A deep red color appeared and the temperature *fell.* The mixture was warmed to room temperature and held 15 min at 25 °C; the red color became a murky yellow-orange. The mixture was then refluxed for 1–2 h, during which mononitropolystyrene precipitated from solution. The soft, sticky material could be washed with methylene chloride, or it could be washed with water in a blender to remove nitric acid. It could also be oxidized with dilute nitric acid with no washing. Well-washed material, when dried, weighed 99.6% of theory for mono-ni-

tropolystyrene. Typical Dumas nitrogen analyses were in the range 9.23–9.41%; theory 9.39%.

In the preferred method a solution of polystyrene (0.8–1.0 M) in methylene chloride at 5 °C was treated with mixed acid (HNO$_3$ 36.0, H$_2$SO$_4$ 52.5, H$_2$O 11.5 wt %) containing 2.0 mol of nitric acid over 10 min. The mixture was then brought to reflux (40 °C). The nitro polymer precipitated in about 5 min. The mixture was held at reflux for 2–4 h, and the methylene chloride was decanted from the polymer. The solvent can be reused directly. The polymer was washed three times with methylene chloride and three times with hot water prior to analysis, which showed 99.0% of mononitration.

Nitric Acid Oxidations. The nitrated bibenzyl (or diphenylpropane) mixtures were oxidized by heating 0.1 mol of nitro compound, 0.5 mol of 70% nitric acid, and 160 mL of water in a titanium-lined shaker tube at 180 °C for 5–6 h. The crude product was collected on a filter, washed with water, then dissolved in dilute sodium bicarbonate or ammonia solution to permit separation of about 1 g of deep yellow neutral material, mp 130–190 °C, a mixture of starting material with dinitrobenzyl. The filtrate was acidified to yield p-nitrobenzoic acid. From pure 4,4'-dinitrobibenzyl, 27.0 g, 81% was obtained, mp 243.5–244.5 °C. Dinitrodiphenylpropane was oxidized similarly to 41% of p-nitrobenzoic acid.

Nitropolystyrene was oxidized similarly, but it was then discovered that 10–20% of the p-nitrobenzoic acid was destroyed during the prolonged treatment. Presumably, the yields in the preceding paragraph could have been higher with shorter contact times. Optimum yields were obtained by accepting less than quantitative conversions. Nitropolystyrene was heated with 22.2% HNO$_3$ (6.4 mol per ring) for 1 h at 180 °C. Product isolation as described above gave 20–30% of

neutral material (which can be recycled) and 87–89% of p-nitrobenzoic acid (corrected for unoxidized starting nitropolystyrene). Oxidation at 150 °C, 6 h or 210 °C, 1 h, was much less satisfactory. With 11% nitric acid, the oxidation was very sluggish.

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Quaternary Ammonium Thickening of Sewage Sludge in Magnetic Field

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A sludge dewatering method was investigated for simultaneous settling and thickening of nonmagnetic sludge by magnetic fields. The investigation concerned an improved sewage sludge dewatering technique involving chemical addition, flocculation, polarization, sedimentation, and disinfection. Finely divided iron oxide particles were added to the sewage sludge (an organic nonmagnetic sludge) as both the weighing agent and the polarization inducing agent. Quaternary ammonium compounds were added as both the flocculating agent and the disinfectant. The agglomerates (or flocs) containing sludge solids, iron oxide, and quaternary ammonium compound were flocculated and then passed through a magnetic field for further polarization. The polarized iron ores associated with the sludge agglomerate (or sludge floc) attract each other to form very high weight-to-surface-area floc particles. The condensed flocs, with or without treatment by secondary flocculation, then settled rapidly. The supernatant and the settled sludge were simultaneously disinfected by the added quaternary ammonium compound.

Introduction

A sewage treatment plant generates two principal end products: effluent and sludges. The former is discharged into receiving waters or deposited on land; the latter needs to be processed prior to ultimate disposal.

Sewage sludges are semi-liquid wastes containing mainly putrescible organic solids. Thousands of gallons of these putrescible and presumptively dangerous sewage sludges are removed from each million gallons of municipal sewage undergoing treatment. The sludge handling and processing