32. *The Nitration of Alkyl Benzenes. Part II. Nitro-derivatives of* n-*Propylbenzene.*

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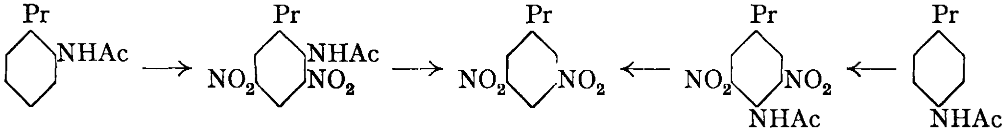
Nitration of the higher alkyl benzenes is apt to yield a variety of products, including some where substitution or oxidation has occurred in the side chain; consequently, it is difficult, if not impossible, to isolate in the pure condition the nitro-compounds required for reference purposes (see Part I). The principle has therefore been adopted of preparing the required compounds from others which could be purified by crystallisation.

None of the nitro-derivatives of *n*-propylbenzene has so far been described. Schultz and Perl (*Ber.*, 1909, **42**, 3614) mononitrated *n*-propylbenzene and isolated *p*-benzamido-*n*-propylbenzene from the reduced product, but did not isolate a pure nitro-*n*-propylbenzene. From *n*-propylbenzene Konovaloff (*J. Russ. Phys. Chem. Soc.*, 1894, **25**, 532) obtained three phenylnitropropanes by the action of dilute nitric acid, and Wolffenstein and Böters (*Ber.*, 1913, **46**, 585) obtained nitrophenolic compounds by nitration in presence of mercury.

Although we could not isolate either compound pure, we have obtained evidence that 2 : 4-dinitro-*n*-propylbenzene is the main product of the dinitration of *n*-propylbenzene, and that 2 : 4 : 6-trinitropropylbenzene also is formed to some extent on vigorous nitration.

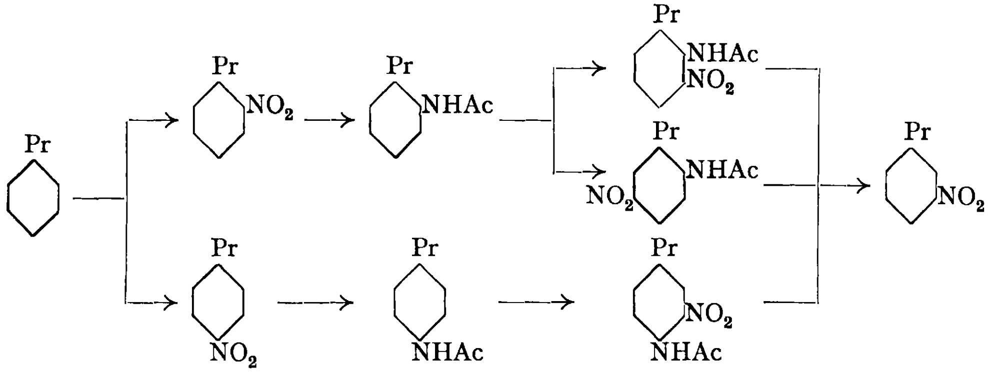
We have prepared o-*nitro*-n-*propylbenzene* from the crude 2 : 4-dinitro-*n*-propylbenzene produced by direct nitration, by reduction with ammonium sulphide to 2-*nitro*-4-*amino*-n-*propylbenzene* and removal of the amino-group. The reduction follows the same course as that of 2 : 4-dinitrotoluene (Beilstein and Kuhlberg, *Annalen*, 1870, **155**, 14), as is shown by the oxidation of the nitropropylbenzene ultimately obtained to *o*-nitrobenzoic acid. 3 : 5-*Dinitro*-n-*propylbenzene* was prepared by reduction of the mixture of *o*- and *p*-nitropropylbenzenes obtained by nitration, dinitration of the acetamido-derivatives, and subsequent removal of the amino group :



2 : 3-*Dinitro*-n-*propylbenzene* was obtained by the nitration of 2-*nitro*-4-*acetamido*-n-*propylbenzene* and removal of the acetamido-group from the 2 : 3-*dinitro*-4-*acetamido*-n-*propylbenzene* produced.

We were unable to isolate 2 : 5-dinitro-4-acetamido-*n*-propylbenzene from the nitration product, though some was undoubtedly present (compare Scott and Robinson, J., 1922, **121**, 844; Page and Heasman, J., 1923, **123**, 3235, who obtained 2 : 3- and 2 : 5-dinitro-4-acetamidotoluenes in the nitration of 2-nitro-4-acetamidotoluene). The orientation of 2 : 3-dinitro-4-acetamido-*n*-propylbenzene was established by the oxidation of the 2 : 3-dinitro-*n*-propylbenzene obtained from it to 2 : 3-dinitrobenzoic acid.

m-*Nitro*-n-*propylbenzene* has been prepared by a method which does not conform to the condition laid down at the beginning of this paper and therefore its purity is open to doubt. The mixture of *o*- and *p*-acetamidopropylbenzenes obtained after reduction of the mononitration product of propylbenzene was mononitrated, and the acetamido-group removed from the mixed product. In accordance with the following scheme, unless any considerable amount of meta-nitration occurs in the nitration of *n*-propylbenzene, the *m*-nitropropylbenzene so obtained should be reasonably pure.



Experimental.

o-*Nitro*-n-*propylbenzene*.—*n*-Propylbenzene (12 g.) was added slowly to a mixture of sulphuric acid (60 c.c., *d* 1·8) and nitric acid (28 c.c., *d* 1·42), kept below 40°. The whole was heated on the water-bath for 30—40 minutes and cooled, and the acid separated. The nitro-compound was washed with water and dilute sodium carbonate solution, dried, and distilled; the main product passed over at 170—173°/11 mm. The crude 2 : 4-dinitropropylbenzene (14 g.) in alcohol (40 c.c.) was boiled for 30 minutes under reflux with alcoholic ammonium sulphide (prepared by mixing 36 c.c. of concentrated aqueous ammonia with an equal volume of alcohol, saturating half this solution with hydrogen sulphide, and adding the other half). The hot solution was separated from sulphur, diluted, and cooled. The precipitate was extracted several times with boiling concentrated hydrochloric acid, and the base precipitated from the extract with dilute sodium hydroxide solution. After crystallising first from dilute alcohol and then from light petroleum, 2-*nitro*-4-*amino*-n-*propylbenzene* formed orange plates, m. p. 59° (Found : C, 59·7; H, 6·6. $C_9H_{12}O_2N_2$ requires C, 60·0; H, 6·7%).

2-*Nitro*-4-*acetamido*-n-*propylbenzene*, prepared by the action of acetic anhydride, crystallised from benzene and light petroleum in pale yellow needles, m. p. 90° (Found : N, 12·8. $C_{11}H_{12}O_3N_2$ requires N, 12·6%).

2-Nitro-4-amino-*n*-propylbenzene (7·5 g.), dissolved in a mixture of fuming sulphuric acid (40 c.c.) and absolute alcohol (110 c.c.), was heated on the water-bath, and dry sodium nitrite (12 g.) added in small portions. After being heated for a further 15 minutes, the mixture was distilled in steam, and the oil extracted from the distillate with ether. After three distillations under reduced pressure o-*nitro*-n-*propylbenzene* was obtained as a pale yellow liquid with an odour similar to that of nitrobenzene but rather sweeter; b. p. 133—136°/26 mm. (Found : C, 64·8; H, 6·6; N, 8·6. $C_9H_{11}O_2N$ requires C, 65·5; H, 6·6; N, 8·5%).

o-Nitropropylbenzene was very slowly attacked by potassium dichromate and dilute sulphuric acid, but boiling for 2 hours with alkaline potassium permanganate and saturation with sulphur dioxide gave *o*-nitrobenzoic acid.

4-*Nitro*-2-*amino*-n-*propylbenzene*.—Crude 2 : 4-dinitro-*n*-propylbenzene (2 g.) in alcohol was heated on the water-bath for 2 hours with stannous chloride (6 g.) in alcohol (10 c.c.) saturated with hydrogen chloride. After dilution, tin was removed as sulphide and the filtrate concentrated and partly neutralised, enough free acid being left to keep the amine in solution. The liquid was again saturated with hydrogen sulphide and these operations were repeated until the solution was free from tin. On addition of dilute sodium hydroxide solution 4-*nitro*-2-*amino*-n-*propylbenzene* separated; it crystallised from dilute alcohol in yellow needles, m. p.

73° (Found: C, 59·7; H, 6·7; N, 15·7. $C_9H_{12}O_2N_2$ requires C, 60·0; H, 6·7; N, 15·6%). This compound was quite different in appearance from 2-nitro-4-amino-*n*-propylbenzene, and a mixture of the two melted below the m. p. of either.

The quantity of the compound obtained was insufficient for the preparation of *p*-nitro-*n*-propylbenzene, and an attempt to obtain a larger quantity was unsuccessful, owing, apparently, to the production of the diamine.

2 : 3-*Dinitro*-n-*propylbenzene*.—2-Nitro-4-acetamido-*n*-propylbenzene (20 g.) was added in small portions to a mixture of sulphuric acid (40 c.c., *d* 1·8) and nitric acid (40 c.c., *d* 1·42) cooled in ice, and the mixture allowed to attain room temperature during 30 minutes and then poured on ice. The yellow oil which was precipitated soon solidified; when it was crystallised from the smallest possible quantity of glacial acetic acid and then from alcohol, 2 : 3-*dinitro*-4-*acetamido*-n-*propylbenzene* separated in yellow plates, m. p. 130° (Found: N, 16·0. $C_{11}H_{13}O_5N_3$ requires N, 16·1%). This compound, on hydrolysis at 100° for 2 hours with 50% sulphuric acid, neutralisation, and crystallisation from alcohol, gave 2 : 3-*dinitro*-4-*amino*-n-*propylbenzene* in orange crystals, m. p. 124° (Found: C, 48·2; H, 4·9. $C_9H_{11}O_4N_3$ requires C, 48·0; H, 4·9%).

The amino-group was removed from the above compound in the manner described in the preparation of *o*-nitropropylbenzene. A solid separated from the steam distillate, which, after crystallising from dilute alcohol, gave 2 : 3-*dinitro*-n-*propylbenzene* in white plates, m. p. 64° (Found: C, 51·6; H, 4·9; N, 13·4. $C_9H_{10}O_4N_2$ requires C, 51·4; H, 4·8; N, 13·3%).

2 : 3-Dinitro-*n*-propylbenzene was heated to boiling for an hour with 50% sulphuric acid and potassium dichromate. After cooling, 2 : 3-dinitrobenzoic acid was collected, recrystallised from hot water, and identified by its m. p. 201° and by conversion by Fischer and Speier's method (*Ber.*, 1895, **28**, 1150) into its methyl ester, m. p. 134° (Brady, Day, and Allam, J., 1928, 981).

3 : 5-*Dinitro*-n-*propylbenzene*.—*n*-Propylbenzene (12 g.) was added slowly to an ice-cooled mixture of sulphuric acid (32 c.c., *d* 1·8), nitric acid (18 c.c., *d* 1·42), and water (8 c.c.) with thorough shaking, the temperature not being allowed to rise above 40°; after 30 minutes, the acid was separated. The nitro-compound was washed with water and alkali and reduced with tin (22 g.) and concentrated hydrochloric acid (60 c.c.). The reduction mixture was distilled in steam to remove unchanged nitro-compound, made alkaline, and again distilled in steam. The mixture of amines was heated with acetic anhydride and one drop of concentrated sulphuric acid, and poured into water; the mixed acetyl derivatives separated as an oil which soon solidified to a paste, which was pressed on a porous tile. The mixture of *o*- and *p*-acetamido-*n*-propylbenzenes (7 g.) was added slowly to nitric acid (70 c.c., *d* 1·5) cooled to −5°. The mixture was kept at 0° for 35 minutes and poured on ice. The well-washed precipitate was hydrolysed with 50% sulphuric acid, and the amino-group removed from the product by diazotisation in boiling alcohol, as previously described. The dinitro-compound was but slowly volatile in steam, and the distillation was carried on for 36 hours. The distillate was extracted with ether. The solid from the ether contained some dinitro-amine, which was removed by warming with concentrated nitric acid, dilution, solution in ether, and washing with dilute sodium hydroxide solution. The ether on evaporation gave 3 : 5-*dinitro*-n-*propylbenzene*, which crystallised from light petroleum in pale yellow prisms, m. p. 51° (Found: N, 13·5. $C_9H_{10}O_4N_2$ requires N, 13·3%). On oxidation with potassium dichromate and 50% sulphuric acid the compound gave 3 : 5-dinitrobenzoic acid.

m-*Nitro*-n-*propylbenzene*.—A mixture (7 g.) of *o*- and *p*-acetamido-*n*-propylbenzenes (Found: C, 65·1; H, 6·7. Calc. for mononitro-compound: C, 65·5; H, 6·6%) was added slowly to an ice-cold mixture of nitric acid (7 c.c., *d* 1·5) and glacial acetic acid (7 c.c.), and kept for an hour at 0°. When the whole was poured on ice, a mixture of a brown and a yellow crystalline solid was obtained, which was hydrolysed with 50% sulphuric acid, and the amino-group removed as in the preparation of *o*-nitropropylbenzene. The steam distillate was extracted with ether, and the extract after drying and removal of solvent was distilled under reduced pressure, m-*nitro*-n-*propylbenzene* being obtained as a yellow liquid, b. p. 136°/16 mm. (Found: N, 8·2. $C_9H_{11}O_2N$ requires N, 8·5%). Oxidation with potassium dichromate and sulphuric acid gave *m*-nitrobenzoic acid.

Di- and Tri-nitration of n-*Propylbenzene*.—*n*-Propylbenzene was dinitrated as described under the preparation of *o*-nitropropylbenzene. The product (b. p. 173°/11 mm.) was not pure (Found: N, 14·3. Calc. for dinitro-compound: N, 13·3%). Oxidation, however, with chromic acid in concentrated sulphuric acid (Curtius and Bollenbach, *J. pr. Chem.*, 1907, **76**, 287) gave 2 : 4-dinitrobenzoic acid. Further nitration of the above material, b. p. 173°, with fuming nitric acid and fuming sulphuric acid at 100° gave a product completely soluble in water, from which only 2 : 4-dinitrobenzoic acid could be isolated. Replacing the fuming sulphuric acid by acid of *d* 1·8 still gave 2 : 4-dinitrobenzoic acid. Nitration of 2 : 4-dinitropropylbenzene (14 g.) with a mixture of nitric acid (14 c.c., *d* 1·5) and sulphuric acid (44 c.c., *d* 1·8) for 3 hours at 70—80°, separation, and washing with water and alkali gave a product which, on reduction with ammonium sulphide by the method used for 2 : 4-dinitropropylbenzene and prolonged fractional crystallisation of the mixture, yielded about 3 g. of 2-nitro-4-amino-*n*-propylbenzene and a small quantity of a brown crystalline solid, m. p. 162°, which was probably 2 : 6-*dinitro*-4-*amino*-n-*propylbenzene* (Found: C, 48·1; H, 5·1; N, 18·8. $C_9H_{11}O_4N_3$ requires C, 48·0; H, 4·9; N, 18·7%). Insufficient was obtained for further investigation, but the formation of this compound suggests that partial trinitration had occurred. The possibility that this product was formed from a compound in which side-chain nitration had occurred seems unlikely, as any dinitrophenylnitropropane would have been removed during the washing of the nitro-compound with sodium hydroxide solution before reduction.

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