

332. *Properties and Reactions of Free Alkyl Radicals in Solution.*
Part XIII. Reactions with Aromatic Nitro-compounds.*

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Benzyl radicals react with 1,3,5-trinitrobenzene to give *ON*-dibenzyl-3,5-dinitrophenylhydroxylamine and benzaldehyde. *m*-Dinitrobenzene reacts similarly but also gives *N*-benzyl-*m*-nitroaniline and *m*-nitroaniline, whilst nitrobenzene yields aniline and *N*-benzylaniline. Further evidence is given of the nuclear methylation of trinitrobenzene. The results give satisfactory explanations of the actions of aromatic nitro-compounds as retarders of free-radical polymerisations and as oxidising agents in hydrogen-transfer processes.

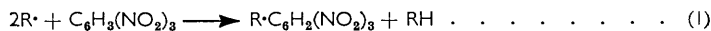
THE mode of action of free alkyl radicals on aromatic nitro-compounds has been a matter of controversy, for whilst 1,3,5-trinitrobenzene can be converted into trinitro-*m*-xylene by free methyl radicals^{1,2} polynitro-compounds are known to be decidedly more efficient

* Part XII, *J.*, 1958, 4632.

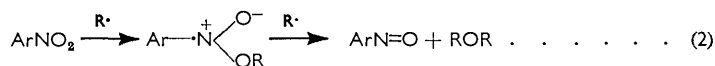
¹ Fieser, Clapp, and Daudt, *J. Amer. Chem. Soc.*, 1942, **64**, 2052.

² Sandin and McCormack, *J. Amer. Chem. Soc.*, 1945, **67**, 2051.

in stopping the radical-catalysed polymerisation of olefins than the process of nuclear alkylation (equation 1), suggested by Price and Durham,³ would indicate.



Bartlett and Kwart⁴ showed that 1,3,5-trinitrobenzene rapidly stops two chains of polymerising styrene, but then, as a slightly weaker inhibitor, stops two more chains and thereafter is still a retarder of polymerisation. Again *m*- and *p*-dinitrobenzene are almost equally effective as inhibitors of the radical polymerisation of allyl acetate,⁵ which would not be the case if nuclear alkylation were occurring. Moreover, the resultant nitrogenous polymers do not yield dinitrobenzoic acids when oxidised. Bartlett and his colleagues therefore suggested that alkyl radicals might reduce nitro-groups as follows:



and that nitroso-compounds, so formed, could also act as inhibitors.

The chain-breaking action of the nitroso-compounds was explained in 1954 by Gingras and Waters⁶ who established that 2-cyano-2-propyl radicals rapidly add to the N=O double bond of nitrosobenzene, forming *ON*-di-(2-cyano-2-propyl)-*N*-phenylhydroxylamine. They reported that from similar reactions both 1,3,5-trinitrobenzene and 1-chloro-2,4-dinitrobenzene could be recovered almost quantitatively. However Inamoto and Simamura⁷ isolated 2.8% of the above hydroxylamine from the decomposition of azo-isobutyronitrile in nitrobenzene and 2.2% of its *m*-nitro-derivative from a similar reaction with *m*-dinitrobenzene. Similar results have been reported by Norris⁸ for reactions of *o*- and *p*-dinitrobenzenes.

As already reported in outline⁹ we have found that free benzyl radicals, which have a close structural similarity to the active radicals $X\cdot CH_2\cdot CHPh\cdot$ in polymerising styrene, easily attack trinitrobenzene, giving *ON*-dibenzyl-*N*-(3,5-dinitrophenyl)hydroxylamine together with benzaldehyde, the latter product not being generated in our reaction mixture (t-butyl peroxide decomposing in an excess of boiling toluene¹⁰) in the absence of the nitro-compound. 4-Chlorobenzyl radicals, generated from *p*-chlorotoluene, react similarly to give the corresponding di-4-chlorobenzylhydroxylamine. Both these hydroxylamines have been oxidised to 3,5,3',5'-tetranitroazoxybenzene. *ON*-Dibenzyl-3,5-dinitrophenylhydroxylamine withstands vigorous acid-hydrolysis but was converted by reductive acetylation into 3,5-diacetamido-*N*-benzylacetanilide, identical with material synthesised by reductive acetylation of *N*-benzylidene-3,5-dinitroaniline.

Benzyl radicals react much less readily with *m*-dinitrobenzene, but from the deeply coloured products it has been possible to isolate *m*-nitroaniline, *N*-benzyl-*m*-nitroaniline and *ON*-dibenzyl-*m*-nitrophenylhydroxylamine together with much benzaldehyde (0.24 mol.). After reaction with nitrobenzene both aniline (6.4%) and *N*-benzylaniline (1%) have been isolated.

It has been reported¹¹ that the pyrolysis of t-butyl peroxide in nitrobenzene gives in very small yield a mixture of isomeric nitrotoluenes together with a much larger bulk of dark brown involatile material, probably formed by partial reduction of the nitro-group and coupling of reduction products. We now find that the decomposition of t-butyl peroxide in boiling chlorobenzene containing 1,3,5-trinitrobenzene yields a mixture of trinitromesitylene (1%) and trinitro-*m*-xylene (5%) in accordance with the results of

³ Price and Durham, *J. Amer. Chem. Soc.*, 1943, **65**, 757.

⁴ Bartlett and Kwart, *J. Amer. Chem. Soc.*, 1952, **74**, 3969.

⁵ Hammond and Bartlett, *J. Polymer Sci.*, 1951, **6**, 617.

⁶ Gingras and Waters, *J.*, 1954, 1920.

⁷ Inamoto and Simamura, *J. Org. Chem.*, 1958, **23**, 408.

⁸ Norris, *J. Amer. Chem. Soc.*, 1959, **81**, 4239.

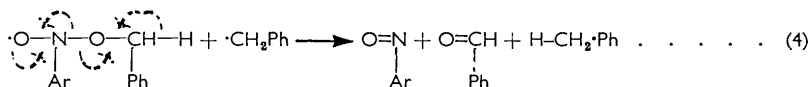
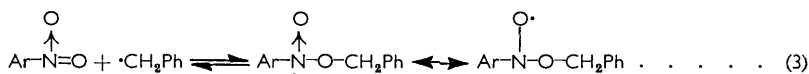
⁹ Jackson, Waters, and Watson, *Chem. and Ind.*, 1959, 47.

¹⁰ Beckwith and Waters, *J.*, 1957, 1001; Watson, D.Phil. Thesis, Oxford, 1958.

¹¹ Cowley, Norman, and Waters, *J.*, 1959, 1799.

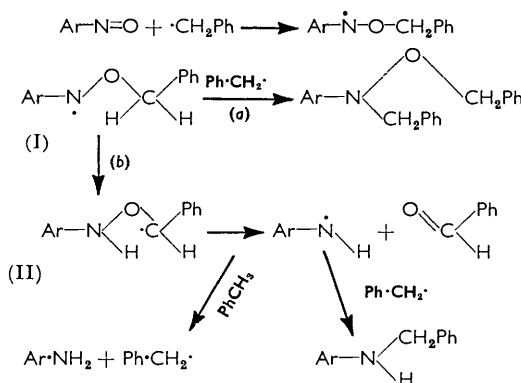
Fieser, Clapp, and Daudt¹ (who generated methyl radicals from lead tetra-acetate) and of Sandin and McCormack² (who used phenyliodosoacetate). Only a trace of an amine could be isolated from our reaction mixture.

Our work helps to clarify modern views^{4,5,12} concerning the inhibiting action of nitro-compounds in vinyl polymerisations and, further, gives some indication of the mode of action of aromatic nitro-compounds as oxidising agents in homolytic hydrogen-transfer processes.¹³ The formation of a large amount of benzaldehyde by attack of benzyl radicals on both trinitro- and dinitro-benzene can be explained by the following reaction sequence,^{3,4} rather than that of Bartlett (equation 2), in which concerted 1-electron movements favour O-N bond breakage in the primary radical adduct to the nitro-compound.



A reduction in this way could not be effected by phenyl radicals, and would be energetically less favoured with $\cdot\text{CH}_3$ radicals than with benzyl on account of the resonance stabilisation of the benzaldehyde formed by the hydrogen-transfer. Evidently the reducing powers of radicals, $\text{PhCH}_2\cdot > \text{CH}_3\cdot > \text{Ph}\cdot$, follow the inverse order of their abilities to effect nuclear substitution of aromatic nitro-compounds.

The homolytic reduction of aromatic nitro-compounds to amines can be explained by the following sequence of reactions:



Subsequently reactions between aromatic amines, hydroxylamines, and nitroso-compounds must inevitably occur.

EXPERIMENTAL

M. p.s are corrected.

Reaction of Benzyl Radicals with 1,3,5-Trinitrobenzene.—Trinitrobenzene (10 g.) and t-butylperoxide (25 ml., 2.9 mol.) were refluxed in toluene (300 ml.) for 72 hr. under nitrogen. Evaporation at 100° gave a brown gum (19.4 g.), 10% of which, in alcohol, was treated with 2,4-dinitrophenylhydrazine to give benzaldehyde 2,4-dinitrophenylhydrazone (0.69 g.) corresponding to the production of 0.42 mol. of benzaldehyde during the reaction. The remaining gum,

¹² Bevington and Ghanera, *J.*, 1959, 2071.

¹³ Jackson and Waters, *J.*, 1958, 4632.

in light petroleum, was chromatographed through alumina (type H) and gave orange-yellow *ON*-dibenzyl-3,5-dinitrophenylhydroxylamine⁹ (4.56 g., 28%), m. p. 121—122° (Found: C, 63.4; H, 4.7; N, 10.6. Calc. for C₂₀H₁₇N₃O₅: C, 63.3; H, 4.5; N, 11.1%). Further elution of the alumina gave a small quantity (0.17 g.) of a brown solid that appeared from its infrared spectrum (band at 2.98 μ) to be a secondary amine, and thereafter some red gum. No trinitrobenzene was recovered; however, this substance suffers some decomposition on the alumina of the column.

Reaction of 4-Chlorobenzyl Radicals with 1,3,5-Trinitrobenzene.—Trinitrobenzene (4 g.) and *t*-butyl peroxide (10 ml.) in *p*-chlorotoluene (42 ml.) were kept at 112° (oil-bath) under nitrogen for 72 hr. From the product there was isolated, as above, *ON*-di-4-chlorobenzyl-3,5-dinitrophenylhydroxylamine (2.4 g., 29%) which crystallised from ethanol-ethyl acetate in yellow needles, m. p. 157.5° (Found: C, 53.3; H, 3.4; N, 8.6, 8.8; Cl, 15.0. C₂₀H₁₅Cl₂N₃O₅ requires C, 53.6; H, 3.4; N, 9.4; Cl, 15.8%).

Reactions of ON-Dibenzyl-3,5-dinitrophenylhydroxylamine.—The compound was recovered unchanged after 24 hours' boiling with concentrated hydrochloric acid or with alcohol (1 part) and concentrated hydrochloric acid (4 parts). Oxidation of the compound (0.3 g.) with chromium trioxide (0.44 g.) in acetic acid (15 ml.) at 100° for 45 min. gave benzoic acid (0.1 g.) and 3,5,3',5'-tetranitroazoxybenzene (0.08 g., isolated chromatographically) which crystallised from methanol-methyl acetate in pale yellow plates, m. p. 185.5° (Found: C, 38.6; H, 1.6; N, 20.6. Calc. for C₁₂H₆N₆O₉: C, 38.1; H, 1.6; N, 22.2%). This gave no m. p. depression and was spectrographically identical with authentic material, m. p. 187—188°, obtained by boiling 1,3,5-trinitrobenzene with aqueous sodium carbonate¹⁴ and also with material (m. p. 184°) obtained by oxidation of *ON*-di-4-chlorobenzyl-3,5-dinitrophenylhydroxylamine. This azoxy-compound was recovered unchanged after being treated at 100° for 1½ hr. with nitric acid and hydrogen peroxide in acetic acid.

Reduction of *ON*-dibenzyl-3,5-dinitrophenylhydroxylamine (1.08 g.) during 3½ hr. in boiling acetic acid-acetic anhydride (50 ml., 1:4) containing sodium acetate (1.05 g.) by gradual addition of zinc dust gave *N*-benzyl-1,3,5-triacetamidobenzene⁹ (0.05 g.), m. p. 250—251° (from methanol-water) (Found: C, 67.1; H, 6.2; N, 12.4. Calc. for C₁₉H₂₁O₃N₃: C, 67.2; H, 6.2; N, 12.4%), identical with material prepared as described below.

3,5-Dinitroaniline,¹⁵ m. p. 161°, was prepared by adding sodium azide (4.5 g.) to 3,5-dinitrobenzoyl chloride (12 g.) suspended in acetic acid (35 ml.), collecting the resulting 3,5-dinitrobenzoyl azide, adding it in small portions to concentrated sulphuric acid (300 ml.), and warming the mixture each time until nitrogen evolution ceased. Treatment of this amine (1 g.) in hot alcohol (15 ml.) with benzaldehyde (0.75 g.) and a few drops of acetic acid gave *N*-benzylidene-3,5-dinitroaniline which crystallised from alcohol in very pale yellow needles, m. p. 139° (Found: C, 57.8; H, 3.1; N, 15.1. C₁₃H₉N₃O₄ requires C, 57.6; H, 3.3; N, 15.5%). This compound (0.3 g.) in ethyl acetate (200 ml.) was hydrogenated at atmospheric pressure, with Adams catalyst, until 7 mol. of hydrogen had been absorbed. After filtration, the solution was treated with an excess of acetic anhydride, and after 24 hr. was poured into aqueous sodium carbonate. The product (25%), on repeated crystallisation from methanol-water, gave 3,5-diacetamido-*N*-benzylacetanilide in colourless prisms, m. p. 252—253° (Found: C, 67.4; H, 6.5; N, 12.3. Calc. for C₁₉H₂₁O₃N₃: C, 67.2; H, 6.2; N, 12.4%).

Reaction of Benzyl Radicals with m-Dinitrobenzene.—*m*-Dinitrobenzene (16.8 g.) and *t*-butyl peroxide (40 ml.) in toluene (300 ml.) were refluxed for 83 hr. under nitrogen. After removal of volatile material the residue was chromatographed through alumina. Light petroleum-benzene (1:1) extracted a yellow solid (16.1 g.) from which some pure *m*-dinitrobenzene (m. p. and mixed m. p. 89°) was isolated by crystallisation from ether. Vapour-phase chromatography at 180° of a portion of the gummy remainder showed the presence of small amounts of two other substances and indicated that the total amount of unchanged dinitrobenzene was 31% of that taken. Further chromatography of this gum with light petroleum-benzene gave yellow prisms (0.5 g.), m. p. 60—61° (from methanol), identified as *ON*-dibenzyl-*m*-nitrophenylhydroxylamine by its analysis (Found: C, 72.0; H, 5.2; N, 8.2. C₂₀H₁₈N₂O₃ requires C, 71.8; H, 5.4; N, 8.4%) and by analogy with the product from trinitrobenzene.

Continued elution of the reaction product with benzene gave a yellow paste from which solid (0.46 g.) was obtained by crystallisation from methanol. After further purification this

¹⁴ Lobry de Bruyn and Van Leent, *Rec. Trav. chim.*, 1894, **13**, 148.

¹⁵ Blanksma and Verberg, *Rec. Trav. chim.*, 1934, **53**, 988.

proved to be *N*-benzyl-*m*-nitroaniline, m. p. 107—108° (Found: C, 68.9; H, 5.4; N, 12.1. Calc. for $C_{13}H_{12}N_2O_2$: C, 68.4; H, 5.3; N, 12.3%). Its infrared spectrum had a single peak at 2.92 μ , indicative of an NH group, and the complete identity of the compound was later proved by synthesis of authentic material by benzylating *N*-toluene-*p*-sulphonyl-*m*-nitroaniline and hydrolysing this (m. p. 124°) with 50% sulphuric acid. The authentic material had m. p. 107° (lit.,¹⁶ 107°) (Found: C, 68.8; H, 5.1; N, 12.2%).

Further elution of the reaction product with methanol gave a brown gum (5.75 g.) which was dissolved in ether and extracted with 6*N*-hydrochloric acid. The acid extract yielded *m*-nitroaniline (0.49 g.), m. p. and mixed m. p. 113° (benzoyl derivative, m. p. and mixed m. p. 156°).

The reaction of benzyl radicals with *m*-dinitrobenzene was repeated, the solvent this time being removed through a fractionating column until no more distilled at 110°. The residue was diluted to 100 ml. with methanol, and the precipitated gum was then dissolved in 250 ml. of benzene. A mixture of 10 ml. of the methanol solution and 25 ml. of the benzene solution was treated with alcoholic dinitrophenylhydrazine and gave 0.69 g. of benzaldehyde 2,4-dinitrophenylhydrazone, m. p. 238—239° after recrystallisation, indicating the formation in the reaction of 0.24 mol. of benzaldehyde. Repeated chromatography of the benzene solution gave, after prolonged elution with benzene, a little *m*-nitroaniline, m. p. and mixed m. p. 113°, showing that this compound is not an artefact produced in the preceding experiment by the acid-extraction.

Reaction of Benzyl Radicals with Nitrobenzene.—Nitrobenzene (5 g.), *t*-butyl peroxide (46 ml.), and toluene (300 ml.) were refluxed together for 38 hr. and then distilled in steam. The aqueous portion of the distillate was extracted with benzene, and this extract, together with the non-aqueous distillate was extracted twice with 6*N*-hydrochloric acid. From the acid extract there was isolated crude aniline which was converted into benzanilide (0.6 g.), m. p. and mixed m. p. 162—163°, corresponding to a 6.4% yield of aniline in the reaction.

Chromatography of the involatile residue gave a brown oil (0.2 g.) with an infrared spectrum similar to that of benzylaniline. Treatment of this with toluene-*p*-sulphonyl chloride in pyridine gave *N*-benzyltoluene-*p*-sulphonanilide, m. p. and mixed m. p. 140°, in amount corresponding to formation of 1% of benzylaniline in the reaction.

Reaction of Methyl Radicals with Trinitrobenzene.—Trinitrobenzene (3 g.) and *t*-butyl peroxide (20.5 ml.) were refluxed in chlorobenzene (100 ml.) for 22 hr. and then steam-distilled. The initial portion of the distillate did not give a dimedone test for formaldehyde. The residue, after being dried by azeotropic distillation, gave a brown solution in benzene and an insoluble brown powder. Chromatography of the solution gave 20 mg. (1.7%) of trinitromesitylene, m. p. and mixed m. p. 233—235° (from methanol), 90 mg. of trinitro-*m*-xylene, m. p. and mixed m. p. 181° (from ethyl acetate) (Found: C, 39.6; H, 2.7; N, 17.5. Calc. for $C_8H_7N_3O_6$: C, 39.8; H, 2.9; N, 17.4%), and a trace (8 mg.) of a secondary amine, m. p. 168—172°, having an infrared absorption peak at 2.90 μ .

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¹⁶ Meldola and Streatfield, *J.*, 1887, **51**, 102.