POLYNITROAROMATICS-II

DICHROMATE-SULFURIC ACID OXIDATIONS OF ALKYLPOLY-NITROBENZENES IN THE PRESENCE OF NITRIC ACID: A NEW REACTION OF TRINITROTOLUENE DERIVATIVES

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Abstract—On the addition of nitric acid to dichromate-sulfuric acid oxidizing mixtures, ring- substituted 2,4,6-trinitrotoluenes are converted to the corresponding derivatives of picric acid rather than of trinitrobenzoic acid. The reaction takes the "conventional" course with the dinitrotoluenes, the only products isolated being the carboxylic acids. With the higher alkyltrinitrobenzenes the reaction leads to acyltrinitrobenzenes.

IN THE first paper of this series² it was reported that the primary reaction product of 3,3'-dimethyl-2,2',4,4',6,6'-hexanitrobiphenyl with a mixture of sodium dichromate, sulfuric acid and nitric acid was unexpectedly 3,3'-dihydroxy-2,2',4,4',6,6'-hexanitrobiphenyl (dipicric acid) rather than the 3,3'-dicarboxylic acid as had been suggested by earlier workers.³ With the same reagent mixture monomethylhexanitrobiphenyl was analogously oxidized to the monohydroxy derivative. To explore the generality of this unusual replacement of methyl by hydroxyl rather than carboxyl when nitric acid was added to conventional⁴ dichromate–sulfuric acid oxidizing mixtures, the reactions of a number of mononuclear dinitrotoluenes and ring- and sidechain-substituted trinitrotoluenes were studied.

2,4,6-Trinitrotoluene itself, when dissolved in a mixture of 90% nitric acid and concentrated sulfuric acid and treated with sodium dichromate dihydrate at ambient temperatures, underwent rapid conversion to pieric acid in 85% yield. The nitric acid: sulfuric acid ratio could be varied over a rather large range with apparently little effect on the course of the reaction; yields of pieric acid ranged from 60 to 85% as this ratio was changed from 1:3 to 30:1. In the complete absence of sulfuric acid the oxidation rate dropped sharply while in the absence of nitric acid there existed, of course, the classical conditions for oxidation to the carboxylic acid⁴ and 2,4,6-trinitrobenzoic acid was, indeed, the only product.

Similar transformations were effected with 3-bromo-2,4,6-trinitrotoluene and 2,4,6-trinitro-*m*-cresol. In the former instance the phenolic (and only) product, *m*-bromopicric acid, was isolated in 52% yield; in the latter case a markedly slower reaction led to extensive degradation with the recovery of only 10% 2,4,6-trinitro-resorcinol. In neither instance nor in the case of T.N.T., itself, was a carboxylic acid or its decarboxylation product identified.

⁴ T. L. Davis, The Chemistry of Powder and Explosives p. 134. John Wiley, New York (1943).

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² J. C. Dacons, H. G. Adolph and M. J. Kamlet, Tetrahedron 19, 791 (1963).

⁸ L. H. Bock, W. W. Moyer and R. Adams, J. Amer. Chem. Soc. 52, 2054 (1930).



On the other hand, the fully substituted 1-t-butyl-3,5-dimethyl-2,4,6-trinitrobenzene, in which the methyl groups were similarly the sites of oxidative attack,⁵ did not give rise to any phenolic species when treated with the dichromate-sulfuric acid-nitric acid mixture. This compound proved quite unreactive under the "standard" conditions and on prolonged oxidation 5-t-butyl-2,4,6-trinitro-*m*-toluic acid (I) was the primary product with lesser amounts of 5-t-butyl-2,4,6-trinitroisophthalic acid (II).



The structure of the dicarboxylic acid was readily derived from its elemental analyses, neutralization equivalent, I.R. spectrum which showed a split carbonyl band with peaks at 1700 and 1725 cm⁻¹ (Fluorolube mull) and ready decarboxylation in boiling aqueous solution to the known 1-t-butyl-2,4,6-trinitrobenzene. Spectral and analytical data, together with its conversion to II, likewise confirmed the structure of the monocarboxylic acid, I.

The dinitrotoluenes also took the "conventional" course when oxidized in the present manner, similar products being formed in the presence of nitric acid as with dichromate-sulfuric acid alone. With both the 2,4- and the 2,6-isomers there was considerable degradation even at reduced temperatures and only 2,4- $(56\cdot4\%)$ and 2,6-dinitrobenzoic acid $(33\cdot6\%)$ were readily isolable.

Nor were phenolic products obtained from the higher alkyl homologs of T.N.T. 1-Ethyl-2,4,6-trinitrobenzene yielded 76% of a non-acidic species, III, whose elemental analyses, together with a strong carbonyl band in the I.R. spectrum, were consistent with the structure of 2,4,6- trinitroacetophenone. Physical properties, however, did not correspond to those recorded by earlier workers⁶ who, giving as evidence only a nitrogen analysis of the phenylhydrazone, had reported 2,4,6-trinitroacetophenone as an orange-red compound deriving from the reaction of trinitrobenzaldehyde with diazomethane. Although such a color seemed improbable for trinitroacetophenone, it appeared that confirmation of the structure of III required independent synthesis.

This was accomplished by reacting 2,4,6-trinitrobenzoyl chloride with ethoxymagnesiomalonic ester. The intermediate diethyl 2,4,6-trinitrobenzoylmalonate was

⁵ The lack of reactivity of the t-butyl group under these conditions is illustrated by failures to oxidize 1-t-butyl-2,4,6-trinitrobenzene (see text).

^e A. Sonn and W. Bülow, Ber. Dtsch. Chem. Ges. 58, 1697 (1925).

not isolated, but hydrolyzed *in situ* with propionic and sulfuric acids to yield about 20% of a material whose I.R. spectrum and melting point were identical with those of III and which gave no depression in melting point on admixture with III.



2,4,6-Trinitroacetophenone was also the primary product from 2,4,6-trinitrocumene. The reaction with the dichromate-sulfuric acid-nitric acid mixture was rather vigorous, but when the oxidation was carried out with adequate cooling it was possible to isolate III in 39% yield.⁷ Contradistinctly, 1-t-butyl-2,4,6-trinitrobenzene was extremely unreactive, most of the starting material being recovered unchanged after sixteen hours at ambient temperatures.

Although no detailed mechanism for the $CH_3 \rightarrow OH$ transformation in the trinitroluene series can yet be offered, a number of conclusions may be drawn from the observed facts.

The failure of ethyl- and isopropyltrinitrobenzene to undergo the reaction may be rationalized on the assumption that carboxylic acids are necessary intermediates for conversion to the phenols. Since, under the present reaction conditions, the longer sidechains were not oxidized past the acetophenone stage, no phenolic products were obtained from these compounds.

This assumption appears justified by the easy conversion of 2,4,6-trinitrobenzoic acid to picric acid in 85–87% yields under the present reaction conditions or, indeed, with dichromate and nitric acid alone, the dichromate being reduced to chromium-III. The reaction did not take place in the absence of dichromate nor was potassium permanganate or potassium chlorate an effective substitute. 3-Hydroxy-2,4,6-trinitrobenzoic acid reacted analogously. The yield of trinitroresorcinol, 10%, was in the same range, probably for similar reasons, as in the oxidation of trinitro-*m*-cresol.

We have already commented² that, in oxidations of dimethylhexanitrobiphenyl, the $CH_3 \rightarrow OH$ reaction was accompanied by a $CH_3 \rightarrow H$ reaction. In addition to 80% 3,3'-dihydroxy-2,2',4,4',6,6'-hexanitrobiphenyl (IV), <1% of the 3-monohydroxy-derivative (V) was obtained as by-product. On the assumption that the carboxylic acid is a precursor to the phenol, this by-product can readily be accounted for by decarboxylation rather than oxidation of the common intermediate VI.

⁷ About 1% of a red crystalline by-product was isolated. This compound, also obtained in good yield from 3-isopropylpicric acid under similar conditions and whose structure has not yet been fully elucidated, will be dealt with in a subsequent communication of this series.



The fact that oxidations of the dinitrotoluenes and of 1-t-butyl-3,5-dimethyl-2,4,6trinitrobenzene did not proceed past the carboxylic acid stage may provide a clue regarding the nature of the COOH \rightarrow OH transformation. A possible and, as we believe, likely explanation is the following:

A dominant feature in the reactivity behavior of polynitroaromatic compounds is the relative ease of nucleophilic displacement of substituents *ortho-para* to the nitro groups. This ease of reaction is ascribed to resonance stabilization of transition state (one-stage mechanism) or reaction intermediate (two-stage mechanism) by canonical structures of the type VIa-c.



Addition of a third nitro group into 2,4-dinitrophenyl compounds has a pronounced effect on rates by providing an additional "seat for the resonating charge" in a further canonical structure corresponding to VIc. Thus, for example, in the reaction with aniline in ethanol at 50°, picryl halides react 7000-20,000 times faster than the corresponding 2,4-dinitrophenyl derivatives.⁸

From the analogous enhanced reactivity of the trinitrobenzoic relative to the dinitrobenzoic acid derivatives, it is not unreasonable that a similar type of displacement plays a part in the COOH \rightarrow OH transformation with simultaneous (one-step mechanism) or subsequent (two-step mechanism) oxidation of the carboxy group to carbon dioxide. One would judge nitrate ion to be the best nucleophile of the species present in the strongly acidic oxidizing medium, which may explain the

⁸ R. E. Parker and T. O. Read, J. Chem. Soc. 9 (1962).

pronounced effects of even relatively small amounts of added nitric acid on the course of the dichromate-sulfuric acid oxidations. It is therefore suggested that the reaction may be represented by



with the formed trinitrophenyl nitrate hydrolyzing, either directly or during the course of the drowning, to picric and nitric acids.

The above can only be a rough picture since nothing is known about the nature of the oxidant nor does it illustrate the failure of permanganate or chlorate to effectively substitute for the dichromate. It does, however, explain the failure in attempts to oxidize 1-t-butyl-3,5-dimethyl-2,4,6-trinitrobenzene to phenolic products. In this highly substituted compound, the nitro groups adjacent to the t-butyl group are twisted completely from the plane of the benzene ring with correspondingly decreased pi-orbital overlap. Canonical structures corresponding to VIb and c contribute very much less to resonance stabilization of the transition state or intermediate with a consequent decrease in reaction rate at least as great as would be effected by removing one of the nitro groups.

The above should not be taken to imply that nitric acid has no other function than to supply nucleophile for the displacement reaction. It should be recalled from paper I of this series² that dimethylhexanitrobiphenyl was unreactive with dichromate and sulfuric acid alone under a variety of conditions, but that, with the addition of nitric acid, oxidation proceeded smoothly at ambient temperatures. Coupled with the requirement that the carboxylic acid be a progenitor to the phenol, failure to form the carboxylic acid in the former instance suggests that the nitric acid played a further part in the $CH_3 \rightarrow COOH$ stage of the overall reaction.

EXPERIMENTAL⁹ (CAUTION¹⁰)

Oxidations of 2,4,6-trinitrotoluene. A well-cooled mixture of 2.57 g trinitrotoluene, 30 ml 97% nitric acid, 7.9 ml 30% oleum and 3.6 ml conc sulfuric acid was treated portionwise (20 min) with 11.6 g sodium dichromate dihydrate. The mixture was stirred 2 hr at 0° and 3 hr at room temp, then poured on ice to yield 1.3 g picric acid, m.p. >115°; extraction of the aqueous mother liquor with methylene chloride furnished an additional 0.9 g. The recrystallized sample did not depress the m.p. of an authentic sample, m.p. 122–123°.

A trial using similar quantities of trinitrotoluene and sodium dichromate with 10 ml 97% nitric acid and 35 ml conc sulfuric acid yielded 1.65 g picric acid. A trial using 30 ml nitric acid and 1 ml conc sulfuric acid yielded 1.80 g picric acid. With 30 ml 100% nitric acid and no sulfuric acid, no picric acid was obtained.

Oxidation of 3-bromo-2,4,6-trinitrotoluene. Bromotrinitrotoluene (10 g) in 100 ml 90% nitric acid and 25 ml 30% oleum was cooled in an ice-bath and treated with 30 g sodium dichromate

- M.ps. are uncorrected. Microanalyses were performed by Prof. Mary Aldridge, Dept. of Chemistry, American University, Washington, D.C.
- ¹⁰ Many of the compounds herein described are explosive in nature. Appropriate precautions should be taken in their handling.

dihydrate. The mixture was stirred 1 hr with ice cooling and for 24 hr at room temp. Pouring on ice, extracting the solid product with dil. sodium bicarbonate solution, and acidifying this filtered extract yielded 5.25 g (52%) crude bromopicric acid, m.p. $145-148^{\circ}$. A recrystallized sample, m.p. $150-151^{\circ}$ showed no depression in m.p. on admixture with an authentic sample prepared by nitration of *m*-bromophenol.

Oxidation of 2,4,6-trinitro-m-cresol. As described above for bromotrinitrotoluene, 2.75 g trinitro-m-cresol was oxidized with 20 ml 100% nitric acid, 4.5 ml 30% oleum and 10 g sodium dichromate dihydrate. On drowning the oxidation mixture there was obtained only 1.1 g starting material. Extraction of the filtrate with methylene chloride, however, furnished 0.20 g (12%) trinitroresorcinol, m.p. 175–180°. A sample recrystallized from ether, m.p. 180°, showed identical U.V. spectrum and no depression in m.p. on admixture with an authentic sample.

Oxidation of 1-t-butyl-3,5-dimethyl-2,4,6-trinitrobenzene (xylene musk). Xylene musk (100 g) was dissolved in 900 ml \sim 100% nitric acid and a mixture of 253 ml 30% oleum and 104 ml conc sulfuric acid was added with cooling. This caused the nitro compound to reprecipitate in a microcrystalline form. After 400 g sodium dichromate dihydrate had been added (1 hr) with the temp maintained between 5 and 10°, the well-stirred mixture was kept in an ice-bath for 4–5 hr and at ambient temp for an additional 15 hr.

After quenching on ice, the mixture was allowed to stand until the resinous lower phase had solidified. This was filtered off, ground, digested with a small amount of saturated sodium bicarbonate solution and filtered again to give 75 g crude 5-t-*butyl*-2,4,6-*trinitro*-m-*toluic acid*. On recrystal-lization from carbon tetrachloride there was obtained 61 g (55%), m.p. 163.5-165.5°. (Found: C, 44.29, 43.98; H, 4.15, 4.23; N, 12.60, 12.93; neut. equiv., 328. Calc. for $C_{12}H_{13}N_3O_8$: C, 44.05; H, 4.00; N, 12.84%; neut. equiv., 327).

The drown liquors and the sodium bicarbonate solution were combined and exhaustively extracted with methylene chloride. Evaporation of solvent from the extract left the crude 5-t-butyl-2,4,6-trinitroisophthalic acid which, after recrystallization from methanol-benzene, weighed 2.4 g (2%), m.p. 216° (dec, sintering from 212°). (Found¹¹: C, 41·10; H, 3·83, N, 11·85, 11·67; neut. equiv., 181. Calc. for C₁₂H₁₁N₈O₁₀: C, 40·40; H, 3·11, N, 11·77%; neut. equiv., 178·6).

A similar run, involving 50 g xylene musk, 450 ml 90% nitric acid, 200 ml 30% oleum and 150 g sodium dichromate dihydrate and a reaction time of 75 hr yielded 18 g (32.7%) monocarboxylic acid and 3.6 g (6%) dicarboxylic acid. Oxidation of the monocarboxylic acid under the same conditions yielded about 5% of the dicarboxylic acid.

Refluxing an aqueous solution of the dicarboxylic acid for several hr yielded >90% 1-t-butyl-2,4,6-trinitrobenzene, m.p. 122.5–124°, identical I.R. spectrum and no depression in m.p. on admixture with authentic sample from nitration of t-butylbenzene.

Oxidation of dinitrotoluenes. The routine procedure (see trinitrotoluene) involved 6.2 g 2,4dinitrotoluene, 30 ml 97% nitric acid, 5 ml 30% oleum, 20 g sodium dichromate dihydrate and 1 hr stirring with ice-cooling. On drowning there was obtained 0.45 g insoluble material which softened at 75-80°, melted partially at about 120°, but did not melt completely below 200°; this material was insoluble in bicarbonate solution. After several days' standing in the refrigerator, there crystallized from the drown liquors 4.15 g 2,4-dinitrobenzoic acid (56.4%), m.p. 178-181° (lit. 180°). Extraction of the mother liquor afforded no phenolic material.

A similar reaction with 3.1 g 2,6-dinitrotoluene gave 1.85 g starting material as the only species insoluble in the drown liquors after 2 hr stirring with ice-cooling. Exhaustive extraction of the mother liquor with chloroform and concentration of the latter yielded 0.5 g (33.6%) 2,6-dinitrobenzoic acid, m.p. 204-206° (lit. 202°).

Oxidation of 1-ethyl-2,4,6-trinitrobenzene. To a mixture of 27·3 g ethyltrinitrobenzene, 300 ml 90–100% nitric acid and 116 g sodium dichromate dihydrate was added dropwise with cooling 50 ml 30% oleum. The mixture was stirred 5 hr at room temp, then drowned on ice. The air-dried product, 24 g, was digested with potassium bicarbonate solution, then recrystallized from chloroform to yield as a first crop 17·0 g 2,4,6-trinitroacetophenone, long colorless needles, m.p. 135–136° and two subsequent crops, totalling 5 g (yield 76%), of slightly less pure material. The analytical sample, m.p. 135·5–136·5°, was obtained on a single further recrystallization from chloroform. (Found: C, 37·89, 37·91; H, 1·96, 2·09; N, 15·91, 16·46. Calc. for $C_8H_6N_8O_7$: C, 37·66; H, 1·98; N, 16·47).

¹¹ In company with other high-melting explosives, elemental analyses of this material were poor as a consequence of its tendency to explode rather than burn smoothly in the combustion tube.

Independent synthesis of 2,4,6-trinitroacetophenone. To a solution of ethoxymagnesiomalonic ester, prepared by the procedure of Bowman¹² from 1.4 g magnesium and 16 g diethyl malonate, was added a solution of 14 g 2,4,6-trinitrobenzoyl chloride in a minimal amount of benzene. The addition, with cooling to maintain the temp around 25°, required 30 min; the mixture was stirred an additional hr at room temp. Several ml propionic acid were added, the benzene was removed *in vacuo*, an additional 50 ml propionic acid and 1 ml conc sulfuric acid were added, the mixture refluxed 3 hr and, after addition of a further 5 ml dil. sulfuric acid, the mixture was refluxed for another 40 min.

Drowning the mixture on ice caused the separation of an oil. After neutralizing the drownmixture with sodium bicarbonate and allowing to stand over the week-end, the oil solidified. This material was filtered, washed with water, air dried and dissolved in chloroform. Concentration of the chloroform solution and addition of hexane caused the separation first of a black tarry material, then of ca. 5 g brown crystals which were reserved, and finally of further tarry material. The tarry fractions were combined, dissolved in methylene chloride and filtered through a column of silicic acid. The slightly colored eluate, on evaporation, left a pale brown oil, ca. 2 g, which solidified on standing. This was combined with the previous 5 g and recrystallized from chloroform to yield: first crop, 3.1 g, m.p. $130-134^{\circ}$; second crop, 1.3 g, m.p. $100-110^{\circ}$; final crop, 2.0 g, half oil-half solid.

A further recrystallization of the first crop from chloroform yielded 2.5 g 2,4,6-trinitroacetophenone, m.p. 135–136°, mixture m.p. with material from the oxidation of ethyltrinitrobenzene, 135–136°. IR spectra of the two samples were identical, showing a carbonyl band at 1710 cm⁻¹ (Fluorolube mull).

Oxidation of 2,4,6-trinitrocumene. An oxidation mixture from 4.75 g trinitrocumene, 50 ml 97% nitric acid, 19 g sodium dichromate dihydrate and 8.5 ml 30% oleum, stirred 2 hr with the temp maintained below 10°, allowed to warm to ambient temp over a 2 hr period and stirred for an additional hr, yielded on drowning 2.5 g of an orange-brown product. Recrystallization of this material from chloroform gave 1.4 g 2,4,6-trinitroacetophenone (29.5%), m.p. 135–136°, identical with material prepared as above. Filtration of the combined concentrated recrystallization mother liquors and a methylene chloride extract of the drown liquors through a column of silicic acid afforded an additional 0.45 g (9.5%) of the acetophenone, m.p. 134–136° together with ca. 50 mg of a higher-melting red crystalline by-product.⁷

Oxidations of 2,4,6-trinitrobenzoic acid. A solution of 2.91 g trinitrobenzoic acid in 30 ml 97% nitric acid was treated with 11.6 g sodium dichromate dihydrate and 5 ml 30% oleum while being cooled in an ice bath. The mixture was stirred overnight at room temp, then drowned on ice to yield 1.45 g picric acid. The mother liquor, extracted several times with methylene chloride and the latter solution concentrated, yielded an additional 0.75 g. Both crops melted at 118–120° and showed no carbonyl band in the infrared.

A similar trial, but without the addition of the oleum, yielded on drowning 1.55 g and from the methylene chloride extract 0.7 g, both crops melting at $115-118^{\circ}$ and showing no carbonyl band.

From 5 g trinitrobenzoic acid, dissolved in 50 ml nitric acid and drowned after 43 hr at room temp, there was obtained only 3.5 g starting material. No picric acid had been formed as evidenced by absence of coloration of aqueous solutions.

Oxidation of 3-hydroxy-2,4,6-trinitrobenzoic acid. The hydroxyacid, 6.2 g, was dissolved in 60 ml 90% nitric acid and 20 ml 30% oleum was added with cooling followed by 23.2 g sodium dichromate dihydrate. The mixture was stirred 1 hr in an ice bath, then at room temp overnight. Drowning on ice yielded 1.15 g of a mixture of styphnic acid and starting material. Extraction of the mother liquor with methylene chloride gave another 0.15 g of the same mixture. The combined crops were recrystallized from ether to yield 0.6 g trinitroresorcinol, m.p. 178–180°, no depression on admixture with authentic sample.

¹² R. E. Bowman, J. Chem. Soc. 322 (1950).