continued for another hour. The reaction mixture, decomposed in the usual way, gave a negative test with copper acetate, and after drying, gave only a trace of precipitate with excess ethylmagnesium bromide. Acid was added and the mixture was steam distilled. The distillate contained 4.38 g. (68%) of pentamethylbenzene which melted at 54–55° and in the distilling flask there remained 1.79 g. of a thick yellow oil.

IV. A Grignard reagent was prepared by refluxing together the bromo compound (10 g.), magnesium (1.46 g.), ether (100 cc.) and ethyl bromide (1 cc.). The reaction was very slow, but a considerable amount of the Grignard reagent had precipitated after three hours. One-fourth (25 cc.) of the solution was removed and this, dropped onto crushed dry ice and worked up in the usual way yielded 0.65 g. (34.5%) of pentamethylbenzoic acid and 1.12 g. of a mixture of bromo compound and pentamethylbenzene which melted at 77–123°. To the remainder of the Grignard reagent was added acetyl chloride (10 cc.). The mixture was refluxed for two hours and then excess crushed dry ice was added. After carbonation there was obtained as alkali soluble material only 0.3 g. of a yellow malodorous oil which, however, gave a deep green color when it was dissolved in ether and shaken with copper acetate. The alkali insoluble material (5.81 g.) was steam distilled. The distillate contained 3.17 g. of pentamethylbenzene which melted at 51–55° and the residue contained 1.59 g. of yellowish impure bromopentamethylbenzene which melted at 130–140°. Thus, although the Grignard reagent was not converted into acetopentamethylbenzene or the triketone by acetyl chloride, nevertheless it was destroyed by this reagent and in the process it was converted into pentamethylbenzene.

V. An experiment similar to IV was carried out starting with bromomesitylene (10 g.), magnesium (1.3 g.), ether (30 cc.) and ethyl bromide (8 drops). Carbonation of an aliquot portion gave the known carboxymesitylene which melted at 146–150° and which showed no depression in melting point when mixed with an authentic specimen. The remainder of the Grignard solution was refluxed for three hours with acetyl chloride (6 cc.). After decomposition in the usual way, a distillate of 2.98 g. of mesitylene (b. p. 53° under 23 mm.) was removed. The residue (3.59 g.) was taken up in ether and added slowly to excess ethylmagnesium bromide.[4] No precipitate of the enolate of acetomesitylene was obtained after the mixture had stood overnight, nor was any obtained when half the ether was evaporated. The mixture was decomposed and steam distilled, giving a distillate containing 1.2 g. of bromomesitylene and a residue of dark, thick oil (0.89 g.). Hence the Grignard reagent from bromomesitylene behaved toward acetyl chloride in the same manner as the reagent from bromopentamethylbenzene.

Summary

1. Contrary to the report of Clément, pentamethylphenylmagnesium bromide does not give acetopentamethylbenzene when it reacts with acetyl chloride. The products of the reaction are pentamethylbenzene and condensation products of the acid chloride.

2. Mesitylmagnesium bromide behaves toward acetyl chloride in the same manner as does the reagent from bromopentamethylbenzene, no acetomesitylene resulting. The behavior of the two methylated Grignard reagents differs from that of 2,4,6-triphenyl-phenylmagnesium bromide, which Kohler and Baltzly found gave the aceto compound with acetyl chloride, and these results indicate that two methyl groups in the ortho position to the functional group of a Grignard reagent offer more hindrance to addition than do two phenyl groups similarly placed.

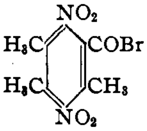
MINNEAPOLIS, MINN. RECEIVED MARCH 15, 1937

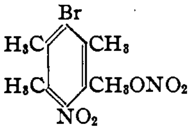
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Polymethylbenzenes. XVIII. The Action of Nitric Acid upon Bromodurene[1]

BY LEE IRVIN SMITH, F. LOWELL TAYLOR AND ISABELLA M. WEBSTER

In a recent paper, Smith and Tenenbaum[2] have shown that the product obtained by Willstätter and Kubli[3] by action of fuming nitric acid upon bromodurene, and regarded by them as dinitrodurylic acid bromide (I), could not possibly be an acid bromide. Moreover, the analyses of Smith and Tenenbaum, as well as those of Willstätter and Kubli, agreed much better with the formula $C_{10}H_{11}O_5N_2Br$ than with the formula $C_{10}H_9O_5N_2Br$ (I). The chief reactions of the substance which was discovered by Smith and Tenenbaum were the ready conversion to 3-bromo-5,6-dinitropseu-


I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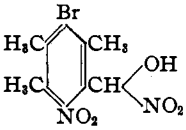
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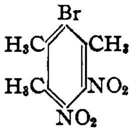
IV

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(1) Paper XVII. THIS JOURNAL, 59, 1078 (1937).

(2) Smith and Tenenbaum, *ibid.*, 57, 1293 (1935).

(3) Willstätter and Kubli, *Ber.*, 42, 4151 (1909).

documene (IV) by action of cold concentrated sulfuric acid, and reduction to aminodurene (V). On the basis of these reactions, Smith and Tenenbaum, assuming that the skeleton of bromonitrodurene was still intact in the substance, suggested provisionally that the substance might possess structure II or III. Further work has shown that II, a benzyl nitrate, is the most probable structure for this substance.

The formation of IV ($C_9H_9O_4N_2Br$) from the W.-K. compound ($C_{10}H_{11}O_5N_2Br$) must proceed by elimination of the elements CH_2O. Close observation of the reaction resulted in the detection of the odor of formaldehyde. It was not possible to obtain enough formaldehyde from the reaction to prepare a derivative, due, no doubt, to the destructive action of sulfuric acid upon formaldehyde. A color test with guaiacol carbonate was apparently positive, but was rather indefinite because of the interfering colors.

The W.-K. compound, warmed in acetic anhydride with a little sulfuric acid, gave a substance (VI) having the composition $C_{12}H_{14}O_4NBr$. This substance was the acetate of a bromonitropseudocumyl alcohol, for it was obtained also by acetylation of the substance $C_{10}H_{12}O_3NBr$ (VII) which resulted *along with nitric* acid when the W.-K. compound in 50% acetic acid was refluxed with dilute (0.1 *N*) sulfuric acid. Only traces of nitrous acid were produced in this reaction. The acetate (VI) was hydrolyzed to the alcohol (VII) by the action of alcoholic hydrochloric acid.

When the W.-K. compound was dissolved in absolute ethanol and subjected to the action of sodium ethoxide; there resulted sodium *nitrite* and an orange-yellow solid having the composition $C_{10}H_{10}O_3NBr$ (VIII) which was an aldehyde. A solution of the aldehyde in acetone when treated with alkali, turned green, then blue, and finally a purple substance precipitated. Because of this color reaction, VIII was considered to be an ortho nitro aldehyde. A synthesis of the *o*-nitro-*m*-bromo aldehyde VIII was attempted, but although 6-nitropseudocumyl aldehyde was readily prepared, it could not be brominated, and the action of bromine on durylic aldehyde apparently converted it to a polybromopolymethylbenzyl benzoate.

Since the action of sulfuric acid converts the W.-K. compound into IV, the skeleton D must be intact. Further since reduction gives rise to aminodurene, the fourth side chain carbon must be in place (E). Starting with E($C_{10}H_9O_2Br$) the elements of water and nitrogen dioxide must be added to make up the composition $C_{10}H_{11}O_5N_2Br$ of the W.-K. compound. While the fourth methyl group has been oxidized, it must be in a state such that it can be reduced to methyl again. Both II and III would account for the reduction to aminodurene, but in addition to these two formulas, structures A, B, and C were considered. The chief objection to formulas II and III was the fact that the W.-K. compound gave different products when hydrolyzed in acid and basic media, respectively. Formula C was eliminated entirely on two counts: it would require migration of a methyl group to form IV, and it would lead to an ortho bromo aldehyde for VIII whereas VIII is quite definitely an ortho nitro aldehyde. Formula B also was discarded because it would require a rearrangement with migration of a nitro group to produce IV. Formula A with the trimethylene oxide ring can account for all of the known reactions of the W.-K. compound without the necessity of recourse to any rearrangements, and at first this formula was selected as best representing the chemical behavior of the W.-K. compound. However, Nef[4] and especially Klason and Carlson[5] have shown that the alkaline hydrolysis of benzyl and other nitrates leads to aldehydes and nitrite[6] and that the intermediate compounds are probably peroxides.

$$RCH_2NO_3 + KOH \longrightarrow RCH_2OOH + KNO_2$$
$$RCH_2OOH \longrightarrow RCHO + H_2O$$

With these facts in view, the chief objection to structure II was eliminated and it became necessary to consider this formula as very likely correct. To decide this point, the alcohol VII was converted to the nitrate *via* the chloride IX, and the iodide X. The nitrate so prepared was identical in all respects with the W.-K. compound. While this proof of the structure of the W.-K. compound is not wholly explicit because the intermediates were themselves derived from the W.-K. compound, yet the synthesis, combined with the reversibility of many of the transformations, constitute good implicit proof. Curiously enough, the alcohol VII cannot be converted to the chloride IX by boiling it for an hour with alcoholic hydrochloric acid, a procedure which con-

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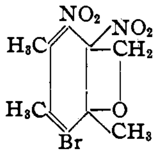
[4] Nef, *Ann.*, **309**, 171 (1899).

[5] (a) Klason and Carlson, *Ber.*, **39**, 2752 (1906); (b) *ibid.*, **40**, 4183 (1907); (c) *ibid.*, **40**, 4191 (1907).

[6] This work was called to the attention of the Authors by the Referee.



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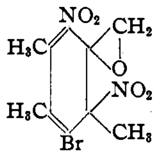

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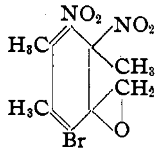

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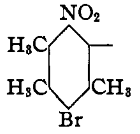

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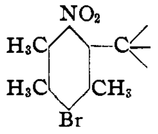
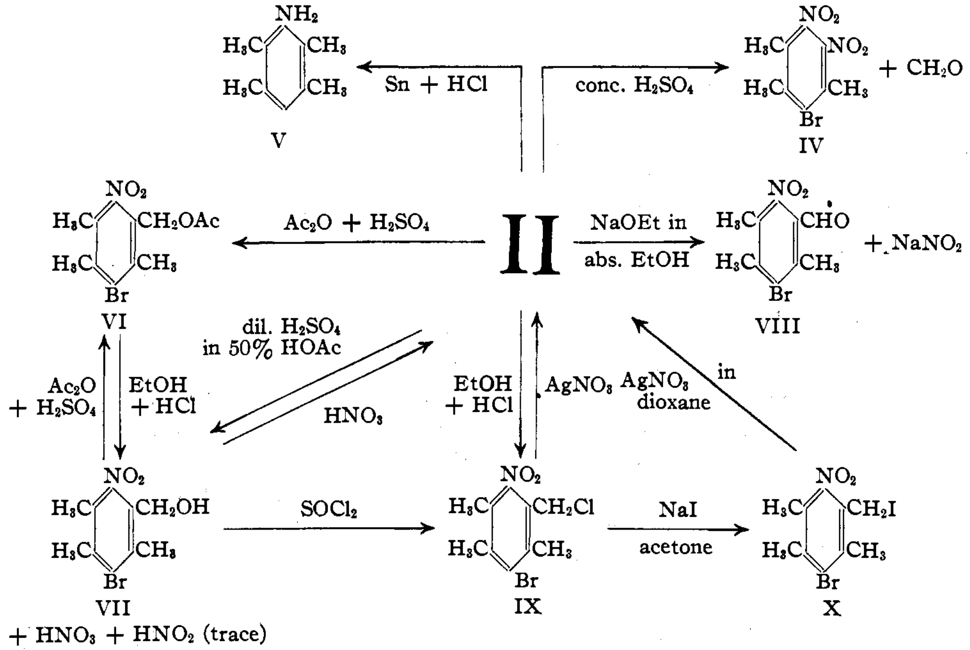


E



verts the W.-K. compound almost quantitatively to the chloride. These facts indicate that the alcohol is not an intermediate in the latter transformation. Moreover, once the chloride is formed, it is not readily hydrolyzed to the alcohol although the acetate can be converted into the alcohol with ease.

The formation of compounds analogous to the W.-K. compound derived from bromodurene appears to be a general reaction of the highly methylated benzenes and their derivatives. Further work, now in progress, indicates that pentamethylbenzene, dibromodurene, dinitrodurene and possibly some other substances all behave toward cold fuming nitric acid in the same manner that bromodurene does.

While the present work establishes definitely the analogy between the W.-K. compound and Nef's benzyl nitrate, the questions as to whether these compounds are actually nitrates, and if so, the mechanism of their hydrolyses in acid and basic solutions, remain unsettled. Klason and Carlson[5] believed that the nitrates were best represented as derivatives of a per-acid HOONO, but this hypothesis merely shifts the scope of the problem from a peculiar basic hydrolysis to a peculiar acid hydrolysis. It may be that a relationship exists among the forms represented by II, III, and A. The exact relationship, if any, is a problem for future work and it is the present opinion of the authors that while II probably best represents the structure for the W.-K. compound, structure A is not yet definitely excluded.

This work was made possible by a grant from the Fluid Research Fund of the Graduate School of the University of Minnesota.

Experimental Part

Action of Concentrated Sulfuric Acid upon the W.-K. Compound.—As shown by Smith and Tenenbaum, the product of this reaction was IV, and the experiments described below were directed toward detection of formaldehyde. Guaiacol carbonate was dissolved in 90% alcohol and the solution was treated with a little ferric chloride. The W.–K. compound was suspended in sulfuric acid (yellow to orange color) and the solution of guaiacol carbonate was added carefully. At the junction of the two solutions a pink to red ring formed (positive test).

Although it was not likely that formaldehyde could be removed from the sulfuric acid in quantity sufficient for the preparation of a derivative, since sulfuric acid polymerizes and dehydrates it, several attempts were made to isolate the aldehyde. The W.–K. compound (0.5 g.) was placed in a small flask with sulfuric acid (5 cc.). The mixture was warmed while a current of air was passed through it (forty-five minutes) and then bubbled through cold water. The water solution gave no precipitate with dimedon. In a similar experiment, the vapors from the decomposition of the W.–K. compound were passed through a liquid air trap. The condensate in the trap was white when cold, but when warmed to room temperature it became red and had a strong odor of oxides of nitrogen. Nevertheless the water solution was neutralized with bicarbonate and treated with dimedon. No precipitate was obtained.

The W.–K. compound (1 g.) was dissolved in dry ether (50 cc.), sulfuric acid (10 cc.) was added and the ether was slowly distilled through a condenser and an adapter dipping below the surface of cold water. As the ether distilled, fresh ether was added and the distillation was continued until 200 cc. of ether had distilled in four hours. The (neutral) water layer was separated, and the ether was extracted once with water. Dimedon (1.1 g.) in alcohol was added to the combined aqueous solutions, the mixture was warmed and allowed to stand overnight. No derivative of formaldehyde resulted.[7]

2,4,5-Trimethyl-3-bromo-6-nitro-benzyl Alcohol (VII).—The W.–K. compound (3 g.) was dissolved in acetic acid (50 cc.) at room temperature. Water (50 cc.) and sulfuric acid (2 *N*, 5 cc.) were added (precipitation) and the mixture was refluxed in an apparatus which was connected to a wash bottle containing aqueous potassium hydroxide (130 cc., 2%). There was no noticeable evolution of gas, and after refluxing for fourteen to fifteen hours, air was drawn through the apparatus in order to sweep out any oxides of nitrogen. Water was then added and the precipitate (1.8 g.) was removed. The filtrate gave a positive test for nitrate ion with ferrous sulfate and sulfuric acid; a test for nitrite ion was negative, and the solution in the wash bottle when acidified with acetic acid and warmed with Griess' reagent (sulfanilic acid and α-naphthylamine in dilute acetic acid) developed only a faint red color. No more than traces of nitrite were present. The precipitate (m. p. 100–150°) was refluxed with ethanol (25 cc.) and hydrochloric acid (10 cc.) for fifteen minutes. The hot solution was filtered and the filtrate was cooled. The product was removed, washed, and crystallized first from alcohol (20 cc.) and then from benzene (12 cc.)–petroleum ether (5 cc.). The substance was white and melted at 188°.

Anal. Calcd. for $C_{10}H_{12}O_3NBr$: C, 43.78; H, 4.41. Found: C, 43.75, 43.50, 43.95, 43.88; H, 4.38, 4.54, 4.41, 4.38.

When the alcohol (0.38 g.) was dropped into fuming nitric acid (10 cc., d. 1.5) at 0°, a red solution resulted which gradually became lighter and a white solid separated. The product (0.43 g., 97%) was the W.–K. compound, m. p. and mixed m. p. 118–122°.

Acetate (VI).—The alcohol was treated with acetic anhydride and a drop of sulfuric acid; dilution of the mixture precipitated the acetate. Crystallized from ethanol it melted at 85°.

The W.–K. compound (3 g.) was covered with acetic anhydride (20 cc.). Sulfuric acid (6 drops) was added and the mixture was warmed gently (not above 40°) for three days. The mixture when poured into ice water precipitated unchanged material. This was removed and while still damp was treated with the same quantities of reagents. There was a vigorous reaction. The mixture was heated at 70° for twenty-one hours. The product, isolated as before, was crystallized first from ethanol (10 cc.) and then from petroleum ether (12 cc.). It weighed 1.35 g. and melted at 86°. There was no depression in the melting point when the substance was mixed with the acetate prepared from the alcohol.

Anal. Calcd. for $C_{12}H_{14}O_4NBr$: C, 45.57; H, 4.46. Found: C, 45.14, 45.41, 45.02; H, 4.10, 4.50, 4.05.

When the acetate (0.21 g.) was refluxed for fifteen minutes with alcohol (6 cc.) and hydrochloric acid (2 cc.), the product was the alcohol VII, m. p. and mixed m. p., 185–190°.

Chloride (IX).—The W.–K. compound (1 g.) was refluxed with alcohol (40 cc.) and hydrochloric acid (20 cc.) for an hour. The clear yellow solution, when cooled, deposited 1.01 g. of white needles which melted at 110–112°. After crystallization from ethanol or dilute acetic acid, the substance melted at 112.5–113.5°. The chloride (0.85 g.) was also formed when the W.–K. compound (2 g.) was refluxed for sixteen hours with acetone (50 cc.), water (10 cc.) and hydrochloric acid (10 cc.), although the product, when prepared this way, was quite impure.[8]

Anal. Calcd. for $C_{10}H_{11}O_2NBrCl$: C, 41.03; H, 3.79. Found: C, 41.55, 41.85, 41.72; H, 4.23, 4.03, 3.78.

The alcohol (VII) was refluxed with alcoholic hydrochloric acid for one hour and the reaction mixture then allowed to stand overnight. The product was unchanged alcohol. Since this procedure converts the W.–K. compound smoothly into the chloride, the alcohol cannot be an intermediate.

The alcohol (VII) (1 g.) was added to thionyl chloride (5 cc.). A clear solution resulted. The mixture was warmed for five minutes, the excess thionyl chloride was removed under reduced pressure and the yellow residue was crystallized from dilute acetic acid. The substance melted at 107–110° and the melting point was not depressed by mixture with a specimen of the chloride prepared directly from the W.–K. compound.

Hydrolysis of the chloride (0.57 g.) by boiling it with alcohol (50 cc.), water (10 cc.) and potassium carbonate (2 g.) yielded 0.44 g. of product which was essentially unchanged chloride, although the melting point was lowered about 15°.

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[7] Klein and Linser, *Mikrochemie*, Pregl Festschr., 204 (1929).

[8] The preparation of the chloride by both methods was first carried out by J. A. Anthes.

Iodide (X).—The chloride IX (0.86 g.) was added to a solution of sodium iodide in acetone (30 cc., 10%). The reaction was practically instantaneous; sodium chloride was precipitated at once. The mixture was warmed gently for two or three minutes and then allowed to stand for half an hour. The precipitate of crude sodium chloride was removed (weight 0.19 g., theoretical, 0.17 g.) and the filtrate was poured into water. The product weighed 0.97 g. (86%) and melted at 111–113°. Addition of the chloride (m. p. 112–113°) depressed the melting point to 91–96°. After two crystallizations from acetone, the substance formed long white needles which melted at 113–115°.

Anal. Calcd. for $C_{10}H_{11}O_2NBrI$: C, 31.26; H, 2.89. Found: C, 31.30, 31.38; H, 3.33, 3.19.

Nitrate (II) (The W.–K. Compound).—Although the chloride (IX) readily reacted with silver nitrate in ether or in alcohol, precipitating nearly the theoretical amount of silver chloride, the organic product was a mixture from which no pure material could be separated. The reaction was apparently complicated by hydrolysis, for the impure material, even the oily residues obtained by evaporating the mother liquors after crystallization, gave the W.–K. compound when they were dropped into fuming nitric acid.

The iodide, however, could be converted smoothly to the nitrate. The iodide (0.65 g.) and silver nitrate (1 g.) were refluxed in dry dioxane (20 cc.) for two hours, and then kept at 100° for seventeen hours longer. The inorganic material was removed and the dioxane solution was poured into water. The precipitated solid (0.43 g.) was removed and crystallized from alcohol. The melting point, 121–122.5°, was not depressed by addition of the W.–K. compound.

2,4,5 - Trimethyl - 3 - bromo - 6 - nitrobenzaldehyde (VIII).—The W.–K. compound (3 g.) was added to absolute ethanol (25 cc.). The mixture was heated to boiling and to it was added dropwise 2–3 cc. of a solution prepared from sodium (0.3 g.) and absolute ethanol (50 cc.). The color became orange yellow and all the solid dissolved. When cooled, unchanged material precipitated. The mixture was heated again and the alkali added, 1–2 cc. at a time until the transient greenish-yellow color became permanent (30 cc. of the alkali, thirty minutes total time). A precipitate of sodium nitrite separated out. The cooled solution was poured into dilute acetic acid and the solid was filtered off. The filtrate was examined for nitrite ion (positive). The product, crystallized first from ethanol (20 cc.)-benzene (10 cc.) and then from petroleum ether, formed faintly orange needles melting at 193°.

Anal. Calcd. for $C_{10}H_{10}O_3NBr$: C, 44.12; H, 3.71. Found: C, 43.89, 44.09; H, 3.81, 3.67.

The aldehyde could be sublimed. It was sensitive to light, which caused a greenish coloration. A small portion in aqueous acetone was warmed with potassium hydroxide. The solution turned green, then blue, and finally a purple solid precipitated. The same color changes were observed when the W.–K. compound was subjected to the action of alcoholic alkali.

Action of Oxidizing Agents upon the W.–K. Compound.—The substance was rather stable toward oxidizing agents, although it was attacked slowly. After refluxing it with permanganate in 50% acetic acid and sulfuric acid (0.5 cc., 2 *N*) for one and one-half hours, the only isolable product was unchanged material (0.1 g. from 0.3 g.). A similar treatment with sodium dichromate (0.4 g.) in acetic acid (10 cc.) also gave unchanged material (0.28 g. from 0.32 g.).

Bromination of Durylic Aldehyde.—Bromine (6.7 g.) was added to a solution of the aldehyde (6 g.) in cold sulfuric acid (20 cc.) and the mixture was allowed to stand at room temperature for twenty-three hours. The solution was poured into ice water; the small amount of free bromine was removed with bisulfite. The product was removed, extracted with petroleum ether, and the solid residue was crystallized from benzene. It formed colorless needles melting at 219–220° and weighed 1.1 g. It was probably α,2,5-tribromoduryl-2,5-dibromodurylate. It was analyzed but was not examined further.

Anal. Calcd. for $C_{20}H_{19}O_2Br_5$: C, 34.75; H, 2.77. Found: C, 34.32; H, 3.07.

Nitration of Durylic Aldehyde.—The aldehyde (3 g.) and sulfuric acid (10 cc.) were cooled in a freezing mixture (−8°) and nitrated by slow addition (one hour) of a solution of potassium nitrate (2 g.) in sulfuric acid (10 cc.). The cherry red solution after standing for thirty minutes at −15° was poured into ice water. The solid was removed, triturated with bicarbonate, and washed with water. It was dissolved in ethanol (25 cc.), the hot solution was filtered and the filtrate, slowly cooled, deposited 1.6 g. of fine plates melting at 139–140°. The aldehyde could not be brominated.

Summary

1. A further study of the reaction between bromodurene and fuming nitric acid has shown that of the formulas heretofore suggested, II, 2-nitro-5-bromo-3,4,6-trimethylbenzyl nitrate, at present best represents the chemical behavior of the product.

2. The reaction appears to be a general property of the highly alkylated benzenes and certain of their derivatives.

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