proved to be better than 95%, and also on the consistency of the other measurements.

We present in Table IV the data for a typical run. The quantity D in the table is

$$\log_{10}\frac{x+c}{x} - \frac{c}{c+r}\log_{10}\frac{x+c+r}{x}$$

which, according to the kinetic equation used, is expected to be proportional to time. Figure 2 shows the plot of this quantity against time.

Summary

The rate of the reaction between methanol and *p*-methoxybenzhydryl chloride in dilute nitrobenzene solution under irreversible conditions has been studied as a function of the methanol concentration from 0.07 to 0.21 M. There is a bimolecular reaction involving one molecule of the chloride and one of methanol and at the same time a trimolecular reaction involving one molecule of chloride and two of methanol. It is suggested that mechanisms of higher order appear as the alcohol is made more concentrated, as seems probable also from the work of Farinacci and Hammett.

Vapor pressure measurements have been made, showing that methanol is not associated in nitrobenzene solutions of the strength used.

The solubility of triethylamine hydrochloride in nitrobenzene is altered markedly by small concentrations of methanol. A series of solubility measurements are interpreted as giving evidence of specific solvation of the chloride ion by one and by two molecules of methanol.

Triethylamine is inert toward *p*-methoxybenzhydryl chloride in nitrobenzene solution, at least in comparison to like concentrations of methanol. This makes it possible to use triethylamine to combine with hydrogen chloride liberated in the alcoholytic reaction and thus to make the reaction effectively irreversible.

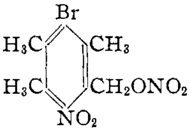
CAMBRIDGE, MASSACHSETTS RECEIVED MARCH 27, 1940

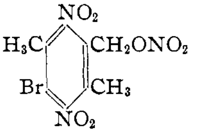
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

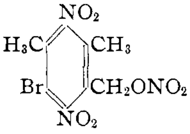
Polymethylbenzenes. XXVI. The Nitration of Bromopentamethylbenzene

BY LEE IRVIN SMITH AND JAMES W. HORNER, JR.[2]

When bromodurene is nitrated under certain circumstances, the product is 6-nitro-3-bromo-2,4,5-trimethylbenzyl nitrate, I.[3] Similarly, 5-bromopseudocumene or its 3,6-dinitro derivative can be attacked at the side chain by nitric acid,[4] and the product has been shown to consist of an inseparable mixture of two benzyl nitrates, II and III.[5]


I


II


III

These nitrates usually can be converted into aromatic nitro compounds by action of sulfuric acid. Peculiar orientation effects frequently are observed when polyalkylbenzenes are converted into substitution products by reactions in which an alkyl group is simultaneously removed or replaced.[6] The most striking of these effects is perhaps that shown by the nitration of pentamethylbenzene[7] and of pentaethylbenzene[8] to dinitrotetraalkylbenzenes in yields of over 70%, and with an ortho orientation of the nitro groups in the methyl derivative and a para orientation in the ethyl derivative. The easy decomposition of benzyl nitrates to nitro compounds indicates that these substances may well be intermediates in those reactions in which alkyl groups are replaced by nitro groups and that the peculiar orientation effects observed in such reactions are due to factors which determine which one of several alkyl groups will be attacked.

In order to study further these effects, the nitration of bromopentamethylbenzene (IV) has been examined. When fuming nitric acid was added to a solution of IV in chloroform, there resulted an oily solid from which was isolated a mixture of two isomeric bromotetramethylbenzyl nitrates, V

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(1) XXV, THIS JOURNAL, **62**, 771 (1940).

(2) Abstracted from a thesis by James W. Horner, Jr., submitted to the Graduate Faculty of the University of Minnesota, in partial fulfilment of the requirements for the Ph.D. degree, January, 1940.

(3) (a) Smith and Tenenbaum, THIS JOURNAL, **57**, 1293 (1935); (b) Smith, Taylor and Webster, *ibid.*, **59**, 1082 (1937).

(4) Huender, *Rec. trav. chim.*, **34**, 25 (1915).

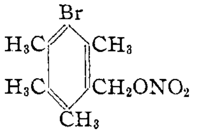
(5) Rinkes, *ibid.*, **57**, 1405 (1938); *ibid.*, **58**, 218, 538 (1939).

(6) (a) Baur, *Ber.*, **27**, 1614 (1894); (b) Barbier, *Helv. Chim. Acta*, **11**, 152, 157 (1928); (c) de Cappeller, *ibid.*, **11**, 426 (1928); (d) Battegay and Kappeler, *Bull. soc. chim.*, **35**, 989 (1924).

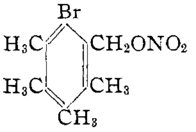
(7) Smith and Harris, THIS JOURNAL, **57**, 1289 (1935).

(8) Smith and Guss, unpublished work.

and VI, and a substance A, melting at 66.5–70° containing halogen but no nitrogen. The two benzyl nitrates formed an inseparable mixture and like the inseparable mixture of II and III, the mixture of V and VI could not be converted into any separable mixture of isomers. When the nitrates were subjected to the action of sulfuric acid, there resulted an inseparable mixture of bromo nitro tetramethylbenzenes, VII and VIII. When this mixture of nitro compounds was reduced by tin and hydrochloric acid, the product was a mixture of bromoaminoisodurene (IX) and aminoprehnitene (X), the halogen having been removed from the *o*-halo nitro compound, and not from the *m*-isomer.[9] The two amines produced in this way were separated; the mixture yielded approximately 0.6 mole of IX and 0.4 mole of X. No trace of any derivative of durene could be obtained from the mixture of amines. It followed, therefore, that the mixture of bromo nitro compounds contained about 60% of VII and 40% of VIII, and, in turn, that the nitration of bromopentamethylbenzene gave, as one of the products, a mixture of the nitrates V and VI containing about 60% of V.



V



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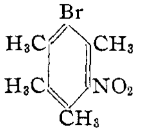
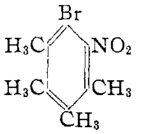
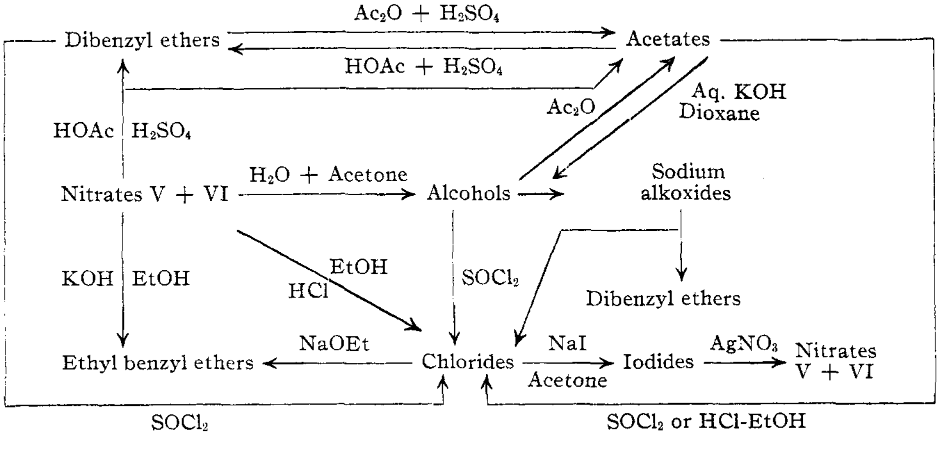


VII



VIII

REACTIONS OF THE BENZYL NITRATES V + VI



The reactions of the nitrates and their derivatives are summarized in the chart. It is particularly noteworthy that these nitrates, in contrast to I, II and III, never produced any aldehydes upon hydrolysis.[10]

Substance A was obtained from the mother liquors after the crude nitration product was crystallized from methanol. Acetylation of A produced the same acetate mixture as that obtained from V + VI. This fact made it possible to prepare all the benzyl derivatives described above directly from the entire solid nitration product rather than from the purified nitrates only. These properties of A, together with the low melting point and the analysis, indicated that A was a mixture of the benzyl methyl ethers derived from V and VI.

The complete series of compounds (chlorides, iodides, acetates and nitrates) derived from each of the bromotetramethylbenzenes, was synthesized. In every case, the melting point of the derivative from bromopentamethylbenzene was not depressed by addition of the synthetic derivative from either prehnitene or isodurene, but a marked change in the melting point resulted when the durene derivative was added.

Experimental Part[11]

Nitration of Bromopentamethylbenzene.—Fuming nitric acid (d. 1.52, 22 cc.) was added over a period of fifteen minutes to a vigorously stirred solution of bromopentamethylbenzene (10 g.) in chloroform (150 cc.) at −11°.

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[9] Nicolet, *et al.*, THIS JOURNAL, **43**, 2081 (1921); **49**, 1796, 1801, 1806, 1810 (1927).

[10] (a) Nef, *Ann.*, **309**, 126 (1899); (b) Klason and Carlson, *Ber.*, **39**, 2752 (1906); *ibid.*, **40**, 4183 (1907); (c) Carlson, *ibid.*, **40**, 4191 (1907).

[11] Microanalyses by J. W. Opie and E. E. Renfrew.

During the reaction, the temperature rose to −1°; the mixture was poured immediately into cold water. The chloroform layer was removed and washed with carbonate (5%) and then with water. Removal of the solvent left a yellow oily solid (13 g.) which was crystallized from methanol (80 cc.) at room temperature. Succeeding crops of crystals were obtained by evaporating the filtrates to half their volume and cooling in ice. In this way the following material was obtained: first crop, 3.56 g., m. p. 69–83°; second crop, 3.00 g., m. p. 53–59°; third crop, 0.77 g., m. p. 55–56°; fourth crop, 0.41 g., oily, m. p. 50–67°; residue, 3.73 g., orange oil. The first crop was principally V + VI. This could be recrystallized from methanol, ethanol, ether, acetic acid, ethyl acetate or petroleum ether. After the two crystallizations from petroleum ether, it melted at 78–84°. Further crystallization sometimes gave a product with a slightly higher melting point, but the melting point range was not decreased.

Anal. Calcd. for $C_{11}H_{14}O_3NBr$: C, 45.83; H, 4.90. Found: C, 46.00; H, 4.90.

After three crystallizations of the fourth crop from methanol, the substance A, m. p. 66.5–70°, was obtained. This substance was most likely a mixture of benzyl methyl ethers. It was not a mixture of the alcohols (m. p. 170°) and bromopentamethylbenzene (m. p. 160°) because a mixture of these two substances melted at 160–164.5°.

Anal. Calcd. for $C_{12}H_{17}OBr$: C, 56.03; H, 6.61. Found: C, 55.57; H, 6.11.

The nature of the nitration product depends greatly upon the amount of acid used, and upon the time allowed for the reaction. More vigorous conditions yield a very oily product from which only the product of exhaustive nitration, 4-bromo-5,6-dinitrohemimellithene, can be isolated. As an example, the following may be cited: pentamethylbromobenzene (29.3 g.) in chloroform (130 cc.) was added slowly (two hours) to a well-stirred mixture of sulfuric acid (381 cc.), fuming nitric acid (d. 1.52, 88 cc.) and chloroform (500 cc.) at 25–31°. The product (34 g.), isolated as in method 1, consisted of 4-bromo-5,6-dinitrohemimellithene, m. p. 201–202° (5.9 g.) and an oil (27.7 g.) which on standing in sulfuric acid slowly deposited more of the bromo dinitro compound. The solid was identified by comparison with an authentic specimen of 4-bromo-5,6-dinitrohemimellithene,[12] and by analysis.

Anal. Calcd. for $C_9H_9O_4N_2Br$: C, 37.38; H, 3.12. Found: C, 37.74; H, 3.49.

The Dibenzyl Ethers.—The nitrates (3.43 g.) were refluxed in acetic acid (50 cc.) containing water (50 cc.) and sulfuric acid (2 *N*, 5 cc.) for four hours. The cooled reaction mixture deposited a white solid (2.27 g.) melting at 80–165°. Extraction of this material with hot ethanol left a residue of the ether mixture (0.83 g.) melting at 202–218°. Crystallization of this material from chloroform–ethanol or benzene did not give a product with a sharper melting point. This mixture of dibenzyl ethers had the widest melting point range of any of the derivatives of the nitrates; since it is derived from two molecules of V and VI, three benzyl ethers probably are present.

Anal. Calcd. for $C_{22}H_{28}OBr_2$: C, 56.40; H, 6.03; active H, 0; carbonyl, 0. Found: C, 56.44, 56.45; H, 5.79, 6.33; active H, 0; carbonyl, 0.

The alcoholic extract, when concentrated and cooled, deposited the acetates (0.86 g.) melting at 72–78°.

The Acetates. (a) The **benzyl ethers** (0.55 g.) were allowed to stand for seventeen hours in acetic anhydride (10 cc.) and sulfuric acid (5 drops). The solution was poured into water and the solid (0.65 g., 100%) was removed and crystallized from petroleum ether. It then melted at 82–83.5°.

Anal. Calcd. for $C_{13}H_{17}O_2Br$: C, 54.73; H, 6.01. Found: C, 54.92; H, 6.27.

(b) The **alcohols** (0.19 g.), after the above treatment, gave the same acetate, m. p. 77.5–83.5° after one crystallization from methanol.

(c) The **chlorides** were largely unchanged when treated as above, but the **iodides** (0.15 g.) were readily converted into the acetates by refluxing in acetic acid (5 cc.) with potassium acetate (0.21 g.) for two hours. The product melted at 81–86°.

When the acetates (0.21 g.) were refluxed for eleven hours in acetic acid (4 cc.) containing water (3 cc.) and sulfuric acid (5 drops), the product (0.17 g.), m. p. 140–170°, was the **dibenzyl ether** mixture. After two crystallizations from chloroform–ethanol, it melted at 211–219°.

(d) Substance A (0.63 g.) was allowed to stand for thirty-five minutes in acetic anhydride (5 cc.) and concentrated sulfuric acid (5 drops). The mixture was poured into water and the solid was removed and crystallized three times from methanol. It weighed 0.21 g., melted at 78–82°, and gave no depression in m. p. when mixed with the acetates prepared in other ways. Similarly, substance A (0.18 g.), hydrolyzed with acetic acid (2 cc.), water (2 cc.) and sulfuric acid (2 *N*, 0.2 cc.) gave an impure product which melted at 60–120°. Acetylation of this material produced the acetates (0.13 g.) melting at 77.5–81.5° without any purification.

(e) The entire nitration product, consisting of the nitrates and substance A, was subjected to successive hydrolysis and acetylation as described under (d). The acetates were obtained in good yield, although apparently there was an impurity present throughout which was best removed by steam distillation before the final acetylation. Further, the crude hydrolysis product could be converted into the alcohols in good yield by the dioxane–potassium hydroxide method, but again the rather persistent impurity was best removed by steam distillation before the final hydrolysis to the alcohols.

The Alcohols.—(a) The acetates (0.67 g.) were refluxed for six hours in dioxane (10 cc.) and potassium hydroxide (25%, 10 cc.). The solution was diluted with water and the solid was removed and crystallized first from ethanol and then from methanol. It weighed 0.35 g. (61%) and melted at 168–171°. It crystallized sometimes as brittle glassy rods, sometimes in clumps of heavy white needles.

Anal. Calcd. for $C_{11}H_{15}OBr$: C, 54.31; H, 6.22; active H, 1 mole; carbonyl, 0. Found: C, 54.30; H, 6.08; active H, 1.0 mole; carbonyl, 0.

(b) The **nitrates** (0.52 g.) were heated with acetone (9 cc.) and water (4 cc.) to 200–240° in a sealed tube for

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[12] Smith and Moyle, THIS JOURNAL, **58**, 9 (1936).

twenty-three hours. The product, after crystallization first from benzene and then from methanol, melted at 168.5–170°.

The chlorides. (a) The **alcohols** (0.97 g.) were refluxed with thionyl chloride for fifteen minutes. Excess reagent was pumped off and the residue (1.04 g., 100%), if it melted below 110–113°, was crystallized from methanol or ethyl acetate.

Anal. Calcd. for $C_{11}H_{14}ClBr$: C, 50.48; H, 5.40. Found: C, 49.88, 50.12; H, 5.47, 5.59.

(b) The **acetates** (0.20 g.), heated with thionyl chloride (3.2 cc.) in a sealed tube at 112° for twenty hours, gave the **chlorides,** m. p. 109–110.5°. When a solution of the acetates (0.40 g.) in ethanol (12 cc.) and hydrochloric acid (4 cc.) was refluxed for five hours, the **chlorides,** m. p. 108–112.5°, were produced.

(c) The **dibenzyl ether** (0.14 g.) was heated for forty-two hours at 122° in a sealed tube with thionyl chloride (3 cc.). The product (0.097 g., 62%) was the chloride. After crystallization from ethanol it melted at 105–110.5°.

(d) The **nitrates** (1.51 g.) were refluxed for a day in ethanol (24 cc.) and hydrochloric acid (8 cc.). The solution was poured into water and the solid (0.18 g.) was removed and crystallized from ethanol. It was the chloride, m. p. 111–112°. The aqueous filtrate contained 1.21 g. of orange oil from which some solid material, m. p. 75–100°, could be isolated, but it could not be purified further. The oil gave an immediate precipitate with silver nitrate.

When the chloride (0.25 g.) in toluene (5 cc.) was refluxed for five hours with the sodium derivative of the alcohols (prepared by refluxing the alcohols (0.23 g.) with sodium (0.023 g.) in toluene (5 cc.) until the white sodium derivative was formed), the product was the **dibenzyl ether.** The reaction mixture was filtered, water was added to the filtrate and the toluene was removed by steam distillation. The residue was extracted with chloroform and crystallized from methanol or benzene. The product melted at 200.5–211°.

The Iodides.—The chlorides (1.04 g.) were warmed briefly with an acetone solution of sodium iodide (10%, 20 cc.) and the solution was then allowed to stand for an hour. Addition of water precipitated a solid (1.34 g., 95%) which was removed and crystallized from acetone or ethyl acetate. It then melted at 133.5–136°.

Anal. Calcd. for $C_{11}H_{14}BrI$: C, 37.40; H, 4.00. Found: C, 37.25; H, 3.97.

The Benzyl Ethyl Ethers.—The nitrates (1.00 g.) were refluxed for eighty-five minutes with ethanol (25 cc.) containing potassium hydroxide (2.19 g.). The inorganic precipitate contained 1.8% of nitrite. The alcoholic filtrate was diluted with water and the solid was removed and crystallized twice from aqueous methanol. It melted at 51–53.5°.

Anal. Calcd. for $C_{13}H_{19}OBr$: C, 57.55; H, 7.06. Found: C, 56.70; H, 7.30.

When the chlorides (0.11 g.) were refluxed for seven hours with sodium ethoxide in ethanol (0.21 g. of sodium, 10 cc. of dry ethanol), the product was the benzyl ethyl ether, m. p. about 50°.

The Bromonitrotetramethylbenzenes, VII + VIII.—Sulfuric acid (8.3 cc.) was added slowly at room temperature to a vigorously stirred solution of the nitrates (0.72 g.) in chloroform (7 cc.). The chloroform layer was removed at once (seven minutes after starting the reaction), washed with carbonate (5%), then with water, and evaporated to dryness, pumping off the last traces of the solvent. The residue, after crystallization from ethanol (charcoal), weighed 0.14 g. (22%) and melted at 163–174.5°. Recrystallization from petroleum ether gave a product melting at 174–177°.

Anal. Calcd. for $C_{10}H_{12}O_2NBr$: C, 46.51; H, 4.69. Found: C, 46.38; H, 4.81.

The mixture of VII + VIII (0.57 g.) in acetic acid (6 cc.) was refluxed for ten hours with granular tin (1.25 g.) and hydrochloric acid (5.5 cc.). The reaction mixture was made strongly alkaline and was steam distilled. The solid (0.25 g.) was removed from the distillate and was sublimed *in vacuo*, first at 100° and then briefly at 150°. The first portion of the sublimate (0.05 g.) melted at 57–62°; the second portion (0.06 g.) melted at 115–136°, and the residue (0.09 g.) melted at 144–147°. The first sublimate, after crystallization from petroleum ether, melted at 64.5–67.5°, gave no depression in m. p. when mixed with aminoprehnitene (m. p. 66–68°), but did give a depression when mixed with aminodurene (m. p. 71.5–74.5°). The residue from the sublimation, after crystallization from petroleum ether, melted at 146–148°. It gave no depression in m. p. when mixed with bromoaminoisodurene (m. p. 145.5–147°). Considering the first sublimate to be pure aminoprehnitene, and the residue to be pure bromoaminoisodurene, and assuming that the *midpoint (125°) of the melting range of the second sublimate is a linear function of the mole fractions of amino*prehnitene (m. p. *ca.* 70°) and bromoaminoisodurene (m. p. *ca.* 147°) present, then the mole fractions of these two amines in the second sublimate are 0.286 and 0.714, respectively, and their respective weights are 0.012 g. and 0.048 g. Hence the total weights of aminoprehnitene and bromoaminoisodurene in the reduction product were 0.062 and 0.138 g., which corresponds with 0.107 g. (41%) of bromonitroprehnitene and 0.156 g. (59%) of bromonitroisodurene in the original mixture of VII + VIII.

The Pure Isomers.—The preparations are described in detail for one set of isomers; other results are given in Table I.

TABLE I

DATA ON PREPARATION OF PURE BROMOTETRAMETHYLBENZYL DERIVATIVES

Bromotetramethylbenzyl derivative	Yield, %	Analyses, % Calcd. C	Calcd. H	Found C	Found H
4,2,3,5,6-chloride	42	50.48	5.40	50.14	5.52
5,2,3,4,6-chloride	45.5	$C_{11}H_{14}ClBr$		50.22	5.53
6,2,3,4,5-chloride	36			50.74	5.62
4,2,3,5,6-iodide	95	37.40	4.00	37.41	4.27
5,2,3,4,6-iodide	100	$C_{11}H_{14}BrI$		37.30	4.36
6,2,3,4,5-iodide	99			37.84	4.37
4,2,3,5,6-acetate	95	54.73	6.01	54.87	6.60
5,2,3,4,6-acetate	84	$C_{13}H_{17}O_2Br$		54.66	6.04
6,2,3,4,5-acetate	93			54.74	5.92
4,2,3,5,6-nitrate	65	45.83	4.90	46.26	5.18
5,2,3,4,6-nitrate	72	$C_{11}H_{14}O_3NBr$		46.27	5.14
6,2,3,4,5-nitrate	92			45.56	4.61

TABLE II

MELTING POINTS (°C.) OF BROMOTETRAMETHYLBENZYL DERIVATIVES

	Chloride	Iodide	Acetate	Nitrate
1. Durene series	105.5–107.5	118.5–120	119.5–122	113–114.5
2. Isodurene series	114–114.5	132.5–134	88.5–90	105–106.5
3. Prehnitene series	114–116	142–143.5	96.5–98	90–92.5
4. Mixture from bromopentamethylbenzene	110–113	133.5–136	82–83.5	78–84
1 + 2	96–101	114–128	89–116	111–114.5
1 + 3	94–100	118–133	97.5–109	84–110
2 + 3	111.5–113	134.5–136	81–92	78–85
1 + 4	Below 99	115–127	83–116	82–110
2 + 4	110–114	134–134.5	83–86	80–91
3 + 4	112.5–114.5	136.5–137	80–94	81–89

Chloromethylations.—The bromohydrocarbon (2.5 g.), hydrochloric acid (10 cc.) and formalin (10 cc., 40%) were stirred vigorously and heated on a water-bath for thirty-two hours while a stream of dry hydrogen chloride was passed through. Occasionally during the reaction, more formalin (total 10 cc.) was added in 2–3 cc. portions. The reaction mixture was extracted with chloroform and the organic layer was washed with water. Removal of the solvent left the solid reaction product, which was crystallized once or twice (charcoal if the product was colored) from ethyl acetate.

Iodides.—The chloride (1.28 g.) was dissolved in a solution of sodium iodide in acetone (20 cc., 10%) and allowed to stand for forty-five minutes to one hour. The solution was poured into water and the solid was removed by filtration or chloroform extraction and crystallized from acetone.

Acetates.—The iodide (0.30 g.) was refluxed for three to five hours in acetic acid (12 cc.) containing potassium acetate (0.50 g.). The mixture was poured into water and the precipitate was removed and crystallized from ethanol.

Nitrates.—The iodide (0.30 g.) was refluxed in dry dioxane (10 cc.) containing powdered silver nitrate (1.50 g.). The reaction mixture was poured into water and the solid was isolated by filtration or, better, by chloroform extraction. It was crystallized from petroleum ether (b. p. 60–68°).

In Table II are given the melting points of the pure substances and their binary mixtures (approximately 50–50) with each other and with the corresponding derivatives (mixture) from bromopentamethylbenzene. It is apparent that many of the mixtures do not show great depressions in melting points, but in all cases the melting points of mixtures of the isodurene and prehnitene derivative are almost identical with, and do not depress, the melting points of the corresponding mixture obtained from bromopentamethylbenzene.

Bromonitrodurene.—A mixture of chloroform (3.5 cc.) and fuming nitric acid (d. 1.57, 1.3 cc.) was added rapidly (4.5 minutes) to a cooled (0°) and well-stirred mixture of chloroform (17 cc.) sulfuric acid (5.5 cc.) and bromodurene (5 g.). The reaction mixture was immediately poured into water, the chloroform layer was removed and partially evaporated. Ethanol was added to replace the chloroform until the hot solution began to crystallize, after which the mixture was chilled. The product (4.03 g., 66%) consisted of light yellow needles which melted at 179–180° after crystallization from chloroform–ethanol.

Anal. Calcd. for $C_{10}H_{12}O_2NBr$: C, 46.51; H, 4.69. Found: C, 46.19; H, 5.14.

Bromonitroisodurene was prepared as above from bromoisodurene (4 g.). The product (2.97 g., 61%), after crystallization from chloroform–ethanol, formed light yellow needles which melted at 176.5–177.5°.

Anal. Calcd. for $C_{10}H_{12}O_2NBr$: C, 46.51; H, 4.69. Found: C, 46.13; H. 4.90.

Bromonitroprehnitene was prepared as above from bromoprehnitene (3.81 g.). The product (1.51 g., 33%) after two crystallizations from chloroform–ethanol formed light yellow needles which melted at 180–181.5°.

Anal. Calcd. for $C_{10}H_{12}O_2NBr$: C, 46.51; H, 4.69. Found: C, 46.88; H, 4.83.

Aminodurene.—Bromonitrodurene (3.28 g.) in acetic acid (35 cc.) was refluxed for four hours with granular tin (7 g.) and hydrochloric acid (32 cc.). The reaction mixture was made strongly alkaline and steam distilled. From the distillate there was isolated 1.45 g. (75%) of aminodurene which, after vacuum sublimation, softened at 68.5° and melted at 71.5–74.5°.[13] A mixture of aminodurene and aminoprehnitene (m. p. 66–68°) was entirely liquid at 51°.

Bromoaminoisodurene.—Reduction of bromonitroisodurene (1 g.) as above gave 0.70 g. (79%) of bromoaminoisodurene which melted at 145.5–147° after crystallization from petroleum ether.

Anal. Calcd. for $C_{10}H_{14}NBr$: C, 52.62; H, 6.19. Found: C, 52.87; H, 6.29.

Aminoprehnitene.—Reduction of bromonitroprehnitene (1.27 g.) as above gave 0.55 g. (75%) of aminoprehnitene, which after vacuum sublimation melted at 66–68°.[14]

Summary

1. The action of fuming nitric acid upon bromopentamethylbenzene produced an inseparable mixture of two benzyl nitrates, 5-bromo-2,3,4,6-tetramethylbenzyl nitrate (V) and 6-bromo-2,3,4,5-tetramethylbenzyl nitrate (VI) in the approximate ratio of 3 to 2. These nitrates were converted into nitro compounds, bromonitroisodurene (VII) and bromonitroprehnitene (VIII), by sulfuric acid.

2. The action of a mixture of fuming nitric

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[13] Ref. 3a, p. 1294; ref. 12, p. 6.

[14] Limpach, *Ber.*, **21**, 644 (1888); Töhl, *ibid.*, **21**, 905 (1888).

and sulfuric acids upon bromopentamethylbenzene gave 4-bromo-5,6-dinitrohemimellithene, in which two methyl groups had been replaced by nitro groups.

3. The benzyl nitrates V and VI were intermediates in the replacement of methyl groups by nitro groups; this may possibly be the course of other aromatic nitrations in which alkyl groups are replaced by nitro groups.

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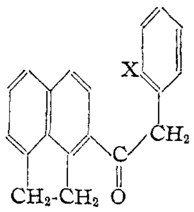
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

7-Cholanthroic Acid

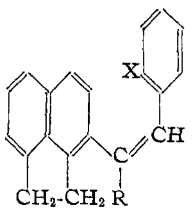
BY LOUIS F. FIESER AND GLEN W. KILMER[1]

The recently described preparation of 1-acetoacenaphthene by the acetylation of the hydrocarbon in the presence of liquid hydrogen fluoride[2,3] has rendered this ketone far more readily available as an intermediate for synthesis than any other 1-substituted acenaphthene, and the present research was undertaken to determine whether this or other 1-acyl derivative obtainable with the use of hydrogen fluoride could be employed as the starting point for the construction of the cholanthrene ring system.

The ready availability of the 1-aceto compound, which in large scale preparations has now been obtained in yields as high as 45% of the theory, is dependent upon the formation of a large proportion of the 1-isomer and also upon the fact that this is less soluble than the 3-ketone present in the mixture and is very easily separated. This favorable combination of factors has not been encountered in such other hydrogen fluoride acylations as have been investigated,[2a] for in the benzoylation, succinoylation and condensation of the hydrocarbon with crotonic acid by the hydrogen fluoride method, the amount of 1-substitution is small or negligible and no greater than in the Friedel and Crafts reaction. Although the prospects of obtaining other 1-acyl derivatives easily by direct hydrogen fluoride acylation are thus none too great, some trial was made of the condensation with phenylacetic acid derivatives with the thought that ketones of the type I might afford a short synthetic route to cholanthrenes. Thus a derived unsaturated compound (II) might be convertible to a cholanthrene by Pschorr ring closure (X = NO_2) or by the alkali fusion method employed by Hewett[4] (X = Br).



I



II

In a preliminary trial the hydrogen fluoride acylation of acenaphthene with phenylacetic acid itself was found to give a difficultly separable ketone mixture which on fractional crystallization afforded in 30% yield a pure compound identified as 3-phenylacetoacenaphthene by hypoiodite oxidation to the corresponding acid. The desired 1-isomer (I, X = H), which was similarly characterized as to structure, was isolated with difficulty and in only small amounts through the picrate. *o*-Bromophenylacetic acid, prepared from *o*-bromobenzoic acid by the Arndt–Eistert[5] reaction in 61% over-all yield, behaved similarly and gave a mixture from which two apparently pure compounds were isolated but only by tedious processing and in very small amounts. In view of these unfavorable indications, this approach was abandoned.

We then undertook to prepare intermediates of the type II starting with 1-acetoacenaphthene (III). Two routes were explored for the conversion of this ketone into 1-acenaphthylacetic acid (VII), the first being via the acid chloride and diazo ketone by the Arndt–Eistert procedure.[5] While the over-all yield of 50% is adequate, the process is time-consuming and not well adapted to the preparation of a quantity of the acetic acid derivative. Furthermore, the purified product probably was contaminated with a trace of the more sparingly soluble 1-acenaphthoic acid, for the melting point was not quite as high as that of

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(1) Du Pont Graduate Fellow, 1939–1940.

(2) (a) Fieser and Hershberg, THIS JOURNAL, **61**, 1272 (1939); (b) **62**, 49 (1940).

(3) Fieser and Cason, *ibid.*, **61**, 1740 (1939).

(4) Hewett, *J. Chem. Soc.*, 1286 (1938).

(5) Arndt and Eistert. *Ber.*, **68**, 203 (1935).