ozonolysis of the tricyclic and tetracyclic ketones IX and X in methanol followed by reduction with trimethyl phosphite yielded, after cyclization, the corresponding 5-membered ring D aldehydes (VIIIa,b) in 54% and 57% over-all yields, respectively with marked saving of time and labor over previous methods.

EXPERIMENTAL[14]

Apparatus. A Welsbach T-23 laboratory ozonizer was used. The ozone-oxygen stream was monitored by a Welsbach model C ozone meter. The ozone was delivered to an Ace Glass Mini-Lab Reactor assembly cat. No. 10104. With appropriate flow meters and potassium iodide traps, the amount of ozone delivered to a reaction mixture and the amount absorbed in a given time could be readily determined by titration of the iodine liberated by the off-gas stream.

General procedure for preparation and reduction of hydroperoxide ozonation cleavage products. Twenty-five millimoles of the olefin was dissolved in about 50 ml. of dry[15] methanol. If low temperature insolubility were encountered, an additional 50 ml. of methylene chloride[15] was also added. The solution was cooled to −65° to −70° in a Dry Ice bath and treated with a 3–4% oxygen-ozone stream until the calculated amount of ozone had been absorbed. A slow nitrogen stream was then bubbled through the cold solution and 5 ml. (about 40 mmoles) of trimethyl phosphite was added. Reduction was usually very rapid and accompanied by a marked temperature rise to around −20° even with strong cooling. Within 5 min. the reduction was complete and the solution was allowed to come to room temperature. Preparation of the carbonyl derivative was effected by addition of about 50–55 mmoles[16] of *p*-nitrophenylhydrazine or semicarbazide in methanol or other appropriate solvent, followed by heating for a short time on a steam bath.

In the case of cinnamic acid, the crude semicarbazones were collected and stirred for 30 min. with 50 ml. of cold 0.5*M* sodium hydroxide solution in order to dissolve out glyoxylic acid semicarbazone. Filtration and acidification served to isolate the latter from benzaldehyde semicarbazone.

l-(−)-anti-trans-3a,7,8,9,9a,9b-Hexahydro-3a-methyl-7-oxo-(1H)-benz[e]indene-3-carboxaldehyde (VIIIa). A solution of 2.14 g. (10 mmoles) of IX[17] was dissolved in 30 ml. of methylene chloride and diluted with 30 ml. of methanol. A standardized ozone-oxygen stream delivering 0.70 mmole of ozone per min. was added at −60° until 10 mmoles of ozone had been absorbed (14.5 min.). Addition of ozone was terminated and 3.0 ml. of trimethyl phosphite was added. A slight temperature rise was noted and the reaction mixture was allowed to come to room temperature over 1 hr. The solvents were removed *in vacuo* on a rotating drier. The clear oily residue was then heated at 60–80° at 0.5 mm. to remove phosphate esters. This crude dialdehyde was then cyclized in benzene using the piperidine-acetic acid method of Woodward.[10] A total of 1.635 g. of crude VIIIa was obtained which yielded sticky crystals on scratching. The crude product was dissolved in ether and was put through a short column of alumina. A total of 1.233 g. (54%) of almost colorless crystals, m.p. 118–123°, was obtained. Two recrystallizations from ether gave the analytical sample, m.p. 124.5–126°.

Anal. Calcd. for $C_{15}H_{16}O_2$: C, 78.91; H, 7.06. Found: C, 79.14; H, 7.25.

(+)-*Δ-9(11),16-Bisdehydro-21-norprogesterone* (VIIIb). One gram (3.55 mmoles) of the (−) tetracyclic ketone X[12] was dissolved in 50 ml. of methylene chloride to which was then added 50 ml. of methanol. The solution was treated for 5.1 min. with ozone at −60° as in the previous experiment. Reduction was effected by addition of 2 ml. of trimethyl phosphite. Subsequent workup and cyclization was also effected as previously described. A first crop of 465 mg., m.p. 154–156°, of essentially pure VIIIb was obtained. Infrared assay of material in mother liquors indicated the presence of another 131 mg. The total yield of useful product amounted to 57%. Recrystallization of first crop material from isopropyl alcohol gave pure material, m.p. 160–161°, showing no melting point depression with authentic material.[12]

In an identical experiment, but with the ozonolysis carried out at 0° instead of −65°, the total yield of VIIIb was only 28%.

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[14] Melting points are uncorrected.

[15] The use of reasonably dry solvents is indicated because of sensitivity of trialkyl phosphites to water. This did not appear to be a stringent requirement, however, as solvents of reagent grade were found to be quite satisfactory.

[16] It is known that carbonyl reagents such as phenylhydrazine, *p*-nitrophenylhydrazine, or hydroxylamine will itself reduce certain ozonation products. See P. S. Bailey, *Ber.*, **87**, 993 (1954), J. P. Wibaut and J. van Dijls, *Rec. trav. chim.*, **64**, 413 (1946), L. W. F. Kampschmidt and J. p. Wibaut, *Rec. trav. chim.*, **73**, 431 (1954), P. W. Haaijman and J. P. Wibaut, *Rec. trav. chim.*, **60**, 842 (1941) and p. H. Bergman and K. DeJong, *Rec. trav. chim.*, **78**, 275 (1959) for examples of this reaction. The relatively high yields of derivative obtained using essentially no excess of reagent indicate that the carbonyl compound is not acting as a reducing agent in the present case.

[17] Q. E. Thompson, *J. Org. Chem.*, **23**, 622 (1958).

Alkylation of Amines by Esters and Lithium Aluminum Hydride

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Ethyl acetate has often been recommended[1] as a reagent for the decomposition of excess lithium aluminum hydride in lithium aluminum hydride reductions. During the preparation of 1,2-propanediamine derivatives as intermediates for our analgesic program,[2] we encountered difficulties which indicated that this reagent should be used with caution in the preparation of amines, since the addition of an ester to a mixture of an amine and lithium aluminum hydride may result in alkylation of the amine.[3]

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[1] (a) W. G. Brown, *Organic Reactions*, John Wiley and Sons, Inc., New York, N. Y., 1951, VI, p. 488; (b) M. D. Banus, *Chem. Eng. News*, **32**, 2424 (1954); (c) N. G. Gaylord, *Reduction with Complex Metal Hydrides*, Interscience Publishers, Inc., New York, N. Y., 1956, p. 1010.

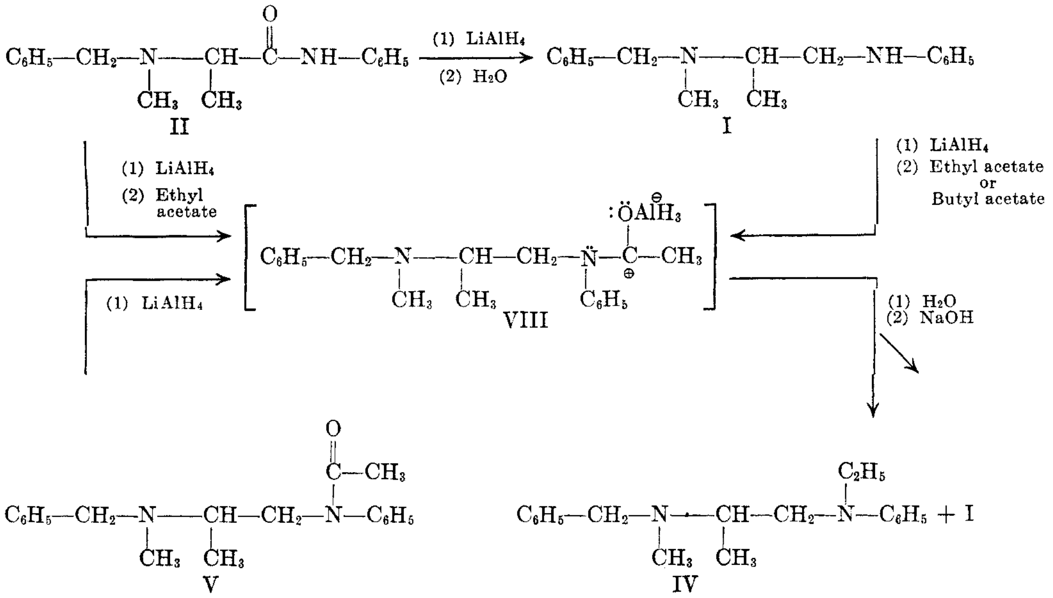
[2] (a) W. B. Wright, Jr., H. J. Brabander, and R. A. Hardy, Jr., *J. Am. Chem. Soc.*, **81**, 1518 (1959); (b) W. B. Wright, Jr., H. J. Brabander, and R. A. Hardy, Jr., 135th National Meeting of The American Chemical Society, Boston, April 1959.

An excellent yield of N^2-benzyl-N^2-methyl-N^1-phenyl-1,2-propanediamine (I) was obtained when 2-(benzylmethylamino)propionanilide (II) was reduced with lithium aluminum hydride in tetrahydrofuran and the excess lithium aluminum hydride was decomposed with water. Reaction of I with propionic anhydride resulted in an almost quantitative yield of *N*-(2-benzylmethylaminopropyl)propionanilide (III), isolated as the hydrochloride. On the other hand, when II was reduced in the same manner but ethyl acetate was used for the decomposition, I was less pure as evidenced by the lower yield, lower index of refraction, and failure of the product to crystallize completely; reaction of this product with propionic anhydride gave a lower yield of III which was less easily purified.

When the mother liquor from the isolation of III in this latter reaction was made basic and the oil was extracted into ether and distilled, a second product was obtained which had an elemental analysis and an infrared absorption spectrum in agreement with the structure N^2-benzyl-N^1-ethyl-N^2-methyl-N^1-phenyl-1,2-propanediamine (IV). Additional evidence for the identity of IV was afforded when this same compound was obtained in 20% yield by the lithium aluminum hydride reduction of *N*-(2-benzylmethylaminopropyl)-acetanilide (V). The major product in this reduction was I, formed by the reductive decomposition of V. This combination of products is to be expected in the lithium aluminum hydride reduction of hindered tertiary amides.[4]

Compound IV was also isolated in about 20% yield when a mixture of I and lithium aluminum hydride in tetrahydrofuran was treated with ethyl acetate or butyl acetate. When ethyl butyrate was used in the final step, N^2-benzyl-N^1-butyl-N^2-methyl-N^1-phenyl-1,2-propanediamine (VI) was obtained. This latter compound was identical with that isolated in low yield when *N*-(2-benzylmethylaminopropyl)butyranilide (VII) was reduced. The crude products from these experiments were examined by gas chromatography. The butyl analog (VI) was not found in the product from the butyl acetate reaction and the ethyl analog (IV) was not found in the product from the ethyl butyrate reaction. These results may be considered as proof that the entering alkyl group was derived from the acyl portion of the ester.

All of these reactions may be explained on the basis of an intermediate state (VIII) as pictured in Chart I. Gaylor[5] has postulated such an intermediate in lithium aluminum hydride reductions of amides and has described the mechanism for conversion to reduction or decomposition products.



EXPERIMENTAL

Chromatography. Crude reaction mixtures were separated by partition chromatography using a heptane–dimethylformamide solvent system and a Celite column. Per cent transmission was measured at 249 mμ and yields were calculated by comparison with pure standards. Gas chromatography was carried out using a Perkin-Elmer vapofractometer, Model 154C, equipped with a Craig polyester-succinate column.

2-(Benzylmethylamino)propionanilide (II). A mixture of 228 g. (1.0 mole) of 2-bromopropionanilide,[6] 242 g. (2.0 moles) of benzylmethylamine and 1200 ml. of benzene was heated at reflux for 4 hr. and then filtered to remove benzylmethylamine hydrobromide. The filtrate was concentrated

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(3) Experiments, to be reported in a later publication, indicate that the one-step akylation of secondary amines by esters and lithium aluminum hydride may be used as a preparative method, often resulting in good to excellent yields of tertiary amines.

(4) (a) V. M. Mićović and M. L. Mihailović, *J. Org. Chem.*, **18**, 1190 (1953); (b) A. W. Burgstahler, *J. Am. Chem. Soc.*, **73**, 3021 (1951); (c) K. Banholzer, T. W. Campbell, and H. Schmid, *Helv. Chim. Acta*, **35**, 1577 (1952).

(5) N. G. Gaylord, *Experientia* **10**, 166, 423 (1954).

(6) A. Tigerstedt, *Ber.* **25**, 2919 (1892).

to remove the benzene and the residue was recrystallized from ethanol. The yield of 2-(benzylmethylamino)propionanilide, m.p. 71–72°, was 80%.

Reduction of 2-(benzylmethylamino)propionalilide (II). *Method A. Decomposition with water.* A solution of 268 g. (1.0 mole) of 2-(benzylmethylamino)propionanilide in 1 l. of tetrahydrofuran was added dropwise, under a nitrogen atmosphere, to a cooled solution of 76 g. (2.0 moles) of lithium aluminum hydride in 2 l. of tetrahydrofuran. The reaction mixture was heated at reflux for 5 hr., allowed to stand overnight, and then treated successively with 76 ml. of water, 228 ml. of 15% sodium hydroxide, and 228 ml. of water. The insoluble portion was filtered and washed with tetrahydrofuran, and the combined filtrates were dried over magnesium sulfate and distilled. The yield of N^2-benzyl-N^2methyl-N^1-phenyl-1,2-propanediamine, b.p. 145–150°/0.3 mm. and n_D^{25} 1.5700, was 221 g. (87%).

Anal. Calcd. for $C_{17}H_{22}N_2$: C, 80.3; H, 8.7; N, 11.0. Found: C, 80.0; H, 8.5; N, 11.0.

This product completely crystallized on standing. A sample recrystallized from ethanol melted at 41–42°.

Method B. Decomposition with ethyl acetate. One mole of 2-(benzylmethylamino)propionanilide was reduced as described above, but 150 ml. of ethyl acetate was added prior to the water and sodium hydroxide. The yield of impure product b.p. 148–164°/0.3 mm. and n_D^{25} 1.5673, was 79%. This material only partly crystallized on standing.

N-(2-Benzylmethylaminopropyl)propionanilide hydrochloride (III). *A. From pure N^2-benzyl-N^2-methyl-N^1-phenyl-1,2-propanediamine*(I). A mixture of 50.8 g. (0.2 mole) of N^2-benzyl-N^2-methyl-N^1-phenyl-1,2-propanediamine, prepared by Method A, and 75 ml. of propionic anhydride was heated on a steam bath for 2 hr. and concentrated to remove the propionic acid and excess propionic anhydride. The residue was dissolved in 330 ml. of ether and treated with 110 ml. of 2*N* ethanolic hydrogen chloride. The reaction mixture was cooled overnight and filtered, and the product was washed with a mixture of ethanol and ether. The yield of *N*-(2-benzylmethylmethylaminopropyl)propionanilide hydrochloride, m.p. 150–152°, was 45.4 g. (65%). Concentration of the mother liquors followed by addition of ether resulted in an additional 14.5 g. (79% total), m.p. 149–151°. Recrystallization from acetone or from ethanol by addition of ether, raised the melting point to 151–152°.

Anal. Calcd. for $C_{20}H_{27}ClN_2O$: C, 69.2; H, 7.8; Cl, 10.2; N, 8.1. Found: C, 69.3; H, 7.9; Cl, 10.4; N, 8.3.

The mother liquor from the filtration of the recovered salt was concentrated to a sirup, treated with aqueous sodium hydroxide, and extracted with ether. The ether layer was concentrated and the residue distilled, b.p. 150–160°/0.1 mm. and n_D^{25} 1.5522. The infrared absorption spectrum of this material was almost identical with that of *N*-(2-benzylmethylaminopropyl)propionanilide, b.p. 146–148°/0.1 mm. and n_D^{25} 1.5491, prepared from the purified hydrochloride. The pure base crystallized on standing and melted at 51–52° after recrystallization from hexane.

Anal. Calcd. for $C_{20}H_{26}N_2O$: C, 77.4; H, 8.4; N, 9.0. Found: C, 77.0; H, 8.5; N, 9.0.

In an alternate reaction the product was not converted to the salt but the base was distilled, b.p. 166–170°/0.3 mm., n_D^{25} 1.5491, and yield 90%.

B. From impure N^2-benzyl-N^2-methyl-N^1-phenyl-1,2-propanediamine (I). A mixture of 100 g. (0.38 mole) of impure diamine, prepared by Method B, and 130 ml. of propionic anhydride was heated on a steam bath for 3 hr. and concentrated to remove the propionic acid and excess propionic anhydride. The residue was dissolved in 550 ml. of ether and 180 ml. of 2.3*N* ethanolic hydrogen chloride was added. Crystallization was slow and the reaction mixture was allowed to stand for 5 days before filtration. The yield, including recoveries, of *N*-(2-benzylmethylaminopropyl)-propionanilide hydrochloride, m.p. 148–151°, was 60%.

N^2-Benzyl-N^1-ethyl-N^2-methyl-N^1-phenyl-1,2-propanediamine (IV). *A. From impure N^2-benzyl-N^2-methyl-N^1-phenyl-1,2-propanediamine* (I). The mother liquor from the filtration of the above salt was concentrated to remove the solvent, treated with dilute sodium hydroxide, and the oil was extracted into ether and fractionally distilled. The fraction with b.p. 133–136°/0.06 mm., n_D^{25} 1.5591, weighed 11.5 g. An infrared absorption spectrum showed a weak carbonyl band but indicated that most of the propionanilide had been removed. This material was further purified by partition chromatography and pure N^2-benzyl-N^1-ethyl-N^2-methyl-1,2-propanediamine, n_D^{25} 1.5635 and b.p. 136–140°/0.3 mm., was obtained.

Anal. Calcd. for $C_{19}H_{26}N_2$: C, 80.8; H, 9.3; N, 9.9; mol. wt., 282. Found: C, 80.5; H, 9.4; N, 9.7; neut. equiv., 279.

The dipicrate was prepared and recrystallized from ethanol, m.p. 89–91°.

Anal. Calcd. for $C_{31}H_{32}N_8O_{14}$: C, 50.3; H, 4.4; N, 15.1. Found: C, 50.7; H, 4.9; N, 14.7.

B. From N-(2-benzylmethylaminopropyl)acetanilide (V). A solution of 14.8 g. (0.05 mole) of *N*-(2-benzylmethylaminopropyl)acetanilide in 50 ml. of tetrahydrofuran was added dropwise, under a nitrogen atmosphere, to a solution of 4.0 g. (0.01 mole) of lithium aluminum hydride in 300 ml. of tetrahydrofuran. The reaction mixture was heated at reflux for 3 hr. and then treated successively with 4 ml. of water, 12 ml. of 15% sodium hydroxide, and 12 ml. of water. The precipitate was filtered and washed with tetrahydrofuran and the filtrates were dried over magnesium sulfate and distilled. The yield of crude products, b.p. 136–140°/0.2 mm. and n_D^{25} 1.5670, was 10.1 g. Partition chromatography indicated a ratio of 72% N^2-benzyl-N^2-methyl-N^1-phenyl-1,2-propanediamine to 28% N^2-benzyl-N^1-ethyl-N^2-methyl-N^1-phenyl-1,2-propanediamine. The products were identical with those obtained by the reduction of 2-(benzylmethylamino)propionanilide using ethyl acetate decomposition, described above, or the reaction of N^2-benzyl-N^2-methyl-N^1-phenyl-1,2-propanediamine with lithium aluminum hydride and ethyl acetate or butyl acetate, described below.

C. From N^2-benzyl-N^2-methyl-N^1-phenyl-1,2-propanediamine (I), *lithium aluminum hydride and ethyl acetate or butyl acetate.* A solution of 5.1 g. (0.02 mole) of N^2-benzyl-N^2-methyl-N^1-phenyl-1,2-propanediamine in 20 ml. of tetrahydrofuran was added to a solution of 2.0 g. (0.05 mole) of lithium aluminum hydride in 100 ml. of tetrahydrofuran. The mixture was heated at reflux for 15 min. and a solution of 0.12 mole of freshly distilled ethyl acetate in 30 ml. of tetrahydrofuran was added. The reaction mixture was allowed to reflux for 1 hr. and was then treated successively with 2 ml. of water, 2 ml. of 15% sodium hydroxide, and 6 ml. of water. The solid was filtered and washed with tetrahydrofuran. The filtrates were concentrated to remove the solvent. Partition chromatography on the residue indicated a ratio of 79% N^2-benzyl-N^2-methyl-N^1-phenyl-1,2-propanediamine to 21% N^2-benzyl-N^1-ethyl-N^2-methyl-N^1-phenyl-1,2-propanediamine.

When butyl acetate was substituted for ethyl acetate in the above procedure, the ratio was 81% to 18%, respectively, of the same products.

N^2-Benzyl-N^1-butyl-N^2-methyl-N^1-phenyl-1,2-propanediamine (VI). *A. From N^2-benzyl-N^2-methyl-N^1-phenyl-1,2-propanediamine* (I), *lithium aluminum hydride and ethyl butyrate.* When ethyl butyrate was substituted for ethyl acetate in the above procedure, the crude product contained N^2-benzyl-N^2-methyl-N^1-phenyl-1,2-propanediamine and N^2-benzyl-N^1-butyl-N^2-methyl-N^1-phenyl-1,2-propanediamine in a ratio of 83% to 17%.

B. From N-(2-benzylmethylaminopropyl)butyranilide (VII). The lithium aluminum hydride reduction of 9.8 g. of *N*-(2-benzylmethylaminopropyl)butyranilide resulted in 6.6 g. of crude oil which largely crystallized on standing. Partition chromatography indicated a ratio of 93% to 7%, respectively, of the same products obtained above.

When a mixture of 4.1 g. of the crude product and 2.5 ml. of ethanol was cooled and filtered, 3.1 g. of N^2-benzyl-N^2-methyl-N^1-phenyl-1,2-propanediamine, m.p. 40–41°, was obtained. The mother liquor was concentrated and the products separated by chromatography. The yield of N^2-benzyl-N^1-butyl-N^2-methyl-N^1-phenyl-1,2-propanediamine, n_D^{25} 1.5497, was 420 mg. The infrared absorption spectrum had a more intense alkyl band than the analogous N^1-ethyl compound and lacked a CO or NH band.

Anal. Calcd. for $C_{21}H_{30}N_2$: C, 81.2; H, 9.7; N, 9.0. Found: C, 80.3; H, 9.8; N, 9.0.

The dipicrate was prepared and recrystallized from ethanol, m.p. 99–100°.

Anal. Calcd. for $C_{33}H_{36}N_8O_{14}$: C, 51.4; H, 4.7; N, 14.6. Found: C, 51.5; H, 5.2; N, 14.4.

N-(2-Benzylmethylaminopropyl)acetanilide (V). This compound was prepared by the reaction of N^2-benzyl-N^2-methyl-N^1-phenyl-1,2-propanediamine with acetic anhydride. The yield of *N*-(2-benzylmethylaminopropyl)acetanilide, b.p. 150–156°/0.1 mm. and n_D^{25} 1.5552, was 86%.

Anal. Calcd. for $C_{19}H_{24}N_2O$: C, 77.0; H, 8.2; N, 9.4. Found: C, 76.7; H, 8.2; N, 9.3.

N-(2-Benzylmethylaminopropyl)butyranilide (VII). This compound, b.p. 165–167°/0.2 mm. and n_D^{25} 1.5446, was obtained in 80% yield by the reaction of N^2-benzyl-N^2-methyl-N^1-phenyl-1,2-propanediamine with butyric anhydride.

Anal. Calcd. for $C_{21}H_{28}N_2O$: C, 77.7; H, 8.7; N, 8.6. Found: C, 77.6; H, 9.0; N, 8.6.

Acknowledgment. We are indebted to Dr. J. H. Clark and associates and to Mr. H. J. Brabander for the preparation of some of the intermediates, to Mr. C. Pidacks and co-workers for the chromatography, and to Mr. L. Brancone and Mr. W. Fulmor and associates for the microanalyses and infrared absorption spectra.

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The Nitration of 4-Nitro-*o*-iodotoluene

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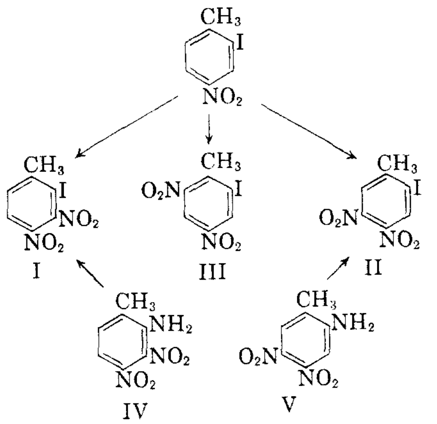
Dinitroiodo compounds have received little attention, as only a few of them are described in the literature. During a program of research on nitration of some iodo[2,3] compounds in this laboratory, nitration of 4-nitro-*o*-iodotoluene was undertaken for detailed investigation. The reaction can be expected to give three dinitro isomers, *viz.*, 3,4-(I); 4, 5-(II) and 4,6-(III) dinitro-*o*-iodotoluenes.

Only two isomers, *i.e.*, 4,5-dinitro-(II) and 4,6-dinitro-*o*-iodotoluene (III), were isolated from the reaction mixture. The identity of 4,5-dinitro-*o*-iodotoluene (II) was confirmed by an unequivocal synthesis from 4,5-dinitro-*o*-toluidine[4] (V) by Sandmeyer's reaction. Attempts to prepare 4,6-dinitro-*o*-iodotoluene (III) from 4,6-dinitro-*o*-toluidine[5] failed. 3,4-Dinitro-*o*-iodotoluene (I) has also been synthesized from 3,4-dinitro-*o*-toluidine[4] (IV). 4,5-Dinitro-*o*-iodotoluene (II) behaves normally with hydrazine hydrate giving 2-nitro-5-iodo-*p*-tolylhydrazine as the main product. The structure is assigned by analogy with other hydrazine preparations.[2]



The various dinitroiodo isomers prepared above can be distinguished readily, by taking advantage of their color reactions in acetone solution with aqueous sodium hydroxide, in which colors ranging from light red to intense green are produced.

EXPERIMENTAL[6]

Nitration of 4-nitro-o-iodotoluene. To a suspension of 4-nitro-*o*-iodotoluene (10 g.) in concd. sulfuric acid (42 ml., d. 1.8), fuming nitric acid (14 ml., d. 1.5) was added dropwise with vigorous shaking. It was then heated on a water bath for about 2 hr. and poured on crushed ice. The yellow crystalline material which separated was repeatedly crystallized successively from ethanol and methanol to give 4,5-dinitro-*o*-iodotoluene (5.2 g.) as yellow flakes, m.p. 97°.

Anal. Calcd. for $C_7H_5O_4N_2I$: I, 41.2. Found: I, 41.0.

The mother-liquor on standing deposited crystals of 4,6-dinitro-*o*-iodotoluene (1 g.) which crystallized from ethanol as pale yellow needles, m.p. 178°.

Anal. Calcd. for $C_7H_5O_4N_2I$: I, 41.2. Found: I, 40.8.

There remained an oil (1.5 g.) which could not be induced to crystallize.

3,4- and 4,5-Dinitro-o-toluidines[4] were prepared according to the method described previously.

4,5-Dinitro-o-iodotoluene. 4,5-Dinitro-*o*-toluidine (0.5 g.) dissolved in concd. sulfuric acid (5 g.) containing a little water was diazotized at 0° with sodium nitrite (0.4 g.). After 0.5 hr. the mixture was treated with a solution of potassium iodide (5 g.) in water. The 4,5-dinitro-*o*-iodotoluene formed was isolated in the usual manner and recrystallized from ethanol as yellow flakes (0.4 g.), m.p. 96°; mixed melting point with a sample of 4,5-dinitro-*o*-iodotoluene obtained by nitration of 4-nitro-*o*-iodotoluene remained undepressed.

3,4-Dinitro-o-iodotoluene was prepared by adopting a procedure, similar to that described above, from 3,4-dinitro-*o*-toluidine as pale yellow needles, m.p. 117°.

Anal. Calcd. for $C_7H_5O_4N_2I$: I, 41.2. Found: I, 40.7.

2-Nitro-5-iodo-p-tolylhydrazine. To a solution of 4,5-dinitro-*o*-iodotoluene (5 g.) in ethanol twice the equivalent

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(1) Present address: Central Drug Research Institute, Lucknow (India).

(2) R. S. Kapil, *J. Chem. Soc.*, **24**, 4127 (1959).

(3) R. S. Kapil, *J. Org. Chem.*, in press.

(4) O. L. Brady and P. N. Williams, *J. Chem. Soc.*, **117**, 1137 (1920).

(5) R. S. Kapil, *J. Indian Chem. Soc.*, in press.

(6) All melting points are uncorrected.