The test described in this paper may also be used for taxonomic studies.

It is difficult to distinguish between the seeds of the medical plants *Ammi visnaga* (L) and *Ammi majus* (L). It was found that the methanol-dioxane extract of the two kinds of seeds behaved differently towards the *m*-dinitrobenzene-alkali reagent; only in the case of *Ammi visnaga* was a positive test obtained. The difference is due to the fact that the seeds of *Ammi visnaga* (L) contain 2-methylchromone derivatives, *e.g.*, khellin (IIb) and visnagin (IIa) whereas *Ammi majus* contains the coumarin derivatives xanthotoxin and imperatorin.

EXPERIMENTAL

The alkali used was 10% aqueous sodium hydroxide. The *m*-dinitrobenzene reagent was prepared by adding a mixture of methyl alcohol and dioxane (1:1 by volume) to an excess of *m*-dinitrobenzene (B.D.H.); after being left at room temperature for 15 minutes, the mixture was filtered. The filtrate (A) was used for the test. The methyl alcohol used was from E. Merck, Darmstadt, Germany. The dioxane used was purified by refluxing over sodium metal, followed by fractional distillation through an efficient column and then was stored out of contact with air.

The filtrate (A) (0.5 cc.) gives practically no color on the addition of two drops of alkali.

Test of the substances listed in Tables I and II. A few crystals of the material to be tested were added to about 0.5 cc. of (A) placed in a micro test tube and one to two drops of alkali were added. In the case of methyl alcohol-dioxane solutions of the substances listed in Table I a violet-red color was developed, either immediately or after a few seconds; this was not the case with such solutions of substances listed in Table II.

Investigation of the seeds of Ammi visnaga (L) and A. majus (L). The dried, ripe, powdered seeds (0.1 g.) were extracted for 30 minutes (using a reflux condenser) with about 2 cc. of a boiling mixture prepared from equal volumes of dioxane and 80% methyl alcohol. The hot mixture was filtered; the filtered extracts in both cases were a light brownish-yellow. Each extract (0.5 cc.) gave, with 2 drops of alkali, an intense yellow color; when about 0.5 cc. of the extract was treated with about 0.2 cc. of A, followed by the addition of 2 drops of alkali, an intense brownish-violet color was developed in one minute in the case of *Ammi visnaga;* in the case *Ammi majus* the color was deep yellow.

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The Synthesis of 4'-Nitro-*o*-terphenyl

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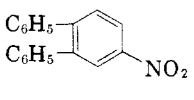
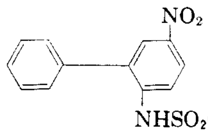
With a view to its use as an intermediate in the preparation of 5,6-diphenyl-1,10-phenanthroline, the synthesis of 4'-nitro-*o*-terphenyl (I) by the use of Gomberg's[1] reaction on 2-amino-5-nitrobiphenyl has been investigated.



I



II

The preparation of 5-nitro-2-(*p*-toluenesulfonamido)biphenyl (II) was carried out by a modification of the method of Smith and Brown[2] using fuming nitric acid (*sp.gr.* 1.5). It was found that the use of concentrated nitric acid as suggested by Bradsher and Jackson[3] failed to bring about nitration. Hydrolysis of II to 2-amino-5-nitrobiphenyl was effected as previously described.[4]

The application of Gomberg's method to 2-amino-5-nitrobiphenyl gave poor yields of I, which were raised slightly by the use of the modification of France, Heilbron, and Hey as described by Bachmann and Hoffman.[5]

Compound I proved to be identical (by the ethod of mixture melting points) with a hitherto unidentified product obtained in low yield by Allen and Burness[6] from the nitration of *o*-terphenyl.

EXPERIMENTAL PART

5-Nitro-2-(p-toluenesulfonamido)biphenyl. To 77 g. of 2-(*p*-toluenesulfonamido)biphenyl in 182 ml. of acetic acid at 60° was added a solution of 17 ml. of fuming nitric acid (*sp.gr.* 1.5) in 35 ml. of acetic acid. The temperature was prevented by cooling from rising above 80°. When the reaction had subsided the mixture was cooled to 15° and the resulting crystals were removed by filtration. The dried product (78.5 g.) melted, without crystallization, at 168–169°; yield, 89.5%. After hydrolysis[4] and acetylation by boiling with acetic anhydride, the resulting 2-acetamido-5-nitrobiphenyl melted at 135–136°. (Bell[7] reports m.p. 133°).

4'-Nitro-o-terphenyl. A solution made by passing nitrosyl chloride into 25 g. of acetic anhydride to a weight increase of 4.5 g. was added dropwise with stirring to a mixture (maintained at 8°) of 13 g. of 2-acetamido-5-nitrobiphenyl, 150 ml. of acetic acid, 75 ml. of acetic anhydride, 8 g. of anhydrous potassium acetate, and 1 g. of phosphoric anhydride. After reaction was complete the mixture was poured on ice, and the resulting nitroso compound was filtered and dried; yield, 13 g. of product melting at 93° (dec). A solution of 13 g. of this compound in 270 ml. of dry benzene was heated at 35° for 12 hours, followed by refluxing for 4–5 hours. Removal of the benzene yielded a tar which was extracted with petroleum ether (b.p. 60–75°). The residue, after evaporation of the petroleum ether, was crystallized from methanol, yielding 1.3 g. (9.3%) of product melting at 118–119° and undepressed when mixed with a

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(1) Gomberg and Bachmann, *J. Am. Chem. Soc.*, **46,** 2339 (1924).

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(3) Bradsher and Jackson, *J. Am. Chem. Soc.*, **74,** 4880 (1952).

(4) Ray and Barrick, *J. Am. Chem. Soc.*, **70,** 1492 (1948).

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(6) Allen and Burness, *J. Org. Chem.*, **14,** 177 (1949).

(7) Bell, *J. Chem. Soc.*, 2774 (1928).

sample of "x-nitro-*o*-terphenyl" obtained from Dr. C. F. H. Allen.

Anal. Calc'd for $C_{18}H_{13}NO_2$: C, 78.53; H, 4.76. Found: C, 78.75; H, 4.74.

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Osmium Tetroxide-Catalyzed Periodate Oxidation of Olefinic Bonds

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The success of the permanganate-catalyzed oxidation of olefinic bonds with periodate[3] prompted the investigation of other catalysts, in particular reagents known to hydroxylate olefins. In the present note the preliminary results of the use of osmium tetroxide as the catalyst are disclosed.[4]

The new method has proved to be successful with some simple mono- and di-substituted olefins. With the permanganate-catalyzed reaction such olefins generally give an aldehyde and a carboxylic acid.[3] The osmium tetroxide technique has the advantage of not proceeding beyond the aldehydic oxidation state, thus affording the same products produced by ozonization followed by reductive cleavage. Catalytic amounts of osmium tetroxide are sufficient because periodate oxidizes osmium in its lower valence forms to the tetroxide, thus regenerating the hydroxylating agent. Hence this combination of two well-known reactions, namely osmium tetroxide hydroxylation of an olefin and periodate cleavage of a 1,2-glycol, permits the use of relatively small amounts of the very expensive and poisonous hydroxylating agent.

Two general procedures were developed. One involved the use of aqueous dioxane (75%), 1 mole-% of osmium tetroxide, and 210 mole-% of solid sodium metaperiodate at 25°. Dodecene-1 and *trans*-stilbene thus were readily oxidized to undecanal and benzaldehyde respectively in 68 and 85% yields (isolated as the 2,4-dinitrophenylhydrazones).

The second procedure involved the use of two immiscible liquid phases, *i.e.* ether and water. In this case a somewhat higher (up to 5 mole-%) proportion of osmium tetroxide was required to give a reasonably rapid reaction. The ether-water system was preferred for the oxidation of olefins giving aldehydes sensitive to self-condensation. Cyclohexene and cyclopentene thus afforded respectively 77 and 76% yields of the 2,4-dinitrophenylhydrazones of adipaldehyde and glutaraldehyde. By the dioxane method cyclohexene gave poor yields, perhaps due to cyclization of the dialdehyde. Dodecene-1, in contrast, gave poorer yields by the ether method.

1-Methylcyclohexene underwent oxidation very slowly and, under the optimum conditions for cyclohexene, gave only about 5% of uncharacterized carbonyl product. A potential use of the new method for selective oxidations is thus indicated.

Cyclohexene can be oxidized satisfactorily by the new method in aqueous medium alone. Acetonitrile also promises to be a useful solvent for these oxidations.

Preliminary experiments indicate that olefins are also oxidized by lead tetraacetate in the presence of catalytic amounts of osmium tetroxide. No noticeable reaction occurred at room temperature in benzene or in acetic acid solution until some water was added whereupon there was rapid consumption of the reagent. Water is evidently required in all of these reactions to effect hydrolysis of the intermediary osmate ester.

EXPERIMENTAL

Oxidation of dodecene-1 and of trans-stilbene. The aqueous dioxane procedure. A mixture of 5 ml. of water, 15 ml. of purified[5] dioxane, freshly distilled from lithium aluminum hydride, 0.77 g. of dodecene-1, and 11.3 mg. of osmium tetroxide was stirred for 5 minutes during which time the mixture became dark brown (due to osmate ester formation). While the temperature of the stirred mixture was maintained at 24–26°, a total of 2.06 g. of finely powdered sodium metaperiodate was added in portions over a period of 30 minutes. The tan-colored slurry then was stirred for an additional 1.5 hours. The mixture (now pale yellow) was extracted thoroughly with ether and the combined organic layers (about 200 ml.) were filtered through anhydrous sodium sulfate. The ether solution then was treated with a solution of 1 g. of 2,4-dinitrophenylhydrazine in 5 ml. of concentrated sulfuric acid, 7.5 ml. of water, and 35 ml. of 95% ethanol. The two phase mixture was stirred for 70 minutes, then was evaporated to a volume of about 50 ml. The yellow 2,4-dinitrophenylhydrazone that separated amounted to 0.95 g., m.p. 98.5–101.5° (reported, m.p. 102°[6] and 106.5°[7]). A second crop obtained by concentration of the

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(1) University of Wisconsin.

(2) University of Ottawa.

(3) R. U. Lemieux and E. von Rudloff, *Can. J. Chem.*, **33**, 1701, 1710 (1955); E. von Rudloff, *Can. J. Chem.*, **33**, 1714 (1955).

(4) The results of the search by M. Mugdan and D. P. Young, *J. Chem. Soc.*, 2988 (1949), for compounds to catalyze the hydroxylation of olefins by hydrogen peroxide have suggested several other possible catalysts for the periodate oxidation of olefins. Preliminary experiments have shown pertungstate, pervanadate, and pervanadic acid to be effective and this matter is receiving further attention. Ruthenium oxide also shows promise as a catalyst; *Cf.* Djerassi and R. R. Engle, *J. Am. Chem. Soc.* **75**, 3838 (1955).

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