to moderate the vigorous reaction. The reaction then was heated to evolve butyl chloride. Distillation of the residue gave dibutyl β-chlorovinyl phosphate (b.p. 96°/0.5, n_D^{25} 1.4392, 85% yield).

Anal. Calc'd for $C_{10}H_{20}ClO_4P$: Cl, 13.0, P, 11.4. Found: Cl, 12.8; P, 11.3.

A mixture of 0.5 g. of the ester, 1 g. of 2,4-dinitrophenylhydrazine, 2 ml. of conc'd hydrochloric acid, and 25 ml. of ethanol were refluxed for 10 minutes, filtered, and the filtrate was allowed to stand. Dark violet-red prisms of the 2,4-dinitrophenylhydrazine (m.p. 196–197° dec., lit. m.p. 198° dec.) were deposited. The filtrate, after removal of the unreacted hydrazine, then deposited a small amount of orange-red crystals of glyoxal 2,4-dinitrophenylosazone, m.p. 324° dec., lit. m.p. 328°. Both the derivative and an authentic osazone sample give the same intense royal-blue color when treated with ethanolic sodium hydroxide.

Triethyl phosphite—Dichloroacetaldehyde. Diethyl β-chlorovinylphosphate was prepared as described above.[2b,e] B.p. 61°/0.5, 112°/8, n_D^{25} 1.4342, 66% yield.

Anal. Calc'd for $C_6H_{12}ClO_4P$: Cl, 16.5; P, 14.4. Found: Cl, 15.9; P, 14.1.

The ester gives a positive Tollens' and Beilstein's test. It does not react with ferric ion or Schiff's reagent; after prolonged boiling with Fehling's solution, a bright purple-red precipitate is deposited, quite unlike the usual brick-red cuprous oxide.

The infrared spectrum, as determined in a Perkin-Elmer Model 21 with a 0.0494-mm. cell, revealed strong olefinic absorption bands at 3.26 and 6.11μ. Absorption in the 10.4μ region, and the lack of an absorption in the 14μ region, indicates, but does not verify, that the vinyl ester is of the *trans* configuration.

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Color Test. Part III. A Color Test for 2-Methylchromones with *m*-Dinitrobenzene and Its Significance for Taxonomic Work

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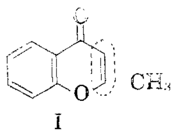
Lately, it has been pointed out[1] that the power of 2-methylchromones to condense with aromatic aldehydes may be explained by considering these chromones as vinylogs of acetophenone (*cf.* I). The

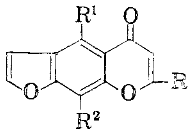

I

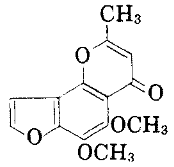
application of this principle to the chemistry of γ-pyrones has now led to the discovery of a most sensitive color test. Bittó[2] has shown that an alcoholic solution containing acetophenone (or acetone) and *m*-dinitrobenzene gives an intense violet-red color on addition of alkali. We found that a deep violet color was developed when the test was applied to 2-methylchromones, and also to 2,6-dimethylpyrone which may be regarded as a vinylog of acetone. The importance of the methyl group in position 2 for this color test is stressed, since chromones (γ-pyrones) which have no methyl group in this position do not give the color. This test, however, is frequently inconclusive in the case of 2-methylchromones containing a phenolic hydroxyl group; this may be due to the fact that many of these chromones dissolve in alkali with color. Demethylated khellin (IIc) a yellow substance for example, dissolves in alkali with a reddish-brown color.[3] One can overcome this difficulty by methylation or acetylation of the phenolic groups before carrying out the test. This new micro test may be regarded as supplementary to the color test described by Schönberg and Sina[4] but it is more sensitive and quicker.

TABLE I

Compounds Giving a Positive Test

2,6-Dimethylpyrone.
2-Methylchromone.
2,6-Dimethylchromone.
2,3,7-Trimethylchromone.
2-Methyl-1,4-α-naphthopyrone.
Visnagin (IIa).
Khellin (IIb).
iso-Khellin (III).
5,7-Dimethoxy-6-formyl-2-methylchromone.
5-Acetoxy-7-methoxy-2,6-dimethylchromone (eugenitin acetate).





IIa: R = CH_3; R^1 = OCH_3; R^2 = H
IIb: R = CH_3; R^1 = R^2═OCH_3
IIc: R = CH_3; R^1 = R^2═OH
IId: R = CH_2OH; R^1 = OCH_3; R^2 = H

III

TABLE II

Compounds Giving a Negative Test

Benzalacetophenone.
2,6-Diphenylpyrone.
3-Methylchromone.
Flavone.
α-Naphthoflavone.
2-Styrylchromone.
2-Styrylvisnagin.
Khellol (IId).
Coumarin.
Xanthotoxin.
Imperatorin.

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(1) Schönberg, Sidky, and Aziz, *J. Am. Chem. Soc.*, **76**, 5115 (1954).

(2) von Bittó, *Ann.* **269**, 377 (1892).

(3) Schönberg and Sina, *J. Am. Chem. Soc.*, **72**, 3396 (1950).

(4) Schönberg and Sina, *J. Chem. Soc.*, 3344 (1950).

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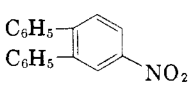
With a view to its use as an intermediate in the preparation of 5,6-diphenyl-1,10-phenanthroline, the synthesis of 4′-nitro-*o*-terphenyl (I) by the use of Gomberg's[1] reaction on 2-amino-5-nitrobiphenyl has been investigated.



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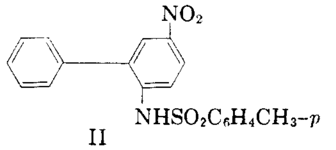

II

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).

(2) Smith and Brown, *J. Am. Chem. Soc.*, **73,** 2438 (1951).

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

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

(5) Bachman and Hoffman, *Org. Reactions*, **2,** 224 (1944).

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

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