with ether giving a dark viscous material. The dark residue was refluxed for 10 hr. with 50 ml. of 20% sodium hydroxide and then washed with ether to remove base-insoluble material. Acidification and extraction with ether gave 1.1 g. of a brown semicrystalline material. The residue was leached with boiling petroleum ether giving 0.8 g. (48% yield base on bond cleavage) of pale yellow crystals which, on treatment with charcoal and recrystallization from water, gave a m.p. of 120.5–121.0° and m.m.p. with authentic benzoic acid of 121.0–122.0°.[6]

B. A solution of 5.0 g. of "anhydro acetophenone disulfide" in 50 ml. of methylene chloride and 25 ml. of pyridine was treated with a dilute stream of ozone in oxygen at −80° (approximately 70% ozonolysis of the double bond occurred.) The ozonolysis solution was allowed to come to room temperature and was warmed gently for 30 min. The mixture was poured into water and extracted with ether. The extract was washed with water and saturated sodium chloride and was dried over sodium sulfate. The solvent was removed under reduced pressure giving 4.0 g. of crude product which did not contain acetophenone when analyzed by infrared and n.m.r. spectroscopy.

"Anhydro Acetophenone Disulfide" from Acetophenone and Dypnone.—A solution of 11 g. (0.05 mole) of dypnone and 6.0 g. (0.05 mole) of acetophenone in 200 ml. of absolute ethanol was cooled in an ice bath. Hydrogen chloride was bubbled through the solution, concurrently with hydrogen sulfide, for 5 hr., the hydrogen sulfide stream being continued for an additional 5 hr. The reaction mixture was placed in a freezer overnight and the yellow precipitate was filtered and dried giving 14.1 g. (75%) of I. One recrystallization from acetone gave a melting point of 106.5–107.5° (lit.,[2a] m.p. 107–108).

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[6] It was shown in a control experiment that acetophenone could not be oxidized to benzoic acid under the above conditions.

The Preparation of *cis*-4-Nitro-4′-methoxystilbene *via* the Wittig Reaction

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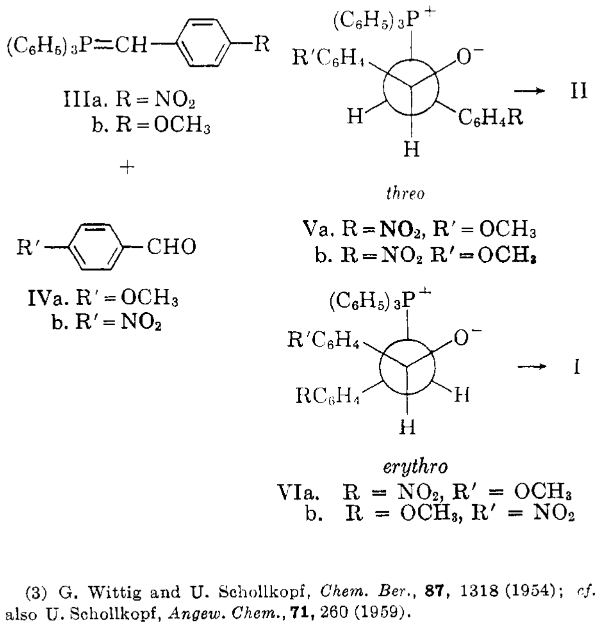
cis-4-Nitro-4′-methoxystilbene (I) has been prepared by the photochemical rearrangement of its *trans* isomer (II).[1] This reaction, however, is not suited for the preparation of relatively large quantities needed for planned biological, physical, and chemical studies. The partial reduction of 4-nitro-4′-methoxytolane did not appear attractive because of the presence of the reducible nitro group. Decarboxylation of either α-(4-methoxyphenyl)-*trans*-4-nitrocinnamic acid or α-(4-nitrophenyl)-*trans*-4-methoxycinnamic acid yielded only *trans*-4-nitro-4′-methoxystilbene (II) rather than the expected *cis* isomer.[2]

The Wittig reaction between benzaldehyde and phenylmethylenetriphenylphosphorane has been reported to afford a mixture of *cis*- and *trans*-stilbene in a ratio of 1:3.[3] In the case of 4-nitro-4′-methoxystilbene we have found that, by the appropriate choice of reactants, this ratio can be made to approach 1:1. The reaction between *p*-nitrophenylmethylenetriphenylphosphorane (IIIa) and anisaldehyde (IVa), affords only the *trans* compound (II) in 89% yield. The reaction of *p*-methoxyphenylmethylenetriphenylphosphorane (IIIb) with *p*-nitrobenzaldehyde (IVb) gave 89% of a mixture which contained 48% *cis* (I) and 52% *trans* isomer (II) which were easily separated by fractional crystallization and chromatography on deactivated alumina.

These results can be interpreted by postulating that the reaction of the stabilized, unreactive phosphorane containing the *p*-nitrobenzal group (IIIa) reacts with the relatively unreactive anisaldehyde (IVa) in a reversible manner to give a mixture of *threo* and *erythro* intermediates (Va and VIa, respectively). The *threo* structure may exist in a stable conformation (Va) capable of *cis* elimination of triphenylphosphine oxide[3] which affords *trans*-4-nitro-4′-methoxystilbene (II). The *erythro* structure (VIa), however, reverts to reactants which are eventually converted to the *trans* product (II) *via* the *threo* intermediate (Va).

On the other hand the less stable, more reactive phosphorane containing the anisal group (IIIb) reacts rapidly and irreversibly with the highly reactive *p*-nitrobenzaldehyde (IVb) to give approximately equal amounts of the *erythro* (VIb) and *threo* (Vb) intermediates each of which lose triphenylphosphine oxide *via* a *cis* elimination[3] to give *cis*- and *trans*-4-nitro-4′-methoxystilbene (I and II), respectively.



IIIa. R = NO$_2$
b. R = OCH$_3$

IVa. R′ = OCH$_3$
b. R′ = NO$_2$

threo

Va. R = NO$_2$, R′ = OCH$_3$
b. R = NO$_2$ R′ = OCH$_3$

erythro

VIa. R = NO$_2$, R′ = OCH$_3$
b. R = OCH$_3$, R′ = NO$_2$

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[1] M. Calvin and H. W. Alter, *J. Chem. Phys.*, **19**, 765 (1951).

[2] L. F. Fieser, "Experiments in Organic Chemistry," 3rd ed., D. C. Heath and Co., Boston, Mass., 1957, p. 185.

[3] G. Wittig and U. Schollkopf, *Chem. Ber.*, **87**, 1318 (1954); *cf.* also U. Schollkopf, *Angew. Chem.*, **71**, 260 (1959).

These observations lead to the conclusion that maximum yields, approaching 50%, of *cis* isomers should be expected when electron-donating substituents are on the phenylmethylenephosphorane and electron-withdrawing substituents on the aldehyde. Conversely, maximum yields, approaching 100%, of *trans* isomers should result from reactions in which the phenylmethylenephosphorane contains electron-withdrawing substituents and the aldehyde electron-donating substituents.

Experimental[4]

p-Nitrobenzyltriphenylphosphonium Chloride.—A solution of 26.3 g. (0.10 mole) of triphenylphosphine and 17.2 g. (0.10 mole) of p-nitrobenzyl chloride in 50 ml. of benzene was refluxed for 2 hr. After cooling, the solid was collected and washed with benzene. The yield was 25.0 g. (58%), m.p. 270–276°. Crystallization from carbon tetrachloride–petroleum ether gave colorless crystals, m.p. 278–280° dec.

Anal. Calcd. for $C_{25}H_{21}NO_2PCl$: Cl, 8.17. Found: Cl, 7.97.

p-Methoxybenzyltriphenylphosphonium Chloride.—A solution of 26.3 g. (0.10 mole) of triphenylphosphine and 15.7 g. (0.10 mole) of p-methoxybenzyl chloride in 50 ml. of benzene was refluxed for 4 hr. After cooling, the product was collected and washed with benzene. The yield was 26 g. (62%), m.p. 236–242°. Crystallization from chloroform–petroleum ether gave colorless crystals, m.p. 241–243°.

Anal. Calcd. for $C_{26}H_{24}OPCl$: Cl, 8.46. Found: Cl, 8.59.

Reaction of p-Nitrophenylmethylenetriphenylphosphorane (IIIa) with Anisaldehyde (IVa).—To a stirred solution of 4.3 g. (0.01 mole) of p-nitrobenzyltriphenylphosphonium chloride in benzene under dry nitrogen was added 0.85 g. (0.013 mole) of butyllithium.[5] After stirring for 2 hr., 1.63 g. (0.012 mole) of anisaldehyde was added and the reaction mixture stirred for an additional 4 hr. The reaction mixture was diluted with petroleum ether and the dark solid collected. Crystallization from alcohol gave 2.23 g. (89%) of yellow crystals of *trans*-4-nitro-4′-methoxystilbene, m.p. 131–132.5° (reported[1] 132–134°).

Reaction of p-Methoxyphenylmethylenetriphenylphosphorane (IIIb) with p-Nitrobenzaldehyde (IVb).—To a stirred solution of 25.2 g. (0.06 mole) of p-methoxybenzyltriphenylphosphonium chloride in benzene under dry nitrogen was added 4.8 g. (0.075 mole) of butyllithium.[5] After stirring for 2 hr., 10 g. (0.066 mole) of p-nitrobenzaldehyde was added and the reaction mixture stirred an additional 4 hr.

The reaction mixture was diluted with water and extracted with ether; the ether extract was dried, concentrated, and diluted with petroleum ether to precipitate most of the *trans*-4-nitro-4′-methoxystilbene. The filtrate was evaporated to dryness, dissolved in benzene–petroleum ether (b.p. 30–60°) 1:1, and chromatographed on Woelm alumina (neutral, activity grade IV). Elution with benzene and crystallization from hexane afforded 6.55 g. (43%) of *cis*-4-nitro-4′-methoxystilbene, m.p. 69–70° (reported[1] 70.2–71.2°). The *trans* isomer obtained from the column was combined with that precipitated earlier, and the entire product was recrystallized from ethanol to give a total yield of 7.05 g. (46%), m.p. 129–130°.

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[4] All melting points are uncorrected.

[5] Obtained from Foote Mineral Co. as a 14.4% solution in pentane–heptane (1:2).

The Formation of 3,4-Benzocoumarin by the Lead Tetraacetate Oxidation of Diphenic Acid

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Lead tetraacetate has been found to react with carboxylic acids in a number of interesting and potentially useful ways. Grob[1] has shown that oxidative decarboxylation of aliphatic 1,2-dicarboxylic acids often gives good yields of olefins. McCoy and Zagalo[2] found that 2-substituted glutaric acids undergo monodecarboxylation to give γ-lactones. This reaction is related to the apparently general oxidative decarboxylation of carboxylic acids by lead tetraacetate[3] to give acetates[4,5] or olefins.[6]

We have examined the behavior of certain aromatic acids toward this reagent. Heating either benzoic acid or phthalic acid at about 80° with lead tetraacetate in acetonitrile containing pyridine resulted in the slow evolution of a gas at a rate which was virtually identical with that obtained in the absence of the carboxylic acids, and the only pure compounds which were isolated were benzoic acid and phthalic anhydride.

When diphenic acid was subjected to the same conditions, somewhat more than a mole of gas per mole of diphenic acid was evolved fairly rapidly and 3,4-benzocoumarin (I) was isolated from the reaction mixture. Employing 1.5 moles of lead tetraacetate (which was free of acetic acid) per mole of diphenic acid gave I in 50% yield (based on diphenic acid). None of this product was obtained and little gas was evolved when the pyridine was omitted or replaced by triethylamine. The use of benzene as a solvent in place of acetonitrile caused very little evolution of gas, and only a trace of 3,4-benzocoumarin was isolated.

A probable intermediate in this reaction is the lead ester II. This species could undergo loss of carbon dioxide, lead acetate, and acetate ion to give I by several paths, two of which are represented by IIa and IIb. The latter either involves nucleophilic substitution at C-2 or loss of the grouping at C-2

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[1] (a) C. A. Grob, M. Ohta, and A. Weiss, *Angew. Chem.*, **70**, 343 (1958); (b) C. A. Grob, M. Ohta, E. Renk, and A. Weiss, *Helv. Chim. Acta*, **41**, 1191 (1958).

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[3] W. A. Mosher and C. L. Kehr, *J. Am. Chem. Soc.*, **75**, 3172 (1953).

[4] J. Jacques, C. Weidmann, and A. Horeau, *Bull. soc. chim. France*, 424 (1960).

[5] D. Ginsburg, *ibid.*, 1349 (1960).

[6] G. Büchi, R. E. Erickson, and N. Wakabayashi, *J. Am. Chem. Soc.*, **83**, 927 (1961).