1,2-Bis(phenylazo)-1,2-diphenylethane (IIIb).—For the isolation of this compound the crude product was crystallized directly from chloroform. Two recrystallizations afforded pale yellow needles, m.p. 186–187°. It gives a deep blue color with sulfuric acid.

Anal. Calcd. for $C_{26}H_{22}N_4$: C, 79.97; H, 5.68; N, 14.36. Found: C, 79.72; H, 5.68; N, 14.22.

Isomerization of IIIb to Benzil Osazone.—A solution of 70 mg. of 1,2-bis(phenylazo)-1,2-diphenylethane (IIIb) in a mixture of 5 ml. of ethanol and 10 ml. of chloroform was treated with 1 drop of 5% aqueous hydrochloric acid and boiled under reflux for 18 hr. The solvent was evaporated and the residue was recrystallized from 10 ml. of cyclohexane, affording 50 mg. (72%) of crude product. After one more recrystallization it had m.p. 220–224° (insert at 200°, rapid rise[12]); m.p. of authentic benzil osazone 229.5–231.5°; mixture m.p. 224.5–227°. Further evidence was furnished by the identity of its infrared spectrum with that of authentic benzil osazone, and the presence of a hydrazone chromophore (λ_{max} 300, 339 mμ) in the ultraviolet. Both the isomerization product and authentic benzil osazone give only a muddy brown color with sulfuric acid.

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[12] The melting point of benzil osazone is very dependent on the rate of heating.

The Structure of "Anhydro Acetophenone Disulfide"

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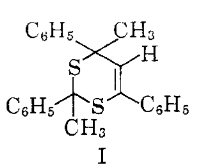
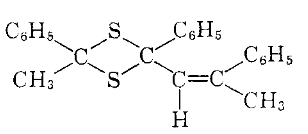
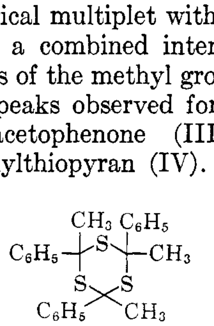
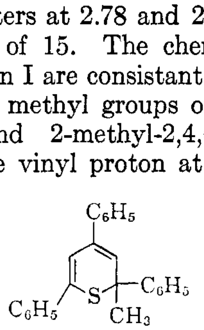
Baumann and Fromm[1] in 1895 isolated a $C_{24}H_{22}S_2$ compound, "anhydro acetophenone disulfide" from the treatment of acetophenone with hydrogen sulfide and hydrogen chloride in absolute ethanol. These authors suggested I and II as possible structures. Campaigne[2a,b] and co-workers have prepared a series of compounds of this type from substituted acetophenones for use as intermediates in the synthesis of 2,4-diaryl thiophenes. Despite the importance of these compounds in chemical synthesis the structure is as yet unknown.[3] The following spectral evidence indicates that the structure is that shown as I, 2,4-dimethyl-2,4,6-triphenyl-2H,4H-1,3-dithiin.


I

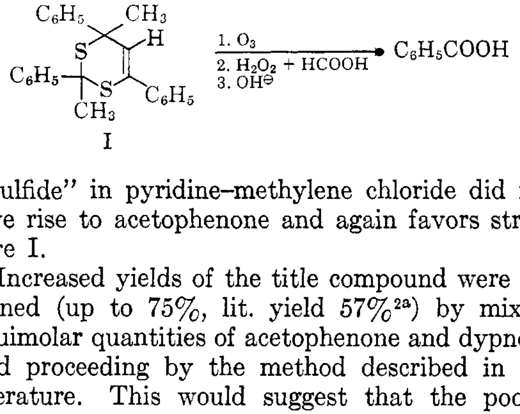

II

The n.m.r. spectrum of "anhydro acetophenone disulfide," recorded on a Varian HR-60 spectrometer, shows singlets at 8.55, 8.21, and 3.76 τ with relative intensities of 3:3:1 and an unsymmetrical multiplet with centers at 2.78 and 2.45 τ with a combined intensity of 15. The chemical shifts of the methyl groups in I are consistant with the peaks observed for the methyl groups of trithioacetophenone (III) and 2-methyl-2,4,6-triphenylthiopyran (IV). The vinyl proton at 3.76 p.p.m. shows no spin-coupling greater than 0.1 c.p.s. with either of the methyl peaks. This evidence would favor structure I where the vinyl proton is separated from the methyl protons by four saturated bonds thus giving rise to a very small coupling constant. Structure II in which the single proton and a methyl group reside on a double bond, would be expected to show spin-coupling between the vinyl proton and methyl protons of 0.5–2.0 c.p.s.[4]


III


IV

Chemical evidence in support of structure I is provided by the isolation of benzoic acid after ozonolysis followed by oxidative work-up and base treatment. Under these conditions structure I would be expected to give benzoic acid whereas II would not. Ozonolysis of "anhydro acetophenone disulfide" in pyridine–methylene chloride did not give rise to acetophenone and again favors structure I.



I

Increased yields of the title compound were obtained (up to 75%, lit. yield 57%[2a]) by mixing equimolar quantities of acetophenone and dypnone and proceeding by the method described in the literature. This would suggest that the poorer yields obtained in the cases of substituted acetophenones might be improved by starting with the substituted acetophenone and corresponding dypnone mixture. Work along this line is under study.

Experimental

Ozonolysis of "Anhydro Acetophenone Disulfide."—A. A solution of 10.0 g. (0.0268 mole) of "anhydro acetophenone disulfide"[2a] in 100 ml. of methylene chloride was treated with a dilute stream of ozone in oxygen at −80°.[5] Formic acid (20 ml.) and 10 ml. of 30% hydrogen peroxide were added and the mixture was allowed to stir overnight at room temperature. The mixture was poured into water and was extracted

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[1] E. Baumann and E. Fromm, *Ber.*, **28**, 895 (1895).

[2] (a) E. Campaigne, *J. Am. Chem. Soc.*, **66**, 684 (1944); (b) E. Campaigne, W. B. Reid, Jr., and J. D. Pera, *J. Org. Chem.*, **24**, 1229 (1959).

[3] E. Campaigne, "Organic Sulfur Compounds," N. Kharash, ed., Pergamon Press, Inc., New York, N. Y., 1961, p. 142.

[4] L. M. Jackman, "Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, Inc., New York, N. Y., 1959, p. 85.

[5] Analysis by n.m.r. of a portion of the crude product indicated approximately 50% of the double bond had been cleaved.

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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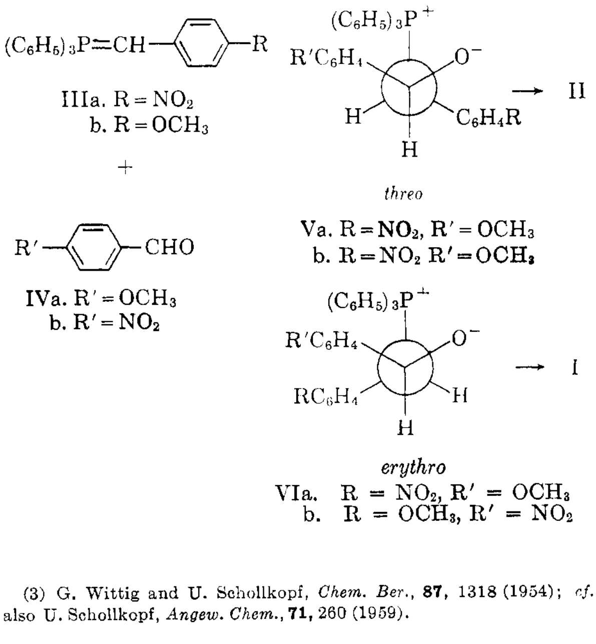
cis-4-Nitro-4′-methoxystilbene (I) has been prepared by the photochemical rearrangement of its *trans* isomer (II).[1] This reaction, however, is not suited for the preparation of relatively large quantities needed for planned biological, physical, and chemical studies. The partial reduction of 4-nitro-4′-methoxytolane 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).