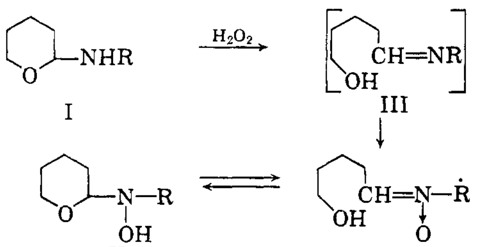

Ia. R = n-C_4H_9
Ib. R = $C_2H_4OC_2H_5$

We did not detect the presence of the tautomeric hydroxylamine derivatives II, although secondary amines are known to be oxidized preferentially to the N,N-disubstituted hydroxylamines.[10] Thus it appears that in the first step of this reaction the O,N-acetal was hydrolyzed to the corresponding azomethine III which was subsequently oxidized by the hydrogen peroxide to the nitrone I. The ready hydrolysis of O,N-acetals of 5-hydroxypentanal by water has been already reported by Glacet and Gaumeton.[9]

There is some indication that the nitrones I tautomerize to the tetrahydropyranylhydroxylamines II in alkaline solution. In 5% sodium hydroxide solution at room temperature the nitrone Ia gave an immediate positive hydroxylamine test with triphenyltetrazolium chloride[11] and reduced silver halide in the cold, whereas the N-n-propyl-C-ethylnitrone IV which was synthesized by Ruppert's method did not. The positive hydroxylamine test with triphenyltetrazolium chloride has to be judged with some caution since any nitrone is expected to be hydrolyzed to a N-alkylhydroxylamine in alkaline solution; however, it appears that this hydrolysis is not rapid at room temperature or else IV would also have caused the immediate reduction of silver halide.

Experimental[12]

N-n-Butyl-C-4-hydroxytetramethylene Nitrone (Ia).—Nine grams of 30% hydrogen peroxide was added dropwise with ice cooling to 11.5 g. of 2-n-butylaminotetrahydropyran.[9] After it had been stirred for 20 hr. at room temperature the reaction mixture was extracted with chloroform. By distillation of the dried chloroform extract was obtained 7.4 g. (58.5%) of N-n-butyl-C-4-hydroxytetramethylene nitrone, b.p. 151–152° (0.1 mm.); n^{25}_{D} 1.4712. $\lambda_{max}^{CHCl_3}$ (infrared) 2.95–3.03, 3.43, 6.03, 6.55, 6.82 μ.

Anal. Calcd. for $C_9H_{19}NO_2$: N, 8.09. Found: N, 8.28.

2-Ethoxyethylaminotetrahydropyran.—A 20.4-g. sample (0.2 mole) of 2-hydroxytetrahydropyran[13] was added dropwise with ice cooling to a stirred suspension of 13 g. of anhydrous potassium carbonate in 17.8 g. (0.2 mole) of ethoxyethylamine. The reaction mixture was stirred for 1 hr. at 0° and for 3 hr. at room temperature. It was then filtered and the insoluble potassium carbonate washed with ether. Distillation of the combined organic solutions gave 29 g. (84%) of 2-ethoxyethylaminotetrahydropyran, b.p. 69–70° (1.4 mm.); n^{23}_{D} 1.4502.

Anal. Calcd. for $C_9H_{19}NO_2$: 8.09. Found: N, 8.03.

N-Ethoxyethyl-C-4-hydroxytetramethylene Nitrone (Ib).—Ten grams of 35% hydrogen peroxide was added dropwise with stirring and ice cooling to 17.3 g. (0.1 mole) of 2-ethoxyethylaminotetrahydropyran. The mixture was stirred for 8 hr. at room temperature and extracted with chloroform. By distillation of the dried chloroform extract was obtained 8.2 g. (43.5%) of N-ethoxyethyl-C-4-hydroxymethylene nitrone, b.p. 168–172° (0.7 mm.); n^{23}_{D} 1.4695. $\lambda_{max}^{CHCl_3}$ (infrared) 2.92–3.02, 3.45, 6.02, 6.55, 6.87, 9.0 μ; (salt plate): 3.05, 3.4–3.5, 6.03, 6.4, 6.87, 8.95.

Anal. Calcd. for $C_9H_{19}NO_3$: C, 57.11; H, 10.12; N, 7.40. Found: C, 57.31; H, 10.25; N, 7.48.

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[10] L. Mamlock and R. Wolffenstein, *Ber.*, **34**, 2500 (1901).

[11] G. A. Snow, *J. Chem. Soc.*, 2588 (1954).

[12] Microanalyses by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

[13] G. F. Woods, Jr., *Org. Syn.*, **27**, 43 (1947).

Oxidative Dimers of Benzaldehyde Phenylhydrazone

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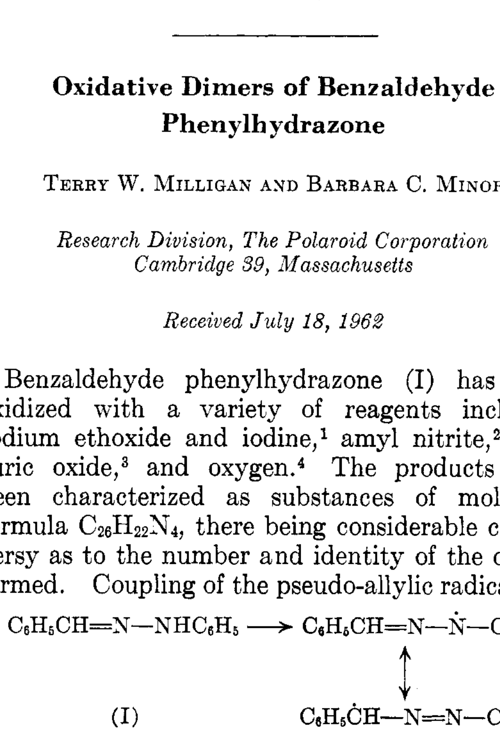
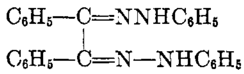
Benzaldehyde phenylhydrazone (I) has been oxidized with a variety of reagents including sodium ethoxide and iodine,[1] amyl nitrite,[2] mercuric oxide,[3] and oxygen.[4] The products have been characterized as substances of molecular formula $C_{26}H_{22}N_4$, there being considerable controversy as to the number and identity of the dimers formed. Coupling of the pseudo-allylic radical (II) in a C—C (IIIa), C—N (IVa) and N—N (V) manner has been proposed. The isomerization of the "N—N" dimer of m.p. 186° to benzil osazone



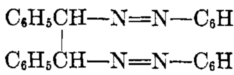
$$\begin{array}{ccc} C_6H_5CH{=}N{-}NHC_6H_5 & \longrightarrow & C_6H_5CH{=}N{-}\dot{N}{-}C_6H_5 \\ & & \updownarrow \\ & & C_6H_5\dot{C}H{-}N{=}N{-}C_6H_5 \end{array}$$

(I) (II)



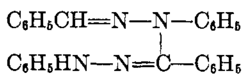
$$\begin{array}{l} C_6H_5{-}C{=}NNHC_6H_5 \\ \quad\;\; | \\ C_6H_5{-}C{=}N{-}NHC_6H_5 \end{array}$$

(IIIa)



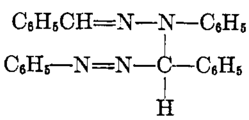
$$\begin{array}{l} C_6H_5CH{-}N{=}N{-}C_6H_5 \\ \quad\;\; | \\ C_6H_5CH{-}N{=}N{-}C_6H_5 \end{array}$$

(IIIb)



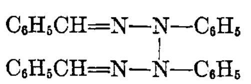
$$\begin{array}{r} C_6H_5CH{=}N{-}N{-}C_6H_5 \\ | \quad\;\;\; \\ C_6H_5HN{-}N{=}C{-}C_6H_5 \end{array}$$

(IVa)



$$\begin{array}{r} C_6H_5CH{=}N{-}N{-}C_6H_5 \\ | \quad\;\;\; \\ C_6H_5{-}N{=}N{-}C{-}C_6H_5 \\ | \quad\;\;\; \\ H \quad\;\;\; \end{array}$$

(IVb)



$$\begin{array}{r} C_6H_5CH{=}N{-}N{-}C_6H_5 \\ | \quad\;\;\; \\ C_6H_5CH{=}N{-}N{-}C_6H_5 \end{array}$$

(V)

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[1] (a) H. Ingle and H. H. Mann, *J. Chem. Soc.*, **67**, 60 (1895); (b) E. Bamberger and J. Grob, *Ber.*, **34**, 523 (1901).

[2] (a) E. Bamberger and W. Pemsel, *ibid.*, **36**, 57 (1903); (b) H. v. Pechmann, *ibid.*, **26**, 1045 (1893).

[3] (a) G. Minnunni, *Gazz. chim. Ital.*, **22**, [2], 217 (1892); (b) G. Minnunni and E. Rap, *ibid.*, **26**, [1], 442, 446 (1896).

was explained as a dissociation into the original radicals which recombined *via* the C—C path. These ideas are recorded in several monographs.[5,6] More recently the structure of the 186° compound has been reassigned as IVb on the basis of its ultraviolet spectrum,[7] which shows it to be an azo compound.

We have examined the oxidation products obtained from benzaldehyde phenylhydrazone using sodium hydroxide and ammoniacal silver nitrate in dimethylformamide as the oxidant.[8] The crude product obtained may be separated by crystallization into two dimers, m.p. 200.5–201° and 187–188°. The first compound has an ultraviolet spectrum ($\lambda_{\max}^{\mathrm{CHCl_3}}$ 298, 335 mμ: ε 19,400, 37,000) indicative of the presence of two phenylhydrazone chromophores (benzil osazone, $\lambda_{\max}^{\mathrm{CHCl_3}}$ 300, 343 mμ; ε 21,000, 36,800). The infrared spectrum confirms the presence of —NH (3330 cm.$^{-1}$) and ArC=N— (1590, 1543, 1485 cm.$^{-1}$) of the phenylhydrazone type.[9] The infrared spectrum is very similar but not identical to the spectrum of benzil osazone recrystallized from the same solvent. Further evidence was sought from the 60 mc. nuclear magnetic resonance spectrum, but unfortunately the —CH=N— proton signal appears buried[10] by the strong complex aromatic hydrogen absorption at −428 c.p.s. (relative to tetramethylsilane) and the —NH signal was too weak to be observed at the solubility limit. Both benzaldehyde phenylhydrazone (−435 c.p.s.) and benzil osazone (−427 c.p.s.) gave similar, but definitely different, n.m.r. spectra in which the —CH=N and —NH signals were not isolable. Our spectroscopic evidence is thus in accord with the previously assigned structure IVa, $N^{\alpha},N^{\beta'}$-diphenyl-N^{β}-benzalbenzhydrazidine, for the 201° compound.

A similar examination of the 187° isomer by spectroscopic and chemical means leads to its identification as 1,2-bis(phenylazo)-1,2-diphenylethane (IIIb), the bisazo tautomer of benzil osazone, and eliminates the two previously assigned structures, IVb and V. Thus, the ultraviolet spectrum of a freshly prepared solution ($\lambda_{\max}^{\mathrm{CHCl_3}}$ 277, 404 mμ; ε 22500, 485) is definitely that of an azo compound,[7,9] while on standing a typical phenylhydrazone chromophore ($\lambda_{\max}$ 300, 345 mμ) was generated. This isomerization was also accomplished preparatively by a trace of acid, and benzil osazone was identified as the product. Further confirmation is available from the infrared spectrum (no —NH, no strong unsaturation absorption 1600–1500 cm.$^{-1}$). Perhaps the most striking evidence, however, is afforded by the n.m.r. spectrum,[11] where in addition to the aromatic multiplet at −436 c.p.s. (20 protons) there is a sharp signal at −343 c.p.s. (4.28 τ) corresponding in position and intensity to that expected for two protons on benzylic carbon atoms substituted by azo-unsaturation.

Experimental

Melting points were obtained in a Mel-Temp capillary melting point apparatus and are corrected. Infrared spectra were determined in potassium bromide disks. Elemental analyses were by A. Bernhardt, Max-Planck-Institut, Mulheim (Ruhr), Germany. The n.m.r. spectra were determined by Mr. Luther Herrick on a Varian HR-60 instrument using tetramethylsilane as an internal standard. Solutions contained 30 mg. of compound in 0.5 cc. of deuteriochloroform. In the case of benzaldehyde phenylhydrazone, precautions were taken to exclude oxygen and to work rapidly to avoid formation of a purple decomposition product. 1,2-Bis(phenylazo)-1,2-diphenylethane was sufficiently soluble only at elevated temperatures. Its spectrum was studied from 30 to 65° and did not change; the data reported are from the 65° spectrum.

Oxidation Procedure.—A mixture prepared by dissolving 2.55 g. (0.015 mole) of silver nitrate in 12 ml. of 28% ammonium hydroxide and adding a solution of 0.6 g. (0.015 mole) of sodium hydroxide in 2 ml. of water was poured into a solution of 2.94 g. (0.015 mole) of benzaldehyde phenylhydrazone in 25 ml. of dimethylformamide. There was an immediate reaction as evidenced by the precipitation of a mixture of metallic silver and the organic products. After stirring for 10 min., the mixture was diluted with 150 ml. of water and filtered. The precipitate was washed with water and air dried. In our earlier experiments, we obtained both isomers from the same crude mixture by tedious fractional crystallization. Best results were later obtained, however, by making a separate run and modifying the work-up to obtain the desired compounds. The crude product (50% yield) has an ultraviolet spectrum indicative of a 7 to 1 mixture of the hydrazidine and azo dimers respectively.

$N^{\alpha},N^{\beta'}$-Diphenyl-N^{β}-benzalbenzhydrazidine (IVa).—The crude solid mixture was recrystallized from cyclohexane. After standing without agitation overnight the first crop, m.p. 190–193°, was collected. It was rich in the 187° isomer and was discarded. On scratching and further standing, the mother liquors deposited a second crop, m.p. 197–197.5° (mixture m.p. with first crop 188–190°). The second crop was recrystallized twice more from cyclohexane and was obtained as nearly colorless needles, m.p. 200.5–201°. It is soluble in cold chloroform and turns green in concentrated sulfuric acid.

Anal. Calcd. for $C_{26}N_{22}H_4$: C, 79.97; H, 5.68; N, 14.35. Found: C, 79.88, 79.98; H, 5.61, 5.75; N, 14.36.

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[4] (a) H. Stobbe and R. Nowak, *Ber.*, **46**, 2887 (1913); (b) M. Busch and H. Kunder, *ibid.*, **49**, 2345 (1916).

[5] H. Wieland, "Die Hydrazine," Verlag von Ferdinand Enke, Stuttgart, 1913, pp. 118–122.

[6] N. V. Sidgewick, "Organic Chemistry of Nitrogen," 2nd ed. revised by T. Taylor and W. Baker, Oxford, 1937, pp. 464, 465.

[7] P. Grammatickakis, *Compt. rend.*, **224**, 1509 (1947). It is interesting that the ultraviolet evidence cited is in itself not consistent with the assigned structure IVb, which contains a remaining hydrazone chromophore.

[8] The composition of the solvent is an important variable. Alkaline solutions of benzaldehyde phenylhydrazone in aqueous alcohols are colorless and do not react with silver ion. An alkaline solution in a polar, nonhydroxylic solvent such as dimethylformamide, dimethyl sulfoxide, or N-methylpyrrolidone is yellow, probably indicating formation of an anion, and reacts rapidly with silver ion.

[9] R. O'Connor and W. Rosenbrook, Jr., *J. Org. Chem.*, **26**, 5208 (1961); R. O'Connor, *ibid.*, **26**, 4375 (1961). The authors consider azo-phenylhydrazone tautomerization in detail.

[10] Other examples of the same difficulty are reported by D. Y. Curtin, J. A. Gourse, W. H. Richardson, and K. L. Rinehart, Jr., *ibid.*, **24**, 93 (1959).

[11] B. H. Arison, A. E. Erickson, N. R. Tienner, and E. F. Schoenewaldt, *Chem. Ind.* (London), 1627 (1958) have used n.m.r. spectroscopy to settle an azo *vs.* phenylhydrazone structural assignment in another system.

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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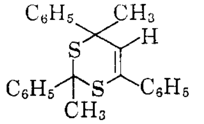
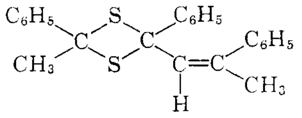
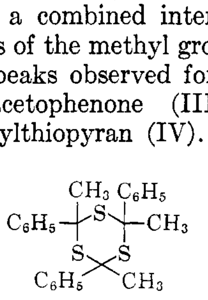
Received July 19, 1962

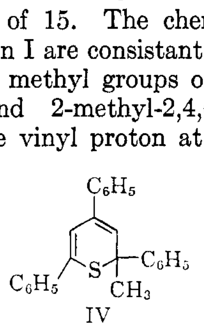
Baumann and Fromm[1] in 1895 isolated a $C_{24}H_{22}S_2$ compound, "anhydro acetophenone disulfide" from the treatment of acetophenone with hydrogen sulfide and hydrogen chloride in absolute ethanol. These authors suggested I and II as possible structures. Campaigne[2a,b] and co-workers have prepared 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

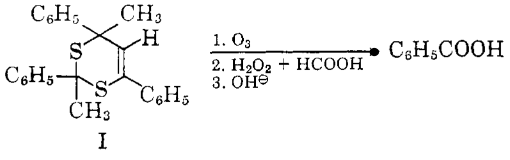

II

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.