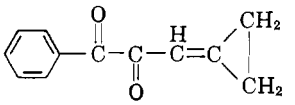
ozonolysis under mild conditions resulted in the formation of a mixture of acids whose infrared spectrum indicated the presence of benzene rings and of ketonic carbonyl groups.

Infrared spectra of the original anomalous product showed absorption characteristic of an $\alpha$-diketone and of a cyclopropane ring, in addition to showing three peaks in the C–H stretching region. No OH stretching absorption was apparent. On the basis of these data, structure II was proposed for the compound. A



II

nuclear magnetic resonance spectrum[4] of the anomalous product was compatible with structure II. The spectrum revealed bands at $\delta$ 7.35 (5 protons), 6.96 (1 proton, a triplet), 4.43 (2 protons, a triplet), and 2.60 (2 protons, a sextet). This spectrum may be interpreted as follows. The triplet centered at $\delta$ 6.96 is the single olefinic proton which is splitting with two protons of one of the methylene groups of the cyclopropane ring. The sextet centered at $\delta$ 2.60 is produced by the two methylene protons of the cyclopropane ring, which are splitting with the olefinic proton and also with the adjacent methylene protons of the cyclopropane ring. The triplet centered at $\delta$ 4.43 represents this latter pair of methylene protons of the cyclopropane ring, which is splitting only with the adjacent ring methylene protons. The stereochemistry imposed by the double bond exocyclic to the cyclopropane ring will permit the protons of only one of the methylene groups of the cyclopropane ring to interact with the olefinic proton.

### Experimental

All melting points are corrected and boiling points are uncorrected. Analyses are by Schwartzkopf Microanalytical Laboratories, Woodside, New York. Infrared spectra were recorded on a Beckman IR-5A spectrophotometer. Ozone was generated by means of a Welsbach T-23 Ozonator, equipped with a Welsbach H 80 ozone analyzer. Microhydrogenations were performed on an Ogg-Cooper microhydrogenation apparatus.

**Ozonolysis. General Method.**—The reaction vessel was a three-neck, round-bottom flask, equipped with a Dry Ice–acetone cold finger condenser and a sintered-glass delivery tube which extended well below the surface of the contents of the flask. The reaction vessel was immersed in an ice–water slurry and was seated on a magnetic stirrer. Oxygen, containing a measured concentration of ozone, was introduced into the solution of the acetylenic alcohol at a known rate of flow for a measured period of time, with efficient stirring. The reaction mixture was extracted with 5% sodium bicarbonate solution, which was acidified with concentrated hydrochloric acid. The resulting cloudy mixture was extracted repeatedly with ether. The combined ethereal extracts were dried over anhydrous magnesium sulfate, filtered, and the ether was removed on a steam bath. The residue was crystallized or was converted to its methyl ester.

**Benzilic Acid.**—Oxygen containing 30 mg./l. of ozone was passed into a solution of 1.50 g. (0.0072 mole) of 1,1-diphenyl-2-propyn-1-ol[5] in 50 ml. of chloroform, at a flow rate of 30 l./hr. for 0.5 hr. The crude benzilic acid was recrystallized from hot water, to afford 1.2 g. (73%), m.p. 148–149°. The infrared spectrum of this product (chloroform) was identical with a similar spectrum of an authentic sample of benzilic acid.

**Cyclopropylphenylglycolic Acid.**—Oxygen containing 20 mg./l. of ozone was passed into a solution of 3.4 g. (0.02 mole) of 1-phenyl-1-cyclopropyl-2-propyn-1-ol[2] in 50 ml. of reagent grade cyclohexane at a flow rate of 20 l./hr. for 3 hr. The crude acid was converted to its methyl ester with diazomethane, to afford 1.54 g. (40%)[6] of an oil, b.p. 80–83° (0.15 mm.), $n^{25}$D 1.5217 (lit.[2] b.p. 84–88° at 0.3 mm., $n^{25}$D 1.5214).

**Cyclobutylphenylglycolic Acid.**—Oxygen containing 25 mg./l. of ozone was passed into a solution of 4.4 g. (0.024 mole) of 1-phenyl-1-cyclobutyl-2-propyn-1-ol[2] in 50 ml. of reagent grade cyclohexane, at a flow rate of 30 l./hr. for 3 hr. The crude acid was converted to its methyl ester with diazomethane, yielding 2.4 g. (47%)[6] of an oil, b.p. 100–104° (0.2 mm.), which slowly crystallized; m.p. 55–56° (lit.[2] m.p. 56–57°).

**9-Hydroxyfluorene-9-carboxylic Acid.**—Oxygen containing 4 mg./l. of ozone was passed at a flow rate of 70 l./hr. for 1 hr. into a solution of 4.12 g. (0.02 mole) of 9-ethynyl-9-fluorenol[7] in 150 ml. of chloroform, to which 100 ml. of 5% sodium hydroxide solution had been added. The aqueous layer was acidified and extracted as described previously. The crude product was converted to its methyl ester with diazomethane, and the ester was recrystallized from benzene–Skellysolve B, to afford 2.5 g. (52%)[6] of material melting at 159–160° (lit.[8] m.p. 160°).

**3-Phenyl-2,3-diketo-1-cyclopropylidenepropane (II).**—Oxygen containing 30 mg./l. of ozone was added at a flow rate of 20 l./hr. for 1 hr. to a solution of 5.2 g. (0.03 mole) of 1-cyclopropyl-1-phenyl-2-propyn-1-ol[2] in 50 ml. of chloroform to which had been added 15 ml. of 5% sodium bicarbonate solution. The aqueous layer was separated and was made slightly acidic to litmus with concentrated sulfuric acid. The resulting cloudy solution was taken to dryness on a flash evaporator at a temperature of 40°, and the dark residue was extracted with hot Skellysolve B. On cooling, white crystals separated, m.p. 98–100°, yielding 0.3 g. (15%).[9] The infrared spectrum (10% in chloroform) exhibited the following significant peaks: 5.83 ($\alpha$-dicarbonyl), 3.31, 3.38, 3.44 (C–H stretching characteristic of CH and $CH_2$ groups), and 9.88 $\mu$ (cyclopropane).

*Anal.* Calcd. for $C_{12}H_{10}O_2$: C, 77.38; H, 5.42; mol. wt., 186. Found: C, 77.01; H, 5.67; mol. wt. (cryscopic in benzene), 179.

Microhydrogenation (with platinum oxide in methanol) data indicated one double bond, 4.05 cc. (calcd. for $C_{12}H_{10}O_2$, 3.94 cc.).

(4) The spectrum was recorded on a Varian Associates A-60 instrument by Dr. Ross G. Pitcher, Varian Associates, Palo Alto, Calif., who assigned the chemical shifts to the protons.

(5) P. Cadiot and A. Willemart, *Bull. soc. chim. France*, 100 (1951).

(6) Yield was based on the amount of acetylenic alcohol subjected to ozonolysis.

(7) G. F. Hennion and B. R. Fleck, *J. Am. Chem. Soc.*, **77**, 3253 (1955).

(8) H. Staudinger, *Ber.*, **39**, 3061 (1906).

(9) Yield was based on the recovery of 3.4 g. of unreacted starting material.

## Photoinduced Condensations of Nitroaromatics

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*Received June 2, 1964*

Aromatic molecular complexes of the electron donor–acceptor type, such as those of picric acid and other aromatic species, appeared intriguing as starting materials for ultraviolet irradiation studies. The initial goal was to determine whether the charge transfer absorption would lead to products, in particular, products in which the two aromatic rings are linked.

Trinitrobenzene and benzene, whose symmetry elements and chemical properties are desirable for the initial studies, gave 3,5,3′,5′-tetranitroazoxybenzene (I) along with a small yield of a second unidentified component, II, instead of an isomerized prod-

(1) Abstracted from the M. S. Thesis of D. J. Holter, University of North Dakota, 1963. This investigation was supported in part by fellowship 15,094 from the Division of Research Grants of the National Institutes of Health, Public Health Service.

uct. The separation of the two required careful alumina chromatography. N.m.r., ultraviolet, and infrared spectra analysis along with molecular weight determination, analysis, and comparison with an authentic sample characterized the product I completely.[2,3] Dinitrobenzene was found to undergo a similar condensation in ethanol to produce 3,3′-dinitroazoxybenzene.

Prolonged irradiation periods only produced further polymerized products and less of I. The irradiation times of 36 hr. gave yields as high as 28% of I along with considerable amounts of a gum which would not elute from an alumina column. The yield of the second component II was consistently low, about 0.5%.

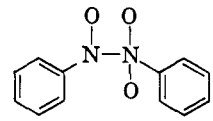
Although photochemical condensations of polynitroaromatic compounds have not been reported, *o*-nitrobenzaldehyde, a substituted mononitrobenzene, is known to condense to form azoxybenzene-*o*,*o*′-dicarboxylic acid among other products under photochemical conditions.[4] Therefore the occurrence of the azoxy-linked product I could be expected if the complex dissociated during or before the absorption of a photon and provided the formation rate of polycondensation products is slow. The formation of azoxybenzene from the parent compound, nitrobenzene, in the presence of benzaldehyde,[5] toluene,[6] and aniline[7] illustrates that the reaction may proceed with an external reducing agent as well.

The trinitrobenzene reaction yields only starting material with benzene as the solvent, but it will proceed in tetrahydrofuran.[8] This substantiates the more obvious fact that a reducing agent other than the nitrobenzene is necessary for the reaction. That ethanol acts as a reducing agent in the present reaction was shown by the isolation of the 2,4-dinitrophenylhydrazone of acetaldehyde from the gases of the reaction mixture. The method used is a convenient, simple way of trapping the elusive acetaldehyde in these reaction mixtures. Nitrogen gas is passed into the solution and the exit gases are exposed to a 2,4-dinitrophenylhydrazine solution. The boiling point of acetaldehyde is low enough to allow it to be carried with the nitrogen gas.

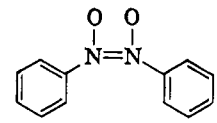
The principal importance of the nitro condensation reactions lies in synthesis. Coupling of trinitrobenzene and dinitrobenzene using various types of bases gives comparable yields, but the isolations of products are difficult.[9]

Because of the multitude of possible oxidation states which aromatic nitrogen molecules can take, there are a number of plausible mechanisms for the condensation. Coupling may be envisioned to occur between (1) two nitro groups, (2) a nitro group and a nitroso group, (3) two nitroso groups, or (4) a nitroso group and a hydroxylamine group *via* classical means. Without further evidence none of the possibilities should be overlooked although the last looks more palatable based on the known condensation under nonphotochemical conditions.[10]

It is likely that the intermediate in these nitro condensation reactions is either III or IV which are the consequences of paths 2 and 3 respectively. That path 3 is possible is shown by the following facts. Nitrosobenzene is known to photochemically generate azoxybenzene.[10] Further, nitrosobenzene dimerizes in the absence of ultraviolet light[11] indicating that reduction may occur on this dimer, IV. We were unable to find any of the ring oxidation products in our reaction mixtures.



III



IV

## Experimental[12]

**Irradiation of 1,3,5-Trinitrobenzene in 95% Ethanol.**—1,3,5-Trinitrobenzene (10 g.) was placed in 500 ml. of 95% ethanol and the suspension was then irradiated for 36 hr. Upon filtration, 4 g. of unreacted starting material was found of m.p. 119–121°. Evaporation of the filtrate gave 5.5 g. of red-brown solid. This solid was taken up in minimum acetone and chromatographed on alumina. Starting material, 2.6 g., m.p. 119–121°, came off the column with 1:1 benzene–petroleum ether (b.p. 60–70°). Further elution with 1:9 petroleum ether–benzene produced 0.96 g. of I, m.p. 181–184°. After two recrystallizations from benzene, the melting point of I was 185–186°, m.m.p. 184–186.2°. The infrared and ultraviolet spectra of I were identical with those of the authentic material.

**Irradiation of 1,3,5-Trinitrobenzene in Tetrahydrofuran.**—1,3,5-Trinitrobenzene (2 g.) was placed in 200 ml. of purified tetrahydrofuran and the solution was irradiated for 68 hr. The brown solution was then evaporated to a brown, tacky residue, 1.9 g., which was taken up in minimal acetone and chromatographed on alumina. The resulting separation provided 0.13 g. of starting material, 0.05 g. of I, and 0.02 g. of II. About 75% of the material put on the column did not come off. Identities were concluded from infrared evidence and elution solvent.

**Acetaldehyde Formation by Irradiation of 1,3,5-Trinitrobenzene.**—1,3,5-Trinitrobenzene (7 g.) in about 500 ml. of 95% ethanol was irradiated for 1.5 hr. Nitrogen was bubbled into the solution and the exit gases were passed near the surface of a 2,4-dinitrophenylhydrazine solution. Large quantities of light-orange needles had precipitated at the end of 1 hr. The recrystallized hydrazone melted at 161–163°; mixture melting point of the authentic acetaldehyde 2,4-dinitrophenylhydrazone was 161–163.5°.

(2) The azoxybenzene I was prepared with difficulty according to the procedure of C. A. Lobry, de Bruyn and A. van Leent, *Rec. trav. chim.*, **13**, 151 (1894). For the ultraviolet spectra of I and related compounds, see P. H. Gore and O. H. Wheeler, *J. Am. Chem. Soc.*, **78**, 2160 (1956). Dr. Gore kindly sent us a sample of the same compound I which also proved identical to our product. The samples were proven the same in all respects by a mixture melting point and infrared and ultraviolet spectra.

(3) The available evidence on the unidentified component II is insufficient for complete characterization; however, the n.m.r. spectrum of II exhibits one set of triplets and one set of doublets ($AX_2$) in contrast to the two sets of each type ($AX_2$-$AX'_2$) for I. The $J$ values for both compounds were in the vicinity of 2 c.p.s., which is consistent with the size of coupling constants between meta protons in benzenoid compounds. These facts rule out the possibility of II being a condensation product between benzene and trinitrobenzene and indicate either a symmetrical dimer or a 1,3,5-trisubstituted monomer with one of the three substituents in a different oxidation state. The $\tau$ values in p.p.m. are I, doublets at 0.53 and 0.69 and triplets at 0.76 and 0.98; II, a doublet at 2.27 and a triplet at 2.04; trinitrobenzene, a singlet at 0.53.

(4) G. Ciamician and P. Silber, *Gazz. chim. acta*, **33**, I, 374 (1901); *cf.* W. Reid and M. Wilk, *Ann.*, **590**, 91 (1954).

(5) G. Ciamician and P. Silber, *Chem. Ber.*, **38**, 1176 (1905).

(6) L. Vecchiotti and G. Zanetti, *Gazz. chim. ital.*, **61**, 798 (1931).

(7) L. Vecchiotti and C. Piccinini, *ibid.*, **61**, 626 (1931).

(8) Tetrahydrofuran can be readily autoxidized to butyrolactone under photochemical conditions. This will be the subject of a future communication.

(9) In a private communication, P. H. Gore reported difficulty in the preparation of I also.

(10) E. Bamberger, *Chem. Ber.*, **35**, 1606 (1902).

(11) B. G. Gowenlock and J. Kay, *J. Chem. Soc.*, 2880 (1962).

(12) The light source employed was a quartz, immersion-type 550-w. Hanovia high pressure mercury arc lamp. The n.m.r. spectrum of I was kindly prepared for us on a Varian HR 60 by D. J. Pasto at the University of Notre Dame and the spectrum of II was run on a Varian A-60. The spectra were obtained with the aid of Perkin-Elmer Infracord and Bausch and Lomb Spectronic 505 spectrophotometers.

**Irradiation of 1,3-Dinitrobenzene.**—1,3-Dinitrobenzene (10 g.) was placed in 500 ml. of absolute ethanol and irradiated for 72 hr. Filtration of the resultant suspension afforded 3.20 g. of starting material. Evaporation of the solvent left 6.80 g. of crude brown material, m.p. 45–70°. Two grams of this crude material was chromatographed on alumina. Starting material, 1.25 g., eluted off in petroleum ether. In 1:5 petroleum ether–benzene eluent, 0.104 g. (2.7%) of crystals was found of m.p. 140–143°; mixture melting point of an authentic sample of 3,3′-dinitroazoxybenzene was 138–142°. The ultraviolet and infrared spectra were identical.

## Formic Ethylcarbonic Anhydride[1]

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*Received April 10, 1964*

The preparation of a number of stable mixed carboxylic carbonic anhydrides,[2] RCOOCOOR′ (R = aryl or alkyl and R′ = alkyl) has prompted us to study the synthesis and properties of formic ethylcarbonic anhydride (A). The symmetrical anhydride of formic acid is unstable[3]; the mixed anhydride of formic and acetic acid is well known,[4] however, and has been used to acylate on oxygen and nitrogen. Formyl chloride, HCOCl, appears to be stable for a few hours[5] at −60°, and formyl fluoride is readily accessible.[3,6]

Treatment of carefully dried formic acid with ethyl chlorocarbonate and triethylamine in ether at −15° for 15–20 min. gave a nearly quantitative yield of triethylamine hydrochloride; the filtrate, after shaking with solid sodium bicarbonate, showed strong bands in the infrared at 1730 and 1793 cm.$^{-1}$, indicative of the presence of mixed carboxylic–carbonic anhydride.[2] Dimethyl ether was also used as solvent in some runs.

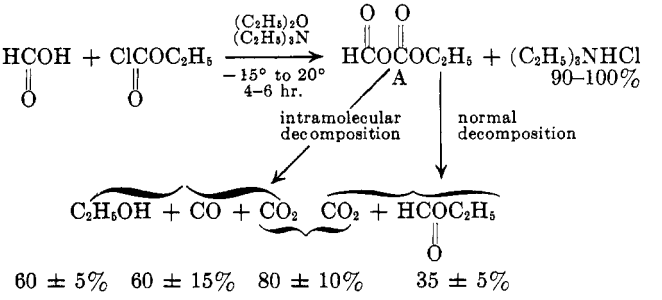
The presence of the mixed anhydride was verified by preparation of the formyl derivative of α-naphthylamine; the latter was added to ethyl chlorocarbonate in ether at 15°, 15 min. after triethylamine was added. The mixture was stirred for 30 min. and the formyl-α-naphthylamine obtained was identical with a known sample.[7]

The residue from the filtrate prepared as above gave a mixture which was shown by v.p.c. analysis and n.m.r. measurements to consist of ethyl alcohol and ethyl formate. Quantitative analyses for ethanol and ethyl formate showed that, in about ten runs, the average yields were 60 ± 5% of alcohol and 35 ± 5% of ester. The triethylamine hydrochloride was obtained in 90–100% yield.

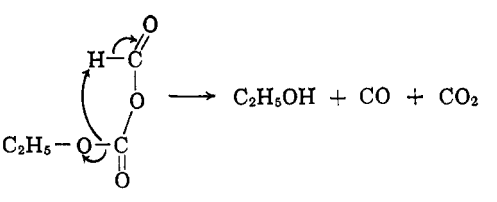
The appearance of ethyl formate can be readily explained by the formation of the mixed anhydride A, which then lost carbon dioxide to form the ester, analogous to other mixed anhydrides, which, however, require temperatures much higher than 0° to decompose in this manner. The formation of carbon dioxide was verified and followed by sweeping the reaction mixture with nitrogen and collecting the carbon dioxide in weighed ascarite tubes. The yields of carbon dioxide were 80 ± 10%, based on complete reaction of the formic acid. It was also observed that 20% of the carbon dioxide was evolved in the first hour and the decomposition was almost complete in 4–6 hr. after the reactants were mixed; the temperature ranged from −15° in the beginning of the reaction to room temperature at the end. Along with the observation from titration experiments that disappearance of formic acid was almost complete 1 hr. after the reactants were mixed, this proved that the mixed anhydride is stable for a short time in that temperature range.

The formation of ethyl alcohol was unexpected; no evidence for the presence of diethyl carbonate could be obtained, but carbon monoxide was shown to be formed by absorbing the gases swept by nitrogen from the reaction mixture of formic acid, ethyl chlorocarbonate, and triethylamine. The carbon monoxide was quantitatively absorbed in a series of bulbs containing cuprous sulfate in sulfuric acid[8] and the yield was 60 ± 15% in about ten runs.

The mixed anhydride appears to decompose by two routes, indicated below, and the yields are in agreement with this.




The decarbonylation of formic acid derivatives[9] is well known, but normally requires more drastic conditions than those prevailing here: solution in ether in essentially neutral solution at 0°. The decomposition of the mixed anhydride to form carbon monoxide, carbon dioxide, and ethanol may involve the following process which may be promoted by traces of catalysts (chloride ion, triethylamine, or protons, depending on circumstances) in the reaction mixture.




(1) Supported by Grant G-11240 from the National Science Foundation.

(2) D. S. Tarbell and N. A. Leister, *J. Org. Chem.*, **23**, 1149 (1958); D. S. Tarbell and E. J. Longosz, *ibid.*, **24**, 774 (1959), and the references therein.

(3) G. A. Olah and S. J. Kuhn, *J. Am. Chem. Soc.*, **82**, 2380 (1960).

(4) A. Béhal, *Compt. rend.*, **128**, 1460 (1899); *Ann. chim. phys.*, [7]**20**, 417 (1900); C. D. Hurd and A. S. Roe, *J. Am. Chem. Soc.*, **61**, 3355 (1939); W. R. Edwards, Jr., and L. H. Reeves, *ibid.*, **64**, 1583 (1942); C. D. Hurd, S. S. Drake, and O. Fancher, *ibid.*, **68**, 789 (1946); B. E. Leach and J. H. Hunter, *Biochem. Prepn.*, **3**, 114 (1953).

(5) H. A. Staab and A. D. Datta, *Angew. Chem.*, **75**, 1203 (1963).

(6) A. N. Nyesmejanov and E. I. Kahn, *Ber.* **87**, 203 (1946).

(7) C. Tobias, *ibid.*, **15**, 2447 (1882).

(8) W. W. Scott, "Standard Methods of Chemical Analysis," D. Van Nostrand Co., Inc., New York, N. Y., 1925, p. 2422.

(9) *Cf.* W. W. Elliott and D. Ll. Hammick, *J. Chem. Soc.*, 3402 (1951), for discussion and leading references.