dodecamethylcyclohexasilane, 19.7 g. (0.0946 mole) of phosphorus pentachloride, and 100 ml. of *sym*-tetrachloroethane was refluxed for 3 hr. The yellow color disappeared rather rapidly. The oil obtained after removal of the solvent and low-boiling materials was distilled under reduced pressure to give 5.4 g. (corresponding to 25.6% of the initial dimethylsilylene groups) of 1,3-dichlorooctamethyltetrasilane, b.p. 89–92° at 15 mm., $n^{20}\text{D}$ 1.4830 (lit.[3] b.p. 82–83° at 11 mm., $n^{20}\text{D}$ 1.4852), and 3.42 g. (17.5%) of 1,4-dichlorooctamethyltetrasilane, b.p. 76–78° at 1.0 mm., $n^{20}\text{D}$ 1.5035.

Anal. Calcd. for $C_8H_{24}Cl_2Si_4$: Cl, 23.4; MR, 92.23. Found: Cl, 23.7, 23.7; MR, 92.70.

In seven other preparations with shorter reflux times ranging from 15 min. to 2 hr., the average yield of the 1,4-dichloro compound was 22.7% based on the dimethylsilylene units in the starting compound, and the yield of 1,3-dichlorohexamethyltrisilane was 17.6%.

In an experiment using carbon tetrachloride in place of *sym*-tetrachloroethane, and refluxing overnight, the yields were 22.1% of 1,2-dichlorotetramethyldisilane, 23.8% of 1,3-dichlorohexamethyltrisilane, and 17.1% of 1,4-dichlorooctamethyltetrasilane (all on the basis of dimethylsilylene units in the starting material).

Decamethyltetrasilane.—From a reaction of 0.148 mole of methylmagnesium iodide in 60 ml. of ether and 7.45 g. (0.0246 mole) of 1,4-dichlorooctamethyltetrasilane in 60 ml. of tetrahydrofuran there was obtained, subsequent to distillation under reduced pressure, 3.98 g. of colorless liquid, $n^{20}\text{D}$ 1.4863. This material was washed first with cold sulfuric acid, then with water, and after drying was redistilled to give 3.11 g. (48%) of decamethyltetrasilane, b.p. 108–109° at 15 mm., $n^{20}\text{D}$ 1.4878 (lit.[3,8] b.p. 109° at 15 mm., $n^{20}\text{D}$ 1.4872).

1,4-Diphenyloctamethyltetrasilane.—From a reaction between 0.084 mole of phenylmagnesium bromide in 70 ml. of tetrahydrofuran and 4.24 g. (0.014 mole) of 1,4-dichlorooctamethyltetrasilane in 30 ml. of tetrahydrofuran was obtained an oil which upon treatment with methanol gave fine crystals. These on recrystallization from methanol gave 2.3 g. (42.5%) of 1,4-diphenyloctamethyltetrasilane, m.p. 59–61°.

Anal. Calcd. for $C_{20}H_{34}Si_4$: C, 62.10; H, 8.85. Found: C, 61.93, 61.81; H, 8.87, 8.90.

The infrared spectrum was quite similar to that of 1,6-diphenyldodecamethylhexasilane. The n.m.r. aromatic–aliphatic proton ratios were 1:2.38, 1:2.36, and 1:2.33 (calculated, 1:2.4).

Reaction of 1,4-Dichlorooctamethyltetrasilane. A. With Sodium.—A reaction mixture of 4.9 g. (0.0162 mole) of 1,4-dichlorooctamethyltetrasilane and 0.75 g. (0.0324 g.-atom) of sodium in 80 ml. of toluene was refluxed overnight subsequent to the addition of a small quantity of sodium–potassium alloy as an initiator. From the reaction mixture was obtained, subsequent to pouring into absolute ethanol containing a small amount of acetic acid, a solid. This was washed with aqueous methanol, then with methanol, and dried to give 0.6 g. of powder. An additional 3 g. of material was obtained after removal of the solvents from the mother liquor. These as yet unidentified polymeric materials are insoluble in toluene, as evidenced by nonextraction of compounds by hot toluene after 5 days. What may be related polymers were also observed under corresponding conditions starting with 1,3-dichlorohexamethyltrisilane.

B. Lithium Catalyzed by Triphenylsilyllithium.—To triphenylsilyllithium (prepared in tetrahydrofuran from 0.31 g. of hexaphenyldisilane and 1.0 g. of lithium) was added 9.47 g. (0.0312 mole) of 1,4-dichlorooctamethyltetrasilane. The addition was effected slowly at room temperature to maintain the characteristic color of silyllithium; then the mixture was stirred at room temperature for 2 hr. After filtering through glass wool to remove excess lithium, the filtrate was worked up as usual to give a crystalline solid. This was recrystallized from acetone to give 3.6 g. (49.6%) of dodecamethylcyclohexasilane which was identified by mixture melting point and comparison of infrared spectrum with an authentic specimen. The only other product so far isolated is 0.1 g. of a polymeric material. From another experiment in which the brown color of silyllithium was intermediately lost, the only pure product isolated was 36.7% of dodecamethylcyclohexasilane.

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[8] G. R. Wilson and A. G. Smith, *J. Org. Chem.*, **26**, 557 (1961).

Ozonolysis of Certain Acetylenic Alcohols[1]

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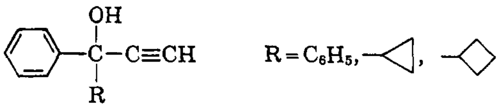
An earlier communication[2] reported the preparation of some phenylcycloalkylglycolic acids by treatment of the corresponding phenylcycloalkylethynyl carbinols with cold, neutral permanganate. The products were difficult to separate from the reaction mixtures, and yields were poor. A possible alternate oxidation procedure involved ozonolysis of the triple bond. Hurd and Christ[3] reported conversion of 1-hydroxy-1-ethynylcyclohexane to 1-hydroxycyclohexane-1-carboxylic acid in 52% yield, by use of a considerable excess of ozone. When phenylcycloalkylethynyl carbinols were treated with a large excess of ozone, quantitative yields of phenylcycloalkyl ketones were isolated, which suggested that the desired glycolic acids were initially formed, but were rapidly decarboxylated by the powerful oxidizing environment. This interpretation was supported by the observation that benzilic acid is rapidly converted to benzophenone by ozone.

When ozonolysis experiments were performed on the acetylenic carbinols I, using carefully controlled and measured amounts of ozone, the glycolic acids were obtained in moderate to good yields. 9-Ethynyl-9-fluorenol was also subjected to ozonolysis, forming 9-hydroxyfluorene-9-carboxylic acid. Ozonolysis appears to be useful in the preparation of otherwise difficultly obtainable, disubstituted glycolic acids.



I

When a variation of the method of ozonolysis and of the isolation procedure was attempted, using 1-phenyl-1-cyclopropyl-2-propyn-1-ol, an anomalous product (which was not a carboxylic acid) was isolated. A molecular weight determination of this product gave a value of 179. Elemental analysis indicated a molecular formula of $C_{12}H_{10}O_2$, which is consistent with the molecular weight determination. The compound decolorized permanganate instantaneously, and microhydrogenation data indicated the presence of one carbon–carbon double bond. Vigorous ozonolysis of the material gave rise to benzoic acid, and a partial

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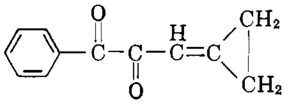
[1] This investigation was supported by Grant MH 07775, National Institute of Mental Health.

[2] S. B. Kadin and J. G. Cannon, *J. Org. Chem.*, **27**, 240 (1962).

[3] C. D. Hurd and R. E. Christ, *ibid.*, **1**, 141 (1936).

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 α-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 δ 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 δ 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 δ 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 δ 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 (α-dicarbonyl), 3.31, 3.38, 3.44 (C–H stretching characteristic of CH and CH_2 groups), and 9.88 μ (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.).

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[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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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-

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(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.