EXPERIMENTAL

Infrared spectra. The infrared spectra were recorded with a Beckman IR-4 double-beam spectrophotometer. Liquids were run as films and the solids as chloroform or carbon tetrachloride solutions, as Nujol mulls, or as potassium bromide pellets.

Ultraviolet and visible spectra. The spectra were taken using a Beckman DK Recording Spectrophotometer or a Beckman DU Spectrophotometer. Solutions were of a concentration sufficient to obtain maximum optical density of 0.8 at the λ_{max}. For initial comparison spectra, all solutions were absolute methanol. Time stability studies were made with methanol or hexane solutions.

Preparation of hydrazones. Excess redistilled reagent grade butanone was refluxed for about 30 min. with the arylhydrazine. Excess butanone was removed by evaporation and the product, when solid, was recrystallized from ethanol to a constant melting range. Liquid hydrazones were distilled under reduced pressure until a product of constant refractive index was obtained.

Phenylhydrazine, N-methylphenylhydrazine, p-nitrophenylhydrazine, p-tolylhydrazine, and *2,4-dinitrophenylhydrazine.* These compounds were obtained from commercial sources and were purified by recrystallization or distillation.

N-Methyl-p-nitrophenylhydrazine. This was prepared by the method of Cuisa and Rastelli.[10] The product melted at 156–158° (reported[10] m.p. 156°).

N-methyl-2,4-dinitrophenylhydrazine. This hydrazine was synthesized by the method of Blanksma and Wackers[11]; m.p. 144–145° (reported[11] m.p. 144°.)

2-Phenylazobutane. A $3 \times 10^{-3}M$ solution of butanone phenylhydrazone in purified hexane was allowed to stand for 30 min. The azo compound formed was not isolated but its visible spectrum was recorded using the original solution and its ultraviolet spectrum was recorded using a solution made by diluting the original one-hundred fold.

2-Methyl-2-p-tolylazopropane. This azo compound was prepared from *t*-butylzinc chloride and *p*-toluenediazonium fluoborate by a method similar to that used by Curtin and Ursprung[8] for synthesis of benzeneazoalkanes. The yield of pure product was 19% (b.p. 90–93°/8 mm.; n_D^{22}, 1.5125).

Anal. Calcd. for $C_{11}H_{16}N_2$: C, 74.95; H, 9.15; N, 15.89. Found: C, 74.86; H, 9.17; N, 16.01.

2-p-Tolylazobutane. This product was prepared by the same method as the 2-methyl-2-*p*-tolylazopropane, yield: 26%; b.p. 96–98°/7 mm.; $n_D^{25°}$, 1.5124.

Anal. Calcd. for $C_{11}H_{16}N_2$: C, 74.95; H, 9.15; N, 15.89. Found: C, 74.77; H, 9.21; N, 15.96.

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[10] R. Cuisa and G. Rastelli, *Gazz. chim. ital.*, **52**, 126 (1922).

[11] J. J. Blanksma and M. L. Wackers, *Rec. trav. chim.*, **155**, 655 (1936).

Pyrolysis of *cis*- and *trans*-3-Hexenedioic Acids

F. BENINGTON AND R. D. MORIN

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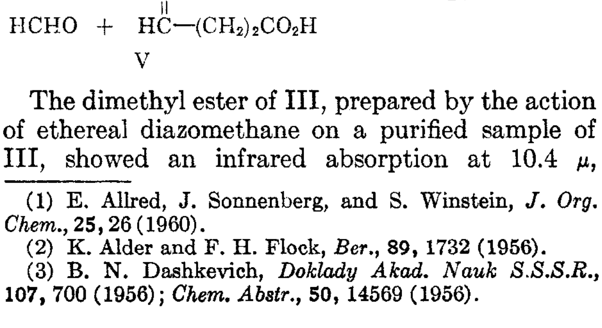
Certain projected syntheses in this laboratory required that we obtain reasonable quantities of 3-cyclopenten-1-ol (I) as an intermediate. Preparation of this cyclic alcohol has been reported by Winstein, *et al.*[1] *via* the hydroboronylation of cyclopentadiene, and by Alder and Flock[2] who reduced the corresponding unsaturated ketone with lithium aluminum hydride; the ketone II was obtained in poor yield by the pyrolysis of dicyclopentadienol-3.

Dashkevich[3] reported that the pyrolysis of calcium acrylate at 450–500° gave 3-cyclopenten-1-one (II) in about 27% yield. This appeared to offer many advantages for the preparation of reasonable quantities of an intermediate which could be converted readily to I. However, in repeated attempts to duplicate this pyrolysis, we were unable to obtain any detectable amount of ketone II.

The fact that certain aliphatic dibasic acids and their alkaline-earth metal salts readily undergo pyrolysis to form cyclic ketones suggested the possibility that the commercially available 3-hexenedioic acid (III) might also be cyclized to the ketone II. Pyrolysis of III at 280–285° yielded a liquid product which exhibited none of the properties reported for the ketone II. This pyrolysis product was found to be an unsaturated monobasic acid having an infrared absorption characteristic of a terminal olefin group. Since ozonolysis of the purified acid yielded both formaldehyde and β-formylpropionic acid (V), the liquid pyrolysis product from III is 4-pentenoic acid (IV).



The dimethyl ester of III, prepared by the action of ethereal diazomethane on a purified sample of III, showed an infrared absorption at 10.4 μ,

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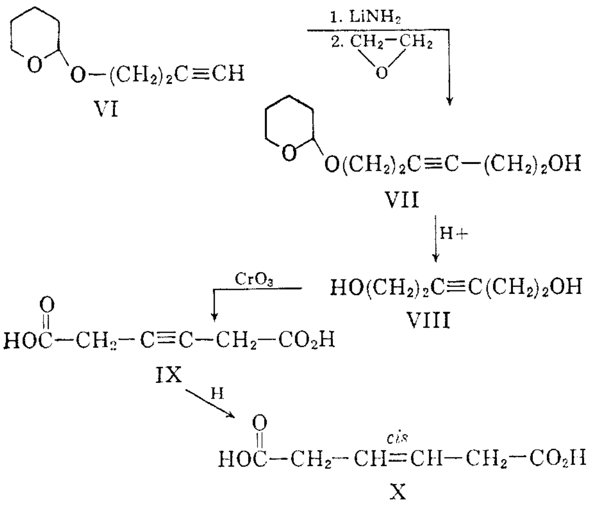
[1] E. Allred, J. Sonnenberg, and S. Winstein, *J. Org. Chem.*, **25**, 26 (1960).

[2] K. Alder and F. H. Flock, *Ber.*, **89**, 1732 (1956).

[3] B. N. Dashkevich, *Doklady Akad. Nauk S.S.S.R.*, **107**, 700 (1956); *Chem. Abstr.*, **50**, 14569 (1956).

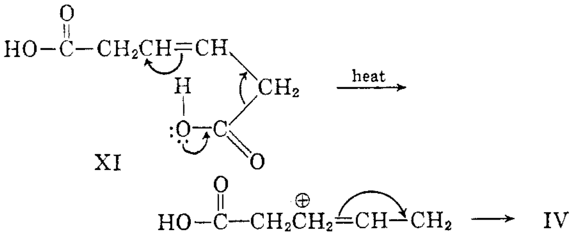
which is characteristic of a *trans* configuration for the olefinic bond in commercial 3-hexenedioic acid. Since a *cis* configuration of this dibasic acid should be more favorable for the cyclization of III to the cyclic ketone II, it was decided to prepare *cis*-3-hexenedioic acid (X) and subject this isomer to pyrolysis under the same conditions which were used for the *trans* acid. 3-Hexynedioic acid[4] (IX) was obtained from the oxidation of 3-hexyne-1,6-diol (VIII) with chromic acid; the latter compound resulted from the reaction of 4-(tetrahydro-2-pyranyloxy)-1-butyne (VI) first with lithium amide and then with ethylene oxide, followed by acid hydrolysis of the intermediate 6-(tetrahydro-2-pyranyloxy)-3-hexyn-1-ol[5] (VII). Stereospecific reduction of the triple bond in the acetylenic dibasic acid (IX) was accomplished by hydrogenation in ethanol using a palladium-on-charcoal catalyst.[6]



The resulting *cis*-3-hexenedioic acid (X) melted at 122–123° (*trans* acid, m.p. 197°[7]) and the corresponding dimethyl ester did not show the 10.4-μ *trans* olefin band.

Pyrolysis of *cis*-3-hexenedioic acid (X) under the same conditions which were used with the *trans* isomer also failed to give the cyclic ketone II. Instead, there was obtained 4-pentenoic acid (IV), demonstrating that both the *cis* and *trans* unsaturated dibasic acids behave in the same manner on pyrolysis.

The decarboxylation of both 3-hexenedioic acids likely occurs through a mechanism first involving protonation of the γ-carbon atom in XI, followed by simultaneous migration of the double bond to the terminal position and displacement of carbon dioxide. This is consistent with the mechanism by which α,β-unsaturated acids undergo thermal decarboxylation *via* isomerization, first to the β,γ-position, followed by shifting of the double bond to the original α-carbon atom.[8]



EXPERIMENTAL[9]

3-Hexynedioic acid (IX). 4-(Tetrahydro-2-pyranyloxy)-1-butyne, b.p. 83–85°/13 mm. (reported b.p. 92–95°/18 mm.) was obtained in 81% yield from 3-butyn-1-ol[10] and 2,3-dihydropyran by the procedure of Jones, *et al.*[11] Treatment of this product with lithium amide and ethylene oxide in liquid ammonia as described by Raphael and Roxburgh[5] resulted in an 80% yield of 6-(tetrahydro-2-pyranyloxy)-3-hexyn-1-ol, b.p. 116–120°/0.4 mm. Conversion to 3-hexyne-1,6-diol, m.p. 81–82° (reported[5] m.p. 77–79°) in 74% yield was effected by treatment with sulfuric acid in methanol. Oxidation of the diol to 3-hexynedioic acid, m.p. 174–175°, with chromic acid in sulfuric acid, was accomplished in 50% yield by the method of Jones, *et al.*[4] The dimethyl ester of the 3-hexynedioic acid melted at 63–64° (reported[4] m.p. 64–65°).

cis-3-Hexenedioic acid (X). A solution of 14.2 g. (0.1 mole) of 3-hexynedioic acid in 220 ml. of ethanol was shaken with hydrogen at an initial pressure of 50 p.s.i.g. in a Parr hydrogenation apparatus in the presence of 1.5 g. of 10% palladium-on-charcoal catalyst. The reaction was stopped as soon as exactly 1 mole of hydrogen was absorbed (about 5 min.), the catalyst was removed by filtration, and the solvent was removed from the filtrate by evaporation under reduced pressure. The solid residue of crude product (14.5 g.) was recrystallized twice from an ethyl acetate-petroleum ether (b.p. 30–60°) mixture to obtain a total of 9.1 g. (63%) of pure *cis*-3-hexenedioic acid, m.p. 122–123°.

Anal. Calcd. for $C_6H_8O_4$: C, 50.0; H, 5.6. Found: C, 50.2; H, 5.7.

The *dimethyl ester*, obtained by treatment of X with ethereal diazomethane, was a liquid, b.p. 75–78°/0.5 mm.; n_D^{25} 1.4412. The infrared spectrum exhibited major bands at 5.75 μ (ester carbonyl), 6.95 μ, and 9.85 μ. The band at 10.3 μ, exhibited by the dimethyl ester of the *trans*-acid (III), was absent.

Anal. Calcd. for $C_8H_{12}O_4$: C, 55.8; H, 7.0. Found: C, 55.8; H, 7.1.

Pyrolysis of trans-3-hexenedioic acid (III). An intimate mixture of 25 g. of *trans*-3-hexenedioic acid[12] and 1.3 g. of barium hydroxide was pyrolyzed in a Claisen distilling flask at about 280 to 285° (internal temperature). The crude pyrolyzate was collected, dissolved in ether, separated from a water layer, dried (anhydrous magnesium sulfate), filtered, and distilled. After removal of ether, a close-boiling

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[4] E. R. H. Jones, G. H. Mansfield, and M. C. Whiting, *J. Chem. Soc.*, 3208 (1958).

[5] R. A. Raphael and C. M. Roxburgh, *J. Chem. Soc.*, 3875 (1952).

[6] *Acetylenic Compounds in Organic Synthesis*, R. A. Raphael, Butterworth's Scientific Publications, London (1955), p. 24.

[7] E. H. Farmer and W. M. Duffin, *J. Chem. Soc.*, 409 (1927).

[8] *Mechanism and Structure in Organic Chemistry*, E. S. Gould, Henry Holt, New York (1959), p. 352.

[9] Melting and boiling points are uncorrected.

[10] Available from Farchan Laboratories, Cleveland, Ohio.

[11] E. R. H. Jones, T. Y. Shen, and M. C. Whiting, *J. Chem. Soc.*, 235 (1950).

[12] Available from Aldrich Chemical Co, Milwaukee, Wis.

liquid, b.p. 70–73°/7 mm., was collected as the sole product of the reaction; yield, 12.5 g. (72%). Almost identical results were obtained when free *trans*-3-hexenedioic acid was pyrolyzed at 280 to 285°. The pyrolysis product was a colorless liquid, b.p. 186–188°/740 mm. (reported[13] b.p. 188°), with a disagreeable odor typical of C_5 fatty acids; it was found to be a monobasic olefinic acid (neut. equiv.: calcd. 100; found: 99). The infrared spectrum showed a terminal double bond and suggested that the compound was 4-pentenoic acid (IV). This structure was verified by ozonolysis of a sample in acetic acid solution; the products after decomposition of the ozonide were found to be formaldehyde (identified as its dimedone derivative, m.p. 191–192°) and β-formylpropionic acid (V), identified as the 2,4-dinitrophenylhydrazone, m.p. 203–204° dec. (reported[14] m.p. 201°). Further substantiating the identity of the pyrolysis product were its refractive index, n_D^{25} 1.4279 (reported[15] n_D^{26} 1.4274), and the *p*-bromophenacyl ester, m.p. 57–58° (reported[15] m.p. 57–58°).

Pyrolysis of cis-3-hexenedioic acid (X). When a mixture of 5 g. of *cis*-3-hexenedioic acid (X) and 0.25 g. of barium hydroxide was heated at about 275 to 285° in a Claisen distilling flask, the sole product in the distillate was 4-pentenoic acid, b.p. 185–188°; yield, 2.3 g. (66%); n_D^{25} 1.4275. This product was identical in all respects (infrared spectrum, melting point of *p*-bromophenacyl ester) with the 4-pentenoic acid obtained from *trans*-3-hexenedioic acid, and there was no evidence that any neutral products were obtained from the pyrolysis reaction. Nearly identical results were obtained when free *cis*-3-hexenedioic acid was pyrolyzed.

Pyrolysis of calcium acrylate. A mixture of 50 g. of calcium acrylate and 80 g. of clean sand was heated in a flask fitted with a gooseneck and condenser with a graphite bath at about 450 to 500°. The mixture darkened and frothed, and a small amount (*ca.* 5 g.) of a dark oil gradually distilled. After being dried with anhydrous magnesium sulfate, the pyrolyzate was distilled and was found to consist of a complex mixture from which no pure compounds were isolated. There was only a trace of material boiling in the range of 130–140° (reported[3] b.p. for 3-cyclopentenone, 133–135°), and it had n_D^{23} 1.4371 (reported[2] for 3-cyclopentenone, n_D^{20} 1.4536) and was not the desired product. Variations in the method of carrying out the pyrolysis failed to effect formation of any detectable amounts of 3-cyclopenten-1-one.

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[13] I. Heilbron, *Dictionary of Organic Compounds*, rev. ed., Vol. I, p. 54 (1953).

[14] H. Kondo and H. Suzuki, *Ber.*, 69B, 2459 (1936).

[15] L. I. Smith and S. Mackenzie, *J. Org. Chem.*, **15**, 74 (1950).

Ozonolysis of Methylnaphthalenes

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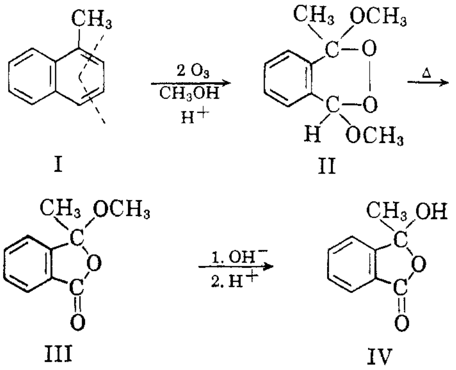
More than fifty years ago, Harries and Weiss[3] reported the isolation of a diozonide from the ozonolysis of naphthalene in chloroform. Investigators have continued to assume that the ozonide of naphthalene is a diozonide because two moles of ozone per mole of naphthalene is absorbed. Examination of the Criegee mechanism[4] for ozonolysis leads one to expect that the naphthalene ring would be cleaved at the 1,2- and 3,4-bonds to yield a monoozonide with two carbons fewer than in naphthalene. Bailey[5] has presented good evidence for the existence of a monoozonide of naphthalene; however, the product was too unstable to analyze and exploded if allowed to dry in chunks. Bailey observed that in methanol, the zwitterion reacted with the solvent to give a 94% yield of a stable crystalline peroxide. It seemed of interest, therefore, to determine whether the ozonolysis of methyl naphthalenes would proceed in a similar manner.

Ozonolysis of 1-methylnaphthalene (I) in methanol at −70° followed by partial evaporation, addition of a few drops of concentrated hydrochloric acid, and recooling to −70° for about sixteen hours gave a 5% yield of a colorless crystalline peroxide. The material was assigned the structure of 3,6-dimethoxy-3-methyl-4,5-benzo-1,2-dioxacyclohexane (II) on the basis of its infrared spectrum and elemental analysis. All attempts to increase the yield of this material were unsuccessful.



I II III IV

During ozonolysis, two molecular equivalents of ozone were absorbed. Furthermore, ozone attacked only in the methylated ring since alkaline permanganate oxidation of the ozonolysis reaction mixture gave only phthalic and no hemimellitic acid. The colorless solution that resulted after ozonolysis evolved oxygen when treated with lead tetraacetate. This reaction is characteristic of hydroperoxides.[6] The hydroperoxide could be destroyed by refluxing the methanolic solution for approximately sixty-eight hours. Evaporation of the solvent led to isolation of a neutral nonperoxidic oil in high

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[2] Present address: United States Steel Corp., Applied Research Laboratory, Monroeville, Pa.

[3] C. Harries and V. Weiss, *Ann.*, **343**, 336 (1905).

[4] R. Criegee, *Record Chem. Progr.*, **18**, No. 2, 111 (1957).

[5] P. S. Bailey and F. J. Garcia-Sharp, *J. Org. Chem.*, **22**, 1008 (1957).

[6] R. Criegee *et al.*, *Chem. Ber.*, **72**, 1799 (1939).