[Contribution from the Department of Chemistry, the Florida State University]

REDUCTION OF TETRAMETHYLENEKETENE DIMER (DISPIRO[4.1.4.1]DODECANE-6,12-DIONE)

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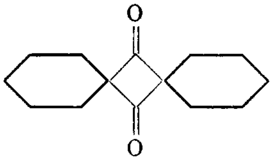
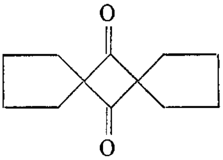
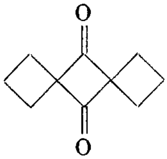
It has recently been demonstrated (1–3), that ketoketene dimers could be reduced to their parent hydrocarbons. One of the methods employed was the application of the Wolfrom-Karabinos (4) technique for carbonyl reduction by the hydrogenolysis of the mercaptol derivative.



I



II



III

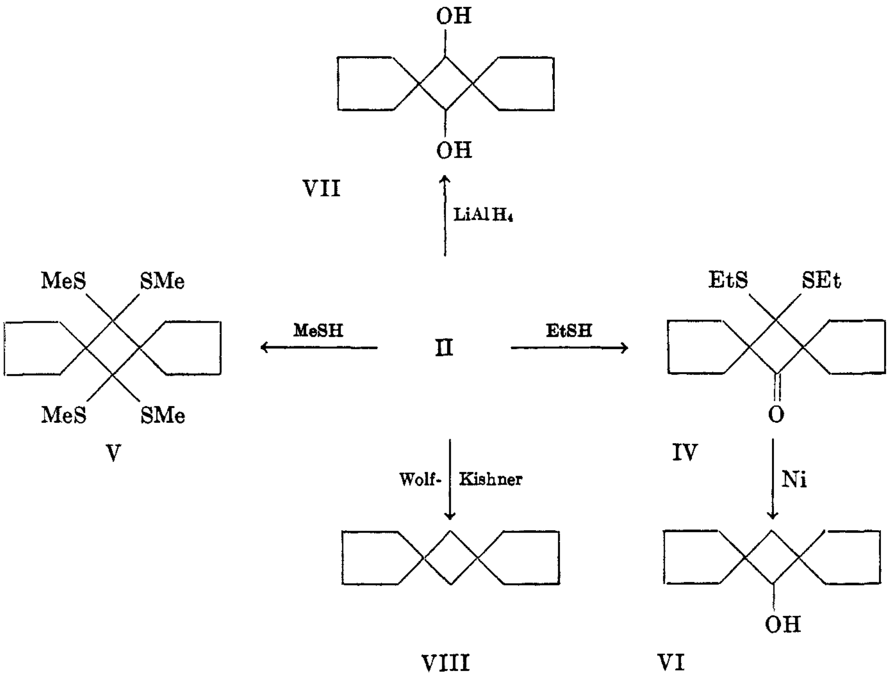
When I was treated with methyl or ethyl mercaptan, only one of the carbonyl groups reacted to give a monomercaptol. The other carbonyl group did not react. The monomercaptol was then subjected to treatment with an excess of mercaptan, but was recovered unchanged.

When III was treated with ethyl or methyl mercaptan in an identical manner (1), both carbonyl groups formed a mercaptol.

In contrast to III with its two planar four-membered rings attached to the cyclobutadione structure, the resistance of I to form a dimercaptol might be due to a steric effect, imposed by its two non-planar six-membered rings. Hauptmann (5) observed a similar difficulty in forming mercaptols of certain α-substituted ketones, which he also ascribes to a steric effect. In these cases mercaptolization was realized by using the most favorable conditions: 1,3-propanedithiol and anhydrous hydrogen chloride. It is interesting to note that when I was subjected to similar conditions, again only one carbonyl group reacted to give IX (see experimental).

It was of interest therefore, to determine the effect of mercaptolization on tetramethyleneketene dimer (II). The five-membered rings in II, although not planar (6), are not as puckered as the six-membered rings in I. II is sterically intermediate between I and III, and might be expected to react more readily with mercaptans than I.

The dimer (II) was synthesized, similar to the preparation of I, as described by Hill (7), in 59% yield, by the action of triethylamine on cyclopentanecarbonyl chloride. When II was treated with ethyl mercaptan, an oily mercaptol was formed. Analysis showed this to be IV, demonstrating that only one carbonyl group had reacted. When II was treated with methyl mercaptan, the mercaptol obtained was shown to be V, in which both carbonyl groups had reacted. Posner (8) had shown earlier that both the mercaptan used, as well as the substituents on β-diketones, were important factors in determining whether one, or both carbonyl groups would react. In the alicyclic series under discussion, the resistance to mercaptolization seems to be steric in nature. The effect decreases on going from non-planar six-membered rings (I), to almost planar five-membered rings (II), and disappears in the planar four-membered rings (III).



By the use of the appropriate mercaptan, one or both carbonyl groups can be made to react. This provides a convenient synthetic route for the reduction of ketoketene dimers.

When IV was subjected to desulfurization with Raney nickel, the product isolated was not the expected ketone as previous experience would have indicated, but was instead, the corresponding alcohol VI. Although a highly active catalyst might conceivably reduce the carbonyl group, the catalyst used in desulfurization was the Mozingo catalyst (9), which was at least a week old.

Previous attempts (10) to reduce ketoketene dimers to glycols by catalytic hydrogenation proved unsatisfactory, since they resulted in mixtures and poor yields. The reduction of II to glycol III was accomplished very successfully with lithium aluminum hydride. Although by no means definitive, the fact that VII did not yield a cyclic acetal derivative (11) with *p*-nitrobenzaldehyde, seems to indicate that the *trans* glycol was formed.

The hydrocarbon VIII was obtained by formation of the disemicarbazone of II (not isolated), and subjection of the crude product to the Huang-Minlon (12) conditions for the Wolf-Kishner reduction (2, 3). The hydrocarbon, a brilliant liquid, was isolated in 44% yield. Its infrared spectrum showed a prominent absorption peak at 11 μ, which is a characteristic absorption for cyclobutane rings (13) (Figure 1[1]).

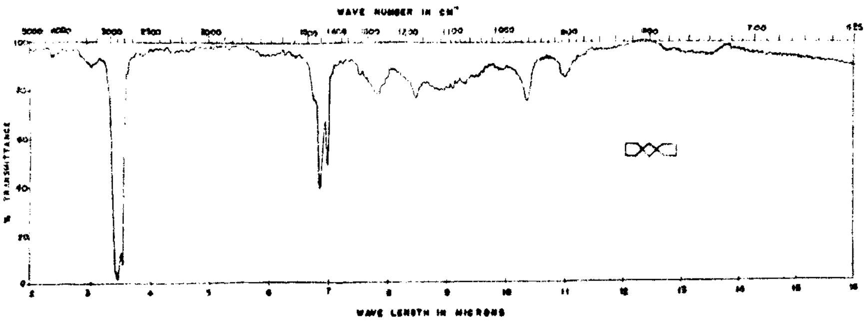


FIGURE 1. INFRARED SPECTRUM OF DISPIRO[4.1.4.1]DODECANE. Baird instrument; c, 10% (vol.) solution in carbon tetrachloride

EXPERIMENTAL[2]

Dispiro[4.1.4.1]dodecane-6,12-dione (II). A solution of 300 cc. of ether and 40 g. (0.3 mole) of cyclopentanecarbonyl chloride (prepared in 95% yield by the action of thionyl chloride on cyclopentanecarboxylic acid; b.p. 94–96° at 92 mm.), was placed in a dry, 500 cc. three-necked flask equipped with a condenser, stirrer, and dropping-funnel, and was kept under a nitrogen atmosphere. Triethylamine (50 g., 0.05 mole) was added to the stirred solution. The reaction mixture was stirred and refluxed for 12 hours. The triethylamine hydrochloride was filtered and the filtrate was washed, first with water and then dilute hydrochloric acid. It was dried and the solvent was evaporated to yield 17 g. (0.089 mole, 59%) of light yellow crystals, m.p. 68–70°. One recrystallization from petroleum ether (60–70°) raised the m.p. to 70–70.5°.

Anal. Calc'd for $C_{12}H_{16}O_2$: C, 74.96; H, 8.39.

Found: C, 75.03; H, 8.37.

The *2,4-dinitrophenylhydrazone* derivative melted at 185–186°, after three recrystallizations from an ethyl alcohol-ethyl acetate mixture.

Anal. Calc'd for $C_{18}H_{20}N_4O_5$: C, 58.03; H, 5.41; N, 15.04.

Found: C, 57.92; H, 5.47; N, 15.00.

6,6-Dithioethyldispiro(4.1.4.1]dodecane-12-one (IV). A mixture of 0.4 g. of anhydrous magnesium sulfate, 1.9 g. (0.01 mole) of II, and 10 cc. of ethyl mercaptan was added to 0.6 g. of freshly fused zinc chloride, spread in a thin film over the lower quarter of a glass bomb. The tube was sealed, shaken, and allowed to stand at room temperature overnight. The bomb was opened, and its contents were poured into a separatory-funnel containing a mixture of ice-water and ether. The ethereal solution was separated, washed several times with 10% sodium hydroxide and once with water, dried, and concentrated. The residual oil was distilled to yield 3 g. (0.01 mole, quant.) of product, b.p. 172–175° at 3 mm.

Anal. Calc'd for $C_{16}H_{28}S_2O$: C, 63.57; H, 8.79; S, 21.48.

Found: C, 63.61; H, 8.73; S, 21.50.

6,6,12,12-Tetrathiomethyldispiro[4.1.4.1]dodecane (V). A mixture of one gram of magnesium sulphate (anhyd.) and 4 g. (0.02 mole) of II was added to 1.5 g. of freshly fused zinc chloride, spread in a thin film over the lower quarter of a glass bomb. The bomb was placed

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[1] Obtained through the courtesy of Dr. C. L. Wilson and the Department of Chemistry of the Ohio State University.

[2] Analyses are by Dr. A. Elek, 4763 W. Adams Blvd., Los Angeles, California.

in a Dry Ice-acetone mixture and 20 cc. of methyl mercaptan was added. The tube was sealed, shaken, and allowed to stand overnight at room temperature. The bomb was opened, and the contents were poured into a separatory-funnel containing a mixture of ice-water and ether. The ethereal solution was separated, washed several times with 10% sodium hydroxide and once with water, dried, and concentrated. The resultant oil (6 g., 0.017 mole, 86%) solidified, and after one recrystallization from ethanol, melted at 112–113°.

Anal. Calc'd for $C_{16}H_{28}S_4$: C, 55.12; H, 8.09; S, 36.79.
Found: C, 55.20; H, 7.99; S, 36.67.

Dispiro[4.1.4.1]dodecane-6-ol (VI). A mixture of 150 g. of Raney nickel and 200 cc. of methanol was placed in a 500-cc. flask equipped with a condenser. Then IV (9 g., 0.03 mole) was added and the mixture was refluxed for 8 hours. The Raney nickel was removed by centrifugation, the supernatant liquids were collected, and the solvent was evaporated. The residual oil was distilled to yield 4.3 g. (0.025 mole, 83%) of product, b.p. 110–112° at 5 mm., n_D^{28} 1.4941. On long standing the sample solidified, m.p. 38–39°.

Anal. Calc'd for $C_{12}H_{20}O$: C, 79.9; H, 11.1.
Found: C, 79.9; H, 11.3.

The *p-nitrobenzoate* derivative was prepared, m.p. 83–85°, from ethanol.

Anal. Calc'd for $C_{19}H_{23}NO_4$: C, 69.3; H, 7.0.
Found: C, 69.4; H, 6.8.

The *p-bromobenzenesulfonate* derivative was prepared, m.p. 58–59° (dec.), but it decomposed rapidly on standing; therefore no analysis was obtained.

Dispiro[4.1.4.1]dodecane-6,12-diol (VII). A solution of 0.2 g. (0.005 mole) of lithium aluminum hydride and 50 ml. of dry ether was placed in a 100-cc., three-necked flask equipped with stirrer, condenser, and dropping-funnel. A solution of 1.9 g. (0.01 mole) of II dissolved in 10 cc. of ether was slowly added. The excess lithium aluminum hydride was decomposed with water and the reaction mixture was acidified with dilute sulphuric acid. The ether extract was dried and evaporated to yield 1.5 g. (0.008 mole, 80%) of product, m.p. 108.5–113°. After three recrystallizations from benzene-petroleum ether, it melted at 120–121.8°.

Anal. Calc'd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27.
Found: C, 73.45; H, 10.20.

Dispiro[4.1.4.1]dodecane (VIII). Diethylene glycol (100 cc.) and 10 g. of sodium were placed in a one-liter flask equipped with a condenser. After the sodium had reacted completely, the solution was heated to 100° and 17 g. (0.055 mole) of the disemicarbazone of II [prepared according to the procedure described by Shriner and Fuson, (14)] was added. The solution was heated at 240° for 5 hours. The reaction mixture was diluted with water and extracted with *n*-pentane. The pentane extract was dried and the solvent was evaporated. The residual oil was washed with concentrated sulphuric acid, water, and then distilled over sodium to yield 4 g. (0.024 mole, 44%), b.p. 133–134° at 100 mm., $n_D^{23.5}$ 1.4730, d_4^{23} 0.862, M_D (calc'd), 51.52, M_D (found), 50.00.

Anal. Calc'd for $C_{12}H_{20}$: C, 87.73; H, 12.26.
Found: C, 87.78; H, 12.24.

Dispiro[5.1.5.1]tetradecane-7,14-dione-7-cyclic trimethylene mercaptol (IX). A mixture of 1 g. of I and 5 g. of 1,3-propanedithiol was placed in a 15-cc. test tube. The tube was surrounded by an ice-bath, and gaseous hydrogen chloride was bubbled in until the solution was saturated (2 hours). The solution was poured into a separatory-funnel containing an ice-water-ether mixture. The ether layer was washed with 10% sodium hydroxide, dried, and then evaporated to yield 1 g. of product, m.p. 112.5–113°, after two recrystallizations from benzene-alcohol.

Anal. Calc'd for $C_{17}H_{26}OS_2$: S, 20.6. Found: S, 21.1.

SUMMARY

Tetramethyleneketene dimer (dispiro[4.1.4.1]dodecane-6,12-dione) has been prepared and subjected to mercaptolization and subsequent desulfurization.

The dimer was also reduced with lithium aluminum hydride to yield dispiro[4.1.4.1]dodecane-6,12-diol and by the Wolf-Kishner method to prepare dispiro[4.1.4.1]dodecane.

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REFERENCES

(1) BUCHMAN, WALBORSKY, AND HERZOG, *J. Am. Chem. Soc.*, in press.

(2) WALBORSKY AND BUCHMAN, *J. Am. Chem. Soc.*, in press.

(3) BUCHMAN AND HERZOG, *J. Org. Chem.*, **16,** 99 (1951).

(4) WOLFROM AND KARABINOS, *J. Am. Chem. Soc.*, **66,** 909 (1944).

(5) HAUPTMANN AND CAMPOS, *J. Am. Chem. Soc.*, **72,** 1405 (1950).

(6) KILPATRICK, PITZER AND SPITZER, *J. Am. Chem. Soc.*, **69,** 2483 (1947).

(7) HILL, Ph.D. Thesis, Cornell University, 1941.

(8) POSNER, *Ber.*, **33,** 2983 (1900); **35,** 493 (1902).

(9) MOZINGO, *Org. Syntheses*, **21,** 15 (1941).

(10) MILLER, Ph.D. Thesis, Cornell University, 1937.

(11) ZERVAS, *Ber.*, **64,** 2289 (1931).

(12) HUANG-MINLON, *J. Am. Chem. Soc.*, **68,** 2487 (1946).

(13) DERFER, PICKETT, AND BOORD, *J. Am. Chem. Soc.*, **71,** 2482 (1949).

(14) SHRINER AND FUSON, *Identification of Organic Compounds*, 2nd ed., John Wiley and Sons, New York, p. 142.