

[CONTRIBUTION FROM SCIENCE HALL, LAWRENCE COLLEGE]

STUDIES IN THE CYCLOPROPENE SERIES.

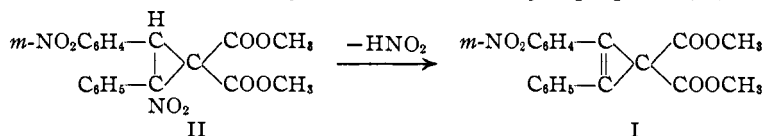
I. DIPHENYLCYCLOPROPENEDICARBOXYLIC ACID

BY S. F. DARLING AND E. W. SPANAGEL

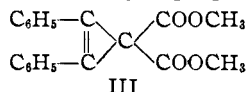
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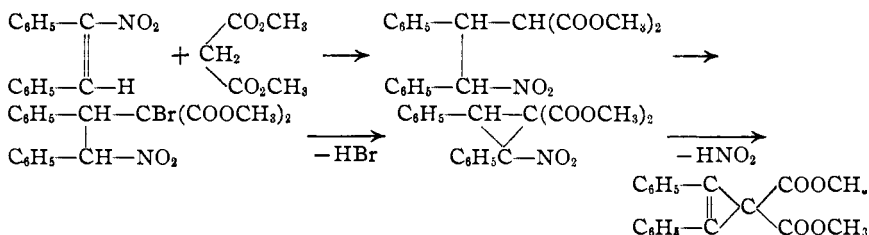
In connection with a study of the behavior of nitrocyclopropane derivatives with bases Kohler and his students¹ have postulated the presence of a substituted cyclopropene derivative intermediate between the nitrocyclopropane and the end-product. Later they actually succeeded in isolating a new type of cyclopropene derivative² (I) as the first product of the action of sodium methylate on the nitrocyclopropane (II). This



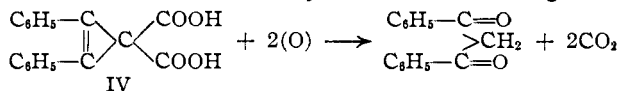
substance suggests many new problems for study but the presence of the nitro group in one of the benzene nuclei is undesirable in certain cases. We have therefore prepared another cyclopropene derivative (III) differing



from the cyclopropene (I) in that both phenyl groups are unsubstituted. The reactions which lead to this substance are as follows



The proof of the structure of this new cyclopropene derivative is analogous to the proof of the constitution of (I). The corresponding dibasic acid (IV) on oxidation with potassium permanganate in alkaline solution forms dibenzoylmethane. Therefore we may write the following reaction

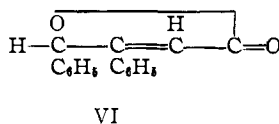
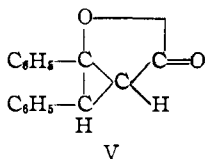


The cyclopropene (III) lends itself much more readily to clean cut reactions than the cyclopropene derivative (I); however, its preparation

¹ Kohler, *THIS JOURNAL*, **44**, 624 (1922).

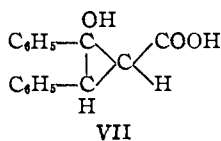
² Kohler, *ibid.*, **52**, 1174 (1930).

entails many difficulties and low yields result. The work described in this paper is confined to the study of the effect of heat on the dibasic acid (IV). This compound melts to a clear, pale yellow liquid at about 190° , with the evolution of carbon dioxide. If this clear melt after cooling is manipulated with appropriate solvents a good yield of a new substance whose composition corresponds to the loss of one molecule of carbon dioxide from the dibasic acid, is obtained. Contrary to our expectations this substance proved to be a lactone instead of a mono basic acid. A little reflection about the matter shows that two formulas for this lactone are probable; the cyclic lactone (V) and the corresponding open-chain unsaturated lactone (VI).



In order to assign the more probable formula to this lactone we have converted it into the corresponding hydroxy acid and subjected this substance to ozonization. There is little doubt that the hydroxy acid derivable from a substance of formula (VI) would form benzoin as one of the products of ozonization. Benzoin could easily be isolated and identified. The hydroxy acid related to a substance of formula (V) should resist ozonization or at most undergo a little general oxidation. The hydroxy acid remained almost totally unchanged in the presence of a moderate stream of ozone and over 75% of the material was recovered unchanged after being subjected to a rapid stream of 6% ozone for three hours. Little

doubt therefore remains that the lactone should be represented by formula (V) and the hydroxy acid by formula (VII). Substances of this type are practically unknown; in fact previous attempts to introduce hydroxyl groups in the cyclopropane ring have led to open-chain compounds. We hope that additional work with cyclopropene derivatives will further characterize this little-known class of compounds.



Experimental Part

The α -Bromo Compound Formed by Indirect Bromination.—Ten grams of dimethyl β,γ -diphenyl- γ -nitro-ethyl-malonate, prepared according to the method of Kohler and Barrett,³ was suspended in 30 cc. of dry methyl alcohol and to this was added 1.3 g. of sodium as sodium methylate. This caused the substance to dissolve and to form a light yellow solution. This solution was cooled and poured slowly into a cold solution of excess bromine in 25 cc. of dry methyl alcohol. The crystals of bromine compound separated promptly and were purified by crystallization from methyl alcohol, from which solvent they separate in stout, colorless crystals which melt at 117 – 118° . The yields vary between 70 and 80% of the theoretical.

³ Kohler and Barrett, THIS JOURNAL, 48, 1770 (1926).

Dimethyl α -Bromo- β , γ -diphenyl- γ -nitro-ethyl-malonate.—This substance is isomeric with the bromine compound prepared by Kohler and Barrett³ by direct bromination of the nitro ester.

Anal. Calcd. for $C_{19}H_{18}O_6NBr$: C, 52.3; H, 4.1. Found: C, 52.1; H, 4.2.

Preparation of the Nitrocyclopropane.—Thirty grams of the above bromine compound was pulverized and added to a solution of 30 g. of potassium acetate in 250 cc. of dry methyl alcohol. The mixture was refluxed for thirty minutes, during which time the substance dissolved, the solution developed a yellow color, and potassium bromide separated. The solution was cooled and to it was added enough water to dissolve the potassium bromide. After standing for several hours the solution deposited 6–7 g. of pure nitrocyclopropane derivative, which melted at 129°. The mother liquor was removed by decantation and after further standing it deposited the isoxazoline oxide, melting point 140°, previously described by Kohler and Barrett.³ After removal of the oxide the solution sometimes deposited a crop of unchanged isomeric bromine compound when the crude bromine compound was used instead of the pure substance melting at 117–118°.

Dimethyl 1,2-Diphenyl-2'-nitro-3,3'-cyclopropane Dicarboxylate.—This substance separates from methyl alcohol in large, lustrous plates which melt at 129°.

Anal. Calcd. for $C_{19}H_{18}O_6N$: C, 64.2; H, 4.8. Found: C, 64.0; H, 4.8.

Preparation of the Cyclopropene Diester.—Five grams of nitrocyclopropane was dissolved in 60 cc. of hot, dry methyl alcohol and to this was added 1 g. of sodium as sodium methylate. The solution was refluxed for fifteen minutes, during which time sodium nitrite separated. In one experiment the sodium nitrite was filtered off and identified. However, in most cases water was added to the cold solution until it precipitated the cyclopropene ester. The yield is about 1–1.5 g. Some cyclopropene dibasic acid can be recovered by acidification of the mother liquors.

Dimethyl 1,2-Diphenyl-3,3'-cyclopropene Dicarboxylate.—After several crystallizations from a mixture of ether and petroleum ether the substance was pure. It separates in beautiful, colorless prisms which melt at 140–142°.

Anal. Calcd. for $C_{19}H_{18}O_4$: C, 74.0; H, 5.2. Found: C, 74.1; H, 5.5.

The Cyclopropene Dibasic Acid.—Two-tenths gram of the cyclopropene ester was refluxed for ten minutes with excess methyl alcoholic potash. The alcohol was removed and the cold solution was acidified. An oil separated which soon solidified. After purification from a mixture of ether and petroleum ether the substance separated in stout, colorless needles which melted with the evolution of carbon dioxide at about 190°.

Anal. Calcd. for $C_{17}H_{14}O_4$: C, 72.9; H, 4.3. Found: C, 73.1; H, 4.6.

Oxidation of the Dibasic Acid.—One-tenth gram of the cyclopropene dibasic acid was dissolved in excess 10% sodium carbonate solution to which was added potassium permanganate solution until the purple color persisted. The solution was cleared with sodium sulfite solution and finally acidified with dilute hydrochloric acid. The substance which separated was extracted with ether and the ethereal solution shaken with a saturated solution of copper acetate. The pale green copper compound which separated melted at 295–300° with decomposition after crystallization from benzene. The copper derivative of dibenzoylmethane melts at 294–301° with decomposition. The remainder of the copper compound was shaken with water containing a small amount of dilute acid and an ether upper layer. The ether layer after evaporation deposited a substance which melted at 75–77°. A mixed melting point with a known sample of dibenzoylmethane showed no depression.

Addition of Bromine to the Cyclopropene Diester.—Two-tenths gram of cyclopropene ester in chloroform solution absorbed bromine from a 5% solution of bromine in

carbon tetrachloride in direct sunlight. The solvent was removed under diminished pressure and the oil which remained crystallized after manipulating with methyl alcohol. It separates in small, colorless crystals from methyl alcohol which melt at $194-5^{\circ}$ with decomposition.

Dimethyl 1,2-Dibromo-1,2-diphenyl-3,3'-cyclopropane Dicarboxylate.—*Anal.* Calcd. for $C_{18}H_{16}O_4Br_2$: C, 48.7; H, 3.4. Found: C, 49.0; H, 3.4.

Decomposition of the Cyclopropene Dibasic Acid. The Lactone.—Two-tenths gram of the cyclopropene dibasic acid was melted in a Pyrex test-tube heated by means of a sulfuric acid bath and maintained at the decomposition point until the carbon dioxide was all evolved. The clear melt was cooled and then taken up in ether, from which it soon separated in colorless crystals. It melts at $149-151^{\circ}$.

Anal. Calcd. for $C_{16}H_{12}O_2$: C, 81.3; H, 5.1. Found: C, 81.2; H, 5.6.

Hydrolysis of the Lactone.—Six-tenths gram of lactone was dissolved in 10 cc. of methyl alcohol to which had been added excess potassium hydroxide solution. A deep purple solution resulted which became lighter as the solution was heated on the water-bath. After removal of the methyl alcohol, which was gradually replaced by water, the clear solution was cooled and acidified. A substance separated which was crystallized from a mixture of ether and petroleum ether. It separates in small, octahedral crystals which melt at $146-148^{\circ}$.

1,2-Diphenyl-2-hydroxy-3-cyclopropane Carboxylic Acid.—*Anal.* Calcd. for $C_{16}H_{14}O_3$: C, 75.5; H, 5.5. Found: C, 75.1; H, 5.6.

Ozonization of the Hydroxy Acid.⁴—Four-tenths gram of the hydroxy acid was ozonized cautiously in ethyl bromide for half an hour, after which almost the whole of the material was recovered unchanged. Finally another 0.4 g. was ozonized in a rapid current of 6% ozone for three hours after which more than 0.3 g. was recovered unchanged. Ozone therefore has no effect on the compound.

Summary

1. Another cyclopropene derivative has been prepared.
2. The dibasic acid obtained from this cyclopropene diester loses carbon dioxide at its decomposition point to form a cyclopropane lactone.

APPLETON, WISCONSIN

⁴ We are indebted to Professor E. P. Kohler of Harvard University who, with Dr. E. M. Nygaard, carried out this experiment for us.