analysis; 35 g. of aluminum chloride was added rapidly with shaking and after three minutes 25 cc. was removed, immediately dissolved in ether and treated with dilute hydrochloric acid to stop the reaction. In the meantime the reaction mixture was refluxed on the water-bath and at various intervals an aliquot was removed and worked up as outlined in the first experiment. The data are given in Table II and indicate that phenylation is extremely rapid—within three minutes the reaction had practically reached completion. If the mixture was allowed to boil too long, a product with a low neutralization equivalent was obtained.

TABLE II

THE EFFECT OF THE LENGTH OF THE REACTION PERIOD

Refluxed, min.	0	3	7	11	30	60	120	180	240
Iodine number	90.8	9.7	11.0	12.1	10.0	13.0	11.5	9.0	13.6
Neut. equiv.[a]	197.0	161.4	160.5	161.0	160.6	159.3	156.0	140.3	133.0

[a] Calcd. for phenylstearic acid, 156.6.

Experiment 4.—The reaction of oleic acid with xylene was studied in a similar manner and was found to proceed with equal rapidity, yielding an oil similar in appearance and properties to phenylstearic acid. The product had an iodine number of 13 and a neutralization equivalent of 144; calcd. for xylylstearic acid, 144.1.

Anal. (silver salt). Subs., 0.5838; Ag, 0.1286. Calcd. for $C_{26}H_{43}O_2Ag$: Ag, 21.77. Found: Ag, 22.02.

Summary

Phenylation of oleic acid with the production of phenylstearic acid proceeded with great speed in the presence of approximately equimolecular quantities of aluminum chloride and oleic acid and an excess of benzene. A considerable excess of aluminum chloride or prolonged boiling of the reaction mixture produced compounds having lower neutralization equivalents than that of phenylstearic acid.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

STUDIES IN THE CYCLOPROPANE SERIES. XIII. A NEW TYPE OF CYCLOPROPENE DERIVATIVE

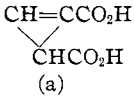
BY E. P. KOHLER AND S. F. DARLING

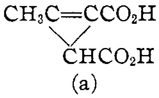
RECEIVED NOVEMBER 1, 1929 PUBLISHED MARCH 6, 1930

In various papers of this series we have discussed the possibility that cyclopropene derivatives might serve as intermediates in the process by which bases convert nitro cyclopropanes into open-chained compounds. The open-chained products are unsaturated and they do not contain the nitro group; but since no cyclopropene derivatives were isolated in any of these cases, the loss of nitrous acid might have occurred either before or after the opening of the ring. We decided, therefore, to determine whether a cyclopropene can actually be formed by eliminating nitrous acid from a suitably constituted nitro cyclopropane.

The choice of suitable material was based on the following consideration.

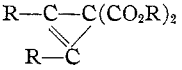
The only type of cyclopropene derivative that is known to be stable in the presence of bases is that represented by the acids



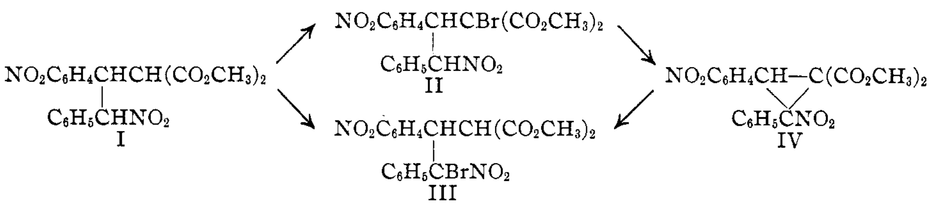


No methods are known for making nitro cyclopropanes which could form derivatives of this type by loss of nitrous acid, and none are available for making the corresponding ketones or other dicarbonyl compounds which would doubtless be equally stable. An inquiry into the reason for the stability of this type, in which all the facts that are known with respect to the preparation and properties of cyclopropene derivatives were considered, led Goss, Ingold and Thorpe[1] to the conclusion that the (a) hydrogen atom is essential for stability. Their argument appears to us to be inconclusive, because it completely ignores the significance of conjugated systems.

It seemed to us that cyclopropene derivatives that contain no conjugated system which would promote the addition of bases, and no hydrogen which by shifting could generate such a conjugated system, should be sufficiently stable to withstand even the intensive action of alkalies that is required for eliminating nitrous acid. We, therefore, decided to prepare a cyclopropene derivative of the type



For our purpose, then, it was essential to start with a nitro cyclopropane derivative which contained but one available hydrogen atom. We planned to secure such a derivative by adding phenylnitromethane to a nitro benzal malonic ester, brominating the addition product in the α- and γ-positions and eliminating hydrogen bromide from one or other of the resulting bromo compounds



The addition product was obtained without difficulty. When it was brominated directly it gave a single monobromo derivative—doubtless the α-bromo compound II because the hydrogen α- to a nitro group cannot be replaced by bromine in neutral or acid solutions. Elimination of hydrogen bromide from the monobromo derivative likewise gave but one product. This is not necessarily the cyclopropane derivative because this reaction

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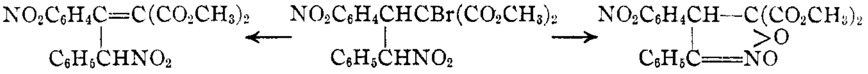
[1] Goss, Ingold and Thorpe, *J. Chem. Soc.*, **123**, 330 (1923).

may result in the formation of an isoxazoline oxide,[2] and, since it is necessary to employ bases for eliminating hydrogen bromide, it is conceivable also that an unsaturated nitro compound might be formed as a secondary product.



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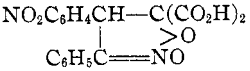
Any unsaturated nitro compound that could possibly result from this reaction would be expected to form a sodium compound, to combine with ozone, and to be readily cleaved into dimethyl malonate and benzoyl phenylnitromethane. Our product undergoes none of these transformations. It was hydrolyzed to the corresponding dibasic acid and when this was boiled with water it ultimately passed into an isoxazole derivative—a behavior that is characteristic of certain isoxazoline oxides.



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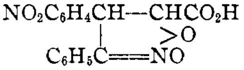

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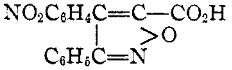
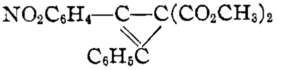


VIII

Since the cyclopropane derivative could not be obtained from this α-bromo compound, it was necessary to undertake the preparation of a γ-bromo compound by way of the sodium compound. The addition product has two hydrogen atoms that are replaceable by metals, but when a solution in sodium methylate was added to bromine, it yielded a single monobromo derivative which was isomeric with the substance obtained by direct bromination. Elimination of hydrogen bromide from this second bromo compound resulted in two isomers which were formed in approximately equal amounts. One of these isomers was the isoxazoline oxide V; this bromo compound, is, therefore, likewise an α-bromo derivative.

Fortunately for our project the second bromine-free product gave none of the typical reactions of isoxazoline oxides. When it was treated with sodium methylate it lost nitrous acid—a reaction that never occurs with these oxides but is characteristic of nearly all nitro cyclopropane derivatives. In this as in a few other cases, therefore, the α-bromo compound yields both oxide and cyclopropane.

Since the product obtained by eliminating nitrous acid from the cyclopropane derivative has no hydrogen atoms that are not tied up in its phenyl and ester groups, the number of its possible formulas is small



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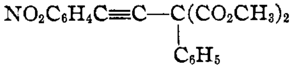
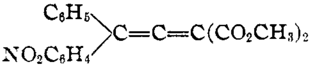


$NO_2C_6H_4C\equiv C-C(C_6H_5)(CO_2CH_3)_2$



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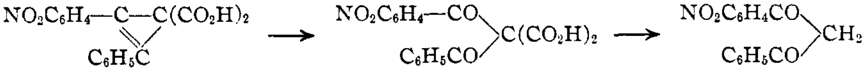
[2] Kohler and Barrett, THIS JOURNAL, **48**, 1770 (1926).

In order to distinguish between these formulas we hydrolyzed the substance to the corresponding dibasic acid and then oxidized this acid with permanganate. The product was nitro dibenzoyl methane, proving conclusively that the substance is the cyclopropene derivative


X XI

The isolation of this cyclopropene derivative justifies the assumption that cyclopropene derivatives may play a role in the passage of nitro cyclopropane derivatives into open-chained compounds. It also proves that the stability of cyclopropene derivatives is not dependent on the presence of a "mobile hydrogen atom." Since it has no conjugated system, the ester is more stable even than the ester of methyl cyclopropene dicarboxylic acid; it is not attacked at all by hot concentrated sodium methylate.

Experimental Part

I. The Isoxazoline Oxide and its Degradation

The reactions that lead to the formation of the isoxazoline oxide are exactly the same as those employed by Kohler and Barrett[2] for making the corresponding compound without the *m*-nitro group, but owing to the influence of the nitro group in diminishing solubility, all operations are much simpler. Since the bromination of the addition product is not easy, it is necessary to use pure material for this step; in all other transformations thoroughly washed and dried crude products serve equally well.

Dimethyl β-(3-Nitrophenyl)-γ-nitro-γ-phenyl-ethylmalonate, I.—A solution of 40 g. of the methyl ester of *m*-nitro benzal malonic acid and 20 g. of phenylnitromethane in 200 cc. of dry methyl alcohol containing a little sodium methylate was boiled for half an hour, then diluted with 100 cc. of ether and a small quantity of water. It deposited 47 g. of addition product. The substance was purified by recrystallization from a mixture of ether and petroleum ether or from methyl alcohol. It is sparingly soluble in ether, moderately soluble in methyl alcohol, and it crystallizes in silky needles which melt at 118–120°.

In a few cases the addition product melted at a considerably lower temperature. In these cases, there were indications of the presence of an isomeric addition product that crystallized in stouter needles. Since this was, doubtless, a stereoisomer, no attempt was made to isolate it.

Anal. Calcd. for $C_{19}H_{18}O_8N_2$: C, 56.7; H, 4.5. Found: C, 57.1; H, 4.5.

The α-Bromo Compound Formed by Direct Bromination, II.—The addition product was brominated by adding excess of bromine to a solution of the substance in chloroform. In order to start the process it was necessary to expose the heated solution to direct sunlight. Once it was started it proceeded under the influence of sunlight alone but took several hours for its completion. When the evolution of hydrogen bromide ceased, the solvent was removed and the oily residue rubbed with a little methyl alcohol until it solidified. The yield of crude, washed and dried solid was 24 g. from 25 g. of substance. The bromo compound was recrystallized from methyl alcohol, from which it separated in fine colorless needles melting at 125°.

Anal. Calcd. for $C_{19}H_{17}O_8N_2Br$: C, 47.4; H, 3.5. Found: C, 47.4; H, 3.6.

Dimethyl 3-Phenyl-4-(3-nitrophenyl)-5,5-isoxazoline Oxide Dicarboxylate, V.—A suspension of 10 g. of the bromo compound and 10 g. of potassium acetate in 100 cc. of methyl alcohol was boiled until all of the bromo compound had disappeared. The light yellow solution was then cooled, the precipitate collected on a filter, washed with water and methyl alcohol and dried; yield, 7.5 g. of pure oxide. The oxide separates from methyl alcohol, in which it is sparingly soluble, in large very pale yellow monoclinic crystals. It melts at 173–174°.

Anal. Calcd. for $C_{19}H_{16}O_8N_2$: C, 57.0; H, 4.0. Found: C, 57.5; H, 4.3.

Hydrolysis to the Dibasic Acid, VI.—A solution of the oxide in cold methyl alcoholic potassium hydroxide is pale yellow in color but it immediately turns red on heating. A red solution like this was heated on a steam-bath for ten minutes, then diluted with a large volume of water and acidified. The precipitated acid was extracted with ether, the ethereal solution filtered, dried and allowed to evaporate. It deposited large pale yellow crystals which melted with vigorous effervescence. The effervescence is due to a molecule of ether, which cannot be completely removed without decomposing the acid, but which appears promptly when the acid is dissolved in bases. The acid will not crystallize in the absence of ether.

Anal. Calcd. for $C_{17}H_{12}O_8N_2 \cdot (C_2H_5)_2O$: C, 56.5; H, 5.0; equiv. wt., 223. Found: C, 56.6; H, 5.3; equiv. wt., 222.

In order to make certain that hydrolysis was not accompanied by rearrangement, the acid was re-esterified by digesting its dry, colorless silver salt with methyl iodide in absolute ether; it gave the original ester in the calculated quantity.

Hydrolysis and Cleavage. 3-Phenyl-4-(3-nitrophenyl)-isoxazoline Oxide Carboxylic Acid, VII.—Two g. of the diester was dissolved in an ice-cold solution containing 2 g. of sodium in the minimum amount of methyl alcohol. The solution turned red as its temperature rose to that of the room. After twenty-four hours at the room temperature it had become deep red in color and had deposited a small quantity of solid. It was cleared by filtration, diluted with water and acidified. The (acid) solution deposited pale yellow needles which became colorless when recrystallized from ether–petroleum ether and then melted with decomposition at about 190°.

Anal. Calcd. for $C_{16}H_{12}O_6N_2$: C, 58.6; H, 3.7; equiv. wt., 328. Found: C, 58.7; H, 4.0; equiv. wt., 323.

The monobasic acid forms a colorless silver salt and a sparingly soluble sodium salt which crystallizes in needles. It is not attacked by ozone and its solution in sodium carbonate does not reduce permanganate.

The Methyl Ester.—The dry silver salt of the monobasic oxido acid was digested with an excess of methyl iodide. The product crystallized from ether–petroleum ether in pale yellow prisms melting at 133°.

Anal. Calcd. for $C_{17}H_{14}O_6N_2$: C, 59.7; H, 4.1. Found: C, 59.9; H, 4.0.

The ester does not dissolve in cold concentrated sodium methylate and it does not form an ozonide. It is therefore neither an unsaturated nitro compound nor a cyclopropane derivative.

3-Phenyl-4-(3-nitrophenyl)-isoxazole Carboxylic Acid, VIII.—When the dibasic acid is heated with water it first loses ether, then dissolves. The resulting clear solution, on longer heating, turns faintly red, becomes turbid and deposits an oil that has the odor of phenylnitromethane. From an ethereal solution of this oil sodium bicarbonate extracts a relatively small quantity of the isoxazole acid. The acid was also obtained as a by-product in the formation of the isoxazoline oxide and cyclopropane esters. It crystallizes in small pale yellow rhombs and decomposes at about 300°.

Anal. Calcd. for $C_{16}H_{10}O_6N_2$: C, 61.9; H, 3.2; equiv. wt., 310. Found: C, 62.1; H, 3.0; equiv. wt., 311.

The acid is very sparingly soluble in ether and in methyl alcohol. It forms a colorless silver salt and a yellow copper salt which decomposes explosively when heated. Its solution in sodium carbonate does not reduce permanganate.

The Methyl Ester.—The ester, made through the silver salt, crystallized in very pale yellow prisms. Its melting point—133°—is the same as that of the methyl ester of the corresponding oxido acid but a mixture of the two substances melts at a much lower temperature.

Anal. Calcd. for $C_{17}H_{12}O_6N_2$: C, 62.9; H, 3.7. Found: C, 63.1; H, 4.1.

II. The Cyclopropene Derivative

For the purpose of getting an isomeric bromine compound the addition product was dissolved in a slight excess of methyl alcoholic sodium methylate and the resulting solution was added to an excess of bromine dissolved in methyl alcohol. This method generally gave an isomeric bromo compound that melted almost at the same temperature as the one that has been described, but all mixtures of the two invariably melted lower. In some cases the bromination resulted in a mixture of these bromo compounds. Since elimination of hydrogen bromide from the pure isomer gave the same two products that were obtained from the mixture, the latter was washed, dried and used without separation.

The Stereoisomeric Bromo Compound, II.—Forty-eight grams of the addition product was dissolved in a solution of 2.8 g. of sodium in 250 cc. of dry methyl alcohol. The orange-yellow solution was poured into 25 cc. of methyl alcohol containing an excess of bromine. The clear solution, on cooling, gradually deposited 46 g. of the monobromo compound, and an additional 3 g. was obtained from the mother liquors. The bromo compound separates from methyl alcohol, in which it is sparingly soluble, in small, almost colorless crystals that melt at 125–126°.

Anal. Calcd. for $C_{19}H_{17}O_8N_2Br$: C, 47.4; H, 3.5. Found: C, 47.2; H, 3.9.

Dimethyl 1-Phenyl-1-nitro-2-(3-nitrophenyl) Cyclopropane Dicarboxylate, IV.—A suspension of 50 g. of the bromo compound and 50 g. of potassium acetate in 300 cc. of dry ethyl alcohol was boiled for fifteen minutes, during which the bromo compound dissolved and the light yellow solution deposited both potassium bromide and cyclopropane derivative. The solution was filtered while hot. The first crop of solid, after washing with water until free from bromide and drying, weighed 11.5 g. It was almost pure cyclopropane derivative.

The filtrate from the first crop, on cooling, deposited 18.5 g. of a mixture of the oxide and the cyclopropane derivative. The mother liquor was diluted with water, extracted with ether—which removed a small quantity of oil and most of the color—and then acidified with a large excess of hydrochloric acid. The acid precipitated 2 g. of the isoxazole carboxylic acid (VIII).

The mixture of cyclopropane derivative and oxide was separated by dissolving in chloroform, in which it is very readily soluble, boiling the solution until the walls were entirely free from solid, and then inoculating it with pure oxide. It deposited 9 g. of almost pure oxide. The filtrate from the oxide yielded cyclopropane.

The cyclopropane diester is sparingly soluble in ether and in methyl alcohol. It crystallizes in colorless leaflets and melts at 167–169°.

Anal. Calcd. for $C_{19}H_{16}O_8N_2$: C, 57.0; H, 4.0. Found: C, 56.8; H, 4.3.

Action of Sodium Methylate, the Cyclopropene Diester, IX.—To a cold solution of 0.25 g. of sodium in 30 cc. of dry methyl alcohol was added 5 g. of finely pulverized cyclopropane derivative. The mixture was heated on a steam-bath until the cyclopropane derivative was replaced by a fine, light yellow crystalline precipitate. The time required for this was ten minutes. The liquid was cooled, the solid collected on a filter and thoroughly washed with water and alcohol. The product was 4 g. of nearly pure cyclopropene derivative. The filtrate deposited a colorless salt which proved to be sodium nitrite.

The cyclopropene derivative is sparingly soluble in nearly all solvents but can be recrystallized from acetone, from which it separates in small pale yellow crystals. It melts at 176–178°.

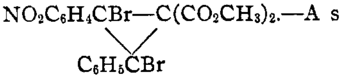
Anal. Calcd. for $C_{19}H_{15}O_6N$: mol. wt. 353; C, 64.6; H, 4.3; N, 4.1; OCH_3, 17.3. Found: mol. wt., 380; C, 64.4; H, 4.6; N, 4.2; OCH_3, 19.2.

The Cyclopropene Diacid, X.—The cyclopropane diester evidently loses nitrous acid more easily than any other nitrocyclopropane derivative that has been studied heretofore. When it is warmed with methyl alcoholic potassium hydroxide it not only undergoes hydrolysis but also loses nitrous acid. The product is the cyclopropene diacid. This acid is also formed when the cyclopropene diester is digested with methyl alcoholic potassium hydroxide. Since it is extremely soluble in methyl alcohol and very sparingly soluble in ether, it was purified by recrystallization from acetone and petroleum ether. From this mixture it separates in fine, colorless needles, containing one molecule of water of crystallization which is lost at 100°.

Anal. Calcd. for $C_{17}H_{11}O_6N \cdot H_2O$: C, 59.5; H, 3.8; N, 4.1; H_2O, 5.2; equiv., 171. Found: C, 59.4; H, 3.8; N, 4.4; H_2O, 5.1; equiv., 171.

The anhydrous acid melts at 216°. Esterification through the silver salt gave the calculated quantity of the ester from which it had been obtained.

Oxidation to Nitro Dibenzoyl Methane, XI.—The acid from 2 g. of the cyclopropene diester was dissolved in an excess of a 5% solution of sodium carbonate. To this canary-yellow solution, concentrated potassium permanganate solution was added in slight excess. After removing oxides of manganese with bisulfite and acid, there remained a gram of brownish colored solid which gave a gray-green copper derivative when its ethereal solution was shaken with aqueous copper acetate. The solid was recrystallized from acetone. The pure substance melted at 135–136°. Its melting point was not changed by admixture with a sample of nitro dibenzoyl methane in the usual way.[3]

Addition of Bromine,  $NO_2C_6H_4CBr{-}C(CO_2CH_3)_2$, C_6H_5CBr.—A small quantity of a dilute solution of bromine in chloroform was added to a solution of one gram of the cyclopropene ester in the same solvent. In diffuse daylight no reaction was perceptible but in direct sunlight the bromine disappeared. More bromine was added in the same manner as long as it disappeared. The excess bromine and the solvent were then removed under diminished pressure. The residue was a yellow oil which solidified when it was rubbed with ether and petroleum ether. The solid was recrystallized from methyl alcohol and water.

Anal. Calcd. for $C_{19}H_{15}O_6NBr_2$: C, 44.4; H, 2.9. Found: C, 44.4; H, 3.2.

The dibromide is readily soluble in chloroform, in ether and in hot methyl alcohol, sparingly soluble in cold methyl alcohol, insoluble in petroleum ether. It crystallizes in colorless needles and melts at 144–145°. The yield was quantitative.

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[3] Bodforss, *Ber.*, **49**, 2803 (1916).

Action of Alkalies.—The dibromide is comparatively insensitive to bases but it slowly reacts with hot alkalies. Thus when 1.5 g. of the substance was boiled with excess of concentrated alcoholic potassium hydroxide it slowly dissolved and when the resulting dark colored solution was acidified it deposited a good yield of the cyclopropene di-acid. Toward concentrated alkalies, therefore, the dibromide behaves essentially like the cyclopropene dibromide discovered by Feist.[4]

The dibromide is also attacked slowly by dilute alkalies but the reaction, which is much more involved, has not yet been cleared up.

Summary

1. It is shown that cyclopropene derivatives can be obtained by eliminating nitrous acid from properly constituted nitro cyclopropane derivatives.

2. A method is described for preparing cyclopropene derivatives which differ from the few known heretofore in that they contain neither a conjugated system nor any hydrogen which by shifting could generate such a system.

3. It is found that the stability of cyclopropene derivatives is not dependent on the presence of a mobile hydrogen atom.

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[Contribution from the Chemical Laboratory of Iowa State College]

THE REACTION BETWEEN MAGNESIUM DIPHENYL AND BROMINE. AN HISTORICAL NOTE ON THE FIRST PREPARATION OF PHENYLMAGNESIUM BROMIDE

By Henry Gilman and Robert E. Brown

Received November 4, 1929 Published March 6, 1930

Introduction

Long years ago Frankland[1] and Fleck[2] publicly called attention to the absence of organomagnesium halides. Fleck[2] purposefully set out to prepare phenylmagnesium bromide (by the *slow* addition of bromine to dry magnesium diphenyl covered with anhydrous ether) by the following reaction written by him

$$(C_6H_5)_2Mg + Br_2 \longrightarrow C_6H_5MgBr + C_6H_5Br \qquad (I)$$

However, because he obtained only bromobenzene and magnesium bromide he pictured the course of reaction as follows

$$(C_6H_5)_2Mg + 2Br_2 \longrightarrow 2C_6H_5Br + MgBr_2 \qquad (II)$$

and wrote, "One may assume that the latter reaction took place and that

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[4] Feist, *Ber.*, **26**, 750 (1893).

[1] Frankland, *J. Chem. Soc.*, **13**, 194 (1861).

[2] Fleck, *Ann.*, **276**, 129 (1893). The results of these studies by Herman Fleck of Philadelphia, working in the laboratory of Lothar Meyer, were published in a dissertation at Tübingen in 1892.