TABLE III.

Substance.	Type of cell.	Temp.	Concentrations.		E. M. F. of cell.	Trans. No. of cation.	Activity ratios a_1/a_2 for		
			C_1.	C_2.			Cl^-.	H^+	
HCl	B	18°	0.006686	0.001665	−0.05614	0.833	3.82	3.84	J.
KCl	B		0.006700	0.001670	−0.03330	0.495			J.
HCl	B	18°	0.008315	0.001665	−0.06487	0.833	4.70	4.74	J.
KCl	B		0.008329	0.001670	−0.03844	0.495			J.
HCl	B	18°	0.01665	0.001665	−0.09235	0.833	8.86	9.38	J.
KCl	B		0.01670	0.001674	−0.05434	0.496			J.
HCl	B	18°	0.03330	0.003329	−0.09162	0.833	8.76	9.14	J.
KCl	B		0.03347	0.003347	−0.05403	0.496			J.
HCl	A	25°	0.05	0.005	−0.11234	.....	8.64	9.16	N. and E.
KCl	A		0.05	0.005	−0.11085	.....			M. and P.
HCl	A	25°	0.1	0.01	−0.1116	.....	8.33	9.23	N. and E.
HCl	A		0.1	0.01	−0.1117	.....			L. B. S.
KCl	A	25°	0.1	0.01	−0.1089	.....			M. and P.
KCl	B		0.1	0.01	−0.0540	0.495			M. and P.

D. A. MACINNES.

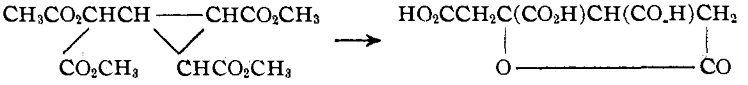
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY.]

STUDIES IN THE CYCLOPROPANE SERIES. VII. NITROCYCLOPROPANES.

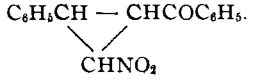
BY E. P. KOHLER AND H. F. ENGELBRECHT.

Received May 31, 1919.

Esters of cyclopropane acids that have either two carboxyl groups or a carboxyl and a ketonic group in combination with one of the ring carbon atoms are almost invariably transformed into open chained compounds by alcoholates, and not infrequently the same change is brought about by concentrated alkalies.[1] Esters of other cyclopropane acids rarely undergo this reaction, the one case known being that reported by Buchner and Miller.[2]



In connection with an investigation of the mechanism of this reaction it became desirable to examine the behavior of a cyclopropane derivative which is so constituted that it can form a metallic derivative without opening the ring. The substance selected for the purpose is benzoylphenyl-nitrocyclopropane.



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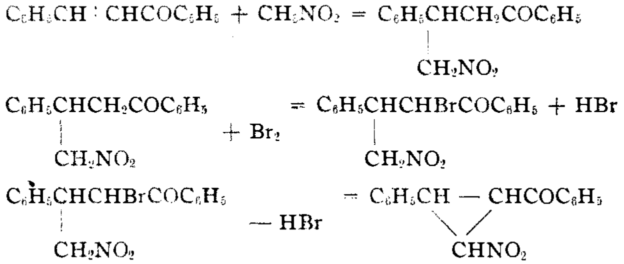
[1] *Ber.*, **36**, 3776 (1903); THIS JOURNAL, **39**, 1406, 1700, 2404 (1917).

[2] *Ber.*, **27**, 871 (1894).

Cyclopropane derivatives in which one of the ring carbon atoms holds a nitro group are unknown, but a feasible plan for preparing such substances was outlined in an earlier paper. This was adopted in the present work, with excellent results. It involves 3 reactions which are represented by the equations

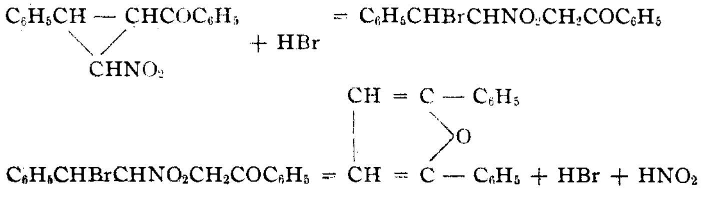


$$C_6H_5CH:CHCOC_6H_5 + CH_3NO_2 = C_6H_5\underset{\displaystyle CH_2NO_2}{\underset{|}{C}}HCH_2COC_6H_5$$

$$C_6H_5\underset{\displaystyle CH_2NO_2}{\underset{|}{C}}HCH_2COC_6H_5 + Br_2 = C_6H_5\underset{\displaystyle CH_2NO_2}{\underset{|}{C}}HCHBrCOC_6H_5 + HBr$$

$$C_6H_5\underset{\displaystyle CH_2NO_2}{\underset{|}{C}}HCHBrCOC_6H_5 - HBr = C_6H_5\underset{\diagdown}{CH} - \underset{\diagup}{CH}COC_6H_5 \quad (CHNO_2)$$

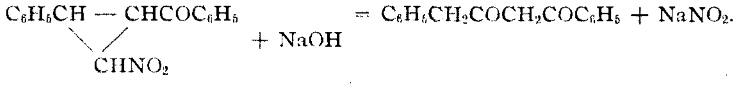
That the resulting nitro compound is a cyclopropane derivative and not an isomeric ethylenic ketone is shown not only by its indifference to permanganate but also by its behavior towards hydrogen bromide. In glacial acetic acid the substance combines with hydrogen bromide as readily as the most active α,β-unsaturated ketone, but the resulting compound is far more stable on heating than any saturated bromine compound which has bromine β to a carbonyl group. By eliminating both hydrobromic acid and nitrous acid it is possible to transform the addition product quantitively into 1,4-diphenyl furane. A compound having two phenyl groups in the 1,4-positions can be formed from one having them in the 1,3-positions only by closing a cyclopropane ring and opening it again at a different point. The reactions involved are therefore represented by the following equations:



$$C_6H_5CH - CHCOC_6H_5\ (CHNO_2) + HBr = C_6H_5CHBrCHNO_2CH_2COC_6H_5$$

$$C_6H_5CHBrCHNO_2CH_2COC_6H_5 = \begin{matrix} CH = C - C_6H_5 \\ | \qquad \rangle O \\ CH = C - C_6H_5 \end{matrix} + HBr + HNO_2$$

The cyclopropane derivative is exceedingly sensitive to all alkaline reagents, the ring being opened even more easily than that of cyclopropane derivatives which have two carbonyl groups in combination with one of the ring carbon atoms. The process is accompanied by replacement of the nitro group and the final product is a β-diketone formed in accordance with the equation



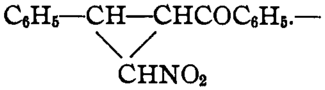
$$C_6H_5CH - CHCOC_6H_5\ (CHNO_2) + NaOH = C_6H_5CH_2COCH_2COC_6H_5 + NaNO_2.$$

The reaction takes place in steps, but no intermediate products could be isolated. The discussion of the mechanism will therefore be deferred until the reaction has been studied with more favorable material.

Experimental Part.

The addition of nitro methane to benzal-acetophenone and the bromination of the product were carried out as described in an earlier paper.[1] The melting points of the isomeric α-bromo compounds are 100° and 106° instead of 100° and 86° as there given. The compound melting at 100°, the principal products can easily be transformed into the higher melting isomer by dissolving it in alcohol and saturating the solution with hydrogen bromide. The isomer separates slowly in almost quantitative yields. The transformation can also be effected by adding a small quantity of either toluidine or diethyl aniline to a methyl alcoholic solution of the lower melting isomer but the yield is much less and the product is contaminated with uncrystallizable red oils.

1-Benzoyl-2-phenyl-3-nitro Cyclopropane,



$C_6H_5—CH—CHCOC_6H_5$.— (ring closed by $CHNO_2$)

The cyclopropane ring can be closed by eliminating hydrogen bromide from the bromine compound with a number of alkaline reagents, but the yields are unsatisfactory with all of them. The best results were obtained with potassium acetate, and the higher melting bromine compound gives a better yield than its isomer. When concentrated solutions of the low melting bromine compound are used, the higher melting isomer frequently crystallizes from the solution and then disappears again during the course of the reaction. Most of the material used in the investigation was made by starting with a thoroughly washed and dried mixture of the bromine compounds. The procedure was as follows:

A concentrated solution of 15 g. of fused potassium acetate in alcohol was added to a suspension of 15 g. of the mixed bromine compounds in 100 cc. of the same solvent. The mixture was allowed to remain at the ordinary temperature for an hour during which the bromine compounds dissolved and considerable quantities of potassium bromide and solid cyclopropane derivative separated. It was then heated on a steam bath for another hour to complete the reaction. The resulting solution, which was pale yellow when pure bromine compounds were used and brown if the materials were impure, was cooled in a freezing mixture and gradually diluted with water while being shaken vigorously. The cyclopropane derivative was precipitated as a crystalline, yellow solid which after one recrystallization from alcohol became colorless and melted at 98°. The yield varied from 55 to 75%—the average of a number of preparations being 61%. The filtrates contained yellow or brown uncrystallizable oils.

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[1] THIS JOURNAL, 38, 889 (1916).

The cyclopropane derivative crystallizes in clusters of stout prisms. It is moderately soluble in alcohol and ether, readily in boiling alcohol, acetone and chloroform. When exposed to sunlight it gradually becomes tinged with pink.

Calc. for $C_{16}H_{13}O_3N$: C, 71.9; H, 4.9. Found: C, 71.6; H, 4.9.

Addition of Hydrogen Bromide.—Thirty g. of finely powdered cyclopropane derivative was added in small portions to 100 cc. of glacial acetit acid which had been saturated with hydrogen bromide. The substancc dissolved rapidly on shaking, the solution became warm, and the produce began to separate in crystalline form as soon as the solution started to cool. The mixture was allowed to stand for an hour during which most of the product separated, then poured into cracked ice. The colorless, pasty precipitate completely solidified when stirred. The solid was thoroughly washed with water, dried in the air and recrystallized from a mixture of acetone and ether.

Calc. for $C_{16}H_{14}O_3NBr$: C, 55.2; H, 4.0. Found: C, 55.5; H, 4.3.

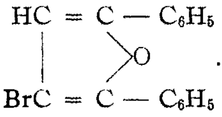
β-Nitro-γ,γ-bromo-phenyl Butyrophenone, $C_6H_5CHBrCHNO_2CH_2CO$-C_6H_5, crystallizes in colorless plates which melt at 115–116° and decompose at 120°. It is an exceedingly sensitive substance. Unless perfectly pure it decomposes spontaneously at the ordinary temperature and in the dark. When the carefully purified compound is kept near the melting point for a short time or exposed to direct sunlight it turns yellow, and the color persists on recrystallization but the melting point remains constant at 115–116° and the composition remains the same.

Calc. for $C_{16}H_{14}O_3NBr$: C, 55.2; H, 4.0. Found: C, 55.3; H, 4.3.

When alcoholic solutions of the bromine compound are boiled they become acid. Qualitative experiments showed that the substance loses both hydrobromic and nitrous acids. The process is very slow but is greatly accelerated by addition of a small quantity of ammonium bromide. Thus 2 g. of ammonium bromide was added to a solution of 5 g. of the bromine compound in 40 cc. of methyl alcohol and the mixture boiled. In less than an hour all the substance had dissolved. The yellow solution, on cooling, deposited the product in pale yellow flakes, which after washing and recrystallization from alcohol melted at 90°.

Calc. for $C_{16}H_{12}O$: C, 87.3; H, 5.5. Found: C, 87.1; H, 5.1.

The substance has the composition of a diphenyl furane, and it was identified as 2,5-diphenyl furane by comparison with a specimen prepared according to Perkin.[1]

1,5-Diphenyl-3-bromo Furane,  .—When the hydro-

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[1] *J. Lond. Chem. Soc.*, **57**, 954 (1890).

bromic acid addition product was heated above the melting point it lost oxides of nitrogen and water but no bromine or hydrobromic acid. The resulting greenish yellow melt was recrystallized from methyl alcohol. It consisted almost entirely of a pale yellow substance which crystallized in thin plates, resembling diphenyl furane, and melted at 77°. These were contaminated with a small quantity of a much yellower product which it was impossible to remove by recrystallization but which was finally got rid of by distillation under diminished pressure.

Calc. for $C_{16}H_{11}OBr$: C, 64.2; H, 3.7. Found: C, 64.6; H, 3.9.

The composition indicated loss of water and nitric oxide from the addition product. The substance is indifferent to permanganate but combines with two atoms of bromine when exposed to the action of bromine vapor. The bromine is completely unreactive—sodium methylate neither replaces it nor eliminates hydrogen bromide. The only open chained formula consistent with these properties is that of an allenic ketone.

$$C_6H_5CHBrCHNO_2CH_2COC_6H_5 = C_6H_5CBr = C = CHCOC_6H_5 + H_2O + NO.$$

We could not, however, secure any evidence of the presence of a carbonyl group, as it was impossible to make either a hydrazone of an oxime. In view of its great stability it seems more probable, therefore, that it is a furane derivative as written. The formation of a furane derivative involves a shifting of the bromine atom, but similar shifts have been observed before in high temperature reactions involving ring formation.

Action of Bases on the Cyclopropane Derivative.—The cyclopropane derivative is readily attacked by all bases but it is difficult to get definite products from the resulting brown or red oils. The following procedure, however, proved fairly satisfactory: An excess of concentrated sodium methylate was added gradually to a well cooled solution of 10 g. of cyclopropane derivative in the minimum quantity of methyl alcohol. The mixture was left at the ordinary temperature for 8 hours, then acidified with hydrochloric acid, and allowed to evaporate in the air. The resulting yellow oil was dissolved in ether and this solution shaken with a saturated aqueous solution of copper acetate. This gave 7 g. of a pale copper derivative. The copper derivative, after decomposition with sulfuric acid in the usual way, yielded a colorless solid which crystallized in plates and melted at 54°.

Calc. for $C_{16}H_{14}O_2$; C, 80.7; H, 5.9. Found: C, 80.6; H, 6.1.

The composition and melting point of the substance as well as the melting point of its copper derivative indicated phenyl-acetyl-acetophenone.

This diketone was therefore made by condensing ethyl phenylacetate with acetophenone. A mixed melting point showed that the two products are identical.

The diketone is not the primary product of the reaction between bases and the cyclopropane derivative. If the alcoholic solution containing the product of the reaction with sodium methylate is acidified with acetic instead of hydrochloric acid, and then allowed to evaporate it leaves an oil that contains no nitrogen but gives only a trace of copper derivative. When this oil is digested for a short time with a dilute solution of hydrochloric acid in methyl alcohol, and then shaken with copper acetate it gives the usual amount of copper derivative, showing that the oil contains an intermediate product which is turned into diketone by the action of mineral acids. All efforts either to isolate this product or to acquire more information about it were unsuccessful.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, KENTUCKY AGRICULTURAL EXPERIMENT STATION.]

THE COMPOSITION OF THE ASH OF CRAB GRASS (DIGITARIA SANGUINALIS) AS AFFECTED BY THE SOIL IN WHICH IT IS GROWN.

BY G. DAVIS BUCKNER.

Received June 4, 1919.

Plant nutrition teaches that the chemical composition of the ash of the same species of plant varies within wide limits when grown in different localities and under different conditions. Plants flourish when grown in soils of widely varying composition and seem to require no definite medium from which to secure the nourishment necessary for normal growth, provided it does not fall below a certain quantitative and qualitative level. The ash of plants grown in different soils will likewise have a variable composition.

In the prosecution of certain experiments in this laboratory it was found desirable to obtain a green plant which contained a large percentage of ash, the composition of which would satisfy given conditions. In the search for such a plant it was noticed that crab grass (*Digitaria sanguinalis*) grew and flourished in the middle of a limestone roadway. From other experiments it was reasoned that here at least would be conditions most favorable for the largest intake of calcium. The comparative analysis of a plant grown under such conditions and that of a sample of the same species grown under normal condition of garden soil would have an added interest. For these reasons plants were carefully selected with regard to form and size, and cut one inch above the ground, and from all external appearances they were similar. Both samples were immediately washed with distilled water to free them from extraneous material and