

Subs., air-dry, 0.5776: Loss, 0.0236 *in vacuo* at 100° over H₂SO₄.

Calc. for C₁₈H₁₈O₇N₂As.H₂O: H₂O, 4.21. Found: 4.09.

Subs., anhydrous, 0.1441: (Kjeldahl), 7.1 cc. 0.1 N HCl. Subs., 0.3292: Mg₂As₂O₇, 0.1231.

Calc. for C₁₈H₁₈O₇N₂As: N, 6.83; As, 18.28. Found: N, 6.90; As, 18.03.

NEW YORK, N. Y.

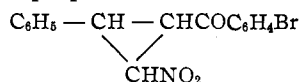
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY.]

STUDIES IN THE CYCLOPROPANE SERIES. VIII. NITRO-CYCLOPROPANE DERIVATIVES.

BY E. P. KOHLER AND H. E. WILLIAMS.

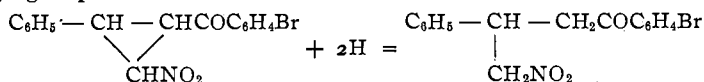
Received June 27, 1919.

In continuation of the work reported in the preceding paper of this series,¹ we have studied another nitro-cyclopropane derivative in the hope that a substance which would give more sparingly soluble products would enable us to isolate some of the intermediate compounds that baffled us in the earlier work. We selected for the purpose *p*-bromobenzoyl-phenyl-nitro-cyclopropane,

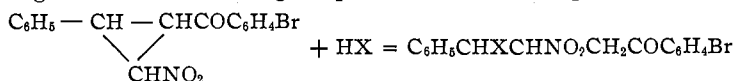


This nitro compound was made without much trouble by the method which had been developed for the bromine-free analog. It has 3 dissimilar asymmetric carbon atoms and 3 of the 4 possible stereoisomers were isolated in the course of the investigation. The structure of all of these is established by the fact that with various reagents they give products in which the carbon chain is not the same, showing that they are formed by opening a cyclopropane ring at different points.

On cautious reduction with zinc and alcohol all of the isomeric cyclopropane derivatives give the same substance that is obtained by addition of nitromethane to benzal-aceto-*p*-bromophenone. The ring is, therefore, opened between the carbon atoms holding the nitro- and *p*-bromobenzoyl groups:



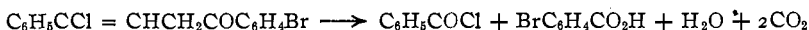
The isomeric cyclopropane derivatives also combine very readily with the halogen acids but the ring is opened at a different point:



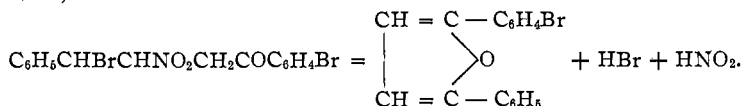
The reactions of the resulting halogen nitro compounds leave no doubt as to their structure. Thus the chlorine compound, when treated with

¹ THIS JOURNAL, 41, 1379 (1919).

cold potassium acetate, loses nitrous acid and forms an unsaturated chlorine compound, which gives benzoyl chloride on oxidation with ozone:

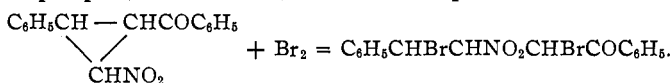


The more sensitive bromine compound loses hydrobromic acid more easily than nitrous acid, therefore forms an unsaturated nitro compound which gives benzaldehyde when oxidized. When boiled with alcohol alone it loses nitrous as well as hydrobromic acid. The result is a furane derivative,



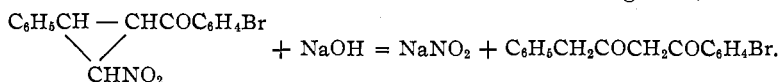
It is worthy of note that while these halogen nitro compounds have reactive hydrogen and halogen in the 1,3-relation they invariably give ethylene and not cyclopropane derivatives when halogen acid is eliminated.

The isomeric cyclopropane derivatives are also attacked by bromine. The principal product is an α,γ -dibromo compound,

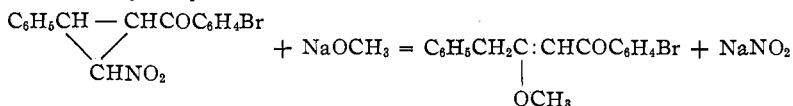


It is possible that this substance may be due to substitution of bromine in the α -position and addition of the resulting hydrogen bromide to the bromo cyclopropane thus formed; but no trace of such a bromo compound could be found among the products.

The reaction of the cyclopropane derivatives which it is most difficult to interpret is that which takes place with alkalis. The final product, like that of the same reaction with the bromine free analog, is a β -diketone,



This diketone is manifestly formed as a result of a number of successive reactions. By using concentrated sodium methylate we succeeded in isolating an unsaturated methoxyl compound which readily gives the diketone on hydrolysis,



It is possible that this is an intermediate product; but it seems more probable that both the methoxyl compound and the diketone are formed from an intermediate acetylenic ketone. In order to reach a definite conclusion, it will be necessary to find a method for detecting an acetylenic ketone in solutions.

Experimental Part.

γ -Nitro- β -phenyl-propyl-(4-bromophenyl) Ketone, $\text{CH}_2(\text{NO}_2)\text{CH}(\text{C}_6\text{H}_5)\text{CH}_2\text{COC}_6\text{H}_4\text{Br}$.—The saturated nitro-ketone that served as the starting point in the investigation was made by adding sodium nitromethane to α -phenyl- γ -(4-bromophenyl) propenone and acidifying the product. This reaction always gives two substances, one of which corresponds to the condensation of a molecule of nitro compound with one, the other with two molecules of the unsaturated ketone. In as much as the sodium compound formed by the addition of sodium nitromethane to the unsaturated ketone is more soluble than either sodium nitromethane or the unsaturated ketone, it is impossible to prevent the formation of considerable quantities of the "dimolecular" product. The following procedure gave the most satisfactory yield of the monomolecular compound.

A finely divided suspension of sodium nitromethane was made by adding 15 g. of nitromethane to a solution of 5 g. of sodium in 75 cc. of 95% alcohol and shaking vigorously until all lumps were broken up. The suspension was added rapidly to 58 g. of unsaturated ketone suspended in 150 g. of alcohol previously warmed to 60°. The mixture warmed up on shaking and the solid gradually disappeared. The resulting yellow to orange colored solution was immediately cooled in ice water and acidified with glacial acetic acid. By adding the acid drop by drop and stirring vigorously it was possible to get a coarsely crystalline product which was easily purified by thorough washing with water and alcohol and recrystallization from alcohol and benzene. The yield of pure substance was 87%.

The yield was not improved by using absolute methyl or ethyl alcohol. It fell to below 50% when the condensation was carried out in solution, or when the sodium nitromethane was added gradually, the principal product being the dimolecular compound. The yield is also less when the solution of sodium salt is acidified rapidly because a mixture of mono- and dimolecular products is precipitated as an oil. This later solidifies but the losses during purification are greater.

The nitro ketone crystallizes in small needles and melts at 101–2°. It is not very soluble in ligroin and alcohol, but dissolves readily in ether, chloroform, acetone and benzene.

Calc. for $\text{C}_{16}\text{H}_{14}\text{O}_2\text{NBr}$: Br, 23.0. Found: Br, 23.3, 23.0.

The semicarbazone of the nitro ketone is sparingly soluble in alcohol, moderately in acetone and in benzene. It melts with decomposition at 168–9°.

Calc. for $\text{C}_{17}\text{H}_{16}\text{O}_3\text{N}_4\text{Br}$: C, 51.5; H, 4.1. Found: C, 51.2; H, 4.2.

The "dimolecular" product, $\text{CHNO}_2(\text{CH}(\text{C}_6\text{H}_5)\text{CH}_2\text{COC}_6\text{H}_4\text{Br})_2$, crys-

tallized from benzene in fine needles. It is sparingly soluble in alcohol, more readily in ether, acetone, chloroform, and benzene.

Calc. for $C_{31}H_{26}O_4NBr_2$: C, 57.3; H, 3.9. Found: C, 57.5; H, 4.2.

γ -Nitro- β -phenyl- α -bromopropyl-(4-bromophenyl) Ketone, $CH_2(NO_2)CH(C_6H_5)CHBrCOC_6H_4Br$.—The nitro ketone was brominated in the usual way in carbon tetrachloride. The solution on evaporation under diminished pressure left a pale yellow oil which slowly solidified when allowed to stand in a cool place in contact with absolute methyl alcohol. The solid was washed with cold methyl alcohol and recrystallized from ordinary alcohol. It was thus separated into 4 substances—3 isomeric monobromo derivatives and one dibromo compound.

The principal product was a monobromo derivative which melted at $114.5-115.5^\circ$. This was most easily purified by crystallization from alcohol containing a small quantity of benzene. It separated in fine needles moderately soluble in alcohol, readily in benzene, acetone, and chloroform.

Calc. for $C_{16}H_{18}O_3NBr_2$: C, 45.0; H, 3.0. Found: C, 45.1; H, 3.4.

The mother liquors slowly deposited clear rhombic tables mixed with a small quantity of thick needles. The two substances were separated mechanically and recrystallized separately from alcohol. The compound which crystallized in rhombic tables melted at $105-6^\circ$.

Calc. for $C_{16}H_{18}O_3NBr_2$: C, 45.0; H, 3.0. Found: C, 45.3; H, 3.3.

The substance crystallizing in needles was obtained only in very small amounts. It was readily soluble in methyl and ethyl alcohols, moderately in ligroin, and melted at 91° .

Calc. for $C_{16}H_{18}O_3NBr_2$: C, 45.0; H, 3.0. Found: C, 45.8; H, 3.1.

The filtrates from the monobromo derivatives contained a small quantity of a dibromo compound which separated in crystalline form when they were allowed to evaporate very slowly in a cold place. By recrystallization from alcohol this was obtained in thin flakes melting $138-9^\circ$.

Calc. for $C_{16}H_{18}O_3NBr_3$: C, 38.0; H, 2.4. Found: C, 38.4; H, 2.6.

The two monobromo compounds melting at 115° and 106° must be stereoisomers because they give the same mono-iodo derivative when digested with potassium iodide. Neither of them undergoes further bromination even when heated with bromine in the sunlight. The third monobromo and the dibromo derivatives were obtained in quantities too small for further investigation.

γ -Nitro- γ -bromo- β -phenyl-propyl-(4-bromophenyl)ketone, $CH_2(NO_2)BrCH(C_6H_5)CH_2COC_6H_4Br$.—Bromination in the position α to the nitro group was accomplished by means of the sodium derivative. This was made by adding the finely powdered nitro ketone to a concentrated solution of sodium methylate in methyl alcohol until some of it remained undissolved after vigorous shaking. The mixture was then

filtered rapidly and the clear solution evaporated over sulfuric acid in a vacuum desiccator. It left a white solid which was powdered and extracted with dry ether to remove a small quantity of nitro ketone.

For the purpose of bromination, the dry powder was added very gradually to a well-cooled solution containing excess of bromine in dry carbon tetrachloride. The reaction was very vigorous but the yield of bromine compound was excellent. This was purified by allowing the solvent to evaporate spontaneously, washing the solid residue thoroughly with water, and recrystallizing from alcohol which contained a small quantity of benzene. The main product crystallized in needles and melted at 127° .

Calc. for $C_{16}H_{13}NO_3Br_2$: C, 45.2; H, 3.0. Found: C, 45.6; H, 3.2.

The filtrates deposited a small quantity of a second product which melted at $99-102^{\circ}$.

γ, γ - Dibromo - γ - nitro - β - phenyl-propyl-(4-bromophenyl) Ketone, $CBr_2NO_2CH(C_6H_5)CH_2COC_6H_4Br$.—The dibromo derivative was obtained without difficulty by alternately adding small quantities of sodium methylate and bromine to a cooled methyl alcoholic solution of the nitro compound, until both methylate and bromine were present in excess. The solid which separated was washed with water and cold alcohol, dried and recrystallized from a mixture of alcohol and benzene. It crystallized in thin plates or needles and melted, not sharply, at $144-6^{\circ}$.

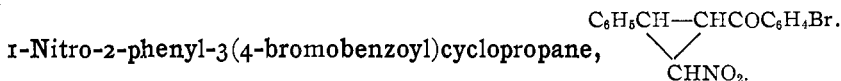
Calc. for $C_{16}H_{12}O_3NBr_3$: C, 38; H, 2.4; Br, 47.4. Found: C, 38.8; H, 2.6; Br, 46.6.

Action of Potassium Iodide on the Bromo Derivatives.—It was shown in an earlier paper that it is possible to distinguish between bromine compounds in which bromine is a α to a nitro group and those in which it is α to a carbonyl by treatment with potassium iodide, the former undergoing reduction while the latter are transformed into the corresponding iodine derivatives. In order to determine whether this reaction is a general one, all the foregoing bromine compounds were boiled with potassium iodide in alcoholic solution. The γ -monobromo compound—which has bromine in the α -position to the nitro group, was quantitatively reduced to the nitro ketone. The γ, γ -dibromo compound was also reduced, giving first the monobromo compound melting at 127° , and finally the nitro ketone. The α -bromo compound gave the corresponding iodo compound in almost the calculated amount.

γ -Nitro- β -phenyl- α -iodo-propyl-(4-bromophenyl) Ketone, $CH_2NO_2CH(C_6H_5)CHICOC_6H_4Br$.—Equal weights of the α -bromo compound and potassium iodide were dissolved in alcohol, and this solution boiled for 20 minutes. The mixture was then cooled and poured into a solution of sodium thiosulfate in order to remove a trace of iodine which had been liberated. The resulting flocculent precipitate was washed, dried and recrystallized from hot alcohol. It separated in pale yellow rhombic plates

and melted at 110° . The same iodo compound was obtained by similar treatment of the lower melting α -bromo compound.

Calc. for $C_{16}H_{18}O_3NBrI$: C, 40.5; H, 2.7. Found: C, 40.6; H, 2.7.



—For the purpose of eliminating hydrogen bromide from the α -bromo compound 12 g. of fused potassium acetate was added to a cooled suspension of 20 g. of the finely powdered bromo compound in 80 cc. of alcohol. The mixture was kept in ice water for 12 hours during which time most of the product separated as fine powder suspended in a brown liquid. The solid was filtered off, washed with alcohol and water until free from bromide, dried, and crystallized from alcohol containing a little benzene. One crystallization gave a pure product melting at 131° . Yield, 17 g., almost the calculated amount.

Calc. for $C_{16}H_{12}O_3NBr$: C, 55.5; H, 3.5; Br, 23.1. Found: C, 55.4; H, 3.7; Br, 22.9.

The cyclopropane derivative crystallizes in fine needles. It dissolves freely in acetone, carbon tetrachloride, benzene, and glacial acetic acid, sparingly in alcohol, and is almost insoluble in petroleum ether. Its solution in acetone does not reduce permanganate. It is more easily purified than the α -bromo compounds. For its preparation in quantity, therefore, it is advantageous to use in place of pure α -bromo compounds the crude mixture as it is obtained by brominating the nitro ketone in carbon tetrachloride and removing the solvent as completely as possible under diminished pressure.

An isomeric cyclopropane derivative was obtained by adding potassium acetate to an alcoholic solution of the γ -bromo compound. The reaction takes place much more slowly than with the α -bromo compound, hence the mixture was allowed to remain at the ordinary temperature for 4 days. The precipitated solid was then washed and recrystallized from alcohol.

Calc. for $C_{16}H_{12}O_3NBr$: C, 55.5; H, 3.5. Found: C, 55.2; H, 3.6.

The substance crystallizes in fine needles and melts at 115° . It is probably formed as a result of the prolonged contact with potassium acetate because we found that the derivative melting at 130° is transformed into the lower melting isomer when its solution in alcohol is boiled for a short time with potassium acetate, or allowed to stand in contact with it for several days.

A third isomeric cyclopropane derivative is formed when an alcoholic suspension of either of the other two is treated with very dilute sodium methylate. Thus a solution of one g. of sodium in 10 cc. of methyl alcohol was added in small portions and with constant shaking to a suspension of 10 g. of the cyclopropane derivative melting at 130° in 150 cc. of

methyl alcohol which was cooled in ice. The solid gradually dissolved and a new product began to separate from the pale yellow solution before all the alkali had been added. The cooling and shaking was continued until the whole volume of the alcohol was filled with solid. The solid was washed with cold alcohol until free from alkali, then recrystallized from boiling alcohol. The substance crystallized in needles and melted $162-3^{\circ}$. Its solution in acetone does not reduce permanganate. The same substance was obtained by treating the isomer melting at 115° in a similar manner.

Calc. for $C_{16}H_{12}O_3NBr$: C, 55.5; H, 3.4. Found: C, 55.3; H, 3.7.

Addition of Hydrogen.—The three isomeric cyclopropane derivatives readily combine with hydrogen when boiled with zinc dust and alcohol, and all three give the same product—the saturated open-chain nitro ketone. The following experiment illustrates the method used for adding hydrogen.

A suspension of 2 g. cyclopropane derivative and 5 g. of zinc dust in 80 cc. of 80% alcohol was boiled for a little more than an hour, then filtered while still hot to remove unchanged zinc and zinc oxide. The filtrate, on cooling, deposited colorless needles which melted at 101° . A mixture of the substance and the saturated nitro ketone melted at the same temperature.

Addition of hydrogen chloride.—The cyclopropane derivative melting at 130° , combined very readily with hydrochloric acid, and gave the calculated amount of addition product. An alcoholic suspension of the substance in a thick walled bottle was cooled in ice water and saturated with hydrogen chloride at 0° . The bottle was then securely stoppered and allowed to stand for 24 hours at the ordinary temperature. The crystalline suspension disappeared and the product separated as an oil which turned into a solid cake. This was crushed, washed until free from acid, and crystallized from alcohol and benzene.

Calc. for $C_{16}H_{12}O_3NCIBr$: C, 50.2; H, 3.6. Found: C, 50.1; H, 3.4.

β -Nitro- γ,γ -phenyl-chloropropyl-(4-bromophenyl) Ketone, $C_6H_5-CHClCHNO_2CH_2COC_6H_4Br$.—The hydrochloric acid addition product crystallizes in long, slender needles which melt at 133° . It is readily soluble in chloroform, acetone, and benzene, sparingly in alcohol and ether, insoluble in ligroin. Alcoholic solutions gradually become strongly acid even at the ordinary temperature and at the boiling point of alcohol the addition product rapidly changes into other substances.

γ,γ -Phenyl-chloroallyl-(4-bromophenyl) Ketone, $C_6H_5CCl = CHCH_2-COC_6H_4Br$.—A suspension of 5 g. of the powdered chloro compound and 5 g. of potassium acetate in 25 cc. of alcohol was allowed to remain at the ordinary temperature for 12 hours during which it changed to an aggregate of well-formed crystals. These were washed with cold alcohol and

water and dissolved in boiling alcohol. The solution yielded two substances in approximately equal amounts.

The first crop consisted mainly of a colorless substance which separated in downy needles and when pure melted at 179–80°. This substance contained no nitrogen, was sparingly soluble in alcohol but dissolved freely in chloroform, acetone and benzene.

Calc. for $C_{16}H_{12}OCIBr$: C, 57.4; H, 3.6. Found: C, 58.2; H, 3.8.

Later crops consisted mainly of a yellow substance which was much more readily soluble in alcohol, separated in plates, and melted at 108–9°.

Calc. for $C_{16}H_{12}OCIBr$: C, 57.4; H, 3.6. Found: C, 57.5; H, 3.9.

These substances are evidently geometrical isomers; they have the same composition, and reduce permanganate with equal ease—showing the presence of an ethylene linkage—and the chlorine is equally unreactive in both, indicating that in each it is connected with an unsaturated carbon atom. Definite proof of the structure of these substances was obtained by oxidation.

The substances rapidly reduced permanganate, but the only organic oxidation products that could be isolated were benzoic and *p*-bromobenzoic acids. It was necessary, therefore, to resort to ozone as oxidizing agent. Ozonized oxygen containing 3% ozone and a trace of moisture was slowly passed through a carbon tetrachloride solution of the yellow substance until ozone was present in excess. The solution gradually deposited a colorless solid, which melted at 244°. This was *p*-bromobenzoic acid—identified by melting a mixture of the substance with a sample on hand.

The filtrate from the bromobenzoic acid, when evaporated under diminished pressure, left a colorless oil which attacked the eyes and had the odor of benzoyl chloride. The liquid was dissolved in dry ether and treated with excess of aniline. This gave a solid which after recrystallization from boiling alcohol melted at 160° and was identified as benzanilide. The principal oxidation products of the yellow compound are, therefore, benzoyl chloride and *p*-bromobenzoic acid. The white isomer, treated in the same way, gave the same products.

These results establish the structure of the hydrochloric acid addition product as well as that of the unsaturated chloro ketones obtained from it. The structure of the latter was determined with great care because this mode of loss of nitrous acid, in which the hydrogen comes from the γ - instead of the α -position was unexpected.



the bromine free analog rapidly lost both hydrochloric and nitrous acids when boiled in alcoholic solution. The product separated in almost the calculated quantity when the solution was allowed to cool.

Calc. for $C_{16}H_{11}OBr$: C, 64.2; H, 3.7. Found: C, 64.1; H, 4.0.

The furane derivative crystallizes in colorless or very pale yellow flakes, and melts at 127° . It is very sparingly soluble in alcohol and ether, more readily in acetone and benzene. Its solution in acetone does not reduce permanganate.

Addition of Hydrogen Bromide.—The cyclopropane derivatives gave two isomeric addition products depending upon the manner in which the addition was brought about. When either the substance melting at 130° , or its isomer melting at 162° , is added to glacial acetic acid which has been previously saturated with hydrogen bromide, it dissolves rapidly, the product begins to separate almost immediately and the reaction is complete in a few minutes. The substance obtained in this way was purified by recrystallization from benzene-ligroin and was thus obtained in colorless needles which melted with decomposition at 144° .

Calc. for $C_{16}H_{13}O_2NBr_2$: C, 45.0; H, 3.0. Found: C, 44.8; H, 3.3.

Each of the two cyclopropane derivatives gave an isomeric substance when solutions in glacial acetic acid were gradually saturated with hydrogen bromide at 0° and then allowed to stand for 12 hours. The product in this case separated in long needles which after crystallization from benzene-ligroin melted at 133° .

Calc. for $C_{16}H_{13}O_2NBr_2$: C, 45.0; H, 3.0. Found: C, 44.9; H, 3.0.

Both of these addition products when boiled with alcohol give the same 1-phenyl-5-(4-bromophenyl) furane; they are, therefore, constituted like the corresponding hydrogen chloride addition product.

γ -Phenyl- β -nitro-alkyl-(4-bromophenyl) Ketone, $C_6H_5CH = CNO_2 \cdot CH_2COC_6H_4Br$.—Unlike the hydrogen chloride addition product, the bromine compound loses halogen acid more easily than nitrous acid. Thus when 10 g. of the substance and 5 g. of potassium acetate were suspended in 30 cc. of alcohol, the substance dissolved rapidly, the solution turned light brown in color and a colorless product separated in a short time. This was washed, dried and recrystallized from a mixture of carbon tetrachloride and ligroin from which it separated in colorless needles, melting, with decomposition, at $162-3^{\circ}$.

Calc. for $C_{16}H_{12}O_3NBr$: C, 55.5; H, 3.5. Found: C, 56.5; H, 3.6.

The substance is extremely unstable, and the high values are doubtless due to loss of nitrous acid during purification.

Addition of Bromine.—The cyclopropane derivatives are not attacked by bromine at the ordinary temperature, even when exposed to

direct sunlight. A slow but complete reaction can be obtained, however, under the combined effect of heat and direct sunlight, provided both the reagents and the solvent are perfectly dry.

α, γ -Dibromo- β -phenyl-propyl-(4-bromophenyl) Ketone, $C_6H_5CHBrCHNO_2CHBrCOC_6H_4Br$.—A saturated carbon tetrachloride solution containing 33 g. of the cyclopropane derivative melting at 130° and 17 g. of bromine were boiled in the sunlight for several days. The only evidence of reaction was a slow deposition of solid from the hot solution, and the boiling was continued as long as this appeared to increase in quantity. The solid was recrystallized from carbon tetrachloride. This gave 33 g. of a colorless product which melted at $162-3^\circ$.

Calc. for $C_{16}H_{12}O_3NBr_3$: C, 37.9; H, 2.4. Found: C, 37.6; H, 2.6.

The filtrate from this substance on slow evaporation deposited two more solid products. These were separated by recrystallization from benzene. The more soluble of the two crystallized in rhombic plates which melted at 137° . The analyses show that this is an isomeric bromine addition product.

Calc. for $C_{16}H_{12}O_3NBr_3$: C, 37.9; H, 2.4. Found: C, 38.2; H, 2.5.

These two bromine addition products were obtained by another reaction that leaves no doubt as to their structure. The γ -bromo compound obtained by adding hydrogen bromide to the cyclopropane derivative readily reacts with bromine, as would be expected, and the two products of the reaction are identical with those obtained by addition of bromine to the cyclopropane derivative:



γ -Phenyl- β -nitro-propenyl-(4-bromophenyl) Ketone,
 $C_6H_5CH_2C : CHCOC_6H_4Br$

$\begin{array}{c} | \\ NC_2 \end{array}$

—The bromine addition products are reactive substances but they gave unmanageable mixtures with nearly all reagents capable of replacing bromine or of eliminating hydrogen bromide. Potassium iodide was an exception, as it gave a crystalline product in good yields. Four g. of potassium iodide was added to a solution of 2 g. of the bromine compound (162°) which had been cooled to 0° . Iodine began to separate at once. The solution was allowed to remain in an ice chest for 2 days, then evaporated in a current of air. The residue was washed with thiosulfate solution, dried, and recrystallized from alcohol and benzene. It crystallized in yellow plates and melted at 115° .

Calc. for $C_{16}H_{12}O_3NBr$: C, 55.4; H, 3.4. Found: C, 55.4; H, 3.9.

The substance is moderately soluble in alcohol, readily in benzene, acetone, and chloroform. Its solution in acetone readily reduces perman-

ganate. The oxidation products, phenylacetic acid melting at 76° and *p*-bromo-benzoic acid, were identified by comparison with specimens on hand. The third product of the reaction between bromine and the cyclopropane derivative was obtained as a very fine crystalline powder which is sparingly soluble in benzene and alcohol and which melts at $190-3^{\circ}$.

Calc. for $C_{16}H_{12}Br_2O$: C, 35.6; H, 2.2. Found: C, 35.8; H, 2.2.

The substance contains no nitrogen. It is very unreactive, undergoing no change when boiled with alcoholic potassium acetate or sodium alcoholate. It is, therefore, probably a furane derivative formed by loss of nitrous acid during the protracted boiling and addition of bromine to the product¹ but the facts at hand do not warrant a definite conclusion.

Action of Sodium Methylate.—As was stated earlier in the paper, dilute sodium methylate turns the lower melting cyclopropane derivatives into the highest melting isomer and the concentrated methylate as well as sodium hydroxide gives a β -diketone. A possible intermediate product in this reaction was obtained as follows: A solution of 5 g. of sodium in the minimum quantity of dry methyl alcohol was added to 60 g. of the finely powdered cyclopropane derivative (130°) previously moistened with a little dry methyl alcohol. The temperature of the mixture was kept at 0° throughout the addition. The cyclopropane derivative slowly dissolved, sodium nitrite deposited on the walls of the vessel while another white solid crystallized from the red solution. The mixture was kept at 0° for several hours, then cooled in a freezing mixture and acidified with a solution of the calculated amount of glacial acetic acid in 300 cc. of ether.

The resulting paste which changed from red to yellow during acidification, was poured into cracked ice contained in a separatory funnel, the ethereal layer washed with water, dried, and allowed to evaporate. The residue contained 8 g. of a colorless solid contaminated with a small quantity of yellow oil. The solid was purified by recrystallization from methyl alcohol.

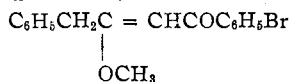
Calc. for $C_{17}H_{16}O_2Br$: C, 61.6; H, 4.6. Found: C, 61.3; H, 4.6.

The substance is readily soluble in alcohol and ether. It crystallizes in thin needles and melts at $102-3^{\circ}$. Its structure was established by oxidation with permanganate which was carried out as follows: 2.5 g. of finely powdered potassium permanganate was added in very small portions to a solution of 3.2 g. of the substance in pure acetone, which was kept at 0° until the reduction of the permanganate was complete. The salts and oxides of manganese were filtered off and the filtrate evaporated under diminished pressure. It left a small quantity of solid imbedded in an oil that had the odor of methyl phenylacetate.

¹ Perkins, *J. Chem. Soc.*, 57, 954 (1890).

The oil was distilled with steam and hydrolyzed with potassium hydroxide. It gave a solid acid which melted at 76°. A mixture of the substance and phenyl acetic acid likewise melted at this temperature. The oily oxidation product was, therefore, methyl phenylacetate.

The solid left behind after removing the ester by steam distillation proved to be unchanged substance, and the acid obtained by treating the salts and oxides of manganese with sodium hydrogen sulfite and dilute acid was identified as bromo-benzoic acid. These oxidation products—methyl phenylacetate and *p*-bromo-benzoic acid—show that the formula of the methoxy compound must be



Phenacetyl-(4-bromobenzyl) Methane, $\text{C}_6\text{H}_5\text{CH}_2\text{COCH}_2\text{COC}_6\text{H}_4\text{Br}$.—The methoxyl compound is easily hydrolyzed when boiled with a few drops of hydrochloric acid in aqueous alcohol. The product separated, on cooling, in rhombic plates melting at 80–1°.

Calc. for $\text{C}_{17}\text{H}_{16}\text{O}_2\text{Br}$: C, 60.5; H, 4.1. Found: C, 60.4; H, 4.3.

The diketone is readily soluble in all common organic solvents except ligroin. When its ethereal solution is shaken with an aqueous solution of copper acetate it forms a pale green copper derivative which is sparingly soluble in ether but dissolves fairly readily in benzene. The diketone can be obtained directly from any of the cyclopropane derivatives by dissolving it with alcoholic sodium hydroxide, acidifying, extracting with ether, and precipitating the diketone as copper derivative.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN.]
**TRIPHENYLMETHYL. XXIX. A STUDY OF THE PROPERTIES
 OF DIPHENYL- α -NAPHTHYLMETHYL.**

BY M. GOMBERG AND C. S. SCHOEPFLE.¹

Received July 22, 1919.

1. Introduction.

Although the existence of a large number of triarylmethyls has been established, the various investigators in this field have been content to prepare the free radicals in solution only and to show that such solutions on exposure to air give rise to the corresponding peroxides. In a limited number of cases the triarylmethyls were actually isolated and the molecular weight of the free radical determined, and in a few instances absorption spectra have been taken. But in no case except that of triphenylmethyl have the chemical and physical properties of the free

¹ The work described in this article and in the article published in *THIS JOURNAL*, 39, 1652 (1917), forms part of a thesis presented by C. S. Schoepfle in partial fulfillment of the requirements for the degree of Doctor of Science in the University of Michigan.