

We are unable to explain fully the lower values now being found and the lack of concordance of the results. The latter fact would indicate the presence of some unknown catalyzer, possibly the surface of the glass vessels in which the reaction takes place.

The work is being pushed forward as rapidly as possible, and we hope in the near future to throw more light on this phase of the problem.

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CORRECTIONS.

"The Calomel Standard Cell," by G. F. Lipscomb and G. A. Hulett, THIS JOURNAL, 38, 20.

Page 24. Column "July 12," 0.67098 should be 0.67078.

Column "Apr. 24," 0.67044 should be 0.67024.

Page 25, line 9. .0525(T — 25)² should be —.000025(T — 25)².

Page 25, line 15. For 0.67159 read 0.67139.

Page 25, line 18. For 0.67159 read 0.67139 and for 30060 read 30047.

Page 25, line 22. For HgCl₂ read Hg₂Cl₂.

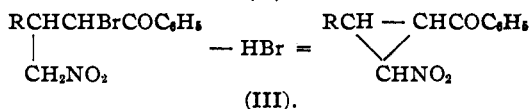
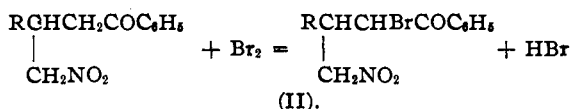
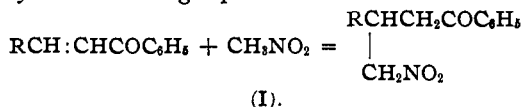
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY.]

THE ADDITION OF ALIPHATIC NITRO COMPOUNDS TO UNSATURATED COMPOUNDS.

By E. P. KOHLER.

Received January 20, 1916.

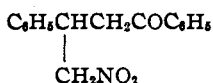
The object of this investigation was to find a method for preparing cyclopropane derivatives that have a nitro group in combination with one of the carbon atoms of the ring. Substances of this type are unknown and they cannot be made by any of the means commonly employed for making aliphatic nitro compounds. It was necessary, therefore, to make a suitable aliphatic nitro compound first and then to close the cyclopropane ring. A promising series of reactions for this purpose is represented by the following equations:



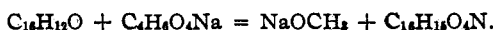
The first step in this sequence involves the addition of a nitroparaffin to an unsaturated compound. This has apparently not been tried heretofore; but since nitromethane, in the presence of alkalis, condenses with aldehydes it is evident that the metallic derivatives of the nitroparaffins combine with the carbonyl group, and it seemed probable that they would also combine with substances containing the system



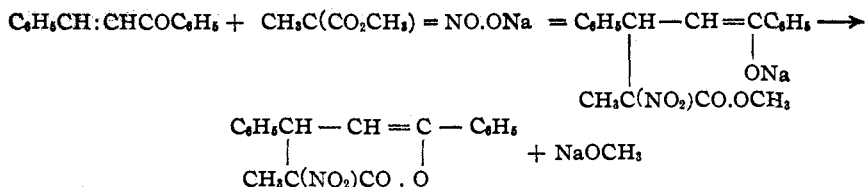
It was found that sodium nitromethane readily combines with benzalacetophenone to form a metallic derivative which, on treatment with acid, gives a product that has the composition $C_{16}H_{15}O_3N$. This substance does not reduce permanganate but forms a semicarbazone and gives the reactions of primary aliphatic nitro compounds. It is therefore the saturated nitroketone



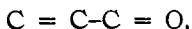
Other nitroparaffins, both primary and secondary, can be used in place of nitromethane; addition takes place more slowly but the final result is essentially the same. The reaction even takes place with nitroesters, but gives a mixture of substances unless the nitro compound is secondary, when the sole product is a lactone. When sodium nitropropionic ester, for example, reacts with benzalacetophenone the product is a crystalline solid, $C_{18}H_{15}O_4N$, formed in accordance with the equation



When the substance $C_{18}H_{15}O_4N$ is digested with hydrochloric acid it loses carbon dioxide and passes into the same nitroketone that is obtained by adding nitroethane to benzalacetophenone. It is therefore a lactone formed as follows:



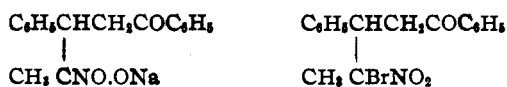
The formation of this lactone indicates that the mode of addition of sodium nitroparaffins to substances that have the system



is exactly like that of organic magnesium compounds and other metallic derivatives, the metal going to oxygen and the remainder of the molecule to the carbon in the 4-position. The sodium compounds actually obtained, however, do not have sodium in combination with carbonyl oxygen;

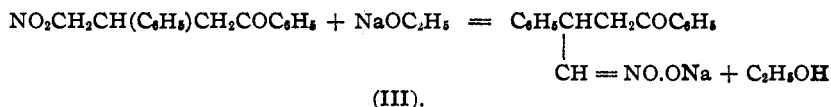
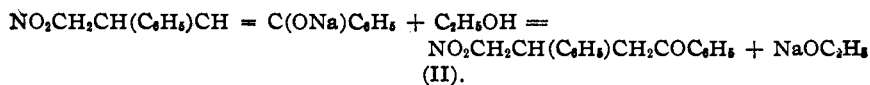
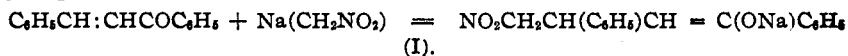
their entire behavior shows that they are constituted like the metallic derivatives of the nitroparaffins. Thus the sodium compound obtained by adding sodium nitromethane to benzalacetophenone, does not react with alkyl halides but readily reacts with bromine, giving sodium bromide and two isomeric monobromo derivatives of the nitroketone. These isomeric bromine compounds are soluble in sodium methylate, and the solutions rapidly decolorize one equivalent of bromine. Both solutions yield the same dibromo derivative, $C_{16}H_{13}O_3NBr_2$. This behavior is typical of the metallic derivatives of nitroparaffins. There is also direct evidence as to the structure of these bromine compounds. Halogen nitro compounds in which the halogen is in combination with the carbon that holds the nitro group are easily reduced. When bromonitroethane, for example, is boiled with alcoholic potassium iodide, iodine is liberated and the bromine compound is rapidly reduced to nitroethane. All the bromine compounds described above give the same reaction, and give it with the same ease, the dibromo compound passing into one of the monobromo derivatives and the two monobromo derivatives being reduced to the nitroketone.

The sodium compound obtained by adding sodium nitroethane to benzalacetophenone also readily reacts with bromine, but the resulting monobromo derivative is no longer soluble in sodium methylate, showing the absence of hydrogen on the carbon atom that holds the nitro group. The structure of the sodium and bromine compounds is therefore represented by the formulas



The result obtained with benzalacetophenone and sodium β -nitropropane supports these conclusions. The reaction in this case does not give a metallic derivative but gives, instead, the nitroketone and sodium alcoholate.

These facts show that the product obtained from the reaction between benzalacetophenone and sodium nitromethane is the result of the following steps:



When bromine is allowed to react with the nitroketones themselves it forms another pair of bromine substitution products quite different from those obtained from the sodium derivative. Alcoholic potassium iodide transforms these, quantitatively, into the corresponding iodine compound, and sodium alcoholate rapidly removes hydrobromic acid to form a cyclopropane derivative. These bromine compounds therefore have bromine in the α -position to carbonyl, and the problem of getting nitrocyclopropane derivatives is solved.

Although this paper deals only with the addition of nitroparaffins to benzalacetophenone, work now in progress shows that, under proper conditions, aliphatic nitro compounds combine quite generally with α,β -unsaturated ketones, with many unsaturated esters, unsaturated nitriles, and even with unsaturated nitro compounds. The products obtained by these reactions are far more tractable substances than the nitroparaffins with simpler alkyl groups, and we expect them to be useful not only in connection with the chemistry of cyclopropane but also with that of nitro compounds.

EXPERIMENTAL PART.

I. Benzalacetophenone and Nitromethane.

Nitromethane itself apparently does not combine with benzalacetophenone. A solution of the ketone in the nitro compound can be boiled for days without any effect beyond a very slow decomposition of the nitro compound. The result is the same when a solution of the two substances in a perfectly dry, indifferent solvent, like ligroin or benzene is heated. In boiling alcohols and in the presence of water the nitro compound disappears, but the ketone remains unchanged. By adding a small quantity of diethylamine or piperidine the addition can be carried out in any suitable solvent. In the case of methyl ketones like benzalacetone and mesityl oxide this is the best procedure, but with benzalacetophenone a better yield and a purer product can be obtained by using sodium alcoholate as condensing agent.

A small quantity of sodium alcoholate is sufficient to cause rapid disappearance of both ketone and nitro compound; but under these conditions the result is always a mixture of complex products. These are due to the fact that the sodium compound formed from one molecule each of ketone and sodium nitromethane readily combines with more of the unsaturated ketone. In order to prevent the formation of complex products, therefore, it is necessary to have an excess of sodium nitromethane *in solution*. The following procedure gives satisfactory results: A solution of 15 g. of sodium in 120 g. of dry methyl alcohol is added, with constant shaking, to a solution of 104 g. of benzalacetophenone and 37.5 g. of nitromethane in 175 g. of the same solvent. The solutions should

be at about 40° at the outset in order to prevent separation of solid sodium nitromethane, and the alcoholate should be added as rapidly as is possible without separation of solid sodium compound. The reaction is complete a few minutes after the last alcoholate has been added. The yellow liquid is then cooled and immediately acidified with glacial acetic acid. A part of the nitroketone usually begins to separate as an oil, but this soon solidifies and the remainder is slowly deposited in clear, white needles. The flask containing the product is finally cooled in a freezing mixture, the solid filtered off, thoroughly washed with weak alcohol and water, and purified by recrystallization from alcohol. A small additional amount of the product can be obtained by combining aqueous and methyl alcoholic filtrates but the resulting precipitate is far less pure and should be recrystallized separately. The best yield obtained was 92% of pure product, the average yield in a number of preparations 88.5%.

Calc. for $C_{16}H_{15}O_2N$: C, 71.4%; H, 5.4%. Found: C, 71.3%; H, 5.7%.

γ -Nitro- β -phenylbutyrophenone, $NO_2CH_2CH(C_6H_5)CH_2COC_6H_5$, crystallizes in thin, white needles that melt at 103° . It is readily soluble in benzene, acetone, chloroform, and hot alcohols; sparingly in cold alcohol and ether; insoluble in petroleum ether. A solution in acetone does not reduce permanganate, indicating the absence of unsaturation. When treated with semicarbazide in the usual way, it gives a sparingly soluble semicarbazone, proving the presence of carbonyl. The semicarbazone crystallizes in small plates and melts at 165° .

Calc. for $C_{17}H_{15}O_2N_4$: N, 17.1%. Found: N, 17.5%.

Sodium Aci-nitrophenylbutyrophenone.—The nitroketone dissolves very sparingly in concentrated aqueous alkalis, somewhat better in alcoholic potassium hydroxide, very readily in solutions of alcoholates. The pure solid sodium derivative was obtained by three different methods, all of which ultimately gave the same substance. When a mixture of dry ether and ligroin is added to the concentrated methyl alcoholic solution obtained by adding sodium methylate to nitromethane and benzalacetophenone, it generally produces a pale yellow crystalline precipitate. This was filtered off in a current of dry air, washed with absolute ether and analyzed. Analyses from different preparations gave variable amounts of sodium, but all of them lost weight (methyl alcohol) when kept over sulfuric acid in a vacuum desiccator. The final results were as follows:

Calc. for $C_{16}H_{14}O_2NNa$: Na, 7.9%. Found: Na, 7.6%

All these preparations were tinged with yellow.

A better method for getting the sodium compound is to saturate a cold solution of sodium methylate in methyl alcohol with pure nitroketone, filter from excess of ketone, and allow the filtrate to evaporate in a vacuum desiccator containing sulfuric acid. Here too a product

containing methyl alcohol crystallizes at first, but this slowly loses weight and, in case the alcohol used was perfectly dry, leaves a pure, white powder.

Calc. for $C_{16}H_{14}O_2NNa$: Na, 7.9%. Found: Na, 7.7%.

The quickest way to get pure sodium compound is to add the calculated quantity of metallic sodium to a solution of the nitroketone in dry benzene and heat. The metal disappears rapidly, and the sparingly soluble derivative separates as a white microcrystalline powder, much less sensitive to atmospheric moisture than previous preparations, and admirably adapted for further transformation. The yield of sodium compound is about 90%. After washing with benzene and dry ether this preparation gave

Calc. for $C_{16}H_{14}O_2NNa$: Na, 7.9%. Found: Na, 7.7%.

The sodium compounds from all sources behaved alike towards water, acids, alcohols, bromine and allyl halides.

In cold water the sodium compound dissolves readily and gives a clear, colorless, very feebly alkaline solution. This soon becomes milky, however, and in less than an hour practically all of the substance is hydrolyzed to sodium hydroxide and nitroketone. Dry alcohols also dissolve large quantities of the metallic derivative. The solutions remain clear and colorless and on evaporation under diminished pressure, they deposit a crystalline sodium compound containing alcohol. The reaction between the sodium compound and acids is much cleaner than that of the metallic derivatives of the simpler nitroparaffins; the result is the same with weak as with strong acids and whether the acid is added to the sodium compound or *vice versa*. The product is an oil that quickly solidifies, and on crystallization gives the calculated quantity of pure nitroketone.

γ -Bromo- γ -nitro- β -phenylbutyrophenone, $NO_2CHBrCH(C_6H_5)CH_2CO-C_6H_5$.—The dry sodium compound was added, gradually, to a well cooled solution of slightly more than one equivalent of dry bromine in chloroform. Reaction is immediate even at the temperature of a freezing mixture. The product was poured into water, the excess of bromine removed with bisulfite, the chloroform layer dried, and freed from chloroform by evaporation under diminished pressure. This left a colorless solid that, on repeated recrystallization from methyl alcohol, gave colorless needles melting at 90° , and thin plates or flat needles that melted at 93° . A mixture of the two substances began to melt at about 70° .

Calc. for $C_{16}H_{14}O_2NBr$: Br, 22.7%. Found (90°): Br, 22.8%; (93°): Br, 22.8%.

It is not possible to make these monobromo derivatives by starting with a methyl alcoholic solutions of the sodium compounds. Such solutions react with almost exactly the same amount of bromine as the dry substance, but the result is always a mixture of nitroketone, with its monobromo and dibromo substitution products, and the amount of dibromo

is considerable even when the solution of the sodium compound is dropped into excess of bromine. It is easy to remove the dibromo derivative from this mixture, but the separation of monobromo derivative and nitroketone is tedious and wasteful. Both needles and plates are very readily soluble in all common organic solvents except ligroin.

γ,γ -Dibromo- γ -nitro- β -phenylbutyrophenone, $\text{NO}_2\text{CBr}_2\text{CH}(\text{C}_6\text{H}_5)\text{CH}_2\text{COC}_6\text{H}_5$.—Neither of the monobromo derivatives just described reacts with bromine at low temperatures, but both of them readily dissolve in sodium methylate, and the resulting solutions rapidly decolorize bromine. Both substances give the same product, small, colorless needles, sparingly soluble in alcohol and ether, readily in chloroform. The substance melts at $160\text{--}162^\circ$ and begins to decompose freely as soon as melted.

Calc. for $\text{C}_{16}\text{H}_{15}\text{O}_2\text{NBr}_2$: Br, 37.5%. Found: Br, 37.5%.

The same dibromo compound can be made without starting with the monobromo derivatives; it can be prepared far more easily and with a satisfactory yield by starting, either with a solution of the nitroketone in sodium methylate, or with the methyl alcoholic solution of the sodium compound that is obtained when a solution of sodium nitromethane is added to benzalacetophenone. When bromine is dropped into either of these solutions, cooled in a freezing mixture, it disappears as fast as added. The color of the solution at first changes gradually from pale yellow to deep yellow and orange, then becomes lighter again and finally colorless after a little more than one molecule of bromine has been added. At this stage the mixture contains only dibromo compound, nitroketone, and sodium bromide, the play of colors being due to the intermediate formation of the yellow sodium derivative of the monobromo compound and its subsequent removal by bromine. The mixture does not react with any more bromine, but by adding half the original amount of sodium alcoholate, the nitroketone is once more turned into sodium compound and will decolorize an equivalent quantity of bromine. This cycle can be repeated until enough bromine has been added to transform all of the nitroketone into dibromo compound. Sodium bromide and dibromo compound are then filtered off, washed with dilute alcohol and water and recrystallized from chloroform and alcohol. Yield, 80–85%.

The most characteristic property of these γ -bromo derivatives is the ease with which they are reduced. Solutions of the dibromo compound in acetone or alcohol can be boiled for a long time without appreciable loss, but when an equivalent quantity of potassium iodide or potassium cyanide is added to the solution one of the bromine atoms is rapidly replaced by hydrogen and, in the presence of excess of reducing agent, the resulting monobromo compound is more slowly, but completely, reduced to the nitroketone.

γ -Nitro- β -phenyl- α -bromobutyrophenone, $\text{NO}_2\text{CH}_2\text{CH}(\text{C}_6\text{H}_5)\text{CHBrCO}_2\text{C}_6\text{H}_5$. The procedure used for introducing bromine in the α -position was as follows: A small quantity of bromine was added to a concentrated solution of the nitroketone in chloroform, and the reaction started either by warming on a steam bath or addition of a drop of acetone. The solution was then cooled with running water and treated with bromine until the color showed a slight excess—90 g. of nitroketone dissolved in 150 g. of chloroform reacted with 58 g. of bromine. Excess of bromine, hydrobromic acid, and solvent, were then removed as completely as possible by warming under diminished pressure. The pale yellow oil that remained was dissolved in hot absolute alcohol. This solution, on cooling, slowly deposited large, colorless needles that melted at 100° .

Calc. for $\text{C}_{16}\text{H}_{14}\text{O}_3\text{NBr}$: Br, 22.7%. Found: Br, 22.8%.

Two more substances were obtained from the filtrates. These were formed only in small quantities and were separated with great difficulty. One of these crystallized from alcohol in thin plates and melted at 86° .

Calc. for $\text{C}_{16}\text{H}_{14}\text{O}_3\text{NBr}$: Br, 22.7%. Found: Br, 22.4%.

The total yield of pure monobrom derivatives was 89%. The third product crystallized in prisms or thick needles and melted at 105° . The analyses show that this is a dibromo derivative. This substance constituted only about 4% of the product, its structure has not been determined.

Calc. for $\text{C}_{16}\text{H}_{12}\text{O}_3\text{NBr}_2$: Br, 37.5%. Found: Br, 37.6%.

γ -Nitro- β -phenyl- α -iodobutyrophenone, $\text{NO}_2\text{CH}_2\text{CH}(\text{C}_6\text{H}_5)\text{CHICO}_2\text{C}_6\text{H}_5$.—Slightly more than one equivalent of potassium iodide was added to each of the α -bromo compounds dissolved in the smallest possible quantity of boiling methyl alcohol. Potassium bromide began to separate almost immediately and a very faint yellow color appeared in the solutions. After boiling for half an hour, the solutions were poured into water. This precipitated pale yellow oils that soon solidified. The product from both bromine compounds was found to be the same. It was purified by crystallization from alcohol from which it separated in pale yellow needles that melted at 123° . The iodine compound is less soluble than either of the bromine compounds and separates much more rapidly from solutions.

Calc. for $\text{C}_{16}\text{H}_{14}\text{O}_3\text{NI}$: I, 32.2%. Found: I, 31.9%.

The most characteristic property of the α -halogen compounds is the ease with which they lose hydrobromic acid when treated with alcoholates, potassium acetate, potassium cyanide, and other feebly alkaline reagents. The product in each case is a trimethylene compound melting at 93° . The properties of this substance will be considered in a later paper dealing with the chemistry of cyclopropane and its derivatives.

γ -Bromo- γ -nitro- β -phenyl- α -bromobutyrophenone, $\text{NO}_2\text{CHBrCH}(\text{C}_6\text{H}_5)\text{CHBrCOC}_6\text{H}_5$.—The α -bromo derivatives are not attacked by bromine, and, owing to the ease with which they pass into trimethylene compounds, it is not possible to transform them into sodium compounds. Further bromination of α -bromo compounds is therefore impossible. The γ -bromo compound, on the other hands, can be brominated by the same procedure that was used for getting α -bromo derivatives. The product obtained by brominating the needles (90°) crystallizes from alcohol in thin needles melting at 130° . It is sparingly soluble in cold alcohol and ether, readily in acetone and chloroform.

Calc. for $\text{C}_{16}\text{H}_{15}\text{O}_3\text{NBr}_2$: Br, 37.5%. Found: Br, 37.6%.

When an alcoholic solution of this dibromo derivative is boiled with potassium iodide the principal product is the α -iodo compound melting at 123° . One of the bromine atoms is, therefore, in the α - and the other in the γ -position. When a similar solution is boiled with zinc dust, one of the products is the trimethylene compound melting at 93° , but the yield is very poor.

γ,γ -Dibromo- γ -nitro- β -phenyl- α -bromobutyrophenone, $\text{NO}_2\text{CBr}_2\text{CH}(\text{C}_6\text{H}_5)\text{CHBrCOC}_6\text{H}_5$.—The γ,γ -dibromo derivative can also be brominated directly, but, in order to start the reaction, it is necessary either to expose the reacting mixture to sunlight or to add to it a drop of acetone. The product crystallized from chloroform in large, lustrous needles that melt at 185° . It is sparingly soluble in ether, alcohol, and cold chloroform, readily in boiling chloroform.

Calc. for $\text{C}_{16}\text{H}_{13}\text{O}_3\text{NBr}_3$: Br, 47.4%. Found: Br, 47.7%.

II. Benzalacetophenone and Nitroethane.

γ -Nitro- β -phenylvalerophenone, $\text{CH}_3\text{CH}(\text{NO}_2)\text{CH}(\text{C}_6\text{H}_5)\text{CH}_2\text{COC}_6\text{H}_5$.—The addition of nitroethane was accomplished in exactly the same way as that of nitromethane. As sodium nitroethane is stable on alcoholic solution, the mixture remains colorless throughout the process and, probably because of hindrance due to the methyl group, there is little tendency to form a dimolecular product. When the addition is carried out in a sufficiently concentrated solution in absolute alcohol, a solid sodium compound separates in colorless needles. This, with acids, gives a colorless oil that solidifies very slowly. The solid is a mixture of stereoisomers that have a pronounced tendency to separate from solution as oil and consequently are very hard to separate. Repeated crystallization from dry ether gave very fine needles melting at 72° , and stout needles or plates melting at 100° .

Calc. for $\text{C}_{18}\text{H}_{17}\text{O}_2\text{N}$: C, 72.1%; H, 6.0%. Found (72°): C, 72.0%; H, 6.0%; (100°): C, 72.4%; H, 6.0%.

The reaction is quantitative, but the relative amounts of the two isomers vary with the mode of acidification. Strong acids and low temperatures favor the formation of the higher melting product. That these substances are the two racemic modifications possible because the nitroketone contains two dissimilar asymmetric carbon atoms, is shown by the fact that when either substance is turned into the sodium derivative and this back into the nitroketone, the result is always a mixture of the two.

γ -Bromo- γ -nitro- β -phenylvalerophenone, $\text{CH}_3\text{CBr}(\text{NO}_2)\text{CH}(\text{C}_6\text{H}_5)\text{CH}_2\text{COC}_6\text{H}_5$.—As the nitroketone has only one hydrogen replaceable by metals it is not necessary to have either dry sodium compound or even pure ketone for making the γ -bromo derivative. An excellent yield of the substance was obtained by adding the calculated amount of sodium methylate to a hot solution of benzalacetophenone and nitroethane in dry methyl alcohol, allowing this solution to stand for an hour, then cooling it in a freezing mixture and dropping bromine into it until the color became permanent. Much of the product separated during the process. After crystallization from chloroform and alcohol this was obtained in the form of fine needles sparingly soluble in alcohol and ether, readily in chloroform. The melting point is 17° .

Calc. for $\text{C}_{17}\text{H}_{16}\text{O}_2\text{NBr}$: Br, 22.1%. Found: Br, 22.2%.

The alcoholic filtrates contained a second product that also crystallized in needles, but was more soluble in alcohol and melted at 160° .

Calc. for $\text{C}_{17}\text{H}_{16}\text{O}_2\text{NBr}$: Br, 22.1%. Found: Br, 22.3%.

γ -Nitro- β -phenyl- α -bromovalerophenone, $\text{CH}_3\text{CH}(\text{NO}_2)\text{CH}(\text{C}_6\text{H}_5)\text{CO}\text{C}_6\text{H}_5$.—The nitroketones, dissolved in chloroform, readily react with bromine, but, probably owing to the number of stereoisomers formed, no solid product could be isolated. The residue left after removing the solvent, however, reacts with potassium acetate in the manner of these α -bromo compounds and gives two solid trimethylene derivatives.

III. Benzalacetophenone and β -Nitropropane.

The preparation of any considerable quantity of β -nitropropane is a matter of some difficulty. V. Meyer obtained the substance by adding silver nitrite to isopropyl iodide and distilling, but he does not state his yield. Nef, who later prepared it in the same way, states that the yield is very poor. My yields by this method were 5–6 g. of pure nitro compound per 100 g. of isopropyl iodide. After trying various modifications of this method, I finally adopted the following: 100 g. of finely ground silver nitrite are added, in the course of several hours, to a solution of 100 g. of isopropyl iodide in 300 cc. of dry, alcohol-free ether. Each spoonful of solid produces a sensible reaction in the liquid and if the mixture is shaken during the addition or immediately afterwards, the solid cakes;

but if the reaction is allowed to proceed until the temperature begins to fall after each addition, and the mixture is then shaken vigorously, the solid remains as a loose powder. In order to complete the reaction it is necessary either to boil for about 12 hours or to allow the mixture to stand in a dark place for several weeks. The latter gives the better yield. The ethereal layer is filtered, the solid repeatedly extracted with boiling ether, the ether removed from the solutions and the residue separated by fractional distillation. The yield by this method was 12-15 g. of pure nitro compound boiling at 120° per 100 g. of isopropyl iodide.

γ -Methyl- γ -nitro- β -phenylvalerophenone, $\text{CH}_3\text{C}(\text{CH}_3)(\text{NO}_2)\text{CH}(\text{C}_6\text{H}_5)\text{CH}_2\text{COC}_6\text{H}_5$.—The addition of a secondary nitro compound to an unsaturated compound was of special interest because the product is necessarily a tertiary nitro compound. The sodium compound resulting from the addition of sodium β -nitropropane to benzalacetophenone therefore cannot rearrange to give the type of sodium compound obtained with nitromethane and primary nitroparaffins. It was found that the reaction goes much more slowly than in the cases previously described—doubtless owing to the hindrance caused by the highly branched chain. In absolute ether and in dry benzene there is scarcely any evidence of reaction. In absolute alcohol the addition starts in the usual way, but the resulting sodium compound is rapidly decomposed by the alcohol, hence the solution becomes increasingly alkaline as the reaction proceeds, and the substance that separates is not a sodium compound but the nitroketone itself. With equivalent quantities of benzalacetophenone and sodium β -nitropropane the yield is insignificant, because both sodium nitropropane and the nitroketone are slowly decomposed by excess of sodium alcoholate. In this case, therefore, the best results are obtained by using only a small quantity of sodium alcoholate as condensing agent. The following procedure gave excellent results: equivalent quantities of unsaturated ketone and nitro compound were dissolved in enough absolute methyl alcohol to keep the ketone in solution in the cold, 5 drops of a strong sodium methylate solution were then added, and the mixture set aside in a securely corked flask. The solution slowly turned yellow, and a colorless solid began to separate in the course of a few days. This continued to increase for several weeks, at the end of which the reaction was complete. The product was purified by recrystallization from a mixture of chloroform and alcohol. Yield, 92%.

Calc. for $\text{C}_{18}\text{H}_{19}\text{O}_4\text{N}$: C, 72.7%; H, 6.4%. Found: C, 72.8%; H, 6.6.

The nitroketone is sparingly soluble in alcohol and ether, readily in benzene and in chloroform. It melts at 167°. The difference in solubility and melting point between this substance and the nitroketones

previously described is conspicuous. The melting points of primary and secondary nitroketones as well as those of the halogen substitution products that still have hydrogen in combination with the carbon that holds the nitro group, are relatively low, while all of the isomeric substitution products that no longer have hydrogen in this position melt much higher and are far less soluble.

Nitromethylphenylvalerophenone shows no tendency to form a metallic derivative. Its solubility in dilute sodium alcoholate is no greater than in alcohol. It is readily soluble in concentrated alcoholate but the process is accompanied by extensive decomposition. The solution contains benzalacetophenone, sodium β -nitropropane, sodium nitrite, and other products of unknown structure. Metallic sodium slowly attacks a solution of the nitroketone in dry benzene but in this case also, the result is not the formation of a metallic derivative—sodium nitropropane and a more complex sodium compound are precipitated while benzalacetophenone and other substances remain dissolved in the benzene.

γ -Methyl- γ -nitro- β -phenyl- α -bromovalerophenone, $\text{CH}_3\text{C}(\text{CH}_3)(\text{NO}_2)\text{-CH}(\text{C}_6\text{H}_5)\text{CHBrCOC}_6\text{H}_5$.—When a solution of the nitroketone in chloroform is treated with bromine in the usual way it gives two isomeric monobromo derivatives that are easily separated by crystallization from chloroform and alcohol. One of these crystallizes in thin, diamond-shaped, plates that are sparingly soluble in boiling alcohol and in cold chloroform, and melt at 165° . The other bromine compound is readily soluble in hot alcohol and crystallizes in stout prisms that melt at 125° .

Calc. for $\text{C}_{18}\text{H}_{19}\text{O}_3\text{NBr}$: Br, 21.3%. Found (155°): Br, 21.6%; (125°): Br, 21.4%.

Summary.

1. The metallic derivatives of nitroparaffins combine with unsaturated ketones to form metallic derivatives of nitroketones.
2. The addition takes place in such a manner that the metal goes to the carbonyl oxygen and the nitroparaffin residue to the β -position; but unless the result is a tertiary nitro compound the product immediately rearranges to a metallic derivative in which the metal is in combination with the nitro group.
3. Bromine reacts with the metallic derivatives of nitroketones and replaces hydrogen in the α -position to the nitro group; while the hydrogen in the α -position to carbonyl is replaced in the reaction between bromine and the free nitroketones.

From the halogen derivatives of the nitroketones in which the halogen is α to carbonyl, it is easy to get cyclopropane derivatives that have a nitro group in combination with one of the carbon atoms in the ring.