beginning of the combustion without the aid of the copper roll is sufficient to prevent backward distillation, and it aids the forward movement and partial burning of the gases. After the oil is completely burned the tubes are swept clear of nitrogen with carbon dioxide from the generator, and the reduced copper oxide reoxidized with tank oxygen. If this be done with the tubes hot, after a few evacuations the system is ready for the next analysis. Even with this large surface of copper oxide the combustion cannot be pushed too rapidly for unburned gases will escape. One g. of oil requires two to three hours in safe operation. The average room temperature, 25°, and the average barometer readings 740 mm. were used in the reduction of the volume of nitrogen to standard conditions. In the preceding table are presented the data of the volumetric determinations together with analysis of the same specimens by the Kjeldahl method using 5 g. of the oil, which were made by Professor M. F. Coolbaugh.

Summary.

Proof has been given of the presence of nitrogen in petroleum of all the principal oil fields, in forms of combination that could have had their origin only in the remains of vegetable or animal bodies. Presumptive evidence has been shown that the associated hydrocarbons in petroleum had the same origin.

A special method of analysis for the determination of minute proportions of nitrogen in oils is described.

CLEVELAND, OHIO.

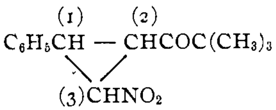
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY.]

STUDIES IN THE CYCLOPROPANE SERIES. IX. NITROCYCLOPROPANE DERIVATIVES.

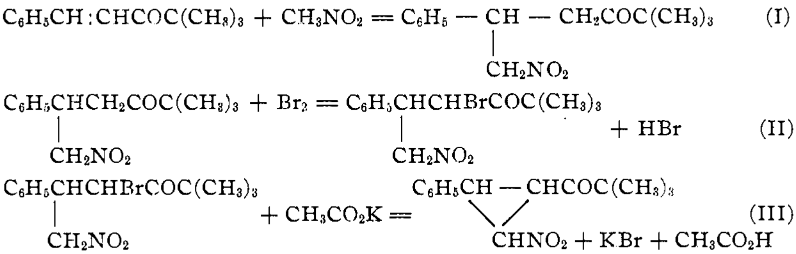
BY ELMER PETER KOHLER AND M. SRINIVASA RAO.

Received August 27, 1919.

The following paper deals with a cyclopropane derivative which has an alkyl group in place of one of the aryl groups contained in all the nitrocyclopropane derivatives described in earlier papers. Substances of this type are not easily made. In order to avoid complications in preparation it finally proved necessary to use tertiary butyl compounds. The substance studied, therefore, was phenyl-trimethylacetyl-nitrocyclopropane:



This substance was made without much difficulty by adding nitromethane to benzalpinacoline, brominating the addition product, and eliminating hydrogen bromide from the resulting bromo compound:



$$C_6H_5CH{:}CHCOC(CH_3)_3 + CH_3NO_2 = C_6H_5-\underset{\displaystyle CH_2NO_2}{\underset{|}{CH}}-CH_2COC(CH_3)_3 \qquad (I)$$

$$\underset{\displaystyle CH_2NO_2}{\underset{|}{C_6H_5CH}}CH_2COC(CH_3)_3 + Br_2 = \underset{\displaystyle CH_2NO_2}{\underset{|}{C_6H_5CH}}CHBrCOC(CH_3)_3 + HBr \qquad (II)$$

$$\underset{\displaystyle CH_2NO_2}{\underset{|}{C_6H_5CH}}CHBrCOC(CH_3)_3 + CH_3CO_2K = \underset{\displaystyle CHNO_2}{\underset{\diagdown\ \diagup}{C_6H_5CH-CHCOC(CH_3)_3}} + KBr + CH_3CO_2H \qquad (III)$$

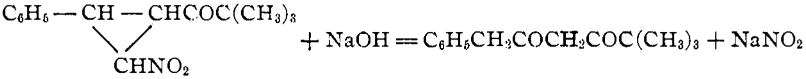
The reactions are similar to those used in the earlier work but the bromo compound does not give up hydrogen bromide nearly so easily as the corresponding substances containing only aryl groups, hence the yield of cyclopropane derivative was smaller.

The substitution of a tertiary butyl for a phenyl group, as was to be expected, does not materially alter the chemical properties of the cyclopropane derivative. Unfortunately it also does not lower the boiling point of the products obtained from the cyclopropane derivative sufficiently to make separations by vacuum distillation feasible—one of the advantages we hoped to gain by the substitution.

The cyclopropane derivative readily combines with other substances; the ring in all cases opens between carbon atoms (1) and (2). The structure of the products was established with less difficulty than we anticipated. Thus with bases the substance gave a product which has the composition $C_9H_{18}O_2$, and which must be a diketone because it gives a copper derivative when shaken with a solution of copper acetate, and two isomeric isoxazole derivatives when treated with hydroxylamine. The structure of this di-ketone was established by synthesis from ethyl phenylacetate and pinacoline:

$$C_6H_5CH_2COOC_2H_5 + CH_3COC(CH_3)_3 = C_6H_5CH_2COCH_2COC(CH_3)_3 + C_2H_5OH.$$

It is evident that this substance can be formed from the cyclopropane derivative only by opening the ring between carbon atoms (1) and (2), the reaction being expressed by the equation:

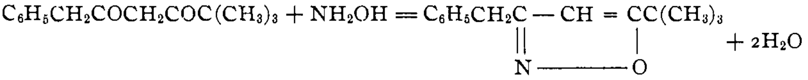


$$\underset{\displaystyle CHNO_2}{\underset{\diagdown\ \diagup}{C_6H_5-CH-CHCOC(CH_3)_3}} + NaOH = C_6H_5CH_2COCH_2COC(CH_3)_3 + NaNO_2$$

The product obtained by adding hydrogen bromide to the cyclopropane derivative has the composition $C_{14}H_{18}O_3NBr$. It very easily loses both nitrous and hydrobromic acids, but by cautious treatment with potassium acetate it is possible to convert it into an unsaturated nitro compound which is isomeric with the cyclopropane derivative, $C_{14}H_{17}O_3N$, and which must have a double linkage next to the phenyl group because it gives benzaldehyde as one of the oxidation products. When this unsaturated nitro compound is treated with hydrogen bromide in glacial acetic acid it not only adds hydrobromic acid but also undergoes reduction, the reaction being expressed by the equation:

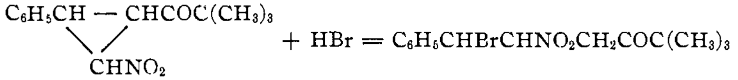
$$C_{14}H_{17}O_3N + 3HBr = C_{14}H_{16}ONBr + Br_2 + 2H_2O.$$

The resulting bromine compound, finally, when reduced with zinc gives one of the isoxazole derivatives that is obtained from the β-diketone in accordance with the equation:



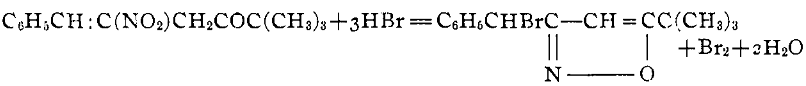
$$C_6H_5CH_2COCH_2COC(CH_3)_3 + NH_2OH = \begin{array}{l} C_6H_5CH_2C - CH = CC(CH_3)_3 \\ \qquad\qquad\;\; \| \qquad\quad | \\ \qquad\qquad\;\; N - - - O \end{array} + 2H_2O$$

This relation establishes the structure of all the intermediate products, the successive reactions being represented by the following equations:

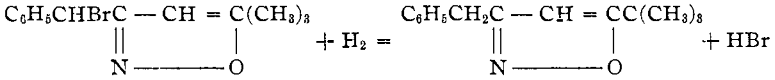


(I)

$$C_6H_5CHBrCHNO_2CH_2COC(CH_3)_3 - HBr = C_6H_6CH{:}C(NO_2)CH_2COC(CH_3)_3 \quad (II)$$



$$C_6H_5CH{:}C(NO_2)CH_2COC(CH_3)_3 + 3HBr = \begin{array}{l} C_6H_6CHBrC - CH = CC(CH_3)_3 \\ \qquad\qquad\quad\; \| \qquad\quad | \\ \qquad\qquad\quad\; N - - - O \end{array} + Br_2 + 2H_2O \quad (III)$$



$$\begin{array}{l} C_6H_5CHBrC - CH = C(CH_3)_3 \\ \qquad\quad\;\; \| \qquad\quad | \\ \qquad\quad\;\; N - - - O \end{array} + H_2 = \begin{array}{l} C_6H_5CH_2C - CH = CC(CH_3)_3 \\ \qquad\quad\; \| \qquad\quad | \\ \qquad\quad\; N - - - O \end{array} + HBr \quad (IV)$$

Experimental Part.

γ-Nitro-β-phenyl-propyl-tertiary butyl ketone, $NO_2CH_2CH(C_6H_5)CH_2COC(CH_3)_3$.—A very concentrated solution of sodium methylate containing 3 g. of sodium was added to a solution of 19 g. of benzalpinacoline and 4 g. of nitromethane in 45 cc. of dry methyl alcohol. The mixture was shaken until all of the sodium nitromethane had gone into solution and then immediately cooled in ice water. The well cooled yellow or orange colored solution was acidified with glacial acetic acid which was added drop by drop while the mixture was stirred vigorously. This precipitated the product as a white powder contaminated with a small quantity of oil and with sodium compounds that are held tenaciously. The powder was washed with cold methyl alcohol to remove the oil and then very thoroughly with water to remove sodium compounds. This left a colorless product which after drying was sufficiently pure for bromination. For the purpose of analysis it was crystallized from methyl alcohol from which it separated in minute colorless plates.

Calc. for $C_{14}H_{19}O_3$: C, 67.4; H, 7.7. Found: C, 67.1; H, 7.5.

The nitro-ketone is readily soluble in all common organic solvents except ligroin. It melts at 74°. The yield was 80 to 90%.

γ-Nitro-β-phenyl-α-bromo-propyl-tertiary butyl ketone, $NO_2CH_2CH(C_6H_5)CHBrCOC(CH_3)_3$.—For the purpose of bromination the nitroketone was, as usual, suspended in a small quantity of chloroform or carbon tetrachloride. With the pure substance the reaction starts promptly at the ordinary temperature, but the crude washed and dried product usually has to be heated to the boiling point of the solvent. The ketone dissolves as the reaction proceeds and the bromo compounds generally begin to separate before it is complete. After adding a slight excess of bromine the solvent was removed under diminished pressure and the solid residue washed repeatedly with small quantities of methyl alcohol. This left a colorless mass composed mainly of two isomeric α-bromo compounds. The yield of mixed bromo compounds was 92%.

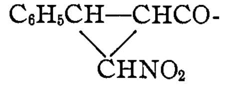
In order to separate the mixture of monobromo compounds it was first extracted two or three times with small quantities of boiling methyl alcohol. The residue—composed mainly of the higher melting substance—after several crystallizations from methyl alcohol gave a product which separated in large needles melting constantly at 143–144°. This bromo compound is sparingly soluble in methyl and ethyl alcohols, moderately in chloroform and carbon tetrachloride, readily in acetone.

Calc. for $C_{14}H_{18}O_3NBr$: C, 51.2; H, 5.5 Found: C, 50.9; H, 5.6.

The lower melting compound was obtained by repeated recrystallization of the solid that separated from the first methyl alcoholic extract of the mixed substances. It separated in colorless plates which melted at 74–75°.

Calc. for $C_{14}H_{18}O_3NBr$: C, 51.2; H, 5.5. Found: C, 51.3; H, 5.8.

1-Phenyl-2-trimethylacetyl-3-nitro cyclopropane,



$C_6H_5CH—CHCO-$ / $CHNO_2$

$C(CH_3)_3$.—The lower melting bromo compound is stable in boiling methyl alcohol but it is rapidly converted into the higher melting isomer by methyl alcoholic potassium acetate. Thus a pure specimen melting at 75° was boiled with methyl alcohol for nearly an hour without change in melting point but when boiled for another hour after a little potassium acetate had been added to the solution it melted sharply at 145°. Both bromo compounds, consequently, give the same cyclopropane derivative. This was, therefore, commonly made by starting with the mixed bromo compounds.

The elimination of hydrobromic acid is so difficult that it is not feasible to transform a given quantity of the bromo compounds completely into cyclopropane derivative in a single operation, for after the concentration of the cyclopropane derivative reaches a certain point, boiling potassium acetate decomposes it as rapidly as it removes hydrogen bromide from the bromo compounds. The most satisfactory procedure was as follows.

A concentrated solution of 25 g. of the mixed bromo compounds in methyl alcohol is boiled with 8 g. of potassium acetate for half an hour.

Eight g. more of potassium acetate is then added gradually to the boiling solution, and the mixture refluxed for another 15 minutes. Half of the methyl alcohol is now distilled off and the residue cooled in a freezing mixture. The resulting solid is washed first with a little methyl alcohol, then with water until free from bromide. The colorless solid remaining is dissolved in the minimum amount of boiling methyl alcohol and the solution allowed to cool. It deposits the cyclopropane derivative in large transparent cubes which after washing with methyl alcohol are analytically pure. The filtrate may deposit some more cubical crystals but the second crop generally is a mixture composed largely of needles of the higher melting bromo compound. While the mixture may be separated mechanically, it is more economical to repeat the treatment with potassium acetate.

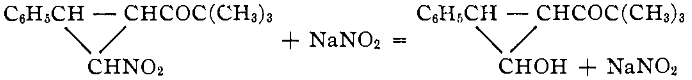
The yield of pure cyclopropane derivative was about 60%—the substance crystallizes in cubes and melts at 94°. It is readily soluble in all common organic solvents except ligroin.

Calc. for $C_{14}H_{17}O_3N$: C, 67.9; H, 6.9. Found: C, 67.5; H, 6.7.

Action of Alkalies.—The cyclopropane derivative is readily attacked by alkalies. These invariably remove nitrous acid from the substance and under most conditions they transform it into a number of oily products from which it is impossible to isolate pure compounds. The following procedure, however, gave a fair yield of a solid product: A concentrated solution of sodium methylate containing 6 g. of sodium in 50 cc. of dry methyl alcohol was added slowly and with constant shaking to a suspension of 20 g. of the cyclopropane derivative in 15 cc. of the same solvent, which was cooled in ice water. The mixture was then vigorously shaken on a machine. After several hours, during which all of the substance dissolved and most of the sodium nitrite separated, it was transferred to a vacuum desiccator and evaporated to complete dryness over sulfuric acid. This left an orange colored residue composed mainly of sodium nitrite and an organic sodium compound. The latter was extracted with methyl alcohol and the well cooled solution cautiously acidified with sulfuric acid. The resulting solid was purified by recrystallization from methyl alcohol.

Calc. for $C_{14}H_{18}O_2$: C, 77.1; H, 8.2. Found: C, 77.2; H, 8.4.

The composition of the substance indicated replacement of the nitro group by hydroxyl:



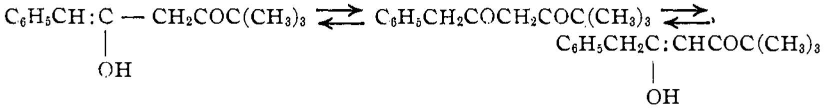
$$\underset{CHNO_2}{C_6H_5CH - CHCOC(CH_3)_3} + NaNO_2 = \underset{CHOH}{C_6H_5CH - CHCOC(CH_3)_3} + NaNO_2$$

The properties of the substance, however, could not be reconciled with such a formula; for while it formed a phenylcarbamate with phenylisocyanate, it gave a color reaction with ferric chloride, formed a sodium derivative with sodium ethylate and a copper derivative with copper acetate, and was converted into an isoxazole by hydroxylamine. These are characteristic reactions of β-diketones.

The two β-diketones that might be formed from the cyclopropane derivative are represented by the formulas: $C_6H_5CH_2COCH_2COC(CH_3)_3$, $C_6H_5COCH_2COCH_2C(CH_3)_3$. Inasmuch as the substance gives phenylacetic acid and pinacoline when boiled with alcoholic potassium hydroxide it can not have a benzoyl group. This excludes the second formula. We therefore undertook the synthesis of phenylacetyl-trimethylacetylmethane. For this purpose 2.3 g. of sodium was added to a well cooled solution of 32 g. of ethyl phenyl acetate and 15 g. pinacoline in 150 cc. of dry ether. The solution was kept in ice water for several hours, then at the ordinary temperature until all of the sodium had disappeared. It was then acidified, extracted with sodium hydrogen carbonate until free from phenylacetic acid, and finally shaken with a cold saturated solution of copper acetate. This precipitated a pale green copper derivative which when shaken with hydrochloric acid and a little ether gave the same substance that had been obtained from the cyclopropane derivative:

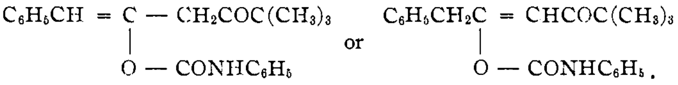
$$C_6H_5CH_2CO.OC_2H_5 + CH_3COC(CH_3)_3 = C_6H_5CH_2COCH_2COC(CH_3)_3 + C_6H_5OH$$

Phenacetyl-trimethyl acetyl-methane is readily soluble in ether, moderately in alcohol, very sparingly in ligroin. It crystallizes in needles and melts at 44°. In alcoholic solution it gives a deep red color with ferric chloride. When it is oxidized with permanganate in acetone it gives almost exclusively benzoic and trimethyl acetic acids while when oxidized in alkaline solution with aqueous permanganate the sole organic products are phenylacetic and trimethylacetic acids. It is, therefore, evidently capable of enolizing in two different ways:



$$C_6H_5CH{:}\underset{\underset{OH}{|}}{C}-CH_2COC(CH_3)_3 \rightleftarrows C_6H_5CH_2COCH_2COC(CH_3)_3 \rightleftarrows C_6H_5CH_2\underset{\underset{OH}{|}}{C}{:}CHCOC(CH_3)_3$$

The phenylcarbamate of the diketone:

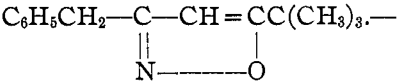


$$C_6H_5CH=\underset{\underset{O-CONHC_6H_5}{|}}{C}-CH_2COC(CH_3)_3 \quad \text{or} \quad C_6H_5CH_2\underset{\underset{O-CONHC_6H_5}{|}}{C}=CHCOC(CH_3)_3.$$

To prepare the carbamate, a mixture of 5 g. of the diketone and 5 g. of phenylisocyanate was heated to 100° for 15 minutes and then to 140–150° for 10 minutes more. The resulting pasty solid was washed with benzene and ether, and recrystallized from methyl alcohol. It is readily soluble in chloroform and acetone, moderately in boiling methyl alcohol, very sparingly in ether. Its melting point is 130–132°.

Calc. for $C_{21}H_{23}O_3N$: C, 74.8; H, 6.8. Found: C, 74.9; H, 6.8.

5-Benzyl-3-tertiarybutyl Isoxazole,

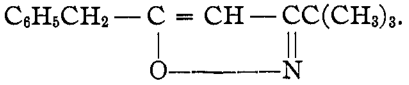


$$\begin{array}{lllll} C_6H_5CH_2\text{—} & C & \text{—}CH= & C & C(CH_3)_3.\text{—} \\ & \| & & | & \\ & N & \text{———} & O & \end{array}$$

A solution of 3 g. of the diketone, 3 g. of hydroxylamine hydrochloride and 5 g. of potassium hydroxide in 100 cc. of methyl alcohol was refluxed for half an hour and then poured into ice water. This precipitated a granular, white solid which after recrystallization from dilute methyl alcohol melted as 51°.

Calc. for $C_{14}H_{17}ON$: C, 78.1; H, 7.9; N, 6.5. Found: C, 78.1; H, 7.8; N, 6.9.

3-Benzyl-5-tertiarybutyl Isoxazole,



$$\begin{array}{lllll} C_6H_5CH_2\text{—} & C & = CH\text{—} & C & C(CH_3)_3. \\ & | & & \| & \\ & O & \text{———} & N & \end{array}$$

—The alkaline filtrate from the isoxazole, on acidification gave another product which after recrystallization from dilute methyl alcohol melted at 63°. The analyses show that this is an isomeric isoxazole.

Calc. for $C_{14}H_{17}OH$: C, 78.1; H, 7.9. Found: C, 78.1; H, 8.0.

β-Nitro-γ-bromo-γ-phenyl-propyl tertiarybutyl Ketone, C_6H_5CHBr-$CHNO_2CH_2NO_2COC(CH_3)_3$.—The nitro cyclopropane combines very readily with hydrobromic acid both when dissolved in alcohol and in glacial acetic acid. A solution in glacial acetic acid cooled in ice water was saturated with hydrogen bromide, allowed to stand for a few minutes, and poured into ice water. This precipitated a colorless oil which solidified when rubbed with a glass rod. The product after washing with ice water until free from acid, and drying *in vacuo* melted at 66–67° and the melting point remained the same after recrystallization from methyl alcohol or from ether and ligroin. The yield was quantitative.

Calc. for $C_{14}H_{18}O_3NBr$: C, 51.4; H, 5.5. Found: C, 51.7; H, 5.5.

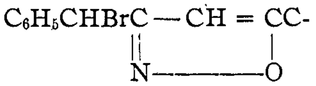
The bromo compound is exceedingly unstable. It loses both nitrous and hydrobromic acids and passes into oily products when boiled with methyl alcohol, and even cold solutions rapidly become acid. When the pure, dry substance is kept in a stoppered bottle it loses nitrous acid, and gradually turns into a brown oil. Potassium acetate, in the cold, eliminates principally hydrobromic acid and forms an unstable nitro compound.

β-Benzal-β-nitro-ethyl tertiarybutyl Ketone, $C_6H_5CH:C(NO_2)CH_2$-$COC(CH_3)_3$.—To an ice cold solution of 9 g. of the hydrobromic acid addition product in 30 cc. of methyl alcohol, 4 g. of powdered potassium acetate was added in small portions and with constant shaking. The solution first turned yellow, then brown, while potassium bromide and a little potassium nitrate was deposited. After standing for 12 hours in an ice chest, most of the organic product had separated as a yellow solid.

This was thoroughly washed with water and recrystallized from methyl alcohol.

Calc. for $C_{14}H_{19}O_3N$: C, 67.9; H, 6.6. Found: C, 67.9; H, 6.9.

The unsaturated nitro compound crystalizes in long, yellow needles and melts at 53–54°. It is readily soluble in the common organic solvents. Its solution in acetone instantly reduces permanganate, and benzaldehyde is a primary oxidation product, showing that the double linkage is next to the phenyl group.

5-Bromobenzyl-3-tertiarybutyl Isoxazole,  $C_6H_5CHBr\underset{N}{\underset{\|}{C}}-CH=\underset{O}{\underset{|}{C}}C(CH_3)_3$.—When hydrogen bromide was passed into a solution of the unsaturated nitro compound, the color of the solution rapidly changed from yellow to red owing to separation of free bromine. The solution was saturated at 0°, allowed to stand for several hours in an ice chest and then poured into ice water. This precipitated an oil which solidified when rubbed. The solid was washed with sodium hydrogen sulfite until colorless, and purified by recrystallization from methyl alcohol.

Calc. for $C_{14}H_{16}ONBr$; C, 57.1; H, 5.4. Found: C, 56.8; H, 5.6.

The isoxazole derivative crystallizes in needles and melts at 77–78°. It is quite stable, being recovered unchanged after having been heated to 150° for 8 hours. The bromine is readily replaced with hydrogen. Thus 0.5 g. of the substance and one g. of zinc dust were heated in acetic acid on a steam bath for half an hour. The solution was filtered into ice water, and the precipitated solid recrystallized from methyl alcohol. It was bromine free, melted at 50°, and the melting point remained the same when it was mixed with a specimen of the lower melting isoxazole which had been obtained by the action of hydroxylamine upon the diketone.

CAMBRIDGE, MASS.

NOTE.

Correction.—In the review of "Chemistry in Old Philadelphia,"[1] line 20, read: Hare's oxy-hydrogen blow pipe and some of Woodhouse's and some of Hare's other contributions. F. B. DAINS.

NEW BOOKS.

Intermediate Text-Book of Chemistry. 1st edition. By ALEXANDER SMITH, Head of Department of Chemistry, Columbia University. The Century Co., New York, 1919. vi + 520 pp. 115 figs. 14 × 21 cm. $2.25.

This is a new member of the successful series of Smith texts, now four in number. Together they carry out the best traditions of chemical in-

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[1] THIS JOURNAL, 41, 1315 (1919).