The **p-bromophenacyl ester of (VII)** was prepared in alcohol, m. p. 193.5–194.5° after four recrystallizations from dioxane–alcohol.

*Anal.* Calcd. for $C_{30}H_{25}O_3Br$: C, 70.17; H, 4.91. Found: C, 70.06; H, 4.90.

No pure compound could be isolated from fractions 1, 2 and 6. Although water-soluble α-methyleneglutaric acid was searched for carefully, it could not be found.

**3,3,3-Triphenylpropanol (X).**—An ether solution of 1.89 g. (0.043 mole) of ethylene oxide was added rapidly to 490 cc. of 0.0805 *N* triphenylmethylsodium reagent. The red color immediately changed to yellow-brown and the ether boiled gently. The reaction mixture was treated with water, the ether separated, dried and evaporated, and the oily residue distilled under reduced pressure. The triphenylpropanol, b. p. 208–212° (3 mm.), crystallized in the receiver; m. p. 106–108° after recrystallization from petroleum ether (b. p. 90–100°) as clusters of glistening white needles; yield, 12 g. (96%). Two more recrystallizations raised the m. p. to 107–108°.

*Anal.* Calcd. for $C_{21}H_{20}O$: C, 87.46; H, 6.99. Found: C, 87.26; H, 7.05.

**3,3,3-Triphenylpropyl Iodide (XI).**—Three grams of triphenylpropanol, 0.103 g. of red phosphorus, and 1.40 g. of iodine were heated in an oil-bath at 165° for five hours. The mixture was taken up in benzene, washed with water and with 5% sodium hydroxide solution, and dried with anhydrous calcium chloride. Evaporation of the solvent gave 3.1 g. (75%) of the iodide, m. p. 173.5–174.5°,[15] after four recrystallizations from benzene–alcohol.

*Anal.* Calcd. for $C_{21}H_{19}I$: C, 63.33; H, 4.81. Found: C, 63.87; 63.90; H, 4.99, 4.81.

(15) Wooster and Morse[16] report m. p. 174.5–175°.

**4,4,4-Triphenylbutyric Acid (VII).**—The Grignard reagent was prepared from 1.3 g. of triphenylpropyl iodide and 0.1 g. of magnesium in 100 cc. of dry ether and 30 cc. of dry benzene. Excess dry carbon dioxide gas was passed into the reaction mixture. The reagent was decomposed with dilute acid, and the ether layer was separated and dried. Removal of the solvent gave 0.2 g. (19%) of the desired acid (VII), m. p. 148–155°. Three recrystallizations from dilute alcohol gave white micro crystals, m. p. 154–156° with sintering from 148°.

*Anal.* Calcd. for $C_{22}H_{20}O_2$: C, 83.51; H, 6.37. Found: C, 83.63; H, 6.32.

The mixed m. p. of this synthetic acid with that obtained from methyl acrylate was 153.5–156°.

The *p*-bromophenacyl ester of (VII) was prepared in alcohol and recrystallized from dioxane–alcohol; m. p. 194–195.5° with sintering from 192°. The mixed m. p. of this ester with that obtained previously from the methyl acrylate reaction was 194–195°.

## Summary

Triphenylmethylsodium does not cause enolization of ethyl crotonate. Instead, 1,4-addition occurs, resulting in the formation of ethyl 3-methyl-4,4,4-triphenylbutyrate in high yield.

Triphenylmethylsodium reacts with methyl acrylate to form a mixture of esters among which are methyl 2-(2,2,2-triphenylethyl)-glutarate and methyl 4,4,4-triphenylbutyrate.

4,4,4-Triphenylbutyric acid has been synthesized by an independent method.

ROCHESTER, NEW YORK RECEIVED JULY 12, 1943

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[COMMUNICATION NO. 945 FROM THE KODAK RESEARCH LABORATORIES]

# Investigation of Pyrazole Compounds. V.[1] The Acylation of 1-Phenyl-3-hydroxy-5-pyrazolone Imide

BY A. WEISSBERGER AND H. D. PORTER

In the preceding paper, structures were assigned to acyl derivatives of 3-phenyl-5-pyrazolone and 3-anilino-5-pyrazolone. The present paper reports on a similar investigation with 1-phenyl-3-hydroxy-5-pyrazolone imide, I.[2]

I, on heating with excess acetic anhydride, forms a **diacetyl derivative melting at 192°** which is hydrolyzed by caustic alkali to a **mono acetyl derivative melting at 233°**. The latter is soluble in carbonate, which excludes O-acylation, and does not form a dye in the film-strip test.[1] It is very stable in caustic alkali, 70% being recovered after heating in 10% sodium hydroxide for two hours on the steam-bath. According to the experience with other pyrazolone derivatives, reported earlier[1] and below, an acetyl group attached to nitrogen would be hydrolyzed under these conditions. The monoacetyl derivative is, therefore, **1-phenyl-3-hydroxy-4-acetyl-5-pyrazolone imide, II.** This assignment is corroborated by the behavior of the 4-acetyl,[3] and the 4-benzoyl[4] derivatives of 1-phenyl-3-methyl-5-pyrazolone, III. Like II, both of these compounds are soluble in carbonate, stable in caustic alkali,[3,4] and do not form a dye in the film-strip test. Acylation in the methylene group of a —$COCH_2C$(NH)— system is not a singularity, but has been observed with a number of open-chain compounds.[5]

The stability of the 4-acetyl compounds makes it unlikely that 3-anilino-4-acetyl-5-pyrazolone, IV, or analogous compounds are intermediates in Worrall's synthesis of anilino pyrazolones.[6] It must rather be assumed that the acetyl group is eliminated before the pyrazolone ring is closed.

With acetic anhydride, II is acetylated to the **diacetyl compound melting at 192°**. The latter is insoluble in carbonate. In caustic alkali at room temperature it hydrolyzes slowly to II. The difference in the carbonate solubility of II and of the diacetyl derivative, and the ease with which the second acetyl group is removed, indi-

(1) Investigation of Pyrazole Compounds. IV, THIS JOURNAL, **65**, 1495 (1943).

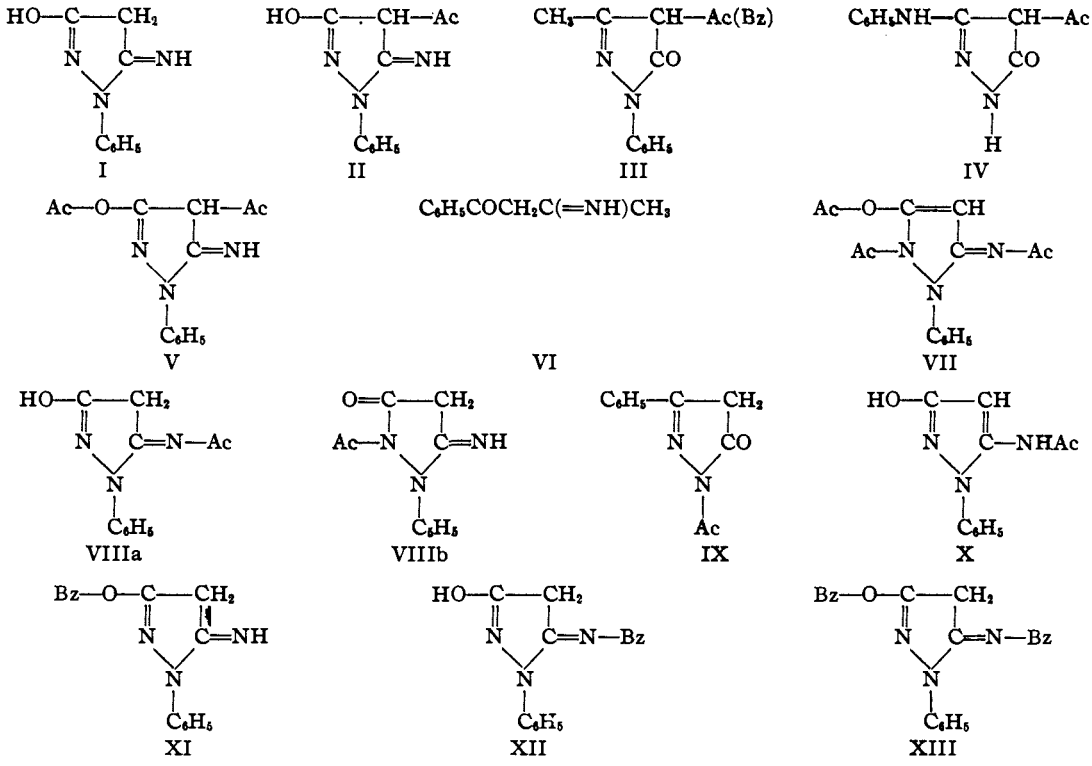
(2) Weissberger and Porter, *ibid.*, **65**, 52 (1943).

(3) Stolte, *J. prakt. Chem.*, **58**, 145 (1897).

(4) Michaelis and Engelhardt, *Ber.*, **41**, 2668 (1908).

(5) Benary and Kerckhoff, *ibid.*, **59**, 2548 (1929).

(6) Worrall, THIS JOURNAL, **44**, 1551 (1922); Weissberger and Porter, *ibid.*, **65**, 732 (1943).




cate that the latter is attached to oxygen in position 3 and that the compound melting at 192° is **1-phenyl-3-acetoxy-4-acetyl-5-pyrazolone imide, V.** An argument that the acetomethine group neighboring a carbonimido group should endow V with solubility in carbonate can be dismissed because benzoylacetone imide, VI, is insoluble in alkali.[7] The tendency for enolization of a carbonyl group in the side chain is obviously much smaller than that of the carbonyl group of the pyrazolone system.

Heating of I on the steam-bath with excess acetic anhydride and pyridine yields a **triacetyl compound** which is insoluble in sodium carbonate. With hot 10% sodium hydroxide, it is hydrolyzed to I, showing that none of the acetyl groups is attached to carbon. Of the remaining structures, that of **1-phenyl-2-acetyl-3-acetoxy-5-acetylimino-$\Delta_3$-pyrazoline, VII,** is the most likely one, the other possible formulas being those of eneamines with two acetyl groups attached to the same nitrogen atom.

When VII is stirred with caustic alkali at room temperature, it dissolves gradually. From the solution, acetic acid precipitates a **monoacetyl compound, melting at 233°.** In spite of the almost identical melting point, the compound differs from II. This is shown by the m. p. of the mixture and by the fact that the monoacetyl derivative obtained from VII forms a magenta dye in the film-strip test. Moreover, like VII, it is readily hydrolyzed to I with hot 10% sodium hydroxide, excluding acetylation at the carbon in position 4. O-acetylation is ruled out by the solubility of the compound in carbonate. This leaves as possible structures those of **1-phenyl-3-hydroxy-5-pyrazolone acetylimide, VIIIa,** and of 1-phenyl-2-acetyl-3,5-pyrazoledione 5-imide, VIIIb. The compound is rather stable in alkali, 75% being recovered after standing in 2% sodium hydroxide for two hours. Of 1-acetyl-3-phenyl-5-pyrazolone, IX, which in the position of the acetyl group corresponds to VIIIb, none was recovered after the same treatment because of hydrolysis.[1] This is evidence against its being structure VIIIb. VIIIa, on the other hand, may be expected to be more resistant to hydrolysis, particularly as the tautomeric 1-phenyl-3-hydroxy-5-acetylaminopyrazole, X. Structure VIIIa is, therefore, assigned to the monoacetyl compound formed by hydrolysis of VII. A small amount of VIIIa can be obtained in the preparation of V from I.

It is noteworthy that no C-acetylation, *i. e.*, formation of II or V, was observed in the preparation of VII, although C-acetylation occurs readily in the absence of pyridine. The latter is known to promote O-acetylation of pyrazole derivatives,[1] and an O-benzoyl derivative of I was actually isolated from the reaction of I with benzoyl chloride in the presence of pyridine. Once O-acylation has taken place, the —$COCH_2C$-(NH)— system responsible for the C-acetylation of I, is destroyed, and C-acetylation can no longer be expected.

(7) Fischer and Bülow, *Ber.*, **18**, 2138 (1885).

It may also deserve some comment that, in the acetylation of II to V, the acetyl group is linked to oxygen while the imino group remains unsubstituted. The acetyl group attached to the neighboring C-atom appears to diminish the reactivity of the imino group for acetylation.

Treatment of I with one mole of benzoyl chloride and pyridine in dioxane gives a **monobenzoyl derivative melting at 105°**. This is insoluble in carbonate and easily saponified to I in agreement with the structure of **1-phenyl-3-benzoyloxy-5-pyrazolone imide, XI**. With two moles of benzoyl chloride and pyridine or with benzoic anhydride in dioxane, I forms a **dibenzoyl derivative melting at 193°**. This is hydrolyzed by caustic alkali at room temperature to a **monobenzoyl derivative melting at 237°**. The latter is soluble in carbonate and hydrolyzed to I by hot caustic alkali. O-acylation and C-acylation are thus excluded, and there remains as the most likely structure for the compound melting at 237°, that of **1-phenyl-3-hydroxy-5-pyrazolone benzoylimide, XII**, which is analogous to VIIIa. Like VIIIa, and at variance with II, XII forms a magenta dye in the film-strip test. A structure corresponding to VIIIb would be less plausible because the benzoyl derivative is even much more stable to alkali than VIIIa. This difference between XII and VIIIa, 80% of the former being recovered under conditions which hydrolyze the latter completely, agrees with other observations on acetyl and benzoyl compounds. Thus, when the 3-N-acetyl- and 3-N-benzoyl derivatives[8] of 1-phenyl-3-amino-5-pyrazolone were heated on the steam-bath in 10% sodium hydroxide for one-half hour, the acetyl derivative was largely hydrolyzed while the benzoyl derivative was not.

As the dibenzoyl derivative, melting at 193°, may be prepared by the benzoylation of either XI or XII, it is **1-phenyl-3-benzoyloxy-5-pyrazolone benzoylimide, XIII**.

## Experimental

**1-Phenyl-3-hydroxy-4-acetyl-5-pyrazolone Imide, II.**—A suspension of 0.7 g. of 1-phenyl-3-acetoxy-4-acetyl-5-pyrazolone imide, IV, in 20 ml. of 2% sodium hydroxide was stirred at room temperature for one-half hour. The resulting solution was acidified with acetic acid and filtered; 0.5 g. (86%) of a white granular powder, m. p. 233–234°, unchanged by recrystallization from 95% ethanol.

*Anal.* Calcd. for $C_{11}H_{11}N_3O_2$: C, 60.7; H, 5.07; N, 19.35. Found: C, 60.85; H, 5.32; N, 19.11.

After heating on the steam-bath in 10% sodium hydroxide solution (10 ml./g.) for two hours, 70% of II[9] was recovered on acidification.

**1-Phenyl-3-acetoxy-4-acetyl-5-pyrazolone Imide, V.**—A solution of 5 g. of 1-phenyl-3-hydroxy-5-pyrazolone imide, I[2], in 10 ml. of acetic anhydride was heated on the steam-bath for one hour, cooled, the resulting sludge slurried with 25 ml. of ethyl ether, filtered, and the residue rinsed with methanol; 1.9 g. (25%), m. p. 190–192°, recrystallized from 95% ethanol; fine white needles, m. p. 192–193°.

*Anal.* Calcd. for $C_{13}H_{13}N_3O_3$: N, 16.2. Found: N, 16.23.

The ethereal filtrate was extracted with 75 ml. of 2% sodium hydroxide and the alkaline solution acidified; 0.9 g. (14%) of 1-phenyl-3-hydroxy-5-pyrazolone acetylimide, VIIIa.[9]

V[9] was also prepared from II following the procedure for V.

**1-Phenyl-2-acetyl-3-acetoxy-5-acetylimino-$\Delta_3$-pyrazoline, VII.**—A solution of 1 g. of 1-phenyl-3-hydroxy-5-pyrazolone imide, I[2], and 1 ml. of pyridine in 5 ml. of acetic anhydride was heated on the steam-bath for one hour, cooled and decomposed in ice water. The precipitated product was filtered and washed with water; 1.1 g. (72%) of white needles, m. p. 83–84°, unchanged by recrystallization from ligroin.

*Anal.* Calcd. for $C_{15}H_{15}N_3O_4$: N, 13.95. Found: N, 13.86.

A small amount of 1-phenyl-3-hydroxy-5-pyrazolone imide, I,[9] was obtained, by concentration of the acidified solution, after heating VII on the steam-bath for one-half hour in 10% sodium hydroxide (7 ml./g.).

**1-Phenyl-3-hydroxy-5-pyrazolone acetylimide, VIIIa,** was prepared from 1-phenyl-2-acetyl-3-acetoxy-5-acetylimino-$\Delta_3$-pyrazoline, VII, following the procedure for the preparation of II from V; 80% yield of white granular powder, m. p. 233–234°, unchanged by recrystallization from 95% ethanol; mixed m. p. with II (equal parts) about 200°.

*Anal.* Calcd. for $C_{11}H_{11}N_3O_2$: N, 19.35. Found: N, 19.42.

After standing in 2% sodium hydroxide solution (20 ml./g.) at room temperature for two hours, 75% of VIIIa[9] was recovered on acidification.

None of VIIIa was recovered after heating on the steam-bath for one-half hour in 10% sodium hydroxide (7 ml./g.). A small amount of 1-phenyl-3-hydroxy-5-pyrazolone imide, I,[9] was obtained by concentration of the acidified solution.[8]

Under the latter conditions, 1-phenyl-3-acetylamino-5-pyrazolone[8] was hydrolyzed to 1-phenyl-3-amino-5-pyrazolone.[8,9]

**1-Phenyl-3-benzyloxy-5-pyrazolone Imide, XI.**—To a solution of 3 g. of 1-phenyl-3-hydroxy-5-pyrazolone imide, I[2], and 1.6 g. of pyridine in 14 ml. of dioxane, heated on the steam-bath, was added dropwise with stirring 2.8 g. of benzoyl chloride. After one-half hour the mixture was cooled, the dioxane solution decanted from an oil, concentrated *in vacuo*, and the residue crystallized from 6 ml. of methanol; 1.95 g. (35%) of short white needles, m. p. 105–106°.

*Anal.* Calcd. for $C_{16}H_{12}N_3O_2$: N, 15.05. Found: N, 14.77.

The oil on triturating with water gave 0.6 g. (10%) of 1-phenyl-3-benzoyloxy-5-pyrazolone benzoylimide, XIII.[9]

Under the conditions for the preparation of XII, XI was hydrolyzed to 1-phenyl-3-hydroxy-5-pyrazolone imide, I,[9] (69%) isolated by concentration of the acidified solution.

**1-Phenyl-3-hydroxy-5-pyrazolone Benzoylimide, XII.**—A mixture of 7 g. of 1-phenyl-3-benzoyloxy-5-pyrazolone benzoylimide, XIII, 150 ml. of 2% sodium hydroxide and 50 ml. of ethanol was stirred at room temperature for one-half hour. The resulting solution was filtered and acidified with acetic acid; 4.75 g. (94%), m. p. 236–237°, recrystallized from acetic acid; white needles, m. p. 237–238°.

*Anal.* Calcd. for $C_{16}H_{21}N_3O_2$: N, 15.05. Found: N, 14.92.

After heating on the steam-bath in 10% sodium hydroxide (7 ml./g.) solution for one-half hour, 80% of XII[9] was recovered on acidification.

Extending the time of heating to two hours and extracting the crude product with 2 ml. of hot water gave a 20% recovery of XII,[9] while 1-phenyl-3-hydroxy-5-pyrazolone imide, I,[9] (32%) crystallized from the filtrate.

Under the former conditions unchanged 1-phenyl-3-benzoylamino-5-pyrazolone[8,9] was recovered.

(8) Weissberger and Porter, THIS JOURNAL, **64**, 2133 (1942).

(9) Identified by m. p. and mixed m. p.

**1-Phenyl-3-benzoyloxy-5-pyrazolone Benzoylimide, XIII.**—To a solution of 5 g. of 1-phenyl-3-hydroxy-5-pyrazolone imide, I,[2] and 4.4 g. of pyridine in 20 ml. of dioxane, on the steam-bath, was added 8 g. of benzoyl chloride, and the heating continued for one-half hour. The product crystallized on cooling, was washed on the filter with 50% ethanol and digested with 100 ml. of 95% ethanol; 7.7 g. (72%) of fine white needles, m. p. 193–194°, unchanged by recrystallization from ethanol.

*Anal.* Calcd. for $C_{23}H_{17}N_3O_3$: N, 10.97. Found: N, 11.03.

XIII[9] was also obtained (69%) from 1-phenyl-3-benzoyloxy-5-pyrazolone imide, XI, or (88%) from 1-phenyl-3-hydroxy-5-pyrazolone benzoylimide, XII, following this procedure.

## Summary

The acetylation and benzoylation of 1-phenyl-3-hydroxy-5-pyrazolone imide, I, is studied.

1 - Phenyl - 3 - hydroxy - 4 - acetyl - 5 - pyrazolone imide, II, 1-phenyl-3-acetoxy-4-acetyl-5-pyrazolone imide, V, 1-phenyl-2-acetyl-3-acetoxy-5-acetylimino-$\Delta_3$-pyrazoline, VII, 1-phenyl-3-hydroxy-5-pyrazolone acetylimide, VIIIa, 1-phenyl-3-benzoyloxy-5-pyrazolone imide, XI, 1-phenyl-3-hydroxy-5-pyrazolone benzoylimide, XII, 1-phenyl-3-benzoyloxy-5-pyrazolone benzoylimide, XIII, are prepared as new compounds, and their properties and structures established.

The C-acetylation in the formation of II is explained by the presence of the $COCH_2C(NH)$- system. When this is destroyed by O-acetylation, C-acetylation no longer occurs.

A suggestion is made for the course of the synthesis of anilinopyrazolones.

ROCHESTER, N. Y. RECEIVED JULY 28, 1943

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AT THE OHIO STATE UNIVERSITY]

# The Preparation of Aldehydes and Ketones by Ozone Oxidation

BY ALBERT L. HENNE AND WARREN L. PERILSTEIN

Specific directions for the preparation in 60 to 70% yields of aldehydes, ketones and acids by hydrolysis or oxidation of an olefin ozonide have been reported in a preceding paper.[1] In the present paper, the ozonide is decomposed by catalytic hydrogenation; the experimental factors are systematically investigated and a redesigned ozonizer is presented which operated well over a period of more than a year.

**Equipment.**—The reasons for redesigning the ozonizer were mainly the heating of the electrodes with consequent destruction of the ozone generated, and the fragility of an outfit made of Berthelot tubes sealed in series. The essential feature of the new design (Fig. 1) is the passage of the gas twice through the length of the tube, first through the annular space between the inner electrode A and tube B, and then between tube B and the outer electrode C. This construction gives a better ozone conversion than a single passage, and completely prevents the rupture of the Pyrex dielectric when tubing of no less than standard thickness is used. Tap water circulating through the outer jacket was used as one electrode; a mercury filled tube cooled only by conduction served as the inner electrode. The grounding of the outer electrode eliminated the necessity of shielding the apparatus for protection of the operator but made it necessary to use a high voltage transformer whose secondary could also be grounded at one end.

A single ozonizer of this type, operated with tap water at about 20°, and with its center electrode at 22 Kv., gave steadily 5.1% and 3.7% by weight of ozonized oxygen, at flow rates of 10 and 20 liters per hour, respectively. This corresponds to 0.64 and 0.93 g. of $O_3$ per hour. Higher concentrations are obtainable by more intense cooling. For instance, a similar but shorter ozonizer immersed in a dry-ice and acetone bath produced 12 and 10% of ozone at 5 and 10 liters per hour, respectively. Cooling of the inner electrode would undoubtedly help further but would also complicate the design. A second ozonizer mounted in series with the first did not improve the ozone output, but placing the two in parallel permitted a slightly higher net yield by decrease of the rate of gas flow through each tube.

The vessel in which ozonization of the olefin took place was water jacketed and is shown in Fig. 2. Catalytic hydrogenation of the ozonide was performed in the same vessel, mounted on a rocking device similar in construction to the Parr outfit.[2]

An electric precipitator operating at 3 Kv. was mounted as shown in Fig. 2; it very effectively corrected the formation of uncondensed fogs and markedly improved the yields.

**Material Tested.**—The catalytic hydrogenation of ozonides was proposed by F. G. Fischer,[3] who recorded yields of aldehydes and ketones ranging from 50 to 70%. To obtain a direct comparison, cyclopentene and cyclohexene were first investigated; our results matched and slightly bettered Fischer's. Later, olefins variously branched were used, namely, 1-octene, 2-octene, 2-methyl-1-heptene, 2-methyl-2-heptene, and 2,3-dimethyl-2-heptene. This group included a representative of each of the five structural types of olefins.[4] It is to be noted that the ozonization of the cyclic olefins yielded high boiling dialdehydes, which are easier to handle without losses than the volatile derivatives of the open chain olefins.

**Solvent.**—To minimize handling, ozonization and hydrogenolysis of the ozonide were carried out in the same solvent and the same container. Methylene chloride (the solvent used in the preceding paper) could not be used here because it prevents catalytic hydrogenation. Instead, ethyl acetate, methanol and absolute ethanol were used; all three were attacked appreciably by ozone but not enough to preclude their use. The concentration of olefin was in general 0.1 mole in 100 ml. of solvent and the temperature of ozonization was in the vicinity of 25°. Variations in concentrations from 0.05 to 0.25 mole per 100 ml. and changes of temperature from −78 to 55° did not significantly affect the yield of carbonyl compounds. Ethanol gave the best and ethyl acetate the worst yields of aldehydes; methanol was intermediate. This was attributed to the formation of acetals which protected the aldehydes against further oxidation. In the preparation of ketones the effect of the solvent was less noticeable, and it was in the opposite direction. The loss of solvents and of olefin was minimized by the use of the reflux condenser and electrical precipitator shown in Fig. 2.

(1) Henne and Hill, THIS JOURNAL, **65**, 752 (1943).

(2) "Organic Syntheses," Coll. Vol. I, 1941, p. 65.

(3) Fischer, Düll and Ertel, *Ber.*, **65**, 1468 (1932).

(4) Boord in "The Science of Petroleum," Oxford University Press, London, 1938, Vol. II, p. 1353.