Summary

We have reported herein the preparation and properties of the enolic geometric isomers of 2,4,6-trimethylbenzylmesitylglyoxal obtained by way of the geometric isomeric α-mesityl-β-mesitoyl ethylene oxides.

WASHINGTON, D. C. RECEIVED AUGUST 7, 1943

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ROCHESTER]

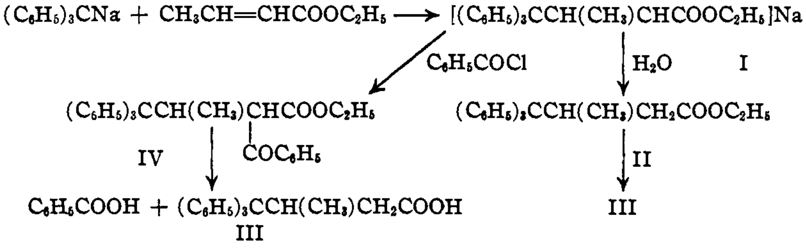
The Reaction of Triphenylmethylsodium with Esters of α,β-Unsaturated Acids

BY WARREN D. MCPHEE AND EDDIE G. LINDSTROM

The use of triphenylmethylsodium has become an important method in synthetic chemistry.[1] The reagent has the ability of forming rather rapidly the sodium salts of the enol forms of most esters which have enolizable hydrogen atoms. It is a more powerful agent than sodium or potassium ethoxide, being capable of forming sodium enolates of esters that are unaffected by these reagents, such as ethyl isobutyrate and ethyl isovalerate.[2]

In the present investigation it was originally hoped that triphenylmethy sodium would be of value in enolizing esters of acetylenic acids prior to condensation with ethyl oxalate. Since sodium and potassium ethoxide are known to add to the triple bond of such esters, giving rise to complex products,[3] they are useless as condensation agents.

Preliminary experiments were carried out with triphenylmethylsodium and ethyl crotonate. It has been found that triphenylmethylsodium adds to the conjugated system of ethyl crotonate and effects little if any enolization of this ester. Ethyl crotonate instantaneously decolorizes the red solution of the reagent with the evolution of heat. Decomposition of the reaction mixture yields ethyl 3-methyl-4,4,4-triphenylbutyrate (II). This ester could not be obtained in crystalline form, but could be hydrolyzed to the corresponding acid (III) in 89% over-all yield. No triphenylmethane, the by-product of enolization, could be isolated.



This new ester (II) undoubtedly arises from the addition of triphenylmethylsodium to the conjugated double bond system of ethyl crotonate forming the organosodium complex (I). Hydrolysis of (I) liberates the ester (II).

In view of the fact that triphenylmethylsodium generally reacts with active hydrogen atoms, its addition to the conjugated system of ethyl crotonate is significant. This is the first case in which enolization, where possible, was not found to occur.[4]

The addition of triphenylmethylsodium to conjugated double bonds has been demonstrated by Ziegler and Jakob[5] in the case of butadiene. Three isomeric triphenylpentenes were obtained and one was shown to be the result of 1,4-addition by its oxidation to triphenylpropionic acid. Recently, Michael and Saffer[6] found that the reagent adds to ethyl and methyl cinnamate to form in low yield the esters of 3,4,4,4-tetraphenylbutyric acid. In all these examples, however, there is no enolizable hydrogen atom in any of the compounds used.

It is of interest that Michael and Saffer[6] did not observe any addition in the case of methyl crotonate. They treated an ether solution of methylcrotonate with triphenylmethylsodium and isolated triphenylmethane in 91% yield. This result is in marked contrast to our experience, namely, the isolation of the 1,4-addition product of ethyl crotonate in 89% yield. In order to determine whether or not the mode of addition could account for the difference, we added the reagent to an ether solution of ethyl crotonate and were able to isolate the acid (III) in 76% yield.

It had been expected that the sodium enolate of ethyl crotonate, if formed by reaction with triphenylmethylsodium, would react with benzoyl chloride to produce ethyl γ-benzoylcrotonate. However, it was found that the product is ethyl 1-benzoyl-3-methyl-4,4,4-tri-

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[1] *Cf.* Hauser and Hudson, "Organic Reactions," Roger Adams, Editor-in-Chief, John Wiley and Sons, Inc., New York, N. Y., 1942, Vol. I, Chapter 9.

[2] Hudson and Hauser, THIS JOURNAL, **63**, 3156 (1941); Hauser and Renfrow, *ibid.*, **59**, 1823 (1937).

[3] Feist, *Ann.*, **345**, 100 (1906); Wislicenus and Schöllkopf, *J. prakt. Chem.*, **95**, 269 (1917).

[4] Baumgarten and Hauser, in a private communication, report an experiment involving the addition of *n*-propyl crotonate to triphenylmethylsodium followed by treatment with solid carbon dioxide. None of the carbonated product could be isolated. This failure to carbonate is indirect evidence that the ester anion is not present.

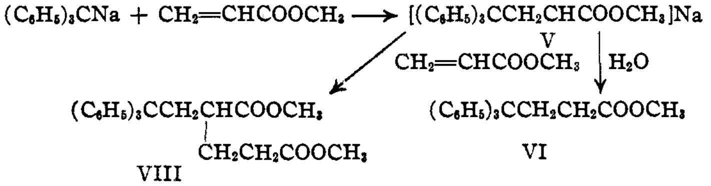
[5] Ziegler and Jakob, *Ann.*, **511**, 45 (1934).

[6] Michael and Saffer, *J. Org. Chem.*, **8**, 60 (1943).

phenylbutyrate (IV). This impure ester was obtained as a glassy solid. Distillation under reduced pressure yielded only triphenylmethane, and other methods of purification, such as attempted crystallization from various solvents, and adsorption on alumina, failed to give the pure ester. Analysis of the glass indicates that it is composed of about 75% of the ester (IV) and 25% of triphenylmethane. The triphenylmethane probably was formed from the ester by pyrolysis,[6] as the sample analyzed had previously been subjected to two unsuccessful low pressure distillations with pot temperatures up to 300°. Hydrolysis of the crude ester leads to benzoic acid and 3-methyl-4,4,4-triphenylbutyric acid (III), the latter being identical with that obtained by direct hydrolysis of (II).

Only "acidic" cleavage of the ester (IV) was found possible. Attempts to obtain 2-methyl-3,3,3-triphenylpropyl phenyl ketone by "ketonic" cleavage, using the hydriodic acid–glacial acetic acid technique of Hudson and Hauser,[7] were unsuccessful. This is probably related to the non-reaction of the carbonyl group of the ester (IV) with 2,4-dinitrophenylhydrazine.

The reaction of triphenylmethylsodium with methyl acrylate also was studied. It is much more complex than that with ethyl crotonate. In general, approximately two moles of methyl acrylate are required to discharge the color of the reagent, whereas only equivalent amounts are necessary when ethyl crotonate is used. In contrast to the nearly quantitative yield of one pure acid after hydrolysis in the case of the reaction with ethyl crotonate, methyl acrylate affords a mixture of esters from which two acids, 4,4,4-triphenylbutyric (VII) and 2-(2,2,2-triphenylethyl)glutaric (IX), were isolated in yields of 16 and 18%, respectively. A substantial amount of triphenylmethane also was observed, although none could be isolated in the reactions with ethyl crotonate.



$$(C_6H_5)_3CNa + CH_2{=}CHCOOCH_3 \longrightarrow \underset{\text{V}}{[(C_6H_5)_3CCH_2CHCOOCH_3]Na}$$

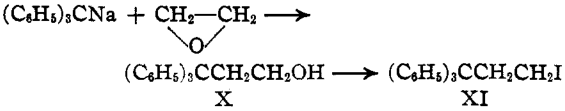
$$\text{V} \xrightarrow{CH_2{=}CHCOOCH_3} \underset{\text{VIII}}{\begin{array}{l}(C_6H_5)_3CCH_2CHCOOCH_3\\ \qquad\quad\ \ |\\ \qquad\quad CH_2CH_2COOCH_3\end{array}} \qquad \text{V} \xrightarrow{H_2O} \underset{\text{VI}}{(C_6H_5)_3CCH_2CH_2COOCH_3}$$

The triphenylbutyric acid (VII) was obtained with considerable difficulty as a crystalline solid after hydrolysis of the reaction mixture containing esters (VI) and (VIII). It forms a crystalline *p*-bromophenacyl ester. The dicarboxylic acid (IX) was also troublesome to isolate from the mixture of esters, (VI) and (VIII). It gives a crystalline S-benzylthiuronium salt and a satisfactory neutral equivalent. The substituted glutaric acid ester (VIII) undoubtedly is formed by the reaction of the organosodium complex (V) with a second molecule of methyl acrylate.

The formation of substantial amounts of triphenylmethane may perhaps be explained by the possibility that the sodio derivative of the dicarboxylic acid ester (VIII), before it is decomposed by water, could supply a proton since it has two α-carbon atoms. This supposition would require the formation of a bivalent anion. Some unpublished observations of Hudson, Baumgarten and Hauser[8] lend support to this theory. These workers report that one mole of ethyl glutarate has been found to decolorize approximately two moles of triphenylmethylsodium, indicating the formation of the ester di-anion.

The consumption of excess methyl acrylate could, perhaps, be accounted for by complex reaction products. Esters other than (VI) and (VIII) involving the condensation of two or even more molecules of methyl acrylate, may be present in the reaction mixture, but their hydrolysis products could not be isolated. For example, von Pechmann[9] has shown that methyl acrylate, under the influence of methanol-free sodium methoxide, is condensed to methyl α-methyleneglutarate. In the present investigation, this ester and its acid could not be shown to be present. Furthermore, the yields of acids (VII) and (IX) are merely minimum values since difficulty was encountered in their isolation. A higher yield of the substituted glutaric acid ester (VIII) would account for some of the excess methyl acrylate.

4,4,4-Triphenylbutyric acid (VII) was synthesized for comparison with the acid obtained from the reaction mixture. Triphenylmethylsodium was treated with ethylene oxide in ether to form the triphenylpropanol (X). This alcohol was readily converted to the iodide (XI) by red phosphorus and iodine, and the iodide formed the Grignard reagent in fair yield. Carbonation of the Grignard reagent gave the desired acid (VII). The synthetic acid is identical with that obtained from methyl acrylate, as is its *p*-bromophenacyl ester.



$$(C_6H_5)_3CNa + \underset{\diagdown O \diagup}{CH_2{-}CH_2} \longrightarrow \underset{\text{X}}{(C_6H_5)_3CCH_2CH_2OH} \longrightarrow \underset{\text{XI}}{(C_6H_5)_3CCH_2CH_2I}$$

The iodide (XI) had been prepared previously[10] by the reaction of triphenylmethylsodium in liquid ammonia with ethyl β-bromoethyl ether and subsequent cleavage of the resulting ether with hydriodic acid. Wooster[10] indicated that there was a slight possibility that his iodide might be 2-iodo-1,1,1-triphenylpropane instead of the expected 3-iodo-1,1,1-triphenylpropane. The present independent synthesis of this iodide and its reactions to form 4,4,4-triphenylbutyric acid (VII) confirm the structure assigned by Wooster.

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[7] Hudson and Hauser, THIS JOURNAL, 63, 3163 (1941).

[8] This information was kindly offered by Professor Hauser.

[9] von Pechmann and Röhm, *Ber.*, 34, 427 (1901).

[10] Wooster and Morse, THIS JOURNAL, 56, 1735 (1934).

It should be mentioned that in several of these reactions with triphenylmethylsodium a considerable amount of material thought to be di-(9-phenylfluoryl) was isolated. This could be produced by the photochemical oxidation of triphenylmethyl[11] which is present at the beginning of the reaction in the preparation of triphenylmethylsodium.

The authors wish to thank Professor Charles R. Hauser of Duke University for permission to mention in the discussion some unpublished results obtained in his laboratory.

Experimental[12]

3-Methyl-4,4,4-triphenylbutyric Acid (III).—To 540 cc. of 0.0967 *N* triphenylmethylsodium reagent in ether, prepared according to Renfrow and Hauser,[13] was added 7.5 cc. of ethyl crotonate (18% excess). The red color was immediately changed to pink and then to dark yellow, and sufficient heat was evolved to boil the ether gently. Within a few minutes water was added and the ether layer separated and dried. Removal of the solvent left a fluid yellow ester which was hydrolyzed by refluxing in 150 cc. of 10% alcoholic potassium hydroxide for two hours. The alcohol was evaporated and the potassium salt was washed with ether to remove neutral material. The aqueous suspension of the salt was acidified with dilute hydrochloric acid and the organic acid filtered. The acid, m. p. 209–213°, weighed 15.3 g. (89%). Two recrystallizations from dilute acetic acid gave white micro crystals, m. p. 213.5–215.5° with sintering.

Anal. Calcd. for $C_{23}H_{22}O_2$: C, 83.60; H, 6.72; neutral equiv., 330. Found: C, 83.32; H, 6.90; neutral equiv.. 341.

The *p*-bromophenacyl ester, prepared in ethanol, gave white micro crystals, m. p. 174–176°, with sintering, after four recrystallizations from ethanol.

Anal. Calcd. for $C_{31}H_{27}O_3Br$: C, 70.58; H, 5.16. Found: C, 70.40; H, 5.39.

3-Methyl-4,4.4-triphenylbutyric acid was also prepared by adding the reagent to ethyl crotonate. To 6.05 g. of ethyl crotonate in 100 cc. of absolute ether a slow stream of 0.107 *N* triphenylmethylsodium was added until the pink color persisted; 390 cc. was required. The product was isolated as before and recrystallized from dilute acetic acid as white needles, m. p. 212–215°; weight, 10.4 g. (76%). Another recrystallization gave needles, m. p. 214–216° with slight sintering.

In both preparations of the acid (III), no triphenylmethane could be isolated from the small amount of neutral material obtained.

Ethyl 1-Benzoyl-3-methyl-4,4,4-triphenylbutyrate (IV).—Ethyl crotonate (13.7 g.. 0.12 mole) was added to 640 cc. of 0.187 *N* triphenylmethylsodium solution. followed immediately by 16.8 g. (0.12 mole) of benzoyl chloride. Heat was evolved during both additions and sodium chloride precipitated. After forty minutes, water was added and the ether layer was separated. washed thoroughly with 10% sodium carbonate, and dried. Evaporation of the ether left 50 g. of a light amber glassy material. Attempts to isolate crystalline solids from it by crystallization from alcohol, ether, benzene and mixtures of these solvents were unsuccessful.

A 22-g. portion of the resinous ester was distilled in a short Claisen flask. Four grams of triphenylmethane distilled at 135-155° (1 mm., bath 225-250°). The hydrocarbon solidified and was recrystallized from ethanol; m. p.. 90-93°. The residue appeared to be unchanged ester, although slightly more colored.

Selective adsorption on alumina[14] failed to give a crystalline product. A solution of the glass in ligroin-benzene was passed over "minus-90" mesh alumina. The middle portion of the ligroin-benzene eluate gave a white powder which was "recrystallized" three times from petroleum ether. This material showed no crystalline form and its m. p. was ill-defined; sintering began at 60° and the material was completely melted at 82°.

Anal. Calcd. for $C_{22}H_{30}O_3$: C, 83.07; H, 6.53. Calcd. for 75% $C_{32}H_{30}O_3$ and 25% $C_{16}H_{16}$: C, 85.68; H, 6.54. Found: C, 85.62; H, 6.65.

The ester does not react with bromine in carbon tetrachloride, but is readily oxidized by permanganate in acetone. The only oxidation product isolated was benzoic acid, identified by its mixed m. p. with known material. The ester would not give a color test with ferric chloride reagent, nor would it yield a 2,4-dinitrophenylhydrazone.

Hydrolysis of (IV).—Four grams of the glassy ester was refluxed for sixteen hours in 40 cc. of 10% potassium hydroxide in 75% alcohol. Evaporation of the alcohol left two salts, one of which was soluble in water. The soluble salt was shown to be potassium benzoate by acidification, filtration, and two recrystallizations from water to give 0.7 g. of benzoic acid, m. p. 121-121.5°. The insoluble salt weighed 2 g. It was suspended in water, acidified, filtered, and recrystallized five times from dilute alcohol; m. p. 212-215°. The mixed m. p. of this acid with 3-methyl-4,4,4-triphenylbutyric acid (III) obtained previously was not depressed.

Triphenylmethylsodium and Methyl Acrylate.—This reaction was carried out several times, using amounts of ester varying from one mole (the expected amount) to more than two moles (the amount necessary to decompose completely the reagent). The following experiment is described because it illustrates well the method used and the results obtained.

Sufficient freshly distilled methyl acrylate (b. p. 80.5–82°) was added to 490 cc. of 0.0985 *N* triphenylmethylsodium reagent to discharge the red color. The equivalent amount of ester was 4.15 g., while 10 g. was required in this case. The reaction mixture was treated with water, and the ether layer was separated, dried and evaporated to yield 21.5 g. of oily ester mixture.

Eighteen and four-tenths grams of the ester mixture was hydrolyzed in 100 cc. of 10% alcoholic potassium hydroxide. and the alcohol removed by evaporation. From the residue 4.1 g. (34%) of triphenylmethane was removed by ether extraction; m. p. 90-93° after recrystallization from alcohol. The salts were acidified with dilute hydrochloric acid and extracted with ether. The ether solution was fractionally extracted by repeated washing with 50-cc. portions of 0.083 *N* potassium hydroxide. The eight basic extracts were acidified and extracted with ether; after being dried, these extracts were evaporated.

2-(2,2,2-Triphenylethyl)-glutaric Acid (IX).—Fractions 3, 4 and 5 were recrystallized as many as seven times (for fraction 4) from benzene–alcohol and the acid was obtained as white micro crystals, m. p. 205-206°; the weight of these fractions. 3.4 g., represents an 18% yield.

Anal. Calcd. for $C_{25}H_{24}O_4$: C, 77.30; H, 6.23; neutral equiv., 194. Found: C, 77.29; H, 6.31; neutral equiv., 194.

The **bis-S-benzylthiuronium salt** of (IX) was prepared in dilute alcohol. m. p. 144-145.5°, after recrystallization from dilute alcohol.

Anal. Calcd. for $C_{41}H_{44}O_4N_4S_2$: C, 68.30; H, 6.15. Found: C, 67.95; H, 6.16.

4,4,4-Triphenylbutyric Acid (VII).—Fractions 7 and 8 were recrystallized four times from dilute alcohol; white micro crystals, m. p. 153-156°; the weight of these fractions, 2.45 g., represents a 16% yield.

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[11] *Cf.* Bowden. *J. Chem. Soc.*, 26 (1939): Bowden and Jones. *ibid.*, **131**, 1149 (1928).

[12] Analyses by Robert Bauman and R. W. King. Melting points are not corrected. Yields are based on triphenylmethylsodium.

[13] Renfrow and Hauser. "Organic Syntheses." **19**, 83 (1939).

[14] Wieland. Ploetz and Indest. *Ann.*, **532**. 186 (1937). separated triphenylmethane and triphenylcarbinol by adsorption on alumina.

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. 173.5–174.50,[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.

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

[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] Stoltz. *J. prakt. Chem.*, **55**, 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).