[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

# Acyl Exchanges between Esters and 1,3-Diketones and β-Keto-esters

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In a study of the reaction of alkyl benzoates with sodium alkoxides[1] it was found that the isopropyl ester yielded, among other products, benzoylacetone and dibenzoylmethane. The formation of these 1,3-diketones was thought to be the result of three consecutive reactions, *viz.*, (a) a reverse Tischtschenko reaction through which the isopropyl benzoate under the influence of the alkoxide broke into benzaldehyde and acetone, (b) the condensation of the resulting acetone with another molecule of the ester to yield benzoylacetone, and (c) an acyl exchange between a third molecule of isopropyl benzoate and the benzoylacetone with the formation of dibenzoylmethane, thus

$$\mathrm{C_6H_5COOCH(CH_3)_2 \xrightarrow{NaOC_3H_7} C_6H_5CHO + CH_3COCH_3} \quad \text{(a)}$$

$$\mathrm{C_6H_5COOC_3H_7 + CH_3COCH_3 \xrightarrow{NaOC_3H_7} C_6H_5COCHNaCOCH_3 + C_3H_7OH} \quad \text{(b)}$$

$$\mathrm{C_6H_5COOC_3H_7 + C_6H_5COCHNaCOCH_3 \longrightarrow C_6H_5COCHNaCOC_6H_5 + CH_3COOC_3H_7} \quad \text{(c)}$$

The results obtained with the various alkyl benzoates that were studied established the validity of reactions (a) and (b).

The present paper is a report of a study of the type of acyl exchange involved in reaction (c). It has been found that such an exchange takes place between esters and both 1,3-diketones and β-ketoesters, and in the case of the latter type the reaction seems to have some preparative value.

When the study of this acyl exchange was started it was thought that the reaction might be carried out by treating a mixture of the 1,3-diketone and an excess of the ester with one equivalent of sodium ethoxide and heating the resultant mixture until the reaction was completed as indicated by the cessation of distillation of such low boiling reaction products as ethyl alcohol and ethyl acetate. After numerous experiments, however, it was found that the alkoxide and the temperatures (130–160°) necessary to bring about the desired acyl exchanges were sufficient to cause the ester (*e. g.*, ethyl benzoate) that was used, to undergo such a considerable amount of the reverse Tischtschenko and consequent reactions[1] that the extent and nature of the acyl exchange reactions were obscured. For this reason, it was found desirable to prepare the sodium enolates of the 1,3-diketones and the β-keto-esters and allow these salts to react with the esters. With this less basic reactant the acyl exchanges in most cases proceeded quite satisfactorily.

The esters and the 1,3-diketones that were studied, together with the reaction conditions and the results obtained, are summarized in Table I. A sufficient excess of the ester, R″COOEt, was used in each case to form a fairly homogeneous reaction mixture at the temperature at which the reactions were run. With the exception of the one in run 6, the reaction temperatures in Table I are temperatures at which the reactions started, as evidenced by distillation of R′COOEt, and were taken in the vigorously stirred reaction mixture. As the reaction proceeded and the ester R′COOEt, together with some ethyl alcohol, distilled out, the reaction mixture turned to a pasty solid and the temperature generally had to be raised about 20° above that shown in the table before the distillation of the ester–alcohol mixture was completed. The time required for the reaction in the cases of both the diketones and keto-esters was usually about four hours.

It may be seen in Table I that there is a fairly good correlation between the yields of the exchange products, R′COOEt and $\mathrm{RCOCH_2COR''}$ in the cases that R″ is phenyl and furyl (runs 1, 4 and 5). In runs 2 and 3 a somewhat smaller amount of ethyl acetate (R′COOEt) distilled from the reaction and in each case a mixture of diketones was formed (see footnote *b*, Table I). It is believed that the di-*p*-chlorobenzoylmethane was formed in run 2 by the reverse Tischtschenko and accompanying reactions rather than from an exchange involving the benzoyl and *p*-chlorobenzoyl groups, since in run 7 it is seen that the latter group does not replace the former. It might be thought that these yields should be higher inasmuch as one of the reaction products is removed from the reaction by distillation as rapidly as it is formed, but the solidification of

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[1] Magnani and McElvain, THIS JOURNAL, **60**, 813 (1938).

TABLE I

ACYL EXCHANGE BETWEEN THE SODIUM ENOLATE OF 1,3-DIKETONES AND ESTERS

$$RCOCHNaCOR' + R''COOEt \longrightarrow RCOCHNaCOR'' + R'COOEt$$

| Run | R is | R' is | R" is | Moles R"COOEt per mole of RCOCH₂COR' | Reaction temp., ° C. | % Yield of R'COOEt | % Yield of RCOCH₂COR" |
|---|---|---|---|---|---|---|---|
| 1 | $C_6H_5$ | $CH_3$ | $C_6H_5$ | 4 | 150 | 49 | 48 |
| 2 | $C_6H_5$ | $CH_3$ | $p$-$C_6H_4Cl$ | 4 | 145 | 33 | [b] |
| 3 | $C_6H_5$ | $CH_3$ | $C_6H_5CH_2$ | 4 | 150 | 43[a] | [b] |
| 4 | $C_6H_5$ | $CH_3$ | $C_4H_3O$[c] | 4 | 140 | 51 | 47 |
| 5 | $CH_3$ | $CH_3$ | $C_4H_3O$[c] | 2 | 135 | 72 | 32[d] |
| 6 | $C_6H_5$ | $C_6H_5$ | $CH_3$ | 6 | 125[e] | 0 | 0[f] |
| 7 | $C_6H_5$ | $C_6H_5$ | $p$-$C_6H_4Cl$ | 3 | 180[g] | 0 | 0 |

[a] In addition to ethyl acetate approximately a 40% yield of ethyl benzoate was obtained. This product had to be separated from a small amount of acetophenone and the excess of ethyl phenylacetate that was used in the reaction. [b] In run 2 a mixture of benzoyl-*p*-chlorobenzoylmethane and di-*p*-chlorobenzoylmethane, b. p. 177–185 (1 mm.), was obtained. These were separated by crystallization from petroleum ether, b. p. 90–100°, into a small sample of the former, m. p. 89° [Bradley and Robinson, *J. Chem. Soc.*, 2356 (1926)] and a considerable amount of the dichloro compound, which was compared with an authentic specimen prepared by the procedure in ref. 1 (see Experimental Part). In run 3 no attempt was made to separate the mixture of benzoylphenylacetylmethane and diphenylacetylmethane that was obtained. [c] $\alpha$-Furyl. [d] In addition to the furoylacetone a 34% yield of difuroylmethane was obtained. [e] This reaction was run in a sealed tube and the temperature is that of the bomb furnace. [f] When dibenzoylmethane, ethyl acetate and NaOEt were used in this run there was some apparent exchange as indicated by the isolation of ethyl benzoate and benzoylacetone from the reaction products. However, these products are believed to result from the alcoholysis of the dibenzoylmethane and the condensation of the resulting acetophenone with ethyl acetate. [g] In this run the reactants were heated to the temperature shown and under 60 mm. of pressure to allow any ethyl benzoate that formed to distil.

the reaction mixture as the reaction proceeds undoubtedly removes the sodium enolates from solution and thus prevents the reaction from going to completion. The most striking feature of the data contained in Table I is absence of reaction in run 7. While the acetyl group is readily replaced by the acyl groups of all the esters that were tried (runs 1–5), the *p*-chlorobenzoyl group (run 7) failed to replace the smaller benzoyl group at a temperature much higher than that used for the other exchanges and under sufficiently diminished pressure to allow any ethyl benzoate that might have formed to distil out of the reaction mixture. In this run the original reactants were recovered practically unchanged. The only explanation that can be offered for the failure of ethyl *p*-chlorobenzoate to form di-*p*-chlorobenzoylmethane in run 7 as it did in run 2 is the greater effectiveness of the more basic sodium enolate of benzoylacetone that was present in run 2 in promoting the reverse Tischtschenko and subsequent reactions. It is not surprising that the acetyl group fails to replace a benzoyl group under the conditions that were used in run 6 (*cf.* footnote *f*, Table I).

The results obtained with the $\beta$-keto-esters are summarized in Table II. With the exception of run 3, the various runs of this table were made with a sufficient excess of the ester to ensure homogeneity of the reaction mixture at the tem-

TABLE II

ACYL EXCHANGE BETWEEN THE SODIUM ENOLATE OF $\beta$-KETO-ESTERS AND ESTERS

$$RCOCR'NaCOOEt + R''COOEt \longrightarrow R''COCR'NaCOOEt + RCOOEt$$

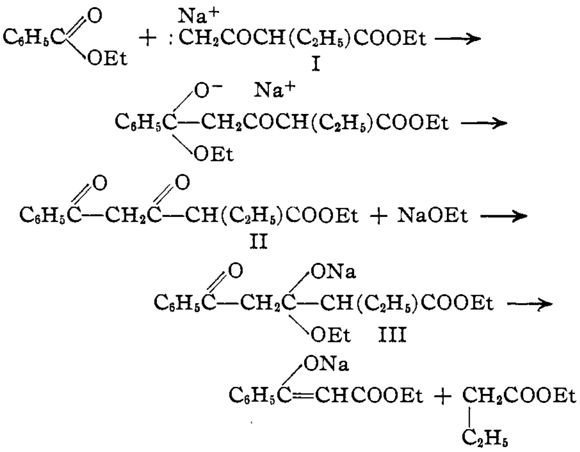
| Run | R is | R' is | R" is | Moles R"COOEt per mole of RCOCHR'COOEt | Reaction temp., ° C. | % Yield of RCOOEt | % Yield of R"COCHR'COOEt |
|---|---|---|---|---|---|---|---|
| 1 | $CH_3$ | H | $C_6H_5$ | 4 | 155 | 51 | 33 |
| 2 | $CH_3$ | H | $C_6H_5$ | 2 | 115 | 56 | 49 |
| 3 | $CH_3$ | H | $C_6H_5$ | 1 | 100 | 46 | 44 |
| 4 | $CH_3$ | $C_2H_5$ | $C_6H_5$ | 2 | 140 | 10[a] | 61[b] |
| 5 | $(CH_3)_2CH$ | $C_2H_5$ | $C_6H_5$ | 2 | 145 | 72 | 50 |
| 6 | $CH_3$ | H | $C_4H_3O$[c] | 2 | 135 | 66 | 38 |
| 7 | $CH_3$ | H | $C_5H_4N$[d] | 2 | 160 | 73 | 4[e] |
| 8 | $C_2H_5O$ | H | $C_6H_5$ | 2 | 135 | 10 | 16 |

[a] The ester distillate was composed of ethyl acetate (10%) and ethyl butyrate (60%). [b] This keto-ester is ethyl benzoylacetate. [c] $\alpha$-Furyl. [d] $\beta$-Pyridyl. [e] The main product of this reaction was a non-distillable tar. This result may be related to the relatively high reaction temperature.

perature at which the reaction started. The reaction temperature has the same significance as it does in Table I, and in general the reactions showed the same behavior.

The extent and the ease of the acyl exchange between the sodium enolate of acetoacetic ester and such an ester as ethyl benzoate suggests the preparative possibilities of this type of reaction. From run 2, Table II, it is seen that ethyl benzoylacetate may be prepared in a quite respectable yield by this reaction. The optimum ratio of ethyl benzoate to the enolate appears to be 2 to 1. With this ratio the reaction starts at a temperature much lower than that of any of the other enolates that have been investigated. The behavior of ethyl furoate and ethyl nicotinate (runs 6 and 7) is interesting. Although the yield of the ester, RCOOEt, which is the most accurate measure of the extent of the exchange reaction, was high in both of these cases, the yield of the corresponding β-keto-ester was lowered (in the case of ethyl nicotinate to practically nothing) by the difficulties encountered in freeing it from the considerable amount of tarry products formed in these reactions. From run 8 it is apparent that the substitution of the malonic ester enolate for that of acetoacetic ester is disadvantageous from a preparative point of view. However, the resistance of the carbethoxy group to replacement enhances the preparative value of the reaction for β-keto-esters since the preferential replacement of the acyl group prevents the contamination of the β-keto-ester that is formed with the 1,3-diketone that would result from the replacement of the carbethoxy group. It would seem, therefore, that an acyl exchange between acetoacetic ester enolate and an ester would be a satisfactory method for preparation of acylacetic esters provided the ester used would have a boiling point sufficiently high to allow ethyl acetate to distil from the reaction mixture.

The behavior of the enolate of α-ethylacetoacetic ester, $CH_3COCNa(C_2H_5)COOEt$, (run 4) is striking. This ester gives as the main products of the exchange ethyl butyrate (60%) and ethyl benzoylacetate (61%) (see footnotes *a* and *b*, Table II). The formation of these products must mean that some sort of an intermediate (II or III), in which the ethyl benzoate is condensed through an acetoacetic ester condensation with the terminal methyl group of the keto-ester, is formed. This intermediate then breaks down into the products that are obtained from the reaction. If the carbanion mechanism[2] is used to explain the formation of the intermediate, the assumption that the anion of I is more prevalent and/or reactive than the isomeric anion, $CH_3COC(C_2H_5)COOEt$, is necessary. The reactions involved in these changes could be represented thus

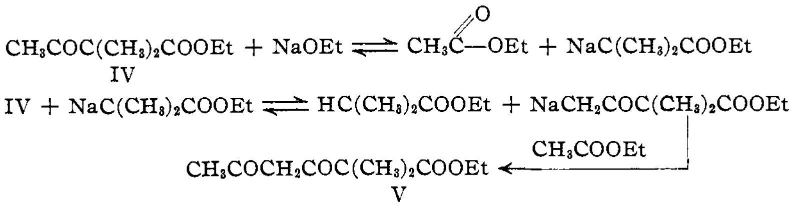


$$C_6H_5C(=O)OEt + {}^{Na^+}:CH_2COCH(C_2H_5)COOEt \ (\text{I}) \longrightarrow C_6H_5C(O^-\,Na^+)(OEt)\text{—}CH_2COCH(C_2H_5)COOEt \longrightarrow$$

$$C_6H_5C(=O)\text{—}CH_2C(=O)\text{—}CH(C_2H_5)COOEt \ (\text{II}) + NaOEt \longrightarrow C_6H_5C(=O)\text{—}CH_2C(ONa)(OEt)\text{—}CH(C_2H_5)COOEt \ (\text{III}) \longrightarrow$$

$$C_6H_5C(ONa){=}CHCOOEt + CH_2(C_2H_5)COOEt$$

Hauser and Hudson[3] recently reported the formation of a compound of type II, ethyl γ-acetyl-α,α-dimethylacetoacetate (V), from the action of sodium ethoxide on ethyl α,α-dimethylacetoacetate (IV). The formation of V was thought to be the result of the reactions



$$\underset{\text{IV}}{CH_3COC(CH_3)_2COOEt} + NaOEt \rightleftharpoons CH_3C(=O)\text{—}OEt + NaC(CH_3)_2COOEt$$

$$\text{IV} + NaC(CH_3)_2COOEt \rightleftharpoons HC(CH_3)_2COOEt + NaCH_2COC(CH_3)_2COOEt$$

$$\underset{\text{V}}{CH_3COCH_2COC(CH_3)_2COOEt} \xleftarrow{CH_3COOEt} NaCH_2COC(CH_3)_2COOEt$$

It should be noted that ester IV carries no α-hydrogen and consequently can enter into an acetoacetic ester condensation only on the terminal methyl group. In contrast to this, the ethyl α-ethylacetoacetate (I) has an α-hydrogen, but in spite of this fact it condenses at the methyl group where much less active hydrogens are present. The behavior of the keto-ester (I) indicates that the acetoacetic ester condensation is more dependent upon the number of hydrogens

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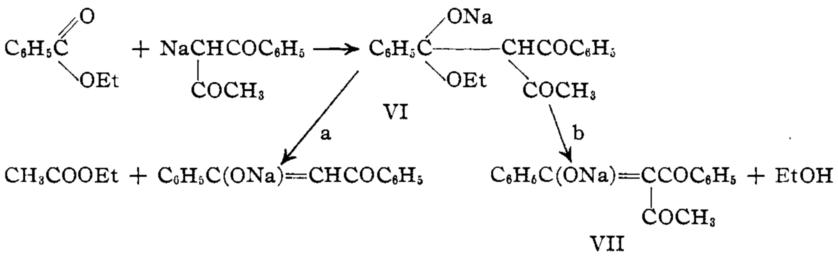
[2] Hauser and Renfrow, This Journal, **59**, 1823 (1937); **60**, 463 (1938).

[3] Hauser and Hudson, *ibid.*, **62**, 62 (1940).

that are present on the carbon that condenses with an ester than it is on the ability of such a hydrogen to enolize.

In run 5 of Table II it is seen that the β-keto-ester, ethyl α-isobutyrylbutyrate, that has a single hydrogen on both the α- and γ-carbon atoms, will exchange an acyl group with ethyl benzoate quite satisfactorily. In this case the isobutyryl group is exchanged, showing that when only a single hydrogen is available any intermediate condensation product that might be formed would be the result of the condensation of the α-carbon (which carries the more active hydrogen and as the enolate would be the expected anionoid center) with the ethyl benzoate.

In most of the acyl exchange reactions listed in Table I considerable alcohol always distilled out of the reaction mixture with the volatile ester. Since the sodium salts that were used had the correct sodium content, this alcohol must have been formed in the reaction. It would seem that its most likely origin is condensation of the reactants to triacylmethane with the resultant formation of alcohol. If the exchange reaction is preceded by the formation of an intermediate such as VI, resulting from the condensation of the enolate carbanion of the 1,3-diketone or β-keto-ester with the ester, it is conceivable that such an intermediate could decompose in two different ways, (a) to form the products of the exchange reaction and (b) into alcohol and a triacyl methane (VII). To illustrate with ethyl benzoate and benzoyl acetone



All attempts to isolate such a triacylmethane from the reactions studied were unsuccessful. Whether or not compounds of type VII were present in the reaction mixture and were hydrolyzed into the diacyl compound and the salt of an acid when the mixture was worked up cannot be definitely stated, but it was found in the few cases that the attempt was made that acids roughly equivalent to the alcohol that distilled from the reaction mixture could be separated from the products of the reaction.

Hauser and Hudson[3] have reported what appears to be an acyl exchange between ethyl isobutyrate and ethyl benzoyldimethylacetate with the formation of ethyl benzoate and ethyl isobutyrylisobutyrate. This reaction proceeds in the presence of sodium ethoxide and triphenylmethane at ordinary temperatures, and was quite satisfactorily explained by these investigators as a series of forward and reverse acetoacetic ester condensations. The exchanges that are reported in the present paper seem to require an intermediate condensation product such as VI or in the special case of ethyl α-ethylacetoacetate an intermediate of type III. The postulation of type VI is the most reasonable explanation of the alcohol that distills with the volatile ester from the reaction mixture, while some such intermediate as III seems absolutely necessary to account for the fact that ethyl butyrate rather than ethyl acetate or alcohol is the main distillate of run 4, Table II.

## Experimental

**Materials Used.**—The esters, ethyl benzoate, ethyl *p*-chlorobenzoate, ethyl phenylacetate, ethyl furoate, ethyl nicotinate, ethyl acetoacetate, ethyl ethylacetoacetate and diethyl malonate that were used were either purified commercial products or were prepared by standard methods described in the literature and boiled over a one degree range.

Diacetylmethane, b. p. 135–136°, was prepared by a standard procedure.[4] Benzoyl acetone, b. p. 90–92° (1 mm.), m. p. 58–58.5°, was prepared by the method of Meerwein.[5] Dibenzoylmethane, b. p. 140–142° (1 mm.), m. p. 78–78.5°, was prepared by the procedure of Magnani and McElvain.[6]

**Ethyl isobutyryl-*n*-butyrate** was prepared from α-isobutyryl-*n*-butyronitrile by a modification of the procedure described by Kroeker and McElvain[7] for the preparation of ethyl isobutyrylacetate. The α-isobutyryl-*n*-butyronitrile was obtained in 33% yield from ethyl isobutyrate and *n*-butyronitrile. It boiled at 89–90° (11 mm.); $n^{25}_D$ 1.4277; $d^{20}_4$ 0.9198.

*Anal.* Calcd. for $C_8H_{13}ON$: N, 10.07. Found: N, 9.93.

Instead of isolating the imino-ether hydrochloride of this nitrile it was directly refluxed on a steam-bath for three to four hours in a solution of 120 g. of concentrated sulfuric acid in 120 ml. of absolute alcohol. The resulting solution was cooled, poured into 200 ml. of water and the aqueous

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(4) *Org. Syntheses*, **20**, 6 (1940).

(5) Meerwein, *J. prakt. Chem.*, **141**, 149 (1934).

(6) Magnani and McElvain, THIS JOURNAL, **60**, 813 (1938).

(7) Kroeker and McElvain, *ibid.*, **56**, 1171 (1934).

solution extracted with three 300-ml. portions of ether. The ether extract was washed with a saturated solution of sodium bicarbonate, dried over sodium sulfate and the ether removed by distillation. The residue, on distillation under diminished pressure, yielded 82 g. (46% based on the nitrile) of ethyl $\alpha$-isobutyryl-$n$-butyrate, b. p. 105–107° (18 mm.); $n^{25}\text{D}$ 1.4239; $d^{20}{}_4$ 0.9480.

*Anal.* Calcd. for $C_{10}H_{18}O_3$: C, 64.53; H, 9.67. Found: C, 64.20; H, 9.81.

The hydrolysis of ethyl $\alpha$-isobutyryl-$n$-butyrate with 5% sodium hydroxide at room temperature for four hours yielded, after acidification and distillation, propyl isopropyl ketone,[8] b. p. 132°; m. p. of the semicarbazone, 117–118°.

**Sodium Enolates of 1,3-Diketones.**—To a solution of 23 g. of sodium in 350 ml. of absolute alcohol in a 2-liter 3-necked flask equipped with a stirrer and reflux condenser was added 1.05 mole of the diketone. The alcohol was then removed under diminished pressure with the application of sufficient heat to keep the mixture at 25°. When the mixture became a pasty mass it was treated with 500 ml. of absolute ether and filtered with suction. After drying in the air for one-half hour the last traces of alcohol and ether were removed by heating the salt in an oil-bath at 130° under diminished pressure. These salts showed the correct sodium content on analysis.

**Reaction of Esters with Sodium Enolates of 1,3-Diketones.**—One mole of the sodium salt of the diketone and the quantity of ester indicated in Table I were placed in a 1-liter 3-necked flask equipped with a stirrer, thermometer and an 8-cm. still head attached to a condenser set for downward distillation. The mixture was heated in an oil-bath until no more distillate came over. The reaction started at the temperature shown in Table I, and generally about four hours were required to complete it. During this time the reaction mixture changed from a homogeneous solution to a pasty solid and the temperature usually had to be raised about 20° above that shown in Table I before the distillation of the volatile reaction products was completed. This distillate upon fractionation yielded, in runs 1–5, a mixture of ethyl acetate and alcohol boiling at 70–78°. The amounts of ethyl acetate shown in Table I were determined by the saponification of an aliquot of these mixtures. The product in the reaction flask was then cooled, dissolved in 500 ml. of water, acidified with 10% sulfuric acid and the insoluble ester layer taken up in ether. The remaining aqueous layer was extracted with three 100-ml. portions of ether. The combined ether extracts were shaken with a saturated solution of sodium bicarbonate to remove the carboxylic acids. From this extract the acids corresponding to the esters used in the reaction could be recovered by acidification. After drying, the ether was removed from the ether extracts and the residue fractionated carefully through a 15-cm. modified Widmer column. After the excess of the reacting ester had distilled out the starting diketone and the one formed in the acyl exchange came over in well defined solid fractions.

In the case of the reaction of the sodium enolate of dibenzoylmethane with ethyl acetate (run 6, Table I) 0.25 mole of the salt and 1.5 mole of ethyl acetate were sealed in a glass bomb tube and heated at 125° for four hours in a bomb furnace. After this time the tube was opened and the reaction mixture worked up as described above. As shown in Table I no exchange occurred and the original reactants were recovered. However, when this run was carried out as described above but with 0.25 mole of sodium ethoxide added to the reactants an 18% yield of benzoyl acetone was obtained when the reaction mixture was worked up. The ethyl benzoate fraction contained some acetophenone and acetoacetic ester.

**Di-*p*-chlorodibenzoylmethane.**—In run 7, Table I, this compound was isolated from the mixture of diketones by recrystallization from petroleum ether (b. p. 90–100°). This compound was compared to an authentic specimen prepared by heating a mixture of 23 g. (0.3 mole) of sodium ethoxide and 280 g. (1.5 mole) of ethyl *p*-chlorobenzoate at 160–180° for one hour. The reaction mixture was worked up as previously described for dibenzoylmethane.[1] The yield of the diketone was 75% of the theoretical based on unrecovered ester. The product after recrystallization from methyl alcohol melted at 158–159°.

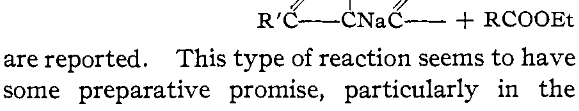
*Anal.* Calcd. for $C_{15}H_{10}O_2Cl_2$: C, 61.47; H, 3.41. Found: C, 61.67; H, 3.80.

**Sodium Enolates of $\beta$-Keto-esters.**—To a solution of 23 g. of sodium in 325 ml. of absolute alcohol in a 500-ml. 3-necked flask fitted with a stirrer, a dropping funnel and a condenser for distillation, was added, over a period of twenty minutes and with stirring, a mole of the $\beta$-keto-ester (or malonic ester). The temperature of the alcohol solution was not allowed to rise higher than 25° during this addition. The alcohol was then removed under diminished pressure at 25°. When about one-half of the alcohol had been removed the mixture became so solid that the stirring had to be discontinued. At this point the salt was heated on the steam-bath under diminished pressure until it appeared dry and then heated for an additional hour at 100° under 2 mm. pressure produced by an oil pump. The salt thus prepared was allowed to cool under this diminished pressure.

**Reaction of Esters with Sodium Enolates of $\beta$-Keto-esters.**—The flask containing the sodium salt as prepared in the preceding section was fitted with a thermometer, a stirrer and an 8-cm. still head attached to a condenser for distillation. The ester was added to the salt and the mixture heated until reaction started (Table II). These reactions required about the same time (four hours) to complete the distillation of the volatile ester as did those with the 1,3-diketones. The resulting reaction mixtures were worked up in the same manner as described above for the 1,3-diketones.

## Summary

A number of acyl exchanges between esters and the sodium enolates of 1,3-diketones and $\beta$-keto-esters according to the reaction



$$\mathrm{R\overset{O}{\overset{\|}{C}}—\overset{|}{C}Na—\overset{O}{\overset{\|}{C}}— + R'COOEt \longrightarrow R'\overset{O}{\overset{\|}{C}}—\overset{|}{C}Na\overset{O}{\overset{\|}{C}}— + RCOOEt}$$

are reported. This type of reaction seems to have some preparative promise, particularly in the cases of the $\beta$-keto-esters.

Although it has not been possible to isolate any

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(8) Meerwein, *Ann.*, **419**, 138 (1919).

intermediate product, evidence is presented to show that these acyl exchanges are preceded by the formation of some sort of a triacyl complex as the result of an acetoacetic ester type of condensation. Through the decomposition of such a complex the various products obtained from the reaction are explained.

MADISON, WISCONSIN RECEIVED MAY 16, 1941

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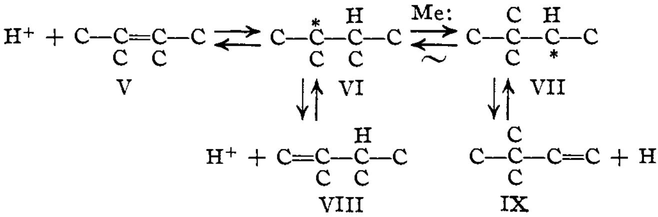
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

# The Polymerization of Olefins. VI.[1] The Dimers Obtained from Tetramethylethylene. Preliminary Paper[2]

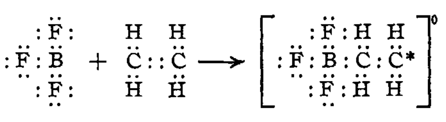
BY FRANK C. WHITMORE AND PAUL L. MEUNIER[3]

The present work was undertaken to throw further light on the mechanism of the polymerization of olefins by acid catalysts.[1,5]

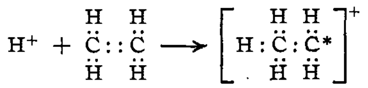
Brunner and Farmer in 1937[4] published their results on the action of boron trifluoride on tetramethylethylene to form 2,2,3,5,6-pentamethyl-3-heptene and a trimethylheptylethylene. These authors[4] discussed various theories of polymerization and concluded that the products were best explained by the Whitmore mechanism.[5] Although the work on tetramethylethylene has been continued, little has been added to the problem as it stood in 1936. Consequently we are now reporting on it although it is still incomplete. Tetramethylethylene was polymerized with 80% sulfuric acid. The dimer mixture was distilled and ozonized. Identified were pinacolone, methylisopropylacetaldehyde, acetone, methyl neopentyl ketone, trimethylacetaldehyde, 3,5,5-trimethyl-2-hexanone, formaldehyde and dineopentyl ketone roughly in that order of decreasing abundance. Our work confirms the formation of 2,2,3,5,6-pentamethyl-3-heptene (I) as found by Brunner and Farmer.[4] We proved their other product to be 2,3,4,6,6-pentamethyl-2-heptene (II). We also found 2,2,4,6,6-pentamethyl-3-heptene (III) and the closely related isomer 1,1-dineopentylethylene (IV). Of these four products the percentages in the dimer were about 50, 10, 25 and 0.2, respectively. No product was found which was directly related to the starting material through the simple application of the Whitmore mechanism.[5] In each case rearrangement apparently took place both before and after the initial addition of a positive activated fragment to an olefin.[5] As was shown earlier[6] tetramethylethylene with an acid catalyst comes to equilibrium with its related isomers



Boron trifluoride[4] functions exactly like the proton from the acid catalyst by adding to one electron pair of the double bond and making the other carbon of the ethylene grouping electronically deficient as indicated by the asterisk. This deficiency can be overcome by the migration of an electron pair with the attached methyl group or proton (Me: ∼ or H: ∼) or by the migration of an electron pair to form a double bond with the liberation of a proton (loss H+).[7] It should be



noted that this activated complex is electrically neutral in spite of its electronically deficient carbon, whereas the activated fragment formed from an olefin by the addition of a proton from the catalyst has an electronically deficient carbon and is electrically positive.



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(1) V, THIS JOURNAL, **63**, 2035 (1941).

(2) Presented at the Pittsburgh meeting of the American Chemical Society, 1936.

(3) Full details are available in the Ph.D. Thesis, 1936, on file in the College Library, Willard P. Lewis, Librarian.

(4) Brunner and Farmer, *J. Chem. Soc.*, 1039 (1937).

(5) Whitmore, *Ind. Eng. Chem.*, **26**, 94 (1934).

(6) Laughlin, Nash and Whitmore, THIS JOURNAL, **56**, 1395 (1934).

(7) *Cf.* ref. 4 and Whitmore, *ibid.*, **54**, 3274 (1932); *cf.* Hunter and Yohe, *ibid.*, **55**, 1248 (1933).