

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Mechanism of the Reactions of Metal Enol Acetoacetic Ester and Related Compounds. II. Sodium Enolates toward Acyl Chlorides

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Claisen and Haase¹ found that O-acetylacetoacetic ester reacts with sodium enol acetoacetic ester at the boiling point of ether to form sodium enol diacetoacetic ester. On the basis of this observation, they suggested as an explanation for the C-acylation of sodium enol acetoacetic ester that O-acetylacetoacetic ester is primarily formed and is subsequently converted by unchanged sodium ester into sodium enol diacetoacetic ester.

Although this interpretation has been generally accepted,² Elion³ had previously concluded from experimental results that acetyl chloride acts upon sodium enol acetoacetic ester in ether solution to form mainly free diacetoacetic ester. In order to gain a better insight into the mechanism of these reactions, and to determine definitely whether a free C-acyl derivative or its sodium derivative is formed, we have investigated the reaction of acetyl and benzoyl chloride upon sodium enol acetoacetic ester semi-quantitatively.

In our experiments, ether suspensions of the sodium ester were added slowly at low temperatures to vigorously stirred ether solutions of the chlorides, excepting experiments V and IX, in which the compounds were added in inverse order and at room temperature. The precipitates were filtered off and their composition determined separately. The experimental data with acetyl chloride are listed in Table A.

There is no evidence from Experiments I, II and IX that acetyl chloride alters the quantitative course of the reaction by mass action.⁴ The

(1) Claisen and Haase, *Ber.*, **33**, 3778 (1900).

(2) See, *e. g.*, (a) Hüchel, "Theoretische Grundlagen des organischen Chemie." 1931, Vol. I, p. 181, who believed it saved the conception of sodium acetoacetic ester as enolate; somewhat further on is stated (p. 229) that only an examination of the reaction velocity of an assumed intermediate substance can determine whether or not it is formed in the course of the reaction. Hüchel evidently overlooked that the properties of the supposed intermediate, O-acetylacetoacetic ester, do not comply with this requirement, and that this was the main reason why Dieckmann [(b) *Ber.*, **37**, 3394 (1904)] and Michael [(c) *ibid.*, **38**, 2084 (1905)] rejected the interpretation.

(3) Elion, *Rec. trav. chim.*, **2**, 34, 202 (1883); **3**, 248, 254 (1884). Only a "small excess" of acetyl chloride was used; the later results of Claisen, Dieckmann and Michael are not pertinent, because the chloride was in excess and water was added. James, *Ann.*, **226**, 211 (1884), used the theory of the chloride and obtained free diacetoacetic ester on working up the products without using water.

(4) This may be explained by assuming the reaction proceeds by decomposition of a "polymolecule," whose intermolecular structure [see preceding paper] is independent of the amount of acetyl chloride

amount of free diacetoacetic ester in the filtrates of I and II was practically the same and the unused chloride in II and III accounts for 74 and 79%, respectively, of the excess used over that in I. The acetoacetic and diacetoacetic esters in the filtrates of Experiments I and II were separated by repeated fractionation before converting the esters into their respective copper derivatives. Considerable mechanical losses were involved in the fractionation; accordingly the amount of regenerated acetoacetic ester in these experiments is less than in Experiment III, in which the esters were partially separated by one fractionation and then precipitated with aqueous copper acetate as copper derivatives. Copper enol diacetoacetic ester separates immediately, since it is not acted upon by dilute acetic acid, whereas copper enol acetoacetic ester separates only after the mixture is neutralized. By separating the esters in this manner, 76% of the calculated amount of regenerated acetoacetic ester was recovered in Experiment III. O-Acetylacetoacetic ester was not detected in these experiments, but its absence cannot be due to interaction with the sodium ester, since during the time of reaction (one and one-half hour, respectively) the temperature was maintained between -26 and -15° , and it was shown^{2c} that the compounds do not act perceptibly upon each other, even at room temperature during an hour.

The decomposition of such polymolecules would be unimolecular. Similar results have been obtained in a number of other reactions, *e. g.*, the action of bromine on acetone. Since the reaction velocity is not only proportional to the concentration of ketone, but also to that of the catalyzing acid, and is independent of the amount of the halogen, it is assumed that the reaction proceeds through slow enolization of the ketone, rapid addition of halogen to the formed enol and halogen hydride elimination from the addition product [Lapworth, *J. Chem. Soc.*, **85**, 30 (1904)]. In opposition to this interpretation, Rice and Fryling [THIS JOURNAL, **47**, 379 (1925)] found that homologs of acetone undergo bromination faster than acetone, and Cohen [*ibid.*, **52**, 2827 (1930), literature in this paper] that the addition of water to dry acetone and bromine greatly retards the reaction. The enolization viewpoint is also advanced to explain α -bromination of aliphatic acids, notwithstanding the experiments of Hell and Mühlhäuser [*Ber.*, **11**, 244 (1878); **12**, 731 (1879)], which showed that the primary products are polymolecules of acid, bromine and hydrogen bromide, and though Michael and Garner [*ibid.*, **34**, 4046 (1901)] showed that chlorination and, partially, bromination of acyl chlorides gave results quite opposed to the enolization assumption [literature in *ibid.*, **46**, 135 (1913)]. All the qualitative and quantitative results in the above reactions accord with the interpretation that they take place primarily with formation of polymolecules of the interacting compounds.—A. M.

TABLE A

35 g. of sodium ester used in each experiment. NaCl determined as AgCl, using 1 and 2 g. samples of precipitate for the analysis. Difference between weight of total solid and sodium chloride accepted as sodium enol diacetoacetic ester. Yields of acetoacetic and diacetoacetic esters based on amount of esters isolated as copper derivatives. Total weight of solids plus weight of crude products from filtrate divided by combined weights of materials used given as materials accounted for in per cent. Unused acid chloride determined as AgCl. Quantitative data on the experimental loss in several of the operations are given under "Experimental."

Experiment	I	II	III	IV	V	
Molecular proportions	1 Na ester to 1 chloride	1 Na ester to 1.5 chloride	1 Na ester to 3 chloride	2 Na ester to 1 chloride	1 Chloride to 2 Na ester	
Time of addn., minutes	60	35	30	20	2	
Temp., °C.	-26-18	-20-15	-25-15	-20-15	36	
Total solid, g.	18.2	14.9	16.0	28.6	28.2	
Sodium chloride	Calcd., g.	13.6	13.6	6.8	6.8	
	Found, g.	..	13.7	13.6	6.7	6.9
Diacetoacetic ester from ppt.	Calcd., g.	4.1	1.1	2.1	19.8	19.8
	Found, g.	2.3	..	0.9	11.8	14.9
Diacetoacetic ester in filt., g.	18.9	16.3	17.0	0.4	None	
Acetoacetic ester in filtrate	2.5	1.1	3.8	9.4	10.1	
O-Acetylacetoacetic ester, g.	None	None	None	..	1.4	
O-Acetyldiacetoacetic ester, g.	7.0	7.1	5.6	1.0	None	
Materials accounted for in %	98.2	93	89	97	95.7	
Unused chloride in %	None	74	79	

On the other hand, O-acetyldiacetoacetic ester⁵ was found in the filtrates of experiments I and II in almost the same amounts, and somewhat less in III, although from the usual conception of mass action the amount should have been somewhat greater. This O-acetate was undoubtedly formed by the action of the chloride upon sodium enol diacetoacetic ester and the latter by the action of the decidedly acidic enol diacetoacetic ester upon unchanged sodium enol acetoacetic ester.

In Experiment IV, two moles of the sodium ester were added to one mole of the chloride. Free diacetoacetic ester practically disappeared to be replaced by sodium enol diacetoacetic ester. A much smaller proportion of the sodium enol diacetoacetic ester was converted into O-acetyldiacetoacetic ester in Experiment IV than in the first three experiments. Partially, this may be due to the slower rate of addition in the first experiments, but the lower concentration of acetyl chloride in Experiment IV may be a factor also. The chloride reacts more rapidly on sodium enol acetoacetic ester than on sodium enol diacetoacetic ester and, since the latter is formed continuously in the presence of a decreasing amount of acetyl chloride, relatively little O-acetyldiacetoacetic ester is formed in the reaction. The reagents were used in the same proportion in Experiment V, but with the order of addition reversed. Diacetoacetic ester, because it reacts quickly upon unchanged sodium ester, appeared

(5) Claisen and Haase, *Ber.*, **33**, 1244 (1900).

in the precipitate as the sodium derivative and the corresponding amount of free acetoacetic ester was recovered from the filtrate. Peculiar to this experiment, is the formation of some O-acetylacetoacetic ester. The temperature of the reaction mixture reached the boiling point of ether in this case and it appears that heat is essential for O-acylation.⁶

Elion³ concluded from his experiments that the main product of the above reaction is diacetoacetic ester, but also observed the formation of some sodium enol diacetoacetic ester. He believed that the latter was converted by the acetyl chloride into free diacetoacetic ester, because the products obtained on boiling these compounds in ether solution for an hour were free diacetoacetic ester and sodium chloride.⁷ Recently, Seidel⁸ stated that acetyl chloride and sodium enol diacetoacetic ester do not interact even at 200°. We found, however, that acetyl chloride reacts on the sodium ester in ether suspension at room temperature, or in acetic ester solution at -15°, to give O-acetyldiacetoacetic ester in yields of 85 and 90%, respectively.

The products formed in the reaction of benzoyl

(6) The higher temperature, and the use of a large excess of acetyl chloride, may account for the formation of the small amount of the O-acetyl derivative in the experiments of Nef [*Ann.*, **266**, 102 (1891)]. This result is directly opposed to that expected from Claisen's interpretation.

(7) This result must have been caused by access of moisture, or by water in the enolate. Further, the O-acetyldiacetoacetic ester formed may have decomposed during distillation at insufficiently reduced pressure.

(8) Seidel, *Ber.*, **65**, 1205 (1932).

TABLE B

Twenty-five grams of sodium ester used in each experiment. Difference between total weight of solid and sodium chloride calculated for complete reaction accepted as sodium enol benzoylacetacetic ester. Difference in weight of low boiling fraction in distillate less the weight of recovered benzoyl chloride computed as acetoacetic ester. Materials accounted for calculated as in Table A. Recovered chloride determined as AgCl. Acetic ester solution of sodium ester added to the chloride in Experiment VIII.

Experiment	VI	VII	VIII	IX
Molecular proportions	1 Na ester to 1 chloride	1 Na ester to 1.5 chloride	2 Na ester to 1 chloride	1 Chloride to 2 Na ester
Time of addition, minutes	15	22	40	0.5
Temperature, °C	-24-15	-22-15	-20-15	36
Total solid, g	13.2	12.4	24.5	25.5
Benzoylacetacetic ester from ppt.	Calcd., g	2.6	19.3	19.3
	Found, g	3.7	2.4	17.1
Benzoylacetacetic ester in filt., g	25.4	25.8	0.3	..
Acetoacetic ester in filt., g	3.0	1.7	8.3	8.8
O-Benzoylacetacetic ester, g	2.4	3.7	1.0	None
Materials accounted for in %	98.5	98.3	93.7	96.5
Recovered chloride in %	11.2	39.3

chloride upon sodium enol acetoacetic ester can be much better separated from each other by fractionation than those obtained with acetyl chloride and can be thus isolated practically quantitatively. The data obtained are given in Table B.

The results obtained in Experiments VI and VII correspond with those in I and II in which acetyl chloride was used, except that the O-acylated esters appear in a smaller and unused acyl chloride in a larger proportion; the latter results agreeing with the smaller reaction velocity of benzoyl chloride. Since benzoyl is decidedly a more negative radical than acetyl, the free chemical energy of sodium in sodium enol benzoylacetacetic ester is better neutralized than in sodium enol diacetacetic ester and for this reason the sodium derivative of the former ester has less tendency to react with acyl chlorides, especially with the slowly acting benzoyl chloride.⁹ Accordingly, in Experiments VI and VII, although sodium enol benzoylacetacetic ester was formed quickly, it was acted upon relatively slowly by benzoyl chloride. On the other hand, acetyl chloride in Experiments I, II and III quickly converted the sodium enol diacetacetic ester into O-acetyldiacetacetic ester, with the result that a lower ratio of diacetacetic ester to its sodium derivative and a larger proportion of O-acetyl derivative was obtained.

In Experiment VIII, two moles of sodium ester were added to one of the chloride and benzoyl-

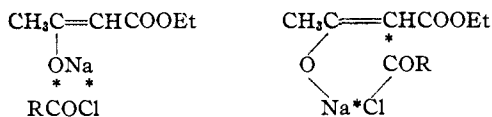
(9) Michael and Ross [THIS JOURNAL, **53**, 2394 (1931); **54**, 387 (1932)] proved that the facility of alkylation and acylation of sodium enolates depends to an extraordinary extent upon the degree of neutralization of the sodium in the enolates examined.

acetoacetic ester appeared almost exclusively as sodium derivative. The result is analogous to that obtained with acetyl chloride in Experiment IV. Likewise, the results of the analogous Experiments IX and V are similar, except that a small amount of O-acetyl-, but no O-benzoyl-acetoacetic ester, was obtained, which is explained by the relative inertness of benzoyl chloride.

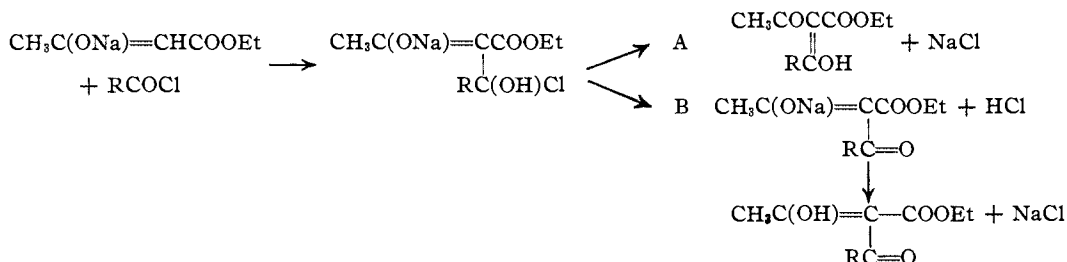
The normal action of acetyl and benzoyl chlorides on sodium enol acetoacetic ester appears most clearly in Experiments I and VI, in which the conditions best subordinate the formation of secondary products. It is evident from the results, that, although the primarily formed free diacetylacetic esters act upon unchanged sodium enol acetoacetic ester at the low temperatures of the experiments to yield a small proportion of the corresponding sodium derivatives, the primary products must be solely free diacetylacetic esters. *The experimental proof that C-diacetylacetic esters are the primary and almost exclusive organic products in these reactions rigorously demonstrates the untenability of the Claisen interpretation, according to which sodium enol diacetylacetic esters, not the free esters, should be the main reaction products.*

Notwithstanding the extensive investigation of the reaction of acyl chlorides upon sodium enol acetoacetic ester, and related enolates, the mechanism of the reaction remains obscure. The reaction is usually conceived as occurring with direct separation of the halogen and acyl group of acyl chloride and thus should take place through the following, intermolecular stereo-structures¹⁰

(10) See preceding paper for this manner of representation and for literature.



This course would lead to O- or C-acylation, or a mixture, and our knowledge of the respective affinity and energy values determining the maximum degradation of the chemical energy does not permit of a decision as to which mode of reaction would be favored. However, Pawlow¹¹ proved experimentally that zinc ethyl acts primarily upon acetyl chloride not by direct union of the chlorine



and zinc, notwithstanding the developed affinity for each other, but by addition of the ZnEt and Et of the zinc ethyl to the unsaturated O and C of the carbonyl, *i. e.*, to form $\text{CH}_3\text{C}(\text{OZnEt})(\text{Et})\text{Cl}$. The acyl halide-enolate reactions involve similar affinity and energy relations and there can be no doubt that in them, and in all corresponding reactions, it is the atoms of the unsaturated group, not the halogen, that function in the primary chemical phase. Further, it has been shown experimentally that sodium enol acetoacetic ester, and similar enolates, react with phenyl isocyanate, not by migration of the sodium, but by the α -hydrogen passing over to the oxygen of the carbonyl group of the reagent, with formation of a C-addition product.¹² The metal remains, there-

(11) Pawlow, *Ann.*, **188**, 104 (1877); Michael, *J. prakt. Chem.*, **60**, 418 (1899); *Ber.*, **38**, 2084 (1905). Later Staudinger and Kon [*Ann.*, **384**, 38 (1911)] came to the same conclusion from certain ketene reactions.

(12) Michael, *Ber.*, **38**, 22 (1905); Michael and Cobb, *Ann.*, **363**, 64 (1908). The migration of the metal may occur only when a stable addition product may be formed, in which the energy of the metal is better neutralized than in the original enolate, but as in all other chemical reactions, the "principle of partition" prevails. Hence the proportion of sodium migrating is directly related to the extent of its neutralization in the used and possible addition product. Phenyl isocyanate is extremely energetic, and is very easily polymerized by alkaline material, while the corresponding thio derivative is a relatively mild reagent and polymerizes with difficulty. On the other hand, the metal in all thio salts is far better neutralized than in the corresponding oxygen derivatives. While phenyl isocyanate reacts violently on sodium enol methylmalonic ester, to form some of a well neutralized sodium salt by deep-seated decomposition, and triphenylisocyanurate [Michael, *Ber.*, **38**, 22 (1905)] phenyl isothiocyanate does not polymerize with the enolate and yields 12-15% of the addition enolate, formed by the intermolecular migration of sodium to the sulfur [Ross, *THIS JOURNAL*, **55**, 3672 (1933)]. In sodium enol

fore, *in situ* in the enolate molecule and the further chemical neutralization of the chemical energy in the system is attained by intermolecular migration of the loosely joined hydrogen attached directly to the Δ - α -C of the enolate. This is facilitated further by the unsaturation of the α -C of the ester and through the highly positive state of the metal of the enolate.¹³

From this, experimentally supported, viewpoint, the action of an acyl chloride upon the sodium enolate must lead to the formation of a C-acyl derivative.¹⁴

The formation of a C- or O-acyl derivative from an enolate therefore depends on the extent of neutralization of the metal of the enolate group. If this is well neutralized, then O-acylation should result entirely, or to a more or less extent; if not, a C-derivative should be formed. The experimental facts at hand agree with this viewpoint.

Acetylmalonic and O-acetyl acetomalonic esters¹⁵ are formed in the action of acetyl chloride upon sodium enol malonic ester, but the quantitative proportions of the reaction products have not been determined. We have investigated the reaction semi-quantitatively, following the procedure used with sodium enol acetoacetic ester. The results are tabulated below.

In Experiment X, the precipitate consisted of sodium chloride and a small amount of sodium enol acetylmalonic ester. The filtrate contained considerable malonic and O-acetylacetomalonic esters; in contrast, Experiment XI gave no acetylmalonic ester and but a small proportion of the O-acetyl compound. In Experiment X, the trimethylcyanoacetic ester, the metal is far better neutralized than in the malonic enolate and here the formation of an addition enolate was so small that it escaped detection.

(13) *J. prakt. Chem.*, **60**, 291, Rule VII (1899); *THIS JOURNAL*, **32**, 990 (1910).

(14) Course A is facilitated by spatial nearness (1,6 position) of Na and Cl and appears more probable than B, but it is possible, depending upon the chemical character of R, that the decompositions may occur simultaneously, with B in a smaller proportion.

(15) The latter compound was formerly considered diacetylmalonic ester, but Michael [*Am. Chem. J.*, **14**, 495 (1892); *Ber.*, **38**, 2087 (1905)] and v. Auwers [*ibid.*, **50**, 243 (1917)] proved the enolic structure.

TABLE C

Thirty-four grams of sodium ester used in each experiment. Difference between weight of total solid and sodium chloride, calculated for complete reaction, accepted as sodium enol acetylmalonic ester.

Experiment	X		XI	
	1 Na ester to 1 chloride		1 Chloride to 2 Na ester	
Molecular proportions				
Time of addition in minutes	25		5	
Temperature, °C.	-15-10		36	
Total solid, g.	13.4		26	
Sodium chloride	Calcd., g.	10.4	5.5	
	Found, g.	10.1	..	
Acetylmalonic ester from ppt.	Calcd., g.	2.9	18.5	
	Found, g.	1.6	16.9	
Acetylmalonic ester from filtrate, g.	2.8		None	
Malonic ester recovered, g.	13.2		14.0	
O-Acetylacetylmalonic ester, g.	14.8		0.7	

marily formed acetylmalonic ester reacted with sodium malonic ester to form the sodium enolate in the presence of acetyl chloride in large excess and O-acetylacetylmalonic ester is therefore the main product of the reaction. In XI, acetylmalonic ester is formed in the presence of a large excess of sodium enol malonic ester and the sodium enolate and malonic ester are formed by interaction; O-acetylacetylmalonic ester appears in small amount, as at no period of the reaction does the enolate come in contact with free acetyl chloride.

The structures of sodium enol malonic and sodium enol acetylmalonic esters may be derived from those of the sodium enolates of acetoacetic and diacetoacetic esters by replacing acetyl by the much less negative carbethoxyl group. Accordingly, the sodium in the first two compounds should be less neutralized than in the latter and acetyl chloride should act more easily on the malonic than on the acetoacetic ester enolates. This relation agrees with the larger proportion of O-acetyl compound, formed under similar conditions, in X than in I, and the much smaller proportion of acetylmalonic ester obtained in X than of diacetoacetic ester in I.

Claisen and Haase¹ interpreted the above O-into C-acyl rearrangement as an intermolecular, direct interchange between the O-acyl and the α -H of the enolate.¹⁶ On the other hand, Erlenmeyer, Jr.,¹⁷ from theoretical considerations and

(16) Later [*Ber.*, **36**, 3677 (1903)] in an analogous reaction, they suggested the addition of the NaO— group to the carbonyl of the O-acetyl, so that the sodium united with the oxygen and the residual radical with the α - Δ -C of the enolate. This large molecule rearranged spontaneously to an acylated enolate. See Michael, *ibid.*, **38**, 1931 (1905), for a criticism of this very improbable view.

(17) Erlenmeyer, Jr., *Ann.*, **316**, 77 (1901).

the observation of Wislicenus and Körber¹⁸ that the O-acetyl ester can be converted into diacetoacetic ester by heating to 240°, concluded that the Claisen rearrangement is intramolecular. However, Bouveault and Bongert¹⁹ and Dieckmann and Stein²⁰ were unable to confirm this result and attributed it to the influence of traces of alkaline material from the glass tubes used by Wislicenus. Later, Wislicenus²¹ repeated the experiment, using an acid washed, hard glass tube, and still observed a slight rearrangement (1%), even when the ester was heated in a platinum vessel, enclosed in the glass tube containing some of the O-acetyl ester. We heated the dry and pure O-acetyl ester at 233° (in the vapor of benzyl cyanide) in Pyrex glass tubes, previously treated with acid and then heated to redness, and obtained only unchanged ester and decomposition products: *viz.*, dehydracetic acid, acetic and acetoacetic esters. The data are summarized in Table D.

TABLE D

Experiment	1	2	3
Material distilled, g.	7.7	6.6	6.5
Time heated, hours	2.5	4.5	2.0
Recovered O-acyl ester, g.	0.1	1.5	4.3
Acetic ester, g.	3.0	1.3	None
Copper acetoacetic ester, g.	0.9	0.3	0.2
Dehydracetic acid, g.	0.05-0.1	None	None

It would seem, therefore, that the O-acetyl ester used by Wislicenus contained a trace of a catalyst, perhaps a trace of the pyridine used in its preparation which is difficult to completely remove, or some of the ester contained in the outside tube entered the platinum vessel.

To determine definitely whether an inter- or intramolecular migration was involved, Dieckmann and Stein²² heated equivalent amounts of sodium enol benzoylacetic and O-acetylacetoacetic esters in ether for four and one-half hours. By fractionation of the portion of the reaction product soluble in aqueous sodium carbonate, there was obtained about 36% of the theoretical yield of impure benzoylacetoacetic, with diacetoacetic ester in one-half the quantity. This proved that the O-acetyl group had migrated and that the rearrangement was intermolecular. We have examined the reaction semi-quantitatively, allowing the mixture to stand a week at room tempera-

(18) Wislicenus and Körber, *Ber.*, **34**, 218, 3768 (1901).

(19) Bouveault and Bongert, *Bull. soc. chim.*, [3] **27**, 1168 (1902).

(20) Dieckmann and Stein, *Ber.*, **37**, 3373 (1904).

(21) Wislicenus, *ibid.*, **38**, 546 (1905).

(22) Dieckmann and Stein, *Ber.*, **37**, 3373 (1904).

ture. The solid and the liquid portions of the reaction products were separated, acidified, the esters fractionated and the fractions converted into copper enolates to attain a sharper separation. Benzoylacetoacetic ester neutralizes the free chemical energy of sodium better than diacetoacetic ester, so more of the former should appear as enolate in the reaction; we found that the respective enolates were formed in the ratio of 1.6:1, and that a 86.5% yield of rearranged esters was obtained.

The reaction between liquid O-benzoylacetoacetic ester²³ and sodium enol acetoacetic ester in ether was also examined semi-quantitatively.

ester from the reaction product. We calcined the carbonate in the air and, after heating the above mixture for three hours, obtained results indicating only 14% of rearranged product. Evidently an extremely small content of water in the carbonate must facilitate enormously the rearrangement. The experiment was repeated with O-benzoylacetoacetic ester and 5% benzoylacetoacetic ester was obtained, but when the carbonate was previously heated at a bright red heat, in a current of carbon dioxide, no evidence of a rearrangement could be detected. It would seem, therefore, that the presence of a trace of water is essential for the migration.²⁴

TABLE E

Experiment.....	I	II	IIIa	IIIb	IVa	IVb	V
Reagents {	-acetoacetic ester.....	O-Benzoyl		Potassium carbonate		O-Acetyl	
	-acetoacetic ester.....	Sodium enol	Copper enol				
Solvent.....		Ether		Acetic ester			
Temperature.....	Room	Boiling point					
Time, hours.....	72	0.75	3	3	3	3	3
C-Acyl ester, g.....	8.6	8.0	0	0	0.5	0	0
Acetoacetic ester, g.....	4.2	3.9	0	0	0	0	0
Recov. O-acyl ester, g.....	1.0	1.6	.	9.6	8.5	9.6	7.2
Conversion, %.....	86	80	0	0	5	0	14

Although the enolate is only sparingly soluble in the mixture, after seventy-two hours at room temperature the solid contained 86% of the theory of C-benzoylacetoacetic ester and a further 10% was isolated from the filtrate, along with 75% of the theory of acetoacetic ester. After warming the mixture for forty-five minutes, practically the same result was obtained.

Benzoyl chloride acts upon copper acetoacetic ester at room temperature to yield a mixture of O- and C-benzoylacetoacetic esters. This may seem to support Claisen's interpretation of primary O-acyl ester formation. We found, however, that the O-benzoyl ester and the copper enolate in ether suspension, or in acetic ester solution, may be heated for hours without undergoing chemical change, and the benzoyl chloride reaction is, therefore, further evidence against Claisen's viewpoint.

Claisen and Haase¹ warmed O-acetylacetoacetic ester in acetic ester solution with "absolutely dry" potassium carbonate for one and one-half hours and isolated about 50% of diacetoacetic

(23) Obtained by treating acetoacetic ester with benzoyl chloride in the presence of pyridine. This compound is stereomeric with the known solid form obtained from copper acetoacetic ester and benzoyl chloride. It appears to rearrange faster to C-benzoylacetoacetic ester than the solid form. Details will be given in a later paper.

Sodium enol acetoacetic ester adds very readily to α,β - Δ -esters and, as O-acyl acetoacetic esters belong to that type, the addition reaction seemed probable. However, the energy and affinity relations in the above chemical systems are also extremely favorable for a facile intermolecular migration. The chemical hindrance to the migration of the α -H of the enolate is slight, since the affinity between it and the attached carbon has been greatly reduced by the developed, positive character of the sodium atom, as is also, in the O-acyl ester, that between the O-acyl and the oxygen joined to it, owing to the relatively negative character of the latter atom. The chemical momentum is connected with the far greater capacity of enolic C-diacylacetic esters than mono-acyl derivatives to neutralize the chemical energy of the metal. This effective neutralization in the diacyl esters is the main reason why the reaction takes place by migration and not by addition. R in the addition product $\text{CH}_3\text{C}(\text{ONa})=\text{C}(\text{R})\text{COOEt}$ would be $\text{CH}_3\overset{\text{I}}{\text{C}}(\text{R})\text{CH}_2\text{COOEt}$ and RCO^- in the product of migration. The energy of the sodium

(24) Contrary to Claisen, *Ber.*, **27**, 3182 (1894), potassium carbonate, well calcined in air, is quite inert toward dry mixtures of acyl chlorides and ketones containing an aliphatic hydrocarbon radical, but addition of a drop of water immediately starts the reaction [Michael, *Ann.*, **390**, 54 (1912)].

is evidently much better neutralized in the latter than in the former enolate, and this should determine the maximum energy degradation.²⁵

That, however, the acyl group in an O-acyl acetoacetic ester under powerful positive influence may migrate intramolecularly is shown by the behavior of liquid O-benzoyl acetoacetic ester toward metallic sodium. The ester, in benzene solution, slowly reacts with the metal, with conversion into a yellow solid and with evolution of hydrogen. From the yellow solid, 57% of O-benzoyl acetoacetic ester was isolated, along with 2% of acetoacetic ester. The mechanism of this reaction can hardly be interpreted otherwise than that the affinity of the sodium for the β -oxygen of the ester expels the α -hydrogen, similarly as has been shown experimentally in the action of the metal on malonic ester derivatives.²⁶ With the metal taking the place of the benzoyl and the latter that of the expelled α -H, the maximum energy degradation of the system is attained by formation of the almost neutral sodium enol benzoyl acetoacetic ester.

Experimental

(a) General Procedure

The apparatus used, when the acyl chloride was added to the sodium ester, consisted of a 500-cc. 3-necked flask equipped with a mechanical stirrer, dropping funnel and a T-tube provided with a thermometer and a calcium chloride tube. A similar apparatus was used in Experiment VIII, in which a solution of the sodium ester in acetic ester (dried by final distillation from sodium) was added to a cold acetic ester solution of benzoyl chloride. The reaction mixture was diluted with 300 cc. of ether and the usual procedure then followed. The apparatus used in the other experiments and the general operation was as follows. A 500-cc. 3-necked flask, provided with a thermometer and a mechanical stirrer, was connected by a 10-mm. tube to the bottom of an ice-jacketed flask, which could be opened or closed at the bottom by means of a rubber plug attached to a glass rod passing through a rubber slip-joint at the top of the flask. The dry sodium enol acetoacetic ester (35 g. in Experiments I-V; 25 g. in Experiments VI-IX) was suspended in 200-250 cc. dry ether in the ice-jacketed flask and added slowly to the ether solution of the acid chloride, kept cold by an ice-hydrochloric acid bath. The reaction mixture was stirred for one-half to one and one-half hours after the final addition, the precipitate allowed to settle for one to three hours (except Experiment VIII, which required six hours) at the low temperature, and the supernatant liquid siphoned off. The solid was collected on a filter and

washed with ether, which was combined with the siphoned liquid. The ether was distilled off and the residual oil fractionated. Acetoacetic and diacetoacetic esters could not be separated completely by fractionation, but were partially separated in this way and the fractions then treated with a saturated copper acetate solution. Copper enol diacetoacetic ester precipitated at once and was filtered off. Copper enol acetoacetic ester was precipitated from the filtrate on neutralizing with dilute ammonia.²⁷ Owing to the considerable difference in the boiling points, the liquid products of Experiments VI-IX could be separated readily by fractionation.

(b) Action of Acetyl Chloride on Sodium Enol Acetoacetic Ester

(I) One Mole of Sodium Ester Added to 1 Mole of Chloride.—Acidification of total solid (18.2 g.) gave 4.5 g. of an oil from which 2.7 g. of copper diacetoacetic ester was obtained. Ether distillate (305 cc.); 25 cc. gave 0.041 g. of AgCl, so 0.3 g. of acetyl chloride remained unchanged. Fractions from liquid product: (1) 28.1 g., b. p. 115-139° at 50 mm.; (2) 5.6 g. of O-acetyldiacetoacetic ester, b. p. 116-122° at 1 mm. Fraction (1) redistilled gave: (1a) 9.7 g., b. p. 108-120° at 41 mm.; (2a) 15.1 g., b. p. 120-130° at 41 mm.; (3a) 3.0 g., b. p. 130-140° at 41 mm.

SEPARATION BY COPPER ACETATE

Fraction	(1a)	(2a)	(3a)
Copper diacetoacetic ester, g.	6.1	15.0	1.2
Copper acetoacetic ester, g.	3.1
O-Acetyl diacetoacetic ester, g.	1.4

(II) One Mole of Sodium Ester Added to 1.5 Moles of Chloride.—Ether distillate (305 cc.); 25 cc. gave 1 g. of AgCl, so 6.7 g. of acetyl chloride was unchanged. Fractions from liquid product: (1) 28.7 g., b. p. 105-120° at 40 mm.; (2) 7.3 g., b. p. 115-120° at 1 mm. Fraction (1) redistilled gave: (1A) 11.2 g., b. p. 105-117° at 38 mm.; (1B) 15.2 g., b. p. 117-130° at 38 mm.; (1C) 2.1 g. distilled at 2 mm. without registering on the thermometer. Fraction (1A) redistilled gave: (1D) 7.1 g., b. p. 90-115° at 38 mm.; and a residual oil (1E), which was combined with fraction (1B) and then distilled, gave fractions: (1F) 1.5 g., b. p. 119° at 38 mm.; (1G) 17.1 g., b. p. 119-123° at 38 mm. Fractions (2) and (1C) were combined and distilled gave: (1) 2 g., b. p. 80-110° at 1 mm.; (H) 7.1 g. of O-acetyldiacetoacetic ester, b. p. 110-115° at 1 mm.

(27) Considerable losses occur on acidification of the sodium enolates and the enolic esters are not quantitatively precipitated as copper enolates. On acidification of an ethereal suspension of 10 g. of sodium enol acetoacetic ester with cold dilute hydrochloric acid (1) 7.7 g.; (2) 7.5 g. of acetoacetic ester (b. p. 89-90° at 32 mm.) was recovered. Separation of enolic esters by sodium carbonate extraction is not satisfactory. A solution of 10 g. of acetoacetic ester in 75 cc. of ether was extracted with three portions (15 cc. each) of a cold 10% sodium carbonate solution and only 9.0 g. of acetoacetic ester was recovered from the dried ether solution. An ether solution (75 cc.) of 10 g. of diacetoacetic ester was extracted with 100 cc. of a 10% potassium carbonate solution (in small portions) until evaporation of the dried ether solution left only 0.5 g. of residual oil. On acidification of the alkaline extract 8.8 g. of diacetoacetic ester (b. p. 114-116° at 30 mm.) was recovered. The yield of copper enolate from pure acetoacetic and diacetoacetic ester is 95 and 85%, respectively.

(25) See Michael, *THIS JOURNAL*, **32**, 990 (1910); **40**, 704 (1918); **42**, 787 (1920).

(26) Michael, *Ber.*, **33**, 3733 (1900); *THIS JOURNAL*, **32**, 1001 (1910).

SEPARATION BY COPPER ACETATE

Fraction	(1D) and (1F)	16.1 g. of (1G)
Copper diacetoacetic ester, g.	2.4	15.8
Copper acetoacetic ester, g.	1.3	...

(III) **One Mole of Sodium Ester Added to 3 Moles of Chloride.**—Acidification of 10 g. of solid liberated 1.4 g. of oil, from which 0.65 g. of copper diacetoacetic ester was obtained. Ether distillate 395 cc.; 25 cc. gave 3.25 g. of AgCl, showing that 28.2 g. of acetyl chloride remained unchanged. Fractions from liquid product: (1) 3.1 g., b. p. 90–103° at 30 mm.; (2) 23.4 g., b. p. 103–125° at 30 mm.; (3) 8.3 g., b. p. 90–120° at 1 mm.

SEPARATION BY COPPER ACETATE

Fraction	(1)	10 g. of (2)	(3)
Copper diacetoacetic ester, g.	0.6	7.3	2.3
Copper acetoacetic ester, g.	1.2	1.5	...
O-Acetyldiacetoacetic ester, g.	5.6

(IV) **Two Moles of Sodium Ester Added to 1 Mole of Chloride.**—Acidification of 27.5 g. of solid gave 16.6 g. of diacetoacetic ester, b. p. 110–123° at 40 mm. Two grams of distillate gave 1.6 g. of copper diacetoacetic ester. Fractions from liquid product: (1) 10.5 g., b. p. 96–105° at 40 mm.; (2) 3.7 g. distilled at 2 mm. below range of thermometer.

Two grams of fraction (1) gave 2.2 g. of the copper enolate. An ether solution of fraction (2) was shaken with copper acetate solution and gave 0.5 g. of copper diacetoacetic ester. The dried ether solution was concentrated and the residual oil gave fractions: (3) 1.3 g., b. p. up to 100° at 2 mm.; (4) 1.0 g. of O-acetyldiacetoacetic ester, b. p. 100–110° at 2 mm. An ether solution of fraction (3) was extracted with a cold 10% sodium hydroxide solution and on concentrating the dried ether solution only 0.3 g. of oil remained. Fraction (4) gave a faint, red coloration with ferric chloride: 1 g. of the ester gave 0.5 g. (calcd. 0.7 g.) of acetphenylhydrazide.

(V) **One Mole of Chloride Added to 2 Moles of Sodium Ester.**—Acidification of 27 g. of solid gave 16.7 g. of diacetoacetic ester, b. p. 118.5–121° at 39 mm. Two grams of distillate gave 2.0 g. of copper diacetoacetic ester.

Fractions from liquid products: (1) 11.1 g. of acetoacetic ester, b. p. 92–96° at 35 mm.; (2) 2.9 g., b. p. 96–120° at 35 mm. Two grams of fraction (1) gave 2.2 g. (calcd. 2.4 g.) of copper acetoacetic ester. An ether solution of fraction (2) was extracted three times with a cold 10% solution of sodium hydroxide, dried, and the ether removed. The residual oil, O-acetylacetoacetic ester (1.4 g.), gave no color with ferric chloride. One gram of the ester with 1.2 g. of phenylhydrazine in ether solution gave 0.7 g. (calcd. 0.87 g.) of acetphenylhydrazide. The concentrated filtrate, with 4–5 drops of acetic acid, gave 0.6 g. of methylphenylpyrazolone.

(c) Action of Benzoyl Chloride on Sodium Enol Acetoacetic Ester

(VI) **One Mole of Sodium Ester Added to 1 Mole of Chloride.**—Acidification of total solid (13.2 g.) gave 3.9 g.

of benzoylacetoacetic ester, b. p. 145–148° at 1 mm. The ester gave 4.2 g. (calcd. 4.4 g.) of copper benzoylacetoacetic ester.

Fractions from liquid products: (1) 5.6 g., b. p. up to 140° at 1 mm.; (2) 26.1 g., b. p. 140–151° at 1 mm.; (3) 2.4 g. of non-volatile oil. Fraction (1) contained 2.6 g. of unused benzoyl chloride. Fraction (2) gave 28.7 g. (calcd. 29.5 g.) of copper benzoylacetoacetic ester.

(VII) **One Mole of Sodium Ester Added to 1.5 Moles of Chloride.**—Acidification of total solid (12.4 g.) gave 3.1 g. of oil, from which 2.7 g. of copper benzoylacetoacetic ester was obtained.

Fractions of liquid products: (1) 14.5 g., b. p. up to 125° at 1 mm.; (2) 27.9 g., b. p. 145–153° at 1 mm.; (3) 3.7 g. of non-volatile oil. Fraction (2) redistilled gave: (2a) 0.9 g., b. p. up to 144° at 1 mm.; (2b) 26.5 g., b. p. 144–150° at 1 mm.

Combined fractions (1) and (2a) contained 13.7 g. of benzoyl chloride. Fraction (2b) gave 29.2 g. (calcd. 30.0 g.) of copper benzoylacetoacetic ester.

(VIII) **Two Moles of Sodium Ester Added to 1 Mole of Chloride.**—Acidification of total solid (24.5 g.) gave 17.1 g. of benzoylacetoacetic ester, b. p. 136–137° at 2 mm.

Fractions of liquid products: ether solution of liquid portion first extracted with a 10% potassium carbonate solution and then distilled, gave: (1) 8.3 g. of acetoacetic ester, b. p. 91–92° at 33 mm.; (2) 1 g. of non-volatile oil. The potassium carbonate extract was acidified and gave 0.5 g. of an oil from which 0.3 g. of copper benzoylacetoacetic ester was obtained.

(IX) **One Mole of Chloride Added to 2 Moles of Sodium Ester.**—Solid (25.5 g.) contained 4.7 g. of sodium chloride. Acidification of 23.9 g. of solid gave 17.0 g. of benzoylacetoacetic ester, b. p. 132–133° at 2 mm.

Fractions from liquid products: (1) 8.8 g. of acetoacetic ester, b. p. 92–93° at 36 mm.; (2) 1.0 g. of oil, b. p. 132–133° at 3 mm.

(d) Action of Acetyl Chloride on Sodium Enol Malonic Ester

(X) **One Mole of Sodium Ester Added to 1 Mole of Chloride.**—A suspension of 33.8 g. of sodium enol malonic ester in 150 cc. ether was added to 14.6 g. of acetyl chloride dissolved in 25 cc. ether. Acidification of 12.4 g. of solid gave 1.5 g. of oil (b. p. 110–125° at 15 mm.) from which 0.6 g. of copper acetylmalonic ester was obtained.

Fractions from liquid product: (1) 20.2 g., b. p. 105–135° at 22 mm.; (2) 12.8 g., b. p. 136–138° at 1 mm. An ether solution of fraction (1) was extracted three times with a 10% sodium carbonate solution, dried and the ether removed. The residual oil gave fractions: (3) 13.2 g. of malonic ester, b. p. 91–100° at 13 mm.; (4) 3.6 g. of O-acetyl acetomalonic ester, b. p. 133–135° at 2 mm. Fraction (3) gave a very slight coloration with ferric chloride and the last drops of (4) no color. The alkaline extract was acidified and gave 1.7 g. of oil, b. p. 120–125° at 17 mm.

An ether solution of fraction (2) was extracted with a 10% sodium hydroxide solution, dried and the ether removed. The residual oil gave 11.2 g. of O-acetylacetomalonic ester, b. p. 154–155° at 15 mm. The alkaline extract was acidified and gave 1.1 g. of an oil from which 0.2 g. of copper acetylmalonic ester was obtained.

(XI) **One Mole of Chloride Added to 2 Moles of Sodium Ester.**—Thirty grams of malonic ester was added at 0° to a suspension of 4.3 g. of powdered sodium in 100 cc. of ether. The mixture was allowed to stand overnight and treated with a solution of 7.4 g. of acetyl chloride in an equal volume of ether. Acidification of the total solid gave 16.9 g. of acetylmalonic ester, b. p. 122–125° at 17 mm.

Fractions of liquid products: an ether solution of the liquid portion was extracted three times with a 10% potassium carbonate solution, dried and the ether removed. The residual oil gave fractions: (1) 14.0 g. of malonic ester, b. p. 109–111° at 35 mm.; (2) 0.7 g. of oil, b. p. 120–122° at 2 mm. Extraction of the acidified alkaline extract gave no material.

(e) **O-Acetate of Diacetoacetic Ester**

(1) **Prepared from Sodium Enol Diacetoacetic Ester.**—An ether suspension of sodium ethylate, prepared from 2 g. of powdered sodium and 4 g. of alcohol, was treated with 15 g. of diacetoacetic ester. After twelve hours, the solvents were removed at reduced pressure, the residue suspended in 200 cc. ether, cooled by running tap water and treated with 6.9 g. of acetyl chloride.

After two days, 7.1 g. of solid (1 g. gave 1.3 g. of AgCl, showing that 3.8 g. of NaCl had formed; calcd. 5.1 g.) was filtered off, and the ether removed. The residual oil gave fractions: (1) 3.2 g., b. p. 80–113° at 2 mm.; (2) 11.8 g., b. p. 113–116° at 2 mm. Fraction (2), which gave a faint color with ferric chloride, was redistilled and collected in two fractions. The last portion gave no immediate coloration with ferric chloride and had the following properties: colorless, b. p. 115–116° at 2 mm., d_{20} 1.1074; n_{20} 1.4522; mol. refract. calcd., 51.23; found, 52.18.

(2) **Prepared by the Pyridine Method.**—Twenty grams of diacetoacetic ester and 17.2 g. of pyridine were treated at 0° with 14 g. of acetyl chloride. After four days the solid was filtered off and washed with ether. The ether was removed from the filtrate and after three fractionations 12.7 g. of a yellow oil was obtained, b. p. 123–124° at 1 mm. The refractive index remained constant after six distillations. The properties of the ester were: perceptibly yellow; b. p. 112–114° at 1 mm.; d_{20} 1.1212, n_{20} 1.4580; mol. refract. calcd., 51.23; found, 52.11. Although several physical properties differ somewhat, the evidence for isomerism is insufficient.

(f) **Rearrangement of O-Acylacetoacetic Esters**

General Procedure.—Ether solutions of O-benzoyl- and O-acetylacetoacetic esters, prepared by the pyridine method, were repeatedly washed with cold, 10% sodium hydroxide solutions, dried and fractionated. The esters gave no coloration with alcoholic ferric chloride. Ten grams of the O-acyl ester was used in each case. In Experiments I and II, the O-ester was added to a suspension of 6.5 g. of sodium enol acetoacetic ester in 50 cc. of ether and the mixture kept in a stoppered flask in a desiccator in one case and, in the other, heated under a reflux. An ether suspension (50 cc.) of 6.8 g. of copper enol acetoacetic ester was used in Experiment III. The ether was distilled off after three hours and replaced by acetic ester (distilled from sodium). After three hours

most of the acetic ester was distilled off, replaced by ether and the unchanged copper ester (6.6 g.) as well as the O-benzoyl ester recovered. The potassium carbonate (11.8 g.) employed in IV (a) was dried by heating to redness in a crucible; that used in IV (b) and V was heated to bright redness in an iron tube through which a current of dry carbon dioxide was passed.

(g) **Attempt to Convert O-Acetyl- into C-Acetylacetoacetic Ester**

General Procedure.—The O-acetate used in Experiment I was prepared by the action of acetyl chloride on copper acetoacetic ester. An ether solution of the O-acetyl ester was washed repeatedly with a cold 10% sodium hydroxide solution, dried and the ether removed. The residual oil was distilled, dried over calcium chloride for twenty-four hours, and redistilled (b. p. 122–123° at 35 mm.). The O-ester used in Experiment II was prepared by the pyridine method. A portion of the same ester was dried for two days longer over calcium chloride, redistilled (b. p. 117° at 30 mm.) and used in Experiment III.

The esters were heated at 235° (in the vapor of benzyl cyanide) in sealed Pyrex tubes previously washed with acid and heated to redness. The tubes were under pressure when opened. Portions of the brown oil obtained were fractionated. The distillate, collected at 30 mm., was dissolved in ether, extracted with a cold 10% sodium hydroxide solution, dried and the solvent removed. The residual oil (recovered O-acetylacetoacetic ester) gave no color with ferric chloride and acetophenylhydrazide (Experiment II) with phenylhydrazine in ether solution. The alkaline extract was acidified, and the liberated oil converted into the copper enolate. The results are given in Table D.

(i) **The Action of Sodium Enol Benzoylacetic Ester on O-Acetylacetoacetic Ester.**—An ethereal suspension of sodium ethylate, prepared from 1.2 g. of powdered sodium and 2.4 g. of alcohol, was treated with 10 g. of benzoylacetic ester. The solvent was removed at reduced pressure, the residue suspended in 100 cc. of ether and treated with 8.9 g. of O-acetylacetoacetic ester. A yellow solid (10.6 g.) was filtered off after one week. The ether was distilled from the filtrate and the residual oil, diluted with petroleum ether, deposited 1.5 g. of solid. On acidification of the combined solids an oil was obtained which gave fractions: (1) 3.4 g., b. p. 78–110° at 1 mm.; (2) 6.5 g., b. p. 137–143° at 1 mm. The petroleum ether extracts were distilled and gave fractions: (3) 2.7 g., b. p. 91–100° at 37 mm.; (4) 3.7 g., b. p. 129° at 1 mm.

YIELDS OF COPPER ENOLATES

Fraction	Copper ester	Crude ester, g.	M. p., °C.	Recryst. ester, g.	M. p., °C.
1	Diacetoacetic	3.2	149–150
2	Benzoylacetoacetic	6.8	205	4.4	232
3	Acetoacetic	2.8	185	1.5	196–197
4	Benzoylacetic	4.0	160	3.4	182–183

(j) **The Action of Sodium on O-Benzoylacetoacetic Ester.**—Ten grams of liquid O-benzoylacetoacetic ester was dissolved in 25 cc. of benzene (dried over sodium) and 1 g. (1 equivalent) of powdered sodium added. The reaction flask was attached by a ground glass joint to a

nitrometer and the gas evolved (120 cc. in 35 hours) collected over petroleum oil. The yellow solid (8.1 g.), filtered off after twelve days, was acidified and 7.1 g. of an oil obtained which gave fractions: (1) 0.6 g., b. p. below 100° at 4 mm.; (2) 5.3 g., b. p. 141–145° at 4 mm. Fraction (1) gave first 0.5 g. of a mixture of copper benzoylacetacetic ester and copper acetoacetic ester (color, bluish; m. p. 155°) and after neutralization with ammonia 0.3 g. of copper acetoacetic ester (m. p. 194°). An ether solution of fraction (2) was washed with a cold, saturated sodium bicarbonate solution, dried and the solvent removed. The residual oil gave 5.2 g. of copper benzoylacetacetic ester (m. p. 227°). On acidification of the alkaline extract 0.7 g. of benzoic acid was obtained.

The benzene filtrate was concentrated, diluted with ether and washed with water. The residual oil (2.1 g.) from the dried ether solution gave no copper enolate. The mixture was extracted with ether and 1 g. of oil recovered (probably unchanged O-ester). Acidification of the aqueous extract gave an oil (1 g.), from which 0.2 g. of impure copper acetoacetic ester was obtained.

Summary

1. The reaction between acetyl and benzoyl chlorides and sodium enol acetoacetic ester has been examined, under varying conditions, semi-quantitatively and the direct, almost quantitative, formation of free diacetoacetic ester rigorously proved. Claisen's interpretation of antecedent formation of O-acyl derivatives is therefore untenable. The direct formation of C-acyl esters has been interpreted as proceeding through addition of the α -methine group of the enolate to the unsaturated carbonyl group of the chloride.

2. Quantitative differences between the results found with acetyl and benzoyl chloride have been explained. An excess of acetyl chloride was found to exert no perceptible mass action effect upon the quantitative outcome. A new interpretation of this result, and corresponding results in

other reactions, now explained by assuming undetectable enolization of the organic compounds, has been advanced and used to explain the phenomena.

3. The action of acetyl chloride upon sodium enol malonic ester has been examined semi-quantitatively and the experimental results coordinated with theory.

4. The described thermal rearrangement of O- into C-acetylacetacetic ester has been re-examined, but could not be confirmed.

5. The structural change has been shown to take place almost quantitatively with sodium enol acetoacetic ester as reagent, forming the sodium enolate of diacyl derivatives. No change could be brought about with copper enol acetoacetic ester, nor with potassium carbonate unless a trace of water was present.

6. The reactions between O-acetylacetacetic and sodium enol benzoylacetacetic esters and O-benzoylacetacetic and sodium enol acetoacetic esters, have been studied semi-quantitatively and the intermolecular character of the O \rightarrow C acyl migration confirmed and explained.

7. It has been shown that metallic sodium converts O-benzoylacetacetic into sodium enol benzoylacetacetic ester, with evolution of hydrogen, obviously by intramolecular migration of benzoyl.

8. It was found that a liquid O-benzoylacetacetic ester was obtained from acetoacetic ester, benzoyl chloride and pyridine, which is apparently stereomeric with the known solid form, obtained from copper enol acetoacetic ester and benzoyl chloride.

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RECEIVED OCTOBER 24, 1934