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I.—Contributions to our Knowledge of Acetoacetic Ether.

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THE investigations of Geuther and Wedel have led them to ascribe the following constitutional formula to acetoacetic ether:—

In what way, however, the action of sodium on the monalkyl acetoacetic ethers takes place is not, according to this formula, at first sight apparent. By the action of sodium on ethylic ethylacetoacetate, for example, sodium ethylacetoacetic ether is produced. According to Geuther's views, there are two possible reactions which may take place here. In the first case, it may be thus formulated:—

or the action of sodium may alter the carboxyl-group. This would be expressed by the following equation:—

If the first reaction took place and the sodium ethylacetoacetic ether were acted on by acetic acid, one would not again obtain ethylacetoacetic ether, but a substance isomeric with it; in the second possibility, it could not be said with any certainty what sort of compound the action of acetic acid would give rise to.

I.—*Action of dilute Acetic Acid on Sodium Ethylacetoacetic Ether.*

The requisite ethylacetoacetic ether was prepared by Wislicenus' method (*Annalen*, **186**, 183), viz., by the action of sodium and ethyl iodide on pure ethylic acetoacetate diluted with benzene. Ethyl bromide was tried in place of the iodide; it cannot however be recommended, as the reaction takes place exceedingly slowly.

By the action of sodium on ethylic ethylacetoacetate, Wislicenus (*Annalen*, **186**, 189) says that considerable decomposition takes place, and that among the products *ethylic butyrate* is found, which is at once recognised by its characteristic odour. He also mentions that the sodium derivative of ethylic ethylacetoacetate is much more easily soluble than that of the ethylic acetoacetate itself. In consequence of this, it may be presumed that if *more* of the diluting liquid were used—instead of $\frac{3}{4}$ to 1 volume of benzene or ether, take say 3 or 4 volumes—a better result would be obtained, and very little decomposition take place, resulting in a higher percentage of the sodium derivative of the substituted ether, without the formation of ethylic butyrate and liquids of high boiling point. This is, as a matter of fact, the case.

Of the four experiments which I have made, ether was used three times, and benzene once, as the diluting liquid. The method of procedure was as follows:—

10 grams of pure ethylic ethylacetoacetate, boiling at 192—194°, were brought into a suitable flask, and diluted with 3 or 4 volumes of absolute ether or benzene. The theoretical quantity of sodium, 1·4 gram, was now introduced in small thin slices, cut under ether. The flask was connected with an inverted condenser by means of a Y-shaped tube which admits of the sodium being easily dropped in from time to time without sustaining any loss of the diluting liquid.

During the reaction, the liquid becomes slightly yellow, but there is not the slightest odour of ethylic butyrate. Nearly the whole quantity of sodium can be dissolved.

The product was now acidified with dilute acetic acid, and the oil which had separated out dried and fractionated. After two rectifications, 7 grams of a liquid which distilled at 192—194° were again obtained. The whole passed over below 200°, and after the ether had been boiled off the thermometer rose rapidly to 190°. The sp. gr. of the oil so obtained was 0·980 at 16°, whereas that of the ethylic ethylacetoacetate operated on was 0·981 at the same temperature.

In order to still further prove the identity of this product with the ethylic ethylacetoacetate used, and at the same time to see if it were possible by the use of more diluting liquid to obtain a better per-

centage than Wislicenus did, I converted it into ethylic diethylacetoacetate.

12 grams of the oil, obtained as above, diluted with 3 to 4 volumes of absolute ether, were operated on, and I ultimately obtained 6.5 grams of pure ethylic diethylacetoacetate, boiling at 210–212° (uncorr.), which is 55 per cent. of the theoretical quantity. Wislicenus (*Annalen*, **186**, 191) obtained only 25 per cent., and his crude oil was always *brown*, whereas the above sample was *colourless*.

From these experiments, there can be scarcely any doubt that *sodium ethylacetoacetic ether*, when acted on with dilute acetic acid, is again converted into *ethylic ethylacetoacetate*.

II.—On certain mixed Di-allyl Acetoacetic Ethers.

Although a number of mixed di-substituted acetoacetic ethers have been prepared, we have no record as to whether the order in which these radicals are introduced is a matter of indifference or not, *i.e.*, whether the same bodies are produced or whether they are isomeric. In order to put this to the test, I chose first of all the radicals allyl and methyl, principally because allyl has not, so far, been used in a di-substituted ether.

1. *Ethylic Allylmethylacetoacetate*.

The ethylic allylacetoacetate (comp. Zeidler, *Annalen*, **187**, 30) was prepared by the general method proposed by Conrad and Limpach (*Annalen*, **192**, 153). Sodium was dissolved in absolute alcohol, ethylic acetoacetate added, and then allyl iodide; the mixture was warmed on a water-bath, the alcohol distilled off, and the residue treated with water until the sodium iodide was just dissolved, which caused the ether to float on the surface as an oil. The sodium iodide solution was now syphoned off, shaken with ether, this extract mixed with the oil, and the whole dried with calcium chloride. After rectifying, a quantity of ethylic allylacetoacetate was obtained, boiling at 198–205°. This substance was now converted into *ethylic allylmethylacetoacetate* by treatment with the required quantity of sodium and methyl iodide.

By the first distillation, nearly the whole quantity distilled at 210°, and after several rectifications the chief portion boiled at 209–211°, each time however a drop or two of a liquid of higher boiling point remained.

An analysis of the liquid boiling at 209–211° gave the following result :—

I. 0.3235 gram gave 0.2540 gram H_2O and 0.7515 gram CO_2 .
 II. 0.3190 „ 0.2555 „ 0.7405 „

		Found.	
		I.	II.
C_{10}	Calculated. 65.2	63.3	63.3
H_{16}	8.7	8.7	8.8
O_3	26.1	—	—
<hr/>			
100.0			

Since ethylic allylmethylacetoacetate, $\text{C}_{10}\text{H}_{16}\text{O}_3$, contains more carbon than was found, it was probable that its boiling point lay somewhat higher. The liquid which had, during the fractionating, remained in the retort, was therefore submitted to distillation, in the hope of obtaining the purer compound, but without success, as the thermometer rose very rapidly from 210° to 360° , and a dark brown syrupy mass was left, which represented more than three-quarters of the whole liquid of high boiling point, only a drop or two having distilled between 210° and 360° .

This ethylic allylmethylacetoacetate has an exceedingly pleasant odour. It produces no coloration with ferric chloride, and is miscible in all proportions with alcohol, ether, and benzene.

2. *Ethylic Methylallylacetoacetate.*

This substance was prepared in a manner precisely similar to the one just described, only with the difference that the methyl-group was first introduced and then the allyl.

I will only remark that when the ethylic methylacetoacetate is poured into the sodium ethylate solution, the mixture becomes solid from separation of white silky needles of the sodium derivative of this ether. On warming on the water-bath with addition of a little more alcohol, it may be dissolved, and the allyl iodide poured in.

On the first distillation I obtained, as in the previous case, a liquid boiling nearly all at 210° , which, after rectification, passed over for the most part at 209 — 211° , but each time a few drops of higher boiling liquid remained in the retort. An analysis gave the result:—

0.3055 gram gave 0.2400 gram H_2O and 0.7170 gram CO_2 .

	Calculated.	Found.
C ₁₀	65.2	63.9
H ₁₆	8.7	8.7
O ₃	26.1	—
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	100.0	

The liquid of higher boiling point was also operated on as before, with a precisely similar result.

This ether has a very pleasant smell, and cannot be distinguished from the former substance in this respect. It gives no coloration with ferric chloride, and is soluble in all proportions in alcohol, ether, or benzene.

As I was unable to obtain either of these substances in the pure state, it cannot be said with certainty that ethylic allylmethyl- and methylallyl-acetoacetates are the same compound.

3. *Ethylic Methylethylacetoacetate.*

I now endeavoured to answer this question by using methyl and ethyl as the substituting radicals, and to this end prepared some ethylic methylethylacetoacetate by Conrad and Limpach's method. The compound finally obtained boiled very constantly between 195—196° (uncorr.).

4. *Ethylic Ethylmethylacetoacetate.*

Saur, who has already prepared this substance (*Annalen*, **188**, 260), employed Wislicenus' method (*ibid.*, **186**, 183 and 187). He gives its boiling point as "198° uncorrected," and also mentions that on the first distillation the chief quantity went over between 195° and 205°. As this boiling point did not correspond with that of the methylethylether which I had made, some ethylic ethylmethylacetoacetate was prepared by Conrad and Limpach's method. It boiled constantly between 195—196° (uncorr.), and by the first distillation all came over below 200°. Perhaps Saur's statement should read "198° corrected" instead of uncorrected.

Since the boiling points of ethylic ethylmethyl- and methylethylacetoacetates are identical, and their odour and action on ferric chloride is the same, it seems very probable that in mixed di-substituted acetoacetic ethers, the order of introducing the radicals is of no importance, and that the same compound is formed either the one way or the other.*

5. *Ethylic Acetylacetoacetate.*†

By the action of acetyl chloride on the product of the action

* Even this, however, is not certain, as the ethylic methylacetoacetate prepared by Geuther (*Jenaische Zeitschrift*, 1865, **2**, 403), boils at 186·8° (corr.), and the methylic ethylacetoacetate, which is *isomeric* with it, boils according to Brandes at 189·7° (corr.) (*Jenaische Zeitschrift*, 1865, **3**, 33), these two substances having nearly the same boiling point.

† In the *Ber.*, **10**, 733, is an abstract on "Acetylacetic ether," taken from a

of sodium on ethylic acetate, Lippmann only obtained ethylic acetoacetate (*Zeitschr. f. Chem.*, 1869, 29); neither could Wedel produce it from acetyl chloride and ethylic acetoacetate (*Annalen*, **219**, 116), I have, however, succeeded in preparing it by the action of acetyl chloride on an ethereal solution of sodium acetoacetic ether. It appears, however, that H. Elion (*Rec. d. Trav. Chim. de Pays-Bas*, **2**, 202—204; also *Ber.*, **16**, 2762, under Diacetylessigäther) has recently prepared this body in a similar manner, and I therefore omit my work here, which will be found in the *Annalen*, **226**, 210, in detail.

It is hardly necessary to mention that for the preparation of the derivatives of ethylic acetoacetate, which are intended to contain acid radicals, Conrad and Limpach's method is inapplicable by reason of the alcohol present.

It would, however, probably give a good result to make the sodium acetoacetic ether by using sodium ethylate, and remove the alcohol by distillation. A solution of the sodium salt in ether or benzene could then be acted on with the chloride of the required radical. In this manner I hope to succeed in preparing perfectly pure substances without resorting to distillation.

Metallic Derivatives of Ethylic Acetylacetoacetate.

Ethylic acetylacetoacetate has the property of a fairly strong acid; for instance, it is capable of expelling acetic acid from its salts, whereas ethylic acetoacetate, although giving rise to a series of "salts," is not able to do this.

Copper acetylacetoacetic ether may be prepared by simply shaking the ether in question with an aqueous solution of neutral copper acetate. 2 grams of ethylic acetylacetoacetate were shaken for some time in a small cylinder with a concentrated solution of copper acetate. The excess of the solution was filtered from the sky-blue crystalline salt which had formed, and this latter washed with water until the liquid passing through was no longer of a distinct blue colour.

On testing for copper with ammonia, a blue colour, although not very intense, is always obtained, a proof that the salt is not altogether insoluble in water.

It was now air-dried until constant in weight, and an analysis gave the following numbers:—

I 0.2615 gram of light blue salt lost 0.0220 gram H_2O by stand-

paper by Demarçay in the *Compt. rend.*, **84**. In this publication Demarçay calls acetoacetic ether "Ether acétyl acétique," and this has been erroneously translated into the *Berichte* as *Acetylacetic ether*.

ing over sulphuric acid, becoming dark blue in colour; heated at 100° the weight remained constant. After ignition in air 0.046 gram of CuO remained.

- II. 0.2730 gram substance lost 0.0225 gram H_2O over sulphuric acid, and 0.0485 gram CuO was obtained.
- III. 0.3210 gram salt, which had been heated to just 150° , whereby it melted to an emerald-green liquid, becoming dark blue and crystalline on cooling: after combustion, it gave 0.159 gram H_2O and 0.5530 gram CO_2 .

Calculated for $(C_8H_{11}O_4)_2Cu + 2H_2O$.		Found.	
		I.	II.
Cu	14.3	14.0	14.2
$2H_2O$	8.2	8.4	8.2
$(C_8H_{11}O_4)_2Cu$.		III.	
C	47.3	47.0	
H	5.4	5.5	

The hydrated salt is sky-blue, and loses its water completely over sulphuric acid, becoming deepened in colour to that of cobalt-blue. At 100° it is blue-grey, and again becomes dark blue on cooling. It melts at 148° to an emerald-green liquid, without suffering the least decomposition; at 128° it re-solidifies to a magnificent blue crystalline mass. If the "salt" be heated to 190 — 200° , a beautifully crystalline colourless substance sublimes, which has not yet been further investigated. The anhydrous salt is easily soluble in alcohol and ether, forming blue liquids; from these solutions it can be obtained in beautiful long silky dark blue needles; the alcoholic solution produces the finest crystals. It also readily dissolves in chloroform and benzene.

Nickel Acetylacetoacetic Ether.—If a nickel sulphate solution be shaken with a few drops of ethylic acetylacetoacetate, with addition of a drop or two of sodium hydroxide, a precipitate is obtained, which is crystalline and of a light green colour. A sample of the salt was air-dried, and the nickel estimated with this result:—

0.2605 gram substance gave, after ignition, 0.440 gram nickel oxide.

Calculated for— $(C_8H_{11}O_4)_2Ni$.		Found.
Ni. . . .	14.5	13.24 per cent.
	13.3 per cent.	

There was not a sufficient quantity of substance left to confirm the percentage of water.

Cobalt sulphate gives the same result as with nickel; the precipitate is rose red.

Lead and zinc acetates produce no insoluble salts.

The strongly acid nature of ethylic acetylacetoacetate, which is manifested by the formation of its copper salt in the simple manner just described, may be employed on account of the comparatively feeble acid nature of ethylic acetoacetate, for the separation, and often very conveniently for the detection, of these two ethers, by converting them into their copper compounds. It is only necessary to shake a mixture of the two ethers with neutral copper acetate solution, when *blue* copper acetylacetoacetic ether separates out, and after filtering it off, to add a few drops of sodium hydroxide solution to the filtrate, which causes *pale-green* copper acetoacetic ether to form. For this purpose, that portion of the distillate boiling below 200° , which is obtained in preparing the acetyl compound, may be used with great advantage.

Decomposition of Ethylic Acetylacetoacetate by Water at the Ordinary Temperature.

This reaction has also been given by H. Elion (*Rec. Trav. Chim.*, July, 1884), and I can substantiate his observations in every way, viz., that ethylic acetylacetoacetate is decomposed into ethylic acetoacetate and acetic acid. For details see *Annalen*, **226**, 215.

Action of Sodium Ethylate on Ethylic Acetylacetoacetate.

I hoped by the action of sodium ethylate on ethylic acetylacetoacetate to produce its sodium compound, and then with methyl iodide to obtain the methyl-derivative, but, on carrying out the experiment, I got a liquid which, after fractional distillation, went over constantly between $179\text{--}180^{\circ}$ (uncorr.), whereas a liquid boiling higher than this was only present in small quantity. This substance boiled at the same temperature as ethylic methylacetoacetate, and an analysis proved that it consisted of this body:—

0.2610 gram gave 0.1960 gram H_2O and 0.5560 gram CO_2 .

	Calculated for ethylic methylacetoacetate.	Found.
C	58.3	58.1
H	8.3	8.3

If the action of the sodium ethylate on the acetyl compound took place in such a way that acetyl and sodium changed places, ethylic acetate would certainly be formed, and, in order to put this to the test, I made the following experiment:—

0.4 gram of sodium was dissolved in 4 c.c. of absolute alcohol, and 3 grams of pure ethylic acetylacetoacetate were poured in. Reaction

began at once, the mixture becoming hot, and a strong smell of ethylic acetate was produced. The alcohol was now distilled off on the water-bath and tested carefully for ethylic acetate by distilling it twice to half its volume, and treating that portion which passed over first after the third distillation with a concentrated solution of calcium chloride, which caused the ethylic acetate to separate on the surface as an oily layer.

The residue which remained in the distilling apparatus, after removing the alcohol, was acidified with dilute acetic acid and the separated oil taken up with ether. After drying and evaporating this, the remainder, weighing 2.5 grams, was distilled. It boiled at 120—200°, and after three rectifications a liquid was obtained which passed over at 175—180°; this was shown to be *ethylic acetoacetate* by converting it into its *green* copper salt. The other portion, about one-third, was easily proved to be undecomposed ethylic acetylacetoacetate by making the *blue* copper salt without the aid of sodium hydroxide.

From this experiment, it is clear that the alkyl-derivatives of ethylic acetylacetoacetate cannot be prepared by the above method, since the latter is decomposed by the alcoholate as shown by the following equation:—

6. *Ethylic Methylacetylacetoacetate.*

This compound was prepared from ethylic methylacetoacetate in a similar manner to ethylic acetylacetoacetate. On distilling, nearly the whole of the oil passed over between 190—220°, and from this I separated, on the third distillation, two portions boiling at 205—215° and 215—220°. I could not succeed in obtaining any constant boiling point, and after each distillation rather a large quantity of dark-brown resinous matter remained, substances of lower boiling points being at the same time produced.

The above liquids were analysed with this result:—

- I. 0.2755 gram gave 0.1990 gram H_2O and 0.5795 gram CO_2 .
 II. 0.3075 „ 0.2195 „ 0.6495 „

Calculated for ethylic methylacetylacetoacetate.		Found.	
		I. 205—215°.	II. 215—220°.
C ₉	58.1	57.34	57.6
H ₁₄	7.5	8.0	7.9
O ₄	34.4	—	—
<hr/>			
100.0			

Ethylacetylacetoacetate is a colourless, mobile, pleasant-smelling liquid, which is decomposed by distillation in the same way as ethylacetoacetate but in a greater degree. It gives a fine raspberry-red coloration with ferric chloride, which is similar to that formed by the acetyl compound. Blue litmus-paper is not reddened unless water is added. It dissolves in alcohol, ether, or benzene, but only slightly in water.

With copper acetate, it gives no precipitate, neither is one formed on adding dilute sodium hydroxide; therefore this ethylacetylacetoacetate forms *no* (insoluble) copper salt. It appears to be only partially decomposed by water.

7. Ethyl Benzoylacetoacetate.

This substance has already been prepared by Bonn (Annalen, 187, 1), and I would only remark, that if the benzoyl chloride is diluted with 2 volumes of ether, cooling with ice is quite unnecessary.

Ethyl benzoylacetoacetate also has the properties of a fairly strong acid, and is capable of displacing acetic acid.

Copper Benzoylacetoacetic Ether.—1 gram of the ether, which smelt slightly of benzoyl chloride, was well shaken with neutral copper acetate solution until the blue oily bead, which was first of all produced, was converted into a dirty green crystalline salt. This was filtered off, washed with cold water, and then air-dried until constant in weight.

On analysing the substance I obtained the following numbers:—

0.2550 gram lost 0.0150 gram H_2O on heating at 100° , and left 0.0400 gram CuO .

Calculated for (C ₁₃ H ₁₃ O ₄) ₂ Cu + 2H ₂ O.		Found.
Cu	11.2	12.5
2H ₂ O	6.4	5.9

As this analysis did not agree with the calculated numbers as well as was expected, I thought the salt was probably mixed with a little copper benzoate which contains some 20 per cent. of copper and no water.

Two crystallisations from absolute alcohol were sufficient to remove a salt which proved to be copper benzoate, it being only sparingly soluble in this liquid. Unfortunately there was not sufficient of the substance which crystallised from the alcoholic solution in dark-blue needles for another analysis.

Since the presence of copper benzoate could only have arisen from the benzoyl compound containing a little benzoyl chloride, the original

product was warmed with absolute alcohol and allowed to remain for 24 hours in order to destroy the influence of the latter by converting it into ethyl benzoate. After this water was added, and some of the separated oil vigorously shaken as before; but this time I could not succeed in breaking the blue oily bead; the mixture was therefore rubbed in a mortar for some time, washed with water, pressed between filter-paper, and dissolved in benzene. In the fine blue crystalline substance which had separated out the copper was determined after removing the benzene by heating at 100° .

0.1750 gram substance after ignition gave 0.0260 gram CuO.

	Calculated for ($C_{13}H_{13}O_4$) ₂ Cu.	Found.
Cu	11.9 per cent.	11.8 per cent.

Copper benzoylacetoacetic ether is light blue in the hydrated state, but becomes a little darker if anhydrous. It melts with decomposition between $180-190^{\circ}$. It dissolves in alcohol, benzene, or ether, but not very easily in the first two solvents: from all three it may be obtained in the crystalline form.