CXXII.—*Ethyl Benzylideneanilineacetoacetate.*

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It was formerly stated (Morrell and Crofts, *Proc.*, 1898, 14, 121) that the purple oil, obtained by the action of anhydrous ferric chloride on ethyl acetoacetate, was decomposed by water into ferric chloride and ethyl acetoacetate, and that the ethyl acetoacetate yielded with benzylideneaniline an additive product melting at 78°. Schiff (*Ber.*, 1898, 31, 207) considered that the additive product melting at 78° was formed by the combination of the ketonic modification of ethyl acetoacetate with benzylideneaniline. The result obtained by Morrell and Crofts seemed to be anomalous, since the benzylideneaniline compound melting at 104° was expected, this temperature being the melting point of the compound obtained from the enolic form of ethyl acetoacetate and benzylideneaniline (Schiff, *loc. cit.*). Recently the existence of three forms of ethyl benzylideneanilineacetoacetate has been challenged by Rabe (*Ber.*, 1902, 35, 3947), who points out that aniline combines with ethyl benzylideneanilineacetoacetate to give a substance which melts at 78°. Rabe, who considered that the change of one form of ethyl benzylideneanilineacetoacetate into another form, as described by Schiff, was attended by the decomposition of the additive product with the liberation of aniline, had grave doubts as to the existence of three desmotropic modifications of ethyl benzylideneanilineacetoacetate.

A few months ago, Francis (*Ber.*, 1903, 36, 937) published his investigations on the forms of ethyl benzylideneanilineacetoacetate, and concluded that one modification exists with a melting point of 104°, and perhaps a second modification melting at 78–80°.

With the intention of confirming the observation made on the ethyl benzylideneanilineacetoacetate obtained from the decomposition of the ferric chloride additive product, we tried a blank experiment with the specimen of ethyl acetoacetate used in our earlier work. The

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substance should be pure, inasmuch as a considerable elevation of the melting point is brought about by the use of the impure solvent (see p. 1295).

The peculiar action of small quantities of sodium ethoxide may perhaps account for the apparent existence of the less fusible modifications, since ethyl benzylidenediaceoacetate is soluble in the same solvents as ethyl benzylideneanilineaceoacetate.

The determination of the molecular weight of ethyl benzylideneanilineaceoacetate in benzene by Landsberger's method gave numbers agreeing with those obtained by Rabe and Biltz (R. Schiff, *Ber.*, 1898, **31**, 208; 1902, **35**, 4326; P. Rabe, *ibid.*, 1902, **35**, 3951; W. Biltz, *ibid.*, 1902, **35**, 4438; Francis, *ibid.*, 1903, **36**, 941). The numbers suggested a gradual dissociation of the substance, since the molecular weight diminished with the dilution. In the case of carbon tetrachloride as solvent, the molecular weight of the ethyl benzylideneanilineaceoacetate diminished steadily with the dilution.

EXPERIMENTAL.

Action of Benzylideneaniline on Ethyl Acetoacetate.

A sample of redistilled ethyl acetoacetate, which had been used in the earlier work and had been kept for three years, was treated with one molecular proportion of benzylideneaniline (m. p. 48°). After some hours, the mixture, which had become quite solid, was powdered and washed with light petroleum; the yellowish-white solid was then found to melt at $84-85^{\circ}$, but after recrystallisation from benzene the melting point fell to 80° , and, when subsequently crystallised from carbon tetrachloride, it melted constantly at 78° .

In order to test a result obtained by one of us (*Proc.*, *loc. cit.*) in which the modification, melting at 78° , was obtained from the decomposition by water of the purple liquid produced by the action of anhydrous ferric chloride on ethyl acetoacetate and the subsequent treatment of the regenerated ethyl acetoacetate with benzylideneaniline, 1.7 grams of redistilled ethyl acetoacetate were dissolved in pure dry ether, the ethereal solution shaken with water, and the ethereal layer evaporated under reduced pressure at 30° . The ethyl acetoacetate was then dried in a vacuum and treated with benzylideneaniline under the foregoing conditions. The yellowish-white solid, when washed with light petroleum, was found to melt at 78° , and when crystallised successively from benzene and carbon tetrachloride the melting point remained constant at 80° . This experiment showed that the benzylideneaniline compound of ethyl acetoacetate, obtained from the ester regenerated from the ferric chloride compound, was the same

as that prepared by the action of benzylideneaniline on redistilled ethyl acetoacetate.

No conclusion as to the constitution of the ferric chloride compound with ethyl acetoacetate could be drawn from the study of the benzylideneaniline compound of the regenerated ethyl acetoacetate. As will be seen from the following results, freshly distilled ethyl acetoacetate with benzylideneaniline gave the more fusible modification. Freshly distilled ethyl acetoacetate (3·4 grams) was mixed with 5 grams of benzylideneaniline. The yellowish-white product, the yield of which was nearly quantitative, melted at 75° after washing with light petroleum; when crystallised from benzene, it melted at 79°, and on recrystallisation from carbon tetrachloride the melting point became constant between 80° and 81°.

0·3005 gave 12 c.c. moist nitrogen at 23° and 771 mm. $N = 4·56$.

$C_{19}H_{21}O_3N$ requires $N = 4·5$ per cent.

When ethyl acetoacetate and benzylideneaniline were mixed in the proportion of two gram-molecules of the ethereal salt to one of the amine, the additive product obtained melted at 78—80° after successive crystallisations from benzene and carbon tetrachloride.

0·3762 gave 14·7 c.c. moist nitrogen at 20° and 771 mm. $N = 4·54$.

$C_{19}H_{21}O_3N$ requires $N = 4·5$ per cent.

The specimen of ethyl acetoacetate supplied by Kahlbaum, and considered by Schiff to be the pure enolic form, yielded, on treatment with benzylideneaniline, an additive product, which, when washed with light petroleum, melted at 83°, and after successive crystallisations from benzene and carbon tetrachloride gave a constant melting point at 81°.

0·2512 gave 0·6735 CO_2 and 0·1525 H_2O . $C = 73·12$; $H = 6·74$.

$C_{19}H_{21}O_3N$ requires $C = 73·33$; $H = 6·7$ per cent.

The effect of impurities in the benzene on the melting point of the benzylideneaniline additive compound when crystallised from this solvent is illustrated by the following data:

The modification, m. p. 78°, after recrystallisation from redistilled but impure benzene, melted at 98—99°, and after recrystallisation from pure crystallisable benzene at 87°. In a duplicate experiment, the melting point after crystallisation from redistilled but impure benzene rose to 86°, whereas the substance melted at 83° when crystallised from pure crystallisable benzene.

The modification, m. p. 81°, when recrystallised from redistilled but impure benzene, melted at 92—93°, but the crystals separating from pure crystallisable benzene melted at 85°.

With ethereal or alcoholic ferric chloride, the additive product immediately gave a purple coloration, which was more intense in ether than in alcohol.

The influence of piperidine on the combination of benzylideneaniline and ethyl acetoacetate is stated by Schiff to bring about the formation of the modification melting at 78°. According to our results, piperidine did not influence the combination in the slightest degree. A mixture of 1.7 grams of ethyl acetoacetate, 2.5 grams of benzylideneaniline, and 2 drops of piperidine became solid after a few hours, and the yellowish-white product, after being washed with ligroin, melted between 72° and 73°; when crystallised from benzene, the substance melted at 79°, and the melting point remained at 81–82° after crystallisation from carbon tetrachloride. The ligroin washings were found to contain free aniline. The numbers are practically the same as those obtained without the use of piperidine.

The influence of sodium ethoxide on the combination of benzylideneaniline and ethyl acetoacetate was very peculiar.* According to Schiff, the addition of a very small quantity of sodium ethoxide causes the formation of the modification melting at 104°. Rabe states that sodium ethoxide decomposes the additive product, aniline being set free. We are able to confirm Rabe's statement, and, moreover, we find that in the presence of a trace of sodium ethoxide, and even in the absence of alcohol, aniline is eliminated from ethyl benzylideneanilineacetoacetate, giving rise to the formation of ethyl benzylidenediacetoacetate. A trace of sodium ethoxide did not influence the melting point of the modification, which was still between 78° and 80°, even when 0.06 gram of sodium ethoxide was employed with 6.4 grams of ethyl acetoacetate. If, however, 0.05 gram of sodium ethoxide was used with 1.7 grams of ethyl acetoacetate, the change in the melting point of the product was very marked.

(a) A mixture of 2.3 grams of ethyl acetoacetate, 3.3 grams of benzylideneaniline, and a trace of powdered sodium ethoxide became solid after some time, and the yellowish-white product, when washed with ligroin, was found to melt at 92°. After successive crystallisations from benzene and carbon tetrachloride, the melting point became constant between 78° and 80°.

(b) A mixture of 6.4 grams of ethyl acetoacetate, 7.5 grams of benzylideneaniline, and 0.06 gram of sodium ethoxide yielded, after several hours, a yellowish-white product which, when washed with ligroin, melted at 77°. After crystallisation from benzene, the melting point rose to 79°. Aniline was found in the ligroin and benzene washings,

* The sodium ethoxide was prepared by the method described by Brühl and Biltz (*Ber.*, 1891, 24, 649), and dried in a vacuum at 100°.

and the mother liquor from the crystallisation in benzene gave, on adding ligroin, a substance which melted at 89° .

The ethyl benzylideneanilineacetoacetate, melting at 79° , was analysed with the following result :

0.1850 gave 0.4965 CO_2 and 0.1142 H_2O . $\text{C} = 73.19$; $\text{H} = 6.85$.

$\text{C}_{19}\text{H}_{21}\text{O}_3\text{N}$ requires $\text{C} = 73.33$; $\text{H} = 6.7$ per cent.

(c) The product obtained in a similar manner from 1.7 grams of ethyl acetoacetate, 2.5 grams of benzylideneaniline, and 0.05 gram of sodium ethoxide, was, when washed with ligroin and crystallised from benzene, found to melt at 124° . Aniline was detected in the ligroin washings.

When alcohol was used instead of benzene, the product melted at 150° . The mother liquor from the benzene crystallisation gave, on the addition of ligroin, a substance which melted at 140° , whereas the compound obtained from the alcoholic mother liquor, on treatment with water, melted at 128° . The substance which melted at 150° was ethyl benzylidenediaceoacetate :

0.1560 gave 0.3750 CO_2 and 0.1015 H_2O . $\text{C} = 65.5$; $\text{H} = 7.2$.

$\text{C}_{19}\text{H}_{24}\text{O}_6$ requires $\text{C} = 65.5$; $\text{H} = 6.9$ per cent.

This compound, which is one of the forms of ethyl benzylidenediaceoacetate described by Rabe (*Annalen*, 1900, 313, 129), did not react with ferric chloride, and the aniline set free in its formation could be easily detected.

(d) The use of a larger amount of sodium ethoxide led to the formation of ethyl benzylidenediaceoacetate, as in the previous experiment, but the liquid mixture of benzylideneaniline and ethyl acetoacetate did not solidify and remained as a gelatinous mass. On treatment with ligroin, the gelatinous mass became solid, and after crystallisation from benzene or carbon tetrachloride the modification melted at 123 — 125° , but after recrystallisation from alcohol the melting point rose to 149 — 150° . The ethyl benzylidenediaceoacetate produced in this way was analysed with the following result :

0.25 gave 0.5912 CO_2 and 0.1549 H_2O . $\text{C} = 65.15$; $\text{H} = 6.84$.

$\text{C}_{19}\text{H}_{24}\text{O}_6$ requires $\text{C} = 65.5$; $\text{H} = 6.9$ per cent.

The alcoholic mother liquor from the crystals melting at 149 — 150° gave, on dilution with water, a crystalline precipitate of flat, rhombic prisms which melted at 137° .

(e) A mixture of 2 grams of ethyl acetoacetate, 2.5 grams of benzylideneaniline, and 0.1 gram of sodium ethoxide also yielded a gelatinous product which, after being washed with ligroin, melted at

136—138° and when recrystallised either from benzene or from carbon tetrachloride, melted at 134—136° or 131—133° respectively. The product contained no nitrogen, and an analysis showed that it was a mixture of the ketonic forms of ethyl benzylidenediacetoacetate.

0.2482 gave 0.5927 CO₂ and 0.1500 H₂O. C = 65.1; H = 6.7.

C₁₉H₂₄O₆ requires C = 65.5; H = 6.9 per cent.

With a still larger quantity of sodium ethoxide, amounting to 0.5 gram for 2 grams of ethyl acetoacetate and 2.5 grams of benzylideneaniline, the gelatinous product, after being washed with ligroin, melted at 138—144°. On crystallisation from benzene, the melting point fell to 128—130°, and when recrystallised from carbon tetrachloride or alcohol the compound melted constantly at 130°. The substances with different melting point, but with the same chemical composition, were identical in crystalline form with those obtained by Rabe (*loc. cit.*). The modification melting at 130° was not homogeneous, but consisted of a mixture of acicular and rhomboidal crystals.

The variation in the values of the molecular weight of the benzylideneaniline additive product is of interest, as will be seen from the numbers obtained in the molecular weight determination by means of Landsberger's method.

Molecular weight in benzene.....	300	303	263	268
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Molecular weight in carbon tetrachloride...	293	280	245	240
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C₁₉H₂₁O₃N requires 311.

These numbers suggest that a dissociation of ethyl benzylideneanilineacetate into its constituents occurs when it is heated to a temperature near its melting point in either benzene or carbon tetrachloride. From Rabe's work, we conclude that the constituents are aniline and ethyl benzylidenediacetoacetate. Biltz obtained the values 210 and 205 for the molecular weight in benzene by Landsberger's method. Rabe's values were 226 and 213, whilst those given by Francis are 292 and 305 in benzene and 302 and 232 in carbon tetrachloride.

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