X.—*Keto-enol Isomerism of Ethylenebisacetylacetone.*

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In their reactions with inorganic reagents acetylacetone and its homologues exhibit the behaviour of three dynamic isomerides : (1) a diketonic form manifested in condensation with tellurium tetrachloride, (2) a *trans*-monoenolic form with selenium tetrachloride, and (3) a *cis*-monoenolic modification with copper acetate, ferric chloride and other metallic salts (Morgan and Drew, J., 1924, **125**, 1044).
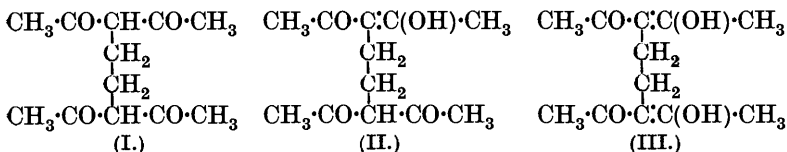
Ordinary acetylacetone consists principally of enolic forms and in 1921 K. Meyer and Hopff, by distilling the diketone under reduced pressure in silica vessels, succeeded in separating the

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enolic and keto-forms, which, however, reverted rapidly to the equilibrium mixture (*Ber.*, 1921, **54**, 579).

With certain derivatives of acetylacetone the individual modifications are more stable. Thus Knoevenagel (*Ber.*, 1903, **36**, 2150) indicated two isomeric forms of methylenebisacetylacetone, one a solid and the other an oil, both of which developed deep violet colorations with ferric chloride. He regarded the oil as the dienolised form, since with ammonia it yielded diacetyldihydrolutidine, whereas the solid, which gave no dihydropyridine derivative with ammonia, he regarded as the monoenolised compound.

Schiff claimed to have isolated no fewer than six isomeric varieties of benzylidenebisacetylacetone, namely, a keto-form, two monoenols (*cis* and *trans*) and three dienols (di*cis*, di*trans* and *cis-trans*). He did not, however, characterise these various modifications (*Annalen*, 1899, **309**, 206).

In the present communication, ethylenebisacetylacetone, prepared by the condensation of sodium acetylacetone and ethylene dibromide, is shown to exist in at least three isomeric forms, which have been identified definitely as a keto-form (I), a monoenolic modification (II), and a dienolic variety (III).

$$CH_3 \cdot CO \cdot \underset{|}{C}H \cdot CO \cdot CH_3 \qquad CH_3 \cdot CO \cdot \underset{|}{C} : C(OH) \cdot CH_3 \qquad CH_3 \cdot CO \cdot \underset{|}{C} : C(OH) \cdot CH_3$$
$$\underset{|}{C}H_2 \qquad\qquad \underset{|}{C}H_2 \qquad\qquad \underset{|}{C}H_2$$
$$\underset{|}{C}H_2 \qquad\qquad \underset{|}{C}H_2 \qquad\qquad \underset{|}{C}H_2$$
$$CH_3 \cdot CO \cdot CH \cdot CO \cdot CH_3 \qquad CH_3 \cdot CO \cdot CH \cdot CO \cdot CH_3 \qquad CH_3 \cdot CO \cdot C : C(OH) \cdot CH_3$$
$$\text{(I.)} \qquad\qquad\qquad \text{(II.)} \qquad\qquad\qquad \text{(III.)}$$

1. keto-*Ethylenebisacetylacetone* (I) is a mobile, colourless liquid of high boiling point; its alcoholic solution only slowly develops a violet colour with ferric chloride.

2. monoenol-*Ethylenebisacetylacetone* (II) is obtained in prismatic crystals, m. p. 99°; its alcoholic solution develops instantaneously a deep violet coloration with ferric chloride.

3. dienol-*Ethylenebisacetylacetone* (III) separates in cubical crystals, m. p. 140—143°, and reacts immediately with ferric chloride. This form is, however, less stable in air than the preceding varieties and the melting point of the crystals soon falls to about 100—110°.

The foregoing isomerides were characterised by an application of Meyer's method for estimating the percentage of enolic modification in a tautomeric substance such as acetylacetone (*Annalen*, 1911, **380**, 212; 1913, **398**, 49; *Ber.*, 1911, **44**, 2718; 1912, **45**, 2843), which depends on the rapid addition of bromine to the enolic modification, but not to the ketonic form. When treated with excess of hydroxylamine, *keto*-ethylenebisacetylacetone and *enol-*

ethylenebisacetylacetone both yield stereoisomeric tetraoximes. In the latter oximation, it is evident that hydroxylamine causes the enolic modification to revert to the ketonic isomeride.

EXPERIMENTAL.

Interaction of Sodium Acetylacetone and Ethylene Dibromide.— Sodium acetylacetone (210 g.) was mixed with excess of ethylene dibromide (600 g.) and refluxed at 160° for 12 hours; the mixture was then allowed to cool and the deposit of sodium bromide washed with ether. The weight of bromide corresponded nearly quantitatively with the amount of sodium originally in the sodium acetylacetone.

The brown ethereal filtrates were distilled, ether and ethylene dibromide being collected up to 135° and acetylacetone from 135° to 145°; the residue was transferred to a Claisen flask and distilled under reduced pressure (3—5 mm.), and the following fractions were collected : (1) b. p. 60—80°—contained the remainder of the ethylene dibromide and acetylacetone; (2) b. p. 80—100°—25 g. of a slightly yellow liquid boiling under ordinary pressure at about 200°. Its alcoholic solution gave no immediate coloration with ferric chloride, but a violet coloration slowly developed; it did not give a copper salt with ammoniacal copper acetate; (3) b. p. 120—130°—8·5 g. of a yellow oil; its alcoholic solution gave an immediate violet colour with ferric chloride and a small precipitate of copper salt with ammoniacal cupric acetate; (4) b. p. 170—200°—19 g. of a brown, viscid oil which gave an instantaneous ferric coloration and a copious precipitate with ammoniacal cupric acetate.

I. keto-*Ethylenebisacetylacetone* (I).—The principal product of the reaction, represented by the second fraction (b. p. 80—100°), was redistilled under reduced pressure, when about 80% distilled between 83° and 85°/4 mm. The resultant liquid was slightly yellow, readily miscible with water, alcohol, benzene, ether, or chloroform, but not with light petroleum; it dissolved in dilute sodium hydroxide to a yellow solution. A sodium salt was formed by adding metallic sodium to the liquid dissolved in ether.

After several distillations under reduced pressure, keto-*ethylenebisacetylacetone* boiled at 97—99°/20 mm. (Found : C, 63·3, 63·9; H, 7·9, 7·9. $C_{12}H_{18}O_4$ requires C, 63·7; H, 8·0%).

II. *Dehydration Product of Ethylenebisacetylacetone.*—The third fraction (b. p. 120—130°) did not solidify on keeping in the ice chest and was therefore dissolved in alcohol and treated with an excess of ammoniacal cupric acetate, when on dilution with water a small amount of copper salt was precipitated, but the major part of the substance evidently remained dissolved in the aqueous-

alcoholic filtrate. By diluting further with water and extracting several times with ether, a light brown oil was obtained, which soon crystallised. After repeated crystallisation from alcohol, the substance separated in colourless, hexagonal plates or laminæ, but only a very small amount was isolated. Its alcoholic solution did not respond to ferric chloride (Found : C, 72·2, 72·4; H, 8·2, 7·3. $C_{24}H_{30}O_5$ requires C, 72·4; H, 7·5%, thus corresponding with a possible dehydration product of ethylenebisacetylacetone : $2C_{12}H_{18}O_4 - 3H_2O = C_{24}H_{30}O_5$) (Knoevenagel, *loc. cit.*).

III. enol-*Ethylenebisacetylacetone* (II).—The fourth fraction (b. p. 170—200°) was cooled in ice, when crystallisation set in. The first deposit consisted of a mass of needles which, after washing with a little ether, were colourless and melted at 134°. Recrystallisation from alcohol or benzene gave a product with indefinite melting point, liquefaction commencing at about 100°, but not being complete until 130°. Its alcoholic solution gave an intense violet colour with ferric chloride and a copper derivative with ammoniacal cupric acetate.

When left in the ice chest for several days, the mother-liquors deposited prismatic crystals; these, when washed free from oil with the aid of ether, melted at 98—99°. Recrystallisation from benzene gave a mass of glistening, white needles, m. p. 99—100°; recrystallisation from alcohol also gave very fine needles melting at 99°. A mixture of the original crystals with those obtained after recrystallisation from alcohol and from benzene also melted at 98°, which indicated a definite substance and not a mixture (Found : C, 63·6, 63·7; H, 8·0, 8·2. $C_{12}H_{18}O_4$ requires C, 63·7; H, 8·0%).

This monoenol-*ethylenebisacetylacetone* (p. 44) when dissolved in alcohol gave an instantaneous deep violet coloration with ferric chloride and a precipitate of a copper salt with ammoniacal cupric acetate. After keeping for some months, its melting point became 146—152°.

IV. dienol-*Ethylenebisacetylacetone* (III). — The mother-liquors from the crystals of the monoenol showed no further signs of crystallisation and were converted into the copper derivative by treating an alcoholic solution with excess of ammoniacal cupric acetate. After drying, the mass was extracted with benzene; a faintly yellow solution was obtained which on evaporation of the solvent left a few drops of a brown oil, whilst the copper salt remained as an insoluble greenish-grey powder. It had no definite melting point, but decomposed above 250°, and was quite insoluble in all organic solvents. It contained 18% of copper. $C_{24}H_{34}O_8Cu$ requires Cu, 12·3 and $C_{12}H_{16}O_4Cu$ requires Cu, 22·1%.

The copper salt was decomposed with sulphuric acid in the presence of ether; a white precipitate was formed and was filtered off, whilst the ethereal layer was allowed to evaporate. The insoluble product with indefinite melting point of 100—107° was subsequently shown to be a mixture of mono- and di-enolic forms. The product separating from the ethereal layer formed colourless. cubic crystals which after washing with ether melted more definitely at 140—143° and consisted chiefly of dienol-*ethylenebisacetylacetone* (Found : C, 63·6; H, 7·9. $C_{12}H_{18}O_4$ requires C, 63·7; H, 8·0%).

When kept for some time, the melting point of the dienol became indefinite; melting commenced at 100°, but was not complete until about 140°. This change in fusibility probably indicated a partial transformation into a mixture of the mono- and di-enolic forms.

V. *Comparative Study of the Behaviour of the Three Isomerides towards Bromine.*—A known weight of the isomeride under investigation, dissolved in sufficient alcohol to give an approximately $M/20$-solution, was treated with $N/10$-bromine (alcoholic) in the cold until the yellow colour persisted; an alcoholic solution oï β-naphthol was then quickly added to absorb the excess of bromine. Potassium iodide was added and the solution gently warmed: iodine was liberated and titrated by means of $N/10$-thiosulphate without the use of an indicator, 1 g.-mol. of iodine being equivalent to one double bond, that is, to one hydroxyl group.

(*a*) *The liquid* keto-*ethylenebisacetylacetone* : 1 g.-mol. liberates $0·033 \times 127$ g. of iodine, corresponding with the presence of about 0·8% of the enolic form.

(*b*) enol-*Ethylenebisacetylacetone*, m. p. 98—99° : 1 g.-mol. liberates 2×127 g. of iodine, corresponding with the pure mono-enolic form of ethylenebisacetylatetone.

(*c*) dienol-*Ethylenebisacetylacetone*, m. p. 140—143° : 1 g.-mol. liberates $2·5 \times 127$ g. of iodine; this indicates the presence of about 1·25 hydroxyl groups per g.-mol. or a mixture of 25% of the dienolic with 75% of the monoenolic form of ethylenebisacetylacetone.

From these results, we conclude that in the case of the liquid and the solid, m. p. 98°, we are dealing with the comparatively stable ketonic and monoenolic forms of ethylenebisacetylacetone. respectively. The other product, m. p. 140—143°, may be an equilibrium mixture; or more probably it represents in the solid state the true dienolic form, which in alcoholic solution becomes transformed into an equilibrium mixture.

Comparative Study of the Ketonic and Monoenolic Forms of Ethylenebisacetylacetone.—Stereoisomeric tetraoximes. The liquid *keto*-ethylenebisacetylacetone and the solid enol modification were each heated on the water-bath for 2 hours in dilute alcohol with

excess of hydroxylamine hydrochloride (6—8 mols.) and sodium acetate. On the mixture being poured into water, the α-*tetraoxime* from the keto-form remained in solution, and was extracted with ether. It separated from the concentrated ethereal extract in colourless crystals, m. p. 165° (Found : N, 19·15. $C_{12}H_{22}O_4N_4$ requires N, 19·6%).

The β-*tetraoxime* from the enol form separated as a white solid crystallisable from hot water in minute, colourless needles decomposing at 220—222° (Found : N, 19·7%).

Tellurium Tetrachloride and keto-*Ethylenebisacetylacetone.*—The liquid keto-form (9 g. = 2 mols.) and 5·4 g. (1 mol.) of tellurium tetrachloride were refluxed in chloroform solution. The mixture immediately blackened, but little or no hydrogen chloride was evolved until after $\frac{1}{2}$ hour; the gas was then freely evolved during 3 hours. The filtrate from tellurium (0·4 g.) was concentrated in a vacuum desiccator. A black tar remained; no crystallisation took place even after one month or on treatment with various solvents. On extraction with *n*-hexane, the tar remained undissolved, but after evaporaton of the hydrocarbon crystalline laminæ were left. By pressing these on a porous plate, white crystals were obtained, which were purified by crystallisation from hexane. Hexagonal prisms resulted, m. p. 79°, yield 1 g. The product was readily soluble in alcohol and the solution gave an immediate intense purple colour with ferric chloride; it also yielded a copper salt. Qualitative tests showed the absence of tellurium, but chlorine was present and could be detached by boiling with aqueous potash (Found : C, 52·0, 51·6; H, 7·0, 6·9. $C_7H_{11}O_2Cl$ requires C, 51·7; H, 6·8%). This analysis corresponds with a removal of one acetylacetone residue and the formation of β-chloroethylacetyl-acetone, $CH_2Cl \cdot CH_2 \cdot CH(CO \cdot CH_3)_2$.

Transformations of enol-*Ethylenebisacetylacetone into its Isomerides.* —*Ketonisation.* The monoenol formed stable, prismatic crystals, m. p. 99°. It was slightly soluble in water and the solution reacted faintly acid to litmus. It readily dissolved in dilute caustic soda to a yellow solution of the sodium salt; no precipitate was produced when this solution was acidified with sulphuric acid in the cold, and extraction with ether yielded an oil which failed to colour ferric chloride and was probably the ketonic form.

Dienolisation. The copper salt, prepared from the monoenolic form by treating a solution in alcohol with excess of ammoniacal cupric acetate, dried to an amorphous, greenish-grey powder quite insoluble in all organic solvents, thus differing from the usual co-ordinated copper derivatives obtained from the β-diketones. It contained 19·3% of copper; the amount calculated for the copper

derivative of the monoenol is 12·3, and for that of the dienol 22·1%. When decomposed in the usual manner with sulphuric acid in the presence of ether, an amorphous, white solid is precipitated which is only sparingly soluble in ether; after washing with ether and drying, this melts at 98° and is the monoenolic form, but the substance which crystallises from the ethereal solution has an indefinite melting point; it softens and loses its crystalline form at 110°, but does not run down the tube to a clear liquid until 130—134°, behaving as a mixture of the di- and mono-enolic forms; Meyer's test indicates the presence of about 20% of the dienolic form with 80% of the monoenolic. It is evident that under the influence of ammoniacal cupric acetate the monoenol changes partly to the dienol.

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