The Structure of Ethyl Dehydroacetate

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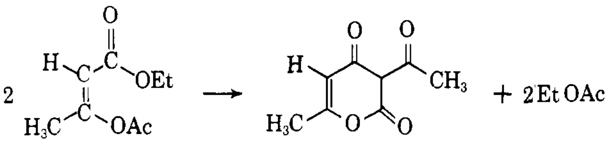
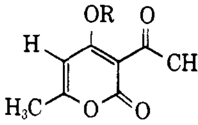
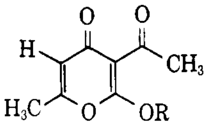
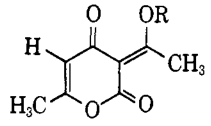
During the course of an attempted diene synthesis employing cyclopentadiene and the enol acetate of ethyl acetoacetate (I), a solid, m.p. 110°, identified as dehydroacetic acid (II), was isolated; no Diels–Alder adduct was formed. Under the vigorous experimental conditions, the enol acetate apparently underwent self-condensation to yield ethyl acetate and dehydroacetic acid (II).


I II

Dehydroacetic acid has been assigned the Feist structure II[3] on the basis of the observed isomerization to 2,6-dimethylpyrone-4-carboxylic acid-3.[4] A re-examination of structure II by Berson[5] has confirmed the structure of the carbon skeleton as formulated. The striking similarity of the ultraviolet absorption spectra of the acid II and its ethyl ester (enol ether) provided compelling evidence that dehydroacetic acid (II) was completely enolized in solution. Furthermore, on the basis of the absorption data, Berson concluded that the conversion of the acid to its ethyl ester occurred with a minimal structural change, *i.e.*, with simple replacement of the hydrogen by an ethyl group. However, no conclusion was drawn as to which of the three possible enol variants (IIa, IIb, or IIc) the acid (and the ethyl ester) possessed. Recently, Forsen and Nilsson[6] have concluded on the basis of the infrared[6,7] and n.m.r. spectra that dehydroacetic acid and its methyl ester posses the α-pyrone structure IIa, although structure IIc was not ruled out.

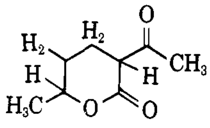

IIa

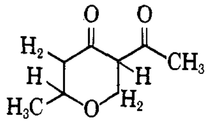

IIb

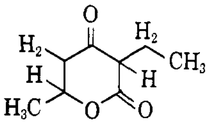

IIc

Investigations of similar substituted 2,4-pyrandione systems have shown that, depending on the method of preparation, the enol ethers which are formed are not necessarily homogeneous. Comparison of the ultraviolet and infrared spectral properties of the enol ethers often allow a simple method of positional assignments.[8] However, the case of dehydroacetic acid (and its esters) is complicated by the presence of the 3-acetyl group. With these considerations in mind, a systematic study of the ultraviolet, infrared, and n.m.r. spectra of dehydroacetic acid and its methyl and ethyl esters was undertaken, employing chemical methods to supplement the spectroscopic information.[9]

Homogeneous esters were obtained in the usual manner by the action of alkyl iodides on the dry silver salt of dehydroacetic acid.[5] Initial comparison of the spectral data gave little more information than had been obtained by Berson[5] and by Forsen and Nilsson[6] as to the enol structure of the acid and its esters. Subjecting the acid to the action of deuterium oxide in the presence of sodium deuterioxide caused rapid deuteration of the 3-acetyl group (observed *via* n.m.r. by the disappearance of the singlet at τ 7.43). This observation was not sufficient to rule out structure IIc inasmuch as the acid may be subject to tautomeric equilibria. The ethyl ester, in which the enol form is fixed, also exhibited rapid deuterium exchange on the 3-acetyl group (disappearance of the singlet at τ 7.55). Hydrogenation of the ethyl ester, m.p. 90–91°, in ethanol using 5% palladium on charcoal as catalyst afforded an oil, $\lambda_{\max}$ 264.5 mμ, which gave a strong positive ferric chloride test. This oil was readily identified as 3-acetyl-6-methyl-2-pyrone (IIIa) by its n.m.r. and ultraviolet spectra. The absence of the characteristic $O{-}C_2H_5$ group in the n.m.r. spectra indicated that the enol ether had cleaved during hydrogenation. The 6-methyl group was now present as a doublet (3H, center at τ 8.63), while the 3-acetyl group showed as a singlet (3H, τ 8.07) which readily underwent deuterium exchange. A single proton showed as a multiplet (center at τ 5.87) corresponding to the 6-position hydrogen. The remaining hydrogens showed as unresolved multiplets. The absence of two extra protons in the region of the n.m.r. spectra occupied by the single proton on the >CH–O– carbon ruled out IIIb, while the deuteration experiments (as well as the absence of a $-C_2H_5$ group in the n.m.r.)[10] precluded IIIc. This combination of spectral data constitutes a simple proof that the enol structure of ethyl dehydroacetate is IIa, and, if the direct relationship of the enol ether to the acid is valid, of the enol structure of dehydroacetic acid.


IIIa


IIIb


IIIc

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[7] H. M. Randall, R. G. Fowler, N. Fuson, and J. R. Dangl, "Infrared Determinations of Organic Structures," Van Nostrand Co., Inc., New York, N. Y., 1949, p. 231.

[8] (a) S. Janiszewska-Drabarek, *Roczniki Chem.*, **27**, 456 (1953); *Chem. Abstr.*, **49**, 3176 (1955); (b) I. Chmielewska, J. Cieslak, and T. Kraczkiewicz, *Roczniki Chem.*, **30**, 1009 (1956); *Chem. Abstr.*, **51**, 8733 (1957); (c) D. Herbst, W. B. Mers, O. R. Gottlieb, and C. Djerassi, *J. Am. Chem. Soc.*, **81**, 2427 (1959); (d) W. Jachymczyk and I. Chmielewska, *Bull. Acad. Polon. Sci., Ser. sci. chim.*, **8**, 155 (1960); *Chem. Abstr.*, **55**, 11401 (1961); (e) J. D. Bu'Lock and H. G. Smith, *J. Chem. Soc.*, 502 (1960); (f) E. A. Chandross and P. Yates, *Chem. Ind.* (London), 149 (1960).

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[10] The $-C_2H_5$ group, for structure IIIc, might have been expected to show up in the $-CH_2-$ region not as a quartet but as a multiplet due to the transient present of the acidic proton on the ring; this situation would have been resolved during the deuteration experiments. Such a situation, however, did not arise. The deuteration experiments were controlled so that no appreciable cleavage of the β-keto esters occurred in any of the cases reported herein.

Experimental

Ultraviolet spectra were obtained on a Beckman Model DB spectrophotometer in 95% ethanol (mean deviation ±1.0 mμ). Infrared spectra were taken on a Perkin-Elmer Model 21 spectrophotometer equipped with sodium chloride optics. The n.m.r. spectra were obtained on a Varian Model A-60 spectrometer using tetramethylsilane as an internal reference and are reported in τ (p.p.m.) units. Melting points were taken in capillaries on a Mel-Temp melting point apparatus.

Dehydroacetic Acid (II).—The enol acetate of ethyl acetoacetate [b.p. 83° (5 mm.), n^{25}D 1.4423, 61.2 g.], freshly distilled cyclopentadiene (19.8 g.), and hydroquinone (0.2 g.) were mixed in a glass liner and placed in a high pressure bomb at 190° for 20.5 hr. under 2000 p.s.i. of an inert gas (hydrogen). On removal from the bomb, 4 g. of polymer was filtered off and the liquid was distilled, yielding three fractions. The low-boiling fraction consisted of mainly cyclopentadiene and was stripped off and discarded. The higher boiling material was fractionated to give 35 g. of unreacted enol acetate and 6.3 g. of a white crystalline material, b.p. 126° (7 mm.), m.p. 99–100°, which melted at 110° following recrystallization from carbon tetrachloride. The solid was identified as dehydroacetic acid, giving no melting point depression on admixture with an authentic sample, m.p. 110°, prepared by the method of Arndt.[11] The acid gave the following spectral properties: ultraviolet, λ_{max} 225.5 mμ (log ε 3.99) and 311.0 mμ (log ε 4.05); infrared, $\lambda_{max}^{CCl_4}$ 5.70 (s), 5.75 (m), 6.06 (s), 6.16 (m), and 6.40 (s) μ; λ_{max}^{Nujol} 5.82 (s), 6.06 (s), 6.16 (s), and 6.42 (s) μ; λ_{max}^{KBr} 5.78 (s), 6.05 (s), 6.17 (m), and 6.40 (s) μ; n.m.r. ($CDCl_3$), τ 7.84 (3H, doublet, J = 0.8 c.p.s.), 7.43 (3H, singlet), and 4.22 (1H, quartet).

A sample of dehydroacetic acid was dissolved in D_2O containing sodium deuterioxide and examination of the n.m.r. spectrum showed rapid deuteration of the 3-acetyl group as indicated by the disappearance of the singlet at τ 7.43. No exchange with the 6-methyl was observed.

Sodium Dehydroacetate.[12]—Sodium dehydroacetate was obtained as a white salt from ethanol–water: λ_{max} 230 mμ (log ε 4.22) and 295.5 mμ (log ε 3.92); λ_{max}^{KBr} 5.93 (s), 6.02 (s), 6.25 (sh), 6.34 (s), and 6.51 (ms) μ; λ_{max}^{Nujol} 5.93 (s), 6.02 (s), 6.31 (m), 6.34 (s), and 6.51 (ms) μ.

Silver Dehydroacetate.[12]—Silver dehydroacetate was obtained as white crystals from hot water which turned gray on drying: λ_{max} 229 mμ (log ε 4.21) and 297 mμ (log ε 3.92); λ_{max}^{KBr} 5.93 (s), 6.03 (s), 6.35 (s), and 6.52 (m) μ; λ_{max}^{Nujol} 5.93 (s), 6.08 (s), and 6.41 (s) μ.

Methyl Dehydroacetate.[12]—Methyl dehydroacetate was obtained as faintly yellow needles on recrystallization from carbon tetrachloride: m.p. 91–92° (lit.[12] m.p. 93–95°); λ_{max} 224.5 mμ (log ε 3.98) and 314.5 mμ (log ε 3.94); $\lambda_{max}^{CCl_4}$ 5.78 (s), 5.83 (s, sh), 5.89 (s, sh), 6.08 (m), and 6.56 (m) μ; λ_{max}^{Nujol} 5.78 (ms, sh), 5.86 (s), 5.98 (s), 6.09 (m), and 6.66 (s) μ; λ_{max}^{KBr} 5.76 (ms, sh), 5.83 (s), 5.95 (s), 6.06 (m), and 6.64 (s) μ; n.m.r. ($CDCl_3$), τ 7.68 (3H, doublet, J = 0.8 c.p.s.), 7.55 (3H, singlet,) 6.04 (3H, singlet), and 3.77 (1H, quartet).

Ethyl Dehydroacetate.[12]—Ethyl dehydroacetate was obtained as white needles on recrystallization from carbon tetrachloride: m.p. 90–91° (lit.[12] m.p. 93–94°); λ_{max} 225.5 mμ (log ε 3.96) and 313.5 mμ (log ε 3.91); $\lambda_{max}^{CCl_4}$ 5.79 (s), 5.87 (s, sh), 6.07 (m), and 6.53 (ms) μ; λ_{max}^{Nujol} 5.83 (s, sh), 5.89 (s), 6.09 (m), and 6.54 (s) μ; λ_{max}^{KBr} 5.69 (m), 5.83 (s), 5.89 (s, sh), 6.07 (m), and 6.54 (s) μ; n.m.r. ($CDCl_3$), τ 8.57 (3H, center of triplet), 7.40 (3H, doublet, J = 0.8 c.p.s.), 7.55 (3H, singlet), 5.78 (2H, center of quartet), and 3.93 (1H, quartet).

A small sample of ethyl dehydroacetate was shaken in D_2O in the presence of sodium deuterioxide for 20 min. and extracted with chloroform-*d*. The diminished singlet at τ 7.55 in the n.m.r. indicated partial deuteration of the 3-acetyl methyl group while no exchange of the 6-methyl was observed.

Ethyl dehydroacetate (2.5 g.) was hydrogenated on a Parr hydrogenation apparatus (60 p.s.i.) using 5% Pd–C (0.5 g.) as catalyst in 35 ml. of absolute ethanol. The catalyst was removed by filtration and the ethanol solution exhibited an ultraviolet λ_{max} at 264.5 mμ. The solvent was removed under vacuum to give 1.5 g. of a dark oil which gave a strong, positive ferric chloride test in both water and alcohol. This material was assigned the structure of 3-acetyl-6-methyl-2-pyrone on the basis of the spectral evidence: $\lambda_{max}^{CCl_4}$, 5.81 (w–m), 6.04 (s), 6.19 (s), and 8.00 (s) μ; λ_{max}^{neat} 5.75 (s), 6.04 (s), 6.19 (s), and 8.00 (s) μ; n.m.r. (CCl_4), τ 8.63 (3H, center of doublet, J = 7 c.p.s.), 8.07 (3H, singlet), 5.87 (1H, multiplet), and 7.84–8.50 (5H, unresolved multiplets). This oil rapidly exchanged deuterium with the 3-acetyl hydrogens as was observed by the disappearance of the singlet at τ 8.07. The deuterium exchange reactions were carried out in D_2O at *ca.* 10–15° with only a trace of sodium deuterioxide present so as to minimize any chance of β-keto ester cleavage. A quantitative hydrogenation of a 1.0-g. sample using 5% Pd–C in absolute ethanol gave absorption of 3.2 mole equiv. of hydrogen. The ethanol solution was examined by ultraviolet and showed an absence of absorptions at 225 and 313 but gave an absorption at 264.5 mμ indicating hydrogenation was complete. Hydrogenation using PtO_2 in ethanol led to a yellow oil, n^{24}D 1.4924, which had λ_{max} 294 mμ and $\lambda_{max}^{CCl_4}$ 5.74 (m, sh,) 5.85 (s), 6.05 (ms), 6.39 (s), 6.90 (ms), 7.21 (ms), 7.41 (m), 7.52 (wm), and 7.81 (s) μ. This material, which was obviously different from the product using Pd–C as catalyst, was not identified.

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The Peroxide-Induced Decarbonylation of Phenoxyacetaldehyde

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Our interest[2] in the neophyl-radical rearrangement prompted an investigation of a possibly analogous oxygen to carbon migration by phenyl. This report concerns our efforts to convert the phenoxymethyl radical (**1**) into the benzyloxy radical (**2**). Several

$$\underset{\mathbf{1}}{\mathrm{Ph{-}O{-}CH_2\cdot}} \xrightarrow{?} \underset{\mathbf{2}}{\mathrm{\cdot O{-}CH_2{-}Ph}}$$

items in the literature made such an investigation seem worthwhile. (1) The rearrangement appeared possible even though no steric compression exists in **1**, since Slaugh[3] found some rearrangement of phenyl in $C_6H_5CH_2CH_2\cdot$ (using labeled compounds) and showed thereby that compressional strain in the radical is not necessary for rearrangement to occur. (2) Oxygen radicals of the type sought do not usually undergo the reverse of the above rearrangement unless three aryl groups are present. Thus, **3** does not rearrange to **4**,[4] while **5** does rearrange to **6** (the Wieland rearrange-

$$\underset{\mathbf{3}}{\mathrm{Ph{-}CH(CH_3){-}O\cdot}} \not\longrightarrow \underset{\mathbf{4}}{\mathrm{CH_3\dot{C}H{-}OPh}}$$

$$\underset{\mathbf{5}}{\mathrm{Ph_3C{-}O\cdot}} \longrightarrow \underset{\mathbf{6}}{\mathrm{Ph_2\dot{C}{-}OPh}}$$

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