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ON THE "TRANS ENOL" OF ETHYL α-sec-BUTYLACETOACETATE[1]

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In our concern with the chemistry of α-alkyl-β-ketoesters,[3] the recent reports of Kabachnik *et al.*[4] on the *trans*-enolization of β-dicarbonyl compounds have been of considerable interest to us. The principal evidence provided by these investigators for the *trans* geometry of the enols of sterically hindered ethyl α-alkylacetoacetates has been the insensitivity of the enol content of such esters to solvent variation and their failure to show a ferric chloride test.[4a,b] In particular, ethyl α-sec-butylacetoacetate (I) stands out as an example of a system with a relatively high "enol" content (~ 14%) which is practically invariant in a range of solvents of widely different solvating capacities. The enol contents were measured bromometrically and their constancy confirmed

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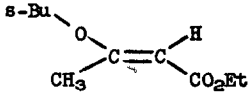
[2] American Chemical Society Scholar, 1962-63.

[3] S. J. Rhoads, J. C. Gilbert, A. W. Decora, T. R. Garland, R. J. Spangler and M. J. Urbigkit, *Tetrahedron*, in press; S. J. Rhoads and A. W. Decora, *ibid.*, in press.

[4] (a) M. I. Kabachnik, S. T. Yoffe and K. V. Vatsuro, *Tetrahedron*, **1**, 317 (1957); (b) M. I. Kabachnik, S. T. Yoffe, E. M. Popov and K. V. Vatsuro, *ibid.*, **12**, 76 (1961); (c) S. T. Yoffe, E. M. Popov, K. V. Vatsuro, E. K. Tulikova and M. I. Kabachnik, *ibid.*, **18**, 923 (1962).

by ultraviolet absorption data ($\lambda_{max} \sim$ 233-240 mμ ; $\epsilon_{max} \sim$ 2000). Moreover, the infrared spectrum of the system showed strong bands at 1738 cm^{-1} (ester carbonyl), 1717 cm^{-1} (ketone carbonyl), and a weaker band at 1619 cm^{-1} attributed to the conjugated double bond of the trans enol. The absence of a band characteristic of a chelated cis enol at $\sim$ 1650 cm^{-1} was also remarked.[4b]

In this communication, we present evidence that the "trans enol" of ethyl α-sec-butylacetoacetate is, in fact, the enol ether II, formed by concurrent O-alkylation of acetoacetic ester.



II

When ethyl acetoacetate is alkylated with sec-butyl iodide under ordinary alkylating conditions (ethanolic sodium ethoxide), the alkylation product contains varying amounts of the O-derivative, II. In our preparations ($\sim$ 0.125 M in sodium enolate), II was present in amounts of 6 to 8% as judged by g.l.p.c., ultraviolet, and n.m.r. analyses. The C- and O-alkylated products could not be separated by fractional distillation but were resolved by g.l.p.c. The properties of the "unpurified" preparations agreed well with those reported by Kabachnik et al.: IR, strong bands at 1741 cm^{-1} and 1719 cm^{-1} and a sharp medium-weak band at 1619 cm^{-1}; UV, λ_{max}^{EtOH} = 238 mμ, $\epsilon \sim$ 1000; bromine titration,[5] 13-14% "enol".

The contaminating O-derivative was removed from the C-alkylated product by shaking with 2 N HCl at room temperature for several hours. Pure ethyl α-sec-butylacetoacetate, recovered from this treatment, had properties

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[5] By the modified-direct method of W. Dieckmann, Ber. 55, 2477 (1922).

which contrasted strongly with those of the original product. In particular, the enol content, determined by bromine titration, had fallen to 0.75 to 1 % and the g.l.p.c. pattern no longer showed the presence of the second component. In the infrared spectrum, the sharp 1619 cm^{-1} peak had disappeared entirely, while the ultraviolet spectrum showed only a low intensity maximum at 265-270 mμ in ethanol and in cyclohexane ($\epsilon^{EtOH} = 70$, $\epsilon^{C_6H_{12}} = 150$), characteristic of an enolizable β-ketoester containing a very small amount of *cis* enolic species.[3] The intense absorption at ~ 240 mμ of the original preparation had vanished and been replaced by a shallow minimum at 245 mμ. The n.m.r. spectrum of I gave no evidence of the vinyl proton resonance at 5.12 τ detected in the unpurified product. It was further noted, contrary to the observations of Kabachnik *et al.*[4a,b] and Henecka,[6] that pure I does give a positive ferric chloride test provided that sufficient sample is used. To be sure, the gray-green coloration is weak and develops slowly, but it is unmistakable.

Finally, we have isolated the contaminating substance by preparative g.l.p.c. techniques and have established its identity with an independently synthesized sample of II. Authentic II, prepared from ethyl β-chlorocrotonate and sodium sec-butylate,[7] has the following pertinent properties:[8] IR, strong bands at 1712 cm^{-1} (conjugated ester carbonyl) and 1619 cm^{-1} (conjugated C=C, intensified by enol ether structure); UV, $\lambda^{EtOH}_{max} = 238$ mμ, $\epsilon \cong 15{,}000$; NMR, vinyl proton signal at 5.12 τ; saponification equiv., 182 (calc'd, 186).

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[6] H. Henecka, *Chemie der Beta-Dicarbonyl-Verbindungen*, p. 125, Springer-Verlag, Berlin, 1950.

[7] D. E. Jones, R. O. Morris, C. A. Vernon and R. F. White, *J. Chem. Soc.* 2349 (1960).

[8] Full details of the ultraviolet, infrared, and nuclear magnetic resonance spectra of O-derivatives of both cyclic and acyclic β-ketoesters will be reported at a later date.

The contention of Kabachnik *et al.* that the enol of *α*-sec-butylacetoacetate exists almost wholly in the *trans* form, based as it is on a case of mistaken identity, must be seriously questioned. The true enol content of I is very low, but if one can deduce geometry on the bases of solvent response and coloration with ferric chloride, then it appears that the enolic species has the usual chelated *cis* structure.

While O-alkylation has been recognized as a component of the reactions of ambident anions under rather special conditions (i.e., selective solvents, highly reactive alkylating agents and suitable substrates)[9], it seems that its importance under quite ordinary alkylating conditions has been underestimated. Work on this general problem is continuing in our laboratories.

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[9] See, *inter alia*, S. J. Rhoads, R. D. Reynolds and R. Raulins, *J. Amer. Chem. Soc.* **74**, 2889 (1952); A. Brändström, *Acta Chem. Scand.* **7**, 223 (1953); N. Kornblum and coworkers, *J. Amer. Chem. Soc.* **77**, 6269 (1955) and later papers; H. D. Zook and T. J. Russo, *ibid.*, **82** 1258 (1960); and I. Forsblad, *Arkiv för Kemi* **15**, 403 (1960).