5. Manske, R. H. F. (Ed.) *The Alkaloids*, **X**, Academic, New York 1968, p. 574.
6. Sakan, T., Fujino, A., Murai, F., Butsugan, Y. and Suzui, A. *Bull. Chem. Soc. Japan* **32** (1959) 315.
7. Torssell, K. and Wahlberg, K. *Acta Chem. Scand.* **21** (1967) 53.
8. Hart, N. K., Johns, S. R. and Lamberton, J. A. *Australian J. Chem.* **21** (1968) 1321.
9. Cavill, G. W. K. and Zeitlin, A. *Australian J. Chem.* **20** (1967) 349.

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Enol-Keto Tautomerism in Diethyl Acylmalonates Studied by NMR

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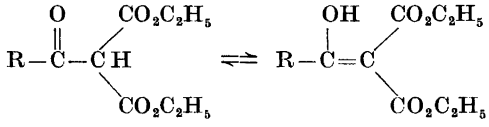
During our investigation of (1-alkylsulfinylalkylidene)-malonic acids at these laboratories [1] we prepared a number of diethyl acylmalonates by the method of Lund.[2] We have now determined the enol content of these compounds and the results are given in Table 1. At the same time we should like to report the chemical shifts for the various protons.



The enol-keto equilibrium positions for the three first compounds in Table 1 have been determined earlier by Meyer [3] and by Auwers and Jacobsen,[4] who titrated the enol with bromine at about 0°C. They found the enol content to be 64 % [3] and 70 %,[4] respectively, for $R=CH_3$. For $R=C_2H_5$ and $R=(CH_3)_2CH$, Auwers and Jacobsen give the values 43 % and 47 %, respectively.[4] These determinations agree rather well with ours.

From Table 1 one can see that the enol content is greater in III than in II, but is reduced to zero in IV where steric interactions destabilize the enol. It is easily appreciated that an ethoxycarbonyl- and a *tert.*-butyl group *cis* to a double bond will produce a rather unfavourable system. Similar effects have also been noted by Campbell and Gilow in their studies on β-diketones.[5] Even in diethyl benzoylmalonate (V) steric effects are of importance diminishing the enol content as compared with diethyl acetylmalonate, in spite of the conjugated system which is formed in the enol of V. Insertion of a benzyl group in place of the phenyl group reduces the steric interaction and gives rise to more enol tautomer.

The enol form is also more favored in newly distilled compounds. A freshly distilled sample of diethyl benzoylmalonate held 18 % enol but after storing for a week only 7 %.

The position of the OH-proton signal does not vary appreciably among the compounds studied and occurs at very low applied fields. This depends upon the presence of intramolecular hydrogen bonds in the enols, which are not as strong as those in the β-diketones studied by Burdett and Rogers,[6] but stronger than those in the β-ketoesters investigated by the same authors. Even for the α-protons the chemical shift does not vary very much, but in the series I—IV the protons will be more deshielded the bulkier the acyl group, due to electronic effects from the acyl groups which increase the electron density at the α-carbon in this way.

The ester groups of the enol form of the compounds are not magnetically equivalent and are also different from the keto tautomer. In compound V, however, the equilibrium is unfavourable for the enol form and when the resolution was insufficiently high, the signals from the enol disappeared under those from the keto form, since the shift difference is small. This small shift difference has also given rise to some uncertainty in the determination of the chemical shift, especially for diethyl propionylmalonate, where an ethyl group is present also in the acyl part of the molecule.

Experimental. Proton magnetic resonance spectra were obtained on the Varian A 60

Table 1. Proton chemical shifts and enol content in pure diethyl acylmalonates. (δ ppm). k=keto, e=enol.

Diethyl acylmalonate	Enol %	OH	α-H	Ester group		R			
$RCOCH(CO_2C_2H_5)_2$				CH_3	CH_2 4.23 k				
I R = CH_3	60	13.50	4.56	1.27	4.27 e 4.20 e	CH_3	2.28 k 2.16 e		
II R = C_2H_5	42	13.44	4.57	1.23 k 1.15 e 1.03 e	4.23 k 4.27 e	CH_3	1.25	CH_2	2.64 k 2.47 e
III R = $(CH_3)_2CH$	50	13.39	4.71	1.26 k 1.24 e 1.13 e	4.21 k 4.25 e	CH_3	1.20	CH	2.91 2.79
IV R = $(CH_3)_3C$	0	—	4.73	1.14	3.93	CH_3	1.09		
V R = C_6H_5 freshly dist. at equilib.	18 7	13.54	4.60	1.14	4.22	C_6H_5	7.35 k 8.02 e		
VI R = $C_6H_5CH_2$	52	13.51	4.68	1.18 1.12	4.13 4.20	C_6H_5	7.05	CH_2	3.78 k 3.87 e

spectrometer. Chemical shift and equilibrium determinations have been made at 38°±2°. Chemical shift values are reported in ppm (δ-values) from internal tetramethylsilane. Equilibrium compositions have been obtained by integration of keto and enol resonance peaks. The samples have not been degassed as this does not produce any measureable effects.[7]

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1. Allenmark, S. and Bohman, O. *Acta Chem. Scand.* **22** (1968) 1404.
2. Lund, H. *Ber.* **67** (1934) 937.
3. Meyer, K. H. *Ber.* **45** (1912) 2855.
4. v. Auwers, K. and Jacobsen, H. *Ann.* **426** (1922) 161.
5. Campbell, R. D. and Gilow, H. M *J. Am. Chem. Soc.* **82** (1960) 2389.
6. Burdett, J. L. and Rogers, M. T. *J. Am. Chem. Soc.* **86** (1964) 2105.
7. Allen, G. and Dwek, R. A. *J. Chem. Soc.***B 32** (1966) 161.

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