3. The Hammett equation applies to the bromination of substituted toluenes by N-bromosuccinimide at all pressures, the ρ value for any such reaction falling off sharply as the pressure rises.

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POSITION OF THE ENOL PROTON IN THE CHELATE FORMS OF UNSYMMETRICAL β-DIKETONES

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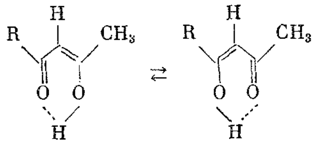
Nuclear magnetic resonance spectra have been used to fix the preferred position of the rapid exchange proton of the intermolecular H bonds of the chelate enol forms of the β-dicarbonyl compounds. Information of this kind has already been obtained for a limited number of types of compounds: the α-acyl derivatives of the cyclic ketones [1, 2], the β-ketoaldehydes [3, 4], and the ring-substituted benzoylacetones [5]. The principal aim of the present work was to determine the position of the point of equilibrium in the intrachelate A ⇌ B equilibrium (ICE) in the aliphatic β-diketones $RCOCH_2COCH_3$ (Ia–d): R = C_2H_5 (Ia), $CH(CH_3)_2$ (Ib), $C(CH_3)_3$ (Ic), and $C(CH_3) = CH_2$ (Id)



(A) (B)

Comparison has also been made of ICE data obtained from study of the ^1H and ^{13}C NMR spectra with the results of quantum-chemical calculations on the relative stabilities of the (A) and (B) forms. The PMR spectra of the various compounds in CCl_4 solution, and the ^{13}C NMR spectrum of compound (Id), were obtained by ourselves; the NMR spectra of the remaining compounds were taken from the literature.

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TABLE 1. Chemical Shifts for the $COCH_3$ Group ^1H and the Carbonyl Group* ^{13}C; Fraction (β) of the (B) Tautomer in the (I) Diketones [CS in ppm; TMS; β = [B]/([A] + [B]), 30°C]

Compound	^1H (CCl_4)	^{13}C (pure liquids)		β, %, from the following data		
	Δ	$\delta(COCH_3)$	$\delta(COR)$ †	Δ	$\delta(COCH_3)$	$\delta(COR)$
(Ia)	–	191,6	196,6 [6] (196,0) [6]	–	48	48
(Ib)	0,15	192,4	199,5 [6] (199,7) [6]	58	51	51
(Ic)	0,13	193,1	201,2 [6] (201,9) [6]	67	53	52
(Id)	0,06	195,3	180,8	96	66	–
(Ie)	0,29	175,5	171,2 [7]	5	5	5
(If)	0,17	190,5 192,1 190,9	190,5 [7] 192,1 [6] 190,9 ‡	50	50	50
(Ig)	0,12	193,4	183,3 ** (185,6)**	70	58††	57

*Chemical shifts from [6, 7] were recalculated to the TMS scale using the formula: δ (TMS) = 192.8-δ (CS_2).

†Values of δ(COR) for the symmetrical $RCOCH_2COR$ diketones are shown in parentheses.

‡In $CDCl_3$ [8].

**In $CDCl_3$ [5].

††From ^{17}O NMR data in benzene solution, $\beta \approx 56\%$ [1, 2].

TABLE 2. Calculated Values of the Energy Difference (ΔE), and Measured Values of the Molar Free Energy Difference ($\Delta G°$), for the (A) and (B) Enol Tautomeric Forms of Compounds from the $RCOCH_2COCH_3$ (I) series

Compound	$E_A - E_B$, kcal/mole	$G^\circ_A - G^\circ_B$, kcal/mole
(Ib)	+2,3	0
(Id)	+3,2	+0,4
(Ih)	−0,5	<−1

DISCUSSION OF RESULTS

Table 1 lists values of the chemical shifts (CS) of the $COCH_3$ protons, and the C=O group ^{13}C nucleus, in the enol forms of the unsymmetrical diketones and in two model compounds: ethyl acetoacetate (Ie, R = OC_2H_5) where the ICE is shifted toward form (A); and acetylacetone (If) where the ICE point is midway between forms (A) and (B). Data on the relative proportions (β) of the two intrachelate tautomers will also be presented, these having been obtained from CS measurements on the PMR and ^{13}C NMR spectra, following the procedures outlined in the experimental section.

Values of β calculated from chemical shift measurements on the ^{13}C NMR spectra of the two C=O groups were almost identical; the value for benzoylacetone (Ig, R = C_6H_5) was close to that obtained from CS measurements on the ^{17}O NMR spectrum [1, 2]. The relative proportion of tautomer (B) with enolized RCO group increased in passing through an R series: $OC_2H_5 \ll C_2H_5 < CH_3 < CH(CH_3)_2 < C(CH_3)_3 < C_6H_5 < C(CH_3) = CH_2$. The total enol content of the $RCOCH_2COOC_2H_5$ (II) β-ketoesters, compounds in which enolization proceeds largely through the RCO group, increases in this same order. This is obviously due to the fact that the R radical – C=O group coupling which stabilizes the keto structure becomes weaker on moving through the series [9]. The value of the $\Delta\sigma_C^+$ constant, a measure of the degree of direct polar coupling, diminishes in passing through the

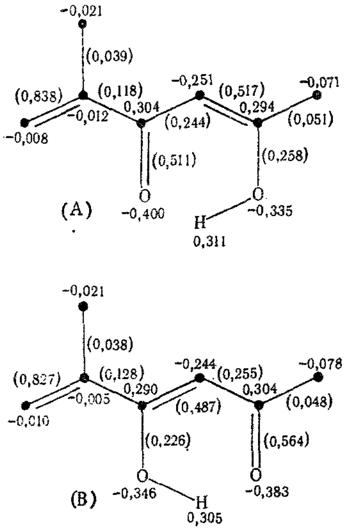

Fig. 1. Charges and π-bond orders (in parentheses) in tautomers (A) and (B) of methacryloylacetone (Id).

first five members of the series [10]. It has been shown [4] that the relative proportion of the chelate forms of the $RCOCH(CH_3)CHO$ aldoketones with enolized RCO group increases in moving through this same R series.

The values of the relative PMR $\Delta = \delta_K^H - \delta_e^H$, ($\delta_K^H$ and δ_e^H are acetyl group δ values for the diketo and enol forms) fell off steadily in going from $R = OC_2H_5$ to $C(CH_3) = CH_2$, this decrease being accompanied by a corresponding increase in the relative proportion of tautomer (B) present in the system. For each ketone, the value of β calculated from Δ was greater than that obtained form the ^{13}C NMR spectrum. We believe that preference should be given to the value obtained from the ^{13}C NMR spectrum. The value of Δ cannot be considered as an exact measure of the position of the ICE equilibrium point. It is seen that Δ is sensitive to direct substituent interaction in the tautomer, and to intermolecular interaction as well, but to a lesser degree than either δ_K^H and δ_e^H. The C=O group CS's in the ^{13}C NMR spectra of the (A) and (B) tautomers are quite different in value ($\delta_B - \delta_A > 30$ ppm); they are more sensitive to change in the ICE point position than are the PMR CS's ($\Delta_A - \Delta_B = 0.24$ ppm), and are only slightly affected by other factors.

The $COCH_3$ signal in the PMR spectrum of the enol form (Ie) has triplet structure with ~0.7 Hz splitting, this being the result of spin–spin coupling with the vinyl and enol protons. In mixtures of (If) and (Id), this signal is a singlet, the signal width at half-wave height being greater for the first compound than for the second, and greater than also the width of the reference TMS lines (0.6, 0.5, and 0.4 Hz, respectively). These observations are consistent with a shift in the ICE point toward the (B) form of (Id), a compound in which there is essentially no H-bond spin–spin coupling between the CH_3 and enol protons [2], and with the fact that the constant for spin–spin coupling with the vinyl protons is no more than 0.2 Hz [11].

Values of the total energy calculated by the CNDO/2 method were used as measures of the relative stabilities of tautomers (A), (B), (Ib), (Id), and (Ih) $R = OCH_3$.* Standard values of the bond lengths and valence angles were used in these calculations. An exception here was the O–H bond length which was set equal to 1.10 Å [12]. Study was made of the various conformers resulting from rotation around the C–R bond. Values of $E_A - E_B$, the difference in total energies of the most favored conformers, are given in Table 2 together with values of $G_A^\circ - G_B^\circ$, the difference in molar free energies calculated from the expression $G_A^\circ - G_B^\circ = RT \ln[\beta/(1-\beta)]$, using β values taken from Table 1. Predictions concerning the effect of R on chelate tautomer stability are consistent with the experimental data. Forms (A) and (B) have essentially the same dipole moments. The methods commonly used for calculating heats of formation are ineffective here because of the peculiarities of the enol form structures (H atom located between two heteroatoms). Figure 1 shows diagrams for the enol tautomers of (Id), together with charges and bond orders calculated by the CNDO/2 method. The degree of π-electron delocalization is higher in the more stable tautomer (B) than in the other tautomer (A).

Thus, experiment and calculation agree in showing that it is form (B) with its long conjugation chain which predominates in (Id), a compound of interest because of its marked tendency toward polymerization. Hydrogenation of (Id) leads to equalization of the equilibrium concentrations of the (A) and (B) forms.

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*There was scarcely any difference between the positions of the ICE points in the (Ih) and (Ie) β-ketoesters.

EXPERIMENTAL

Methacryloylacetone (Id). Compound (Id) was prepared by the method of [13]; bp, 70-72°C (17 mm); n_D^{25} 1.4792; d_4^{25} 0.9982 (literature values: n_D^{25} 1.4506, d_4^{25} 1.001). PMR spectra (CCl_4, δ, ppm): 2.07 s and 2.13 t (J = 0.6 Hz) for the CH_3 group protons of the enol and keto forms, respectively; 3.72 q (J = 0.6 Hz) ($-CH_2-$); 5.67 s ($=CH-$); 15.20 s (enol proton). Multiplet signals at 1.92, 5.39, and 5.92 ($J \sim 1$ Hz) ($-C(CH_3){=}CH_2$). As read from the PMR spectra, (Id) was enolized to the extent of 96.5 and 91.0% in CCl_4 solution and in the pure liquid form, respectively. ^{13}C NMR spectra (pure liquid containing 10% added $CDCl_3$; δ, ppm; TMS): $H_2\overset{1}{C}{=}\overset{2}{C}(\overset{7}{C}H_3)-\overset{3}{C}O\overset{4}{C}H_2\overset{5}{C}O\overset{6}{C}H_3$: 17.9–C-7 (enol and ketone) 26.3 and 30.2–C-6; 96.8 and 53.5–C-4; 121.3 and 126.2–C-1; 139.5 and 144.3–C-2; 180.8 and 194.8–C-3; 195.3 and 201.0–C-5. The first of each of these entries is for the enol form, the second for the diketone form. Data on other 1,3-dicarboxylic compounds were used in carrying out signal assignment in these spectra.

Pivaloylacetone (Ic). A cooled mixture of 33 ml of ethyl acetate and 6.2 ml of methyl tert-butyl ketone was added dropwise to a suspension of 2.3 g of Na in 20 ml of abs. ether, and the solution allowed to stand for 6 h at 0°C. Ten grams of ice were added to the resulting mass, the water layer separated off, washed with water, then poured into a mixture of 5 g of ice and 2 ml of conc. HCl. The organic layer was washed with $NaHCO_3$ solution and then poured into a saturated copper acetate solution. The chelate Cu complex was separated from solution, washed with ether, and broken down with a 15% H_2SO_4 solution. The decomposition product was extracted with ether. The ether was then evaporated off, and the residue redistilled in vacuum; bp 65-67°C (29 mm); yield, 1.2 g. Gas–liquid chromatography showed the product obtained here to be free of contaminants.

Isobutyrylacetone (Ic) was prepared by the method of [14]. The structure of the product was confirmed by PMR spectroscopy. The remaining reagents were analytical grade compounds which had been purified by fractional distillation.

The PMR spectra were obtained with a C-60HL spectrometer, working in 8% CCl_4 solution at 26°C. The error in the measured difference of the CS's of the keto and enol form signals (Δ) was less than 0.01 ppm. The ^{13}C NMR spectra were obtained with an HX-90 spectrometer, working in the Fourier transform mode.

The fractional content of form (B) was calculated from the formula: $\beta = (\delta - \delta_A)/(\delta_B - \delta_A)$ [1, 2]. Here δ is the mean CS for the CO group ^{13}C NMR signal for the enol form of the diketone (I), and δ_A and δ_B the respective CS's for the (A) and (B) tautomers. The quantity δ was set equal to CS's for the corresponding ketoester (II): 175.5 for R = CH_3 (cf. Table 1) and 169 for R = C_6H_5 (not 173 as reported in [5]*). The CS's of the ketoesters (II) with $RCOCH_2COR$ $(\delta_A + \delta_B)/2$ and $C(CH_3)_2$ being unknown and the $\delta_A - \delta_B$ difference only weakly dependent on R, the latter was assumed equal to the corresponding difference for (If), namely, 33.6 ppm. A similar procedure was followed in evaluating β from the PMR data. This method of estimating β values is acceptable in cases in which the R group has only an insignificant effect on the CS of the NMR signal from the distant acyl group of the tautomer [CH_3CO group in (I) diketones]. This condition was satisfied in our ^{13}C NMR spectra, the value of δ(COO) for the enol forms of ketoesters (II) with R = CH_3, C_6H_5, and CF_3 being 172.2 [7], 173, and 171.5, respectively. The error in the determination of β arising from the measurement of the ^{13}C NMR CS was ~1%.

The authors wish to thank Yu. A. Ignat'ev for the ^{13}C NMR spectrum of methacryloylacetone (Id).

CONCLUSIONS

1. The ^1H and ^{13}C NMR spectra of the chelate enol forms of $RCOCH_2COCH_3$ dicarbonyl compounds with R = OC_2H_5, C_2H_5, CH_3, $CH(CH_3)_2$, C_6H_5 and $C(CH)_3{=}CH_2$ have been analyzed.

2. Determination has been made of the relative contents of two possible chelate enol forms of the diketone tautomers, these forms differing in the position of the enol proton. In running through the above R listing, there is an increase in the fraction of the tautomer in which the enol proton is located near the RCO group oxygen.

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*Correction of this value would have no effect on the conclusions of [5]; it resulted from a check carried out with V. A. Gindin at the suggestion of N. N. Shapet'ko.

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NMR SPECTROSCOPIC STUDY OF COUPLING EFFECTS

6. ^{13}C NMR SPECTRA OF ALKYLSELENOBENZENES

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The PhEAlk (E = O, or Se) compounds are simple and effective models for studying the character, and degree, of heteroatom–aromatic ring interaction. The conformational structures of these compounds are affected by geometrical factors and by the coupling of the unshared electron pair, and the vacant heteroatom orbitals, with the unsaturated fragment. The present work was a study of the chemical shifts (CS) in the ^{13}C NMR spectra of the alkylselenobenzenes (Table 1), the data obtained being compared with the results of earlier work on the alkoxy- and alkylthiobenzenes [1].

Study of the p-carbon (C^4) CS's showed the establishment of p–π coupling between the free electron pair of the Se atom and the aromatic portion of the molecule. Thus, the C^4 atom of PhSeMe is more highly shielded than the aromatic ring carbon of benzene (128.5 ppm), and this despite the fact that the molecule contains the inductive electron acceptor group SeMe. Different conditions are required, however, for overlap with the neighboring carbon atom 2p orbitals in ethers, sulfides, and selenides. Comparison of the C^4 CS's in the PhOMe, PhSMe, and PhSeMe (120.61, 124.52, and 125.55 ppm, respectively), led to the conclusion that donor coupling is somewhat less pronounced in the selenides than in the sulfides, and much less pronounced than in the ethers. A diminution of the π-donor effect in the 0 > S > Se series would be entirely consistent with the known variation of the mesomeric effect of atoms with unshared electron pairs in moving through the periodic system [2], the conditions for 2p–π (O) overlap being better than for 3p–π (S) overlap, and still better than for 4p–π (Se) overlap.

Increasing the size of the alkyl substituent in the alkylselenobenzene reduces the p-carbon shielding (cf. Table 1), the result being a stepwise steric breakdown of the p–π coupling similar to that observed earlier in the sulfides [1]. In (V), the p–π coplanarity of the molecule has been lost to such extent that the C^4 CS (128.10 ppm) is almost identical with the ^{13}C CS for unsubstituted benzene (128.50 ppm). This suggests that there is essentially no π-acceptor selenium interaction in these molecules. By applying the same type of analysis of the S-analog (C^4 CS, 128.13 ppm), it was concluded that a certain degree of p–π coupling still prevails in the tert-butoxybenzene molecule despite the breakdown in coplanarity (C^4 CS 122.88 ppm). An analysis of the ^{13}C CS's in the alkylvinyl ethers and sulfides leads to these same conclusions [3, 4].

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