Table II. Nuclear Magnetic Resonance Data on Beta-Diketones

Beta-Diketone	Chemical Shifts[a,b] K	E	OH	% Enol
2,4-Pentanedione	3.58	5.50	15.34	79
2,4-Hexanedione	3.18[c]	5.08[c]	13.46[c]	81
5-Methyl-3,5-hexanedione	3.57	5.50	14.92	89
2,2-Dimethyl-3,5-hexanedione	3.56	5.60	15.58	94
3,5-Heptanedione	3.66	5.66	15.04	76
3,5-Heptanedione	3.18[c]	5.12[c]	14.30[c]	76
2-Methyl-3,5-heptanedione	3.57	5.50	14.92	88
2,2-Dimethyl-3,5-heptanedione	3.56	5.58	15.58	92
2,6-Dimethyl-3,5-heptanedione	3.60	5.50	15.50	94
2,2,6-Trimethyl-3,5-heptanedione	3.54[c]	5.28[c]	15.52[c]	96
2,2,6,6-Tetramethyl-3,5-heptanedione	3.74	5.86	...	...

[a] Chemical shifts in p.p.m. from TMS as internal standards unless otherwise indicated. [b] K = keto; E = enol. [c] Chemical shifts in p.p.m. from TMS as external standard.

lion observed for the CH_2 (keto abbreviated K), CH (enol abbreviated E), and OH protons are presented in Table II. The spectra of the other protons were as expected for the methyl, ethyl, isopropyl, and *tert*-butyl groups. The characteristic patterns were seen for both the keto and enol forms with overlapping of the multiplets being observed.

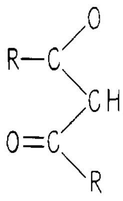
The per cent enol of the beta-diketones was calculated from the following relationship:

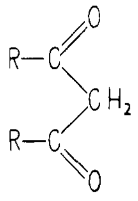
$$200E/(2E + K)$$

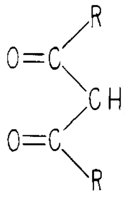
where E is the integrated intensity of the CH (enol) proton and K is the integrated intensity of the CH_2 (keto) protons. The calculated values are presented in Table II. No value was calculated for 2,2,6,6-tetramethyl-3,5-heptanedione because the value of K was very small, making an accurate figure difficult to obtain. Apparently this beta-diketone existed almost completely in the enol form.

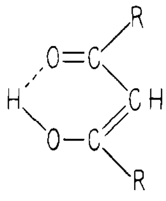
The value for the per cent enol of 2,4-pentanedione obtained in this study (79%) is in agreement with the literature values listed above. No literature values are available for the per cent enol of the other beta-diketones used in this study. The values obtained indicate that in general the per cent enol increases as the alkyl groups become more complex. However, decreases are noted in going from 2,4-hexanedione to 3,5-heptanedione, from 5-methyl-2,4-hexanedione to 2-methyl-3,5-heptanedione, and from 2,4-dimethyl-3,5-hexanedione to 2,2-dimethyl-3,5-heptanedione.

The increase in the amount of enol as the alkyl group becomes larger is mainly attributed to a steric effect. The keto form may take on structures I, II, and III (*4*). Structures I and II minimize the resultant of the dipole moments of the carbonyl groups. However, when the R groups become large, these structures become strained and the keto form is forced into structure III. With 2,2,6,6-tetramethylheptane-3,5-dione a rotation of 30° to 40° away from III cannot take place without introducing some strain (*4*).


I


II


III


IV

The enol form (IV) exists as the intramolecular hydrogen-bonded species (*3*). The hydrogen bond tends to decrease the dipole-dipole repulsion between the carbonyls and thus stabilizes the enol form relative to the keto form. The larger the alkyl groups, the greater the steric interaction forcing the carbonyls closer together and thus the greater the tendency to enolize to reduce the electrostatic repulsion between the carbonyls.

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Benzyltriethylammonium Salts

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A series of benzyltriethylammonium organic and inorganic salts was synthesized and characterized.

A SERIES of benzyltriethylammonium organic and inorganic salts was prepared to study the effect of the anionic species on the biological activity of benzyltriethylammonium salts. We report on the synthesis and characterization of several of these salts (*1*). Table I summarizes yields, melting points, and elemental analyses of the compounds prepared. Characteristic infrared absorption bands for each compound are listed in Table II. In all cases, absorptions at ~700 and ~750 cm.$^{-1}$ for five adjacent hydrogens on the benzene ring were noted.

$$[C_6H_5CH_2N(C_2H_5)_3]^+ Cl^- + AgY \rightarrow [C_6H_5CH_2N(C_2H_5)_3]^+ Y^- + AgCl$$

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Table I. Benzyltriethylammonium Organic and Inorganic Salts, $C_6H_5CH_2N(C_2H_5)_3^+Y^-$

Compound No.	Anion	Y^-	% Yield	M.P., °C.		Analysis[a] % C	% H	%N
1	Chloride	Cl^-	90	197-200	Calcd:	68.7	11.9	6.2
					Found:	68.5	11.7	6.1
2	Nitrate	NO_3^-	84	83-88	Calcd:	61.8	8.7	11.1
					Found:	61.8	8.5	11.0
3	Iodate	IO_3^-	46	125-30	...[b]	...	...	
4	Bicarbonate	HCO_3^-	78	160-64	Calcd:	62.5	8.5	5.2
					Found:	62.0	8.3	5.0
5	Sulfate	SO_4^{2-}	63[c]	115-20	Calcd:	65.0	9.2	5.8
					Found:	64.5	8.7	6.3
6	Thiocyanate	NCS^-	80	69-73		...[b]	...	...
7	Cyanide	CN^-	96	88-90		...[b]	...	...
8	Oxalate	$C_2O_4^{2-}$	64[c]	Oil	Calcd:	71.0	9.3	5.9
					Found:	70.4	8.9	6.3
9	Benzoate	$C_6H_5CO_2^-$	83	88-91		...[b]	...	...
10	Diethyl dithiocarbamate	$(C_2H_5)_2NCS_2$	59[d]	178-85	...[b]	...	...	
11	Ethyl xanthate	$C_2H_5OCS_2$—	35	Oil	Calcd:	61.3	8.3	20.8
					Found:	61.5	8.0	20.3

[a] Elemental analyses performed by Carol K. Fitz, Needham Heights, Mass. [b] Hygroscopic and unstable material, no analysis performed. [c] Two benzyltriethylammonium ions per anion. [d] Refluxed 12 hours.

Table II. Characteristic Infrared Absorptions of Benzyltriethylammonium Salts

Compound No.	Anion	Aliphatic C—H Stretch, $Cm.^{-1}$	C—N Vibration $Cm.^{-1}$	Absorption Characteristics of Anion, $Cm.^{-1}$
2	NO_3^-	2950	1155	1350
3	IO_3^-	3000	1160	820-750
4	HCO_3^-	2950	1155	2600, 1650, 830
5	SO_4^{2-}	3000	1150	1125
6	NCS^-	2980	1150	2050
7	CN^-	3000	1155	2100
8	$C_2O_4^{2-}$	2980	1155	1600
9	$C_6H_5CO_2^-$	3000	1155	1565, 1361
10	$(C_2H_5)_2NCS_2^-$	2967	...	1393, 1136, 1011
11	$C_2H_5OCS_2^-$	3000	1175	1080, 1070, 1040, 1020

EXPERIMENTAL

All reactants were obtained commercially and used without further purification. Infrared spectra were recorded on a Perkin-Elmer Model 21 spectrophotometer in a potassium bromide matrix. The infrared spectrum of each compound was consistent with the desired structure. Melting points were taken on a Hershberg melting point apparatus and are uncorrected.

Benzyltriethylammonium Chloride. A mixture of triethylamine (2 moles) and benzyl chloride (2 moles) in water (1 liter) was refluxed for 2 hours. The solution was concentrated and cooled. Filtration yielded a white crystalline solid in 90% yield.

Benzyltriethylammonium Salts (*1*). Most salts were prepared by refluxing a solution of benzyltriethylammonium chloride (0.1 mole) and the silver salt (0.1 mole) in water for 2 to 3 hours. Exceptions are noted in Table I. Silver chloride was removed by filtration and the filtrate was evaporated to dryness under diminished pressure. The product was dried in vacuo at 50° C. for 2 hours. In the case of the ethylxanthate salt, sodium ethylxanthate in methanol was used.

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