the H-atom shift indicated in eq 9. These results thus suggest that transfer of an active H atom between ligand and metal may be quite general in gas-phase processes involving transition metal ions.

Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, and to the University of Delaware Research Foundation for partial support of this research.

References and Notes

(1) K. J. Klabunde, *Acc. Chem. Res.*, **8**, 393 (1975).
(2) P. L. Timms, *Adv. Inorg. Radiochem.*, **14**, 121 (1972).
(3) K. J. Klabunde, *Angew. Chem., Int. Ed. Engl.*, **14**, 287 (1975).
(4) J. Allison and D. P. Ridge, *J. Organomet. Chem.*, **99**, C11 (1975).
(5) R. R. Corderman and J. L. Beauchamp, *Inorg. Chem.*, **15**, 665 (1976).
(6) R. C. Dunbar, J. F. Ennever, and J. P. Fackler, *Inorg. Chem.*, **12**, 2734 (1973).
(7) M. S. Foster and J. L. Beauchamp, *J. Am. Chem. Soc.*, **97**, 4808 (1975).
(8) J. Müller and W. Goll, *Chem. Ber.*, **106**, 1129 (1973).
(9) S. M. Schildcrout, *J. Am. Chem. Soc.*, **95**, 3846 (1973).
(10) J. Müller, W. Holzinger, and W. Kalbfus, *J. Organomet. Chem.*, **97**, 213 (1975).
(11) R. F. Heck, "Organotransition Metal Chemistry", Academic Press, New York, N.Y., 1974, pp 76–110.
(12) P. C. Wailes, R. S. P. Coutts, and H. Weigold, "Organometallic Chemistry of Titanium, Zirconium, and Hafnium", Academic Press, New York, N.Y., 1974.
(13) W. Mowat et al., *J. Chem. Soc., Dalton Trans.*, 533 (1972).
(14) W. Mowat and G. Wilkinson, *J. Organomet. Chem.*, **38**, C35 (1972).
(15) W. Mowat and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 1120 (1973).
(16) J. L. Beauchamp, *Annu. Rev. Phys. Chem.*, **22**, 527 (1971).

J. Allison, D. P. Ridge*
Department of Chemistry, University of Delaware
Newark, Delaware 19711

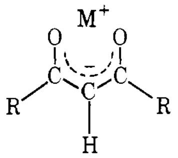
Received July 2, 1976

Alkali β-Ketoenolates as Ion Pairs

Sir:

We are presently engaged in a physico-chemical study which aims to cast light on the structure and dissociation of alkali enolate salts in solution. We present here far-infrared spectral evidence for cation–anion interactions and relate it to corresponding conductance and ^1H NMR data. Results from these independent techniques are mutually consistent and provide concrete evidence for the previously inferred ion-pair structure of the alkali β-ketoenolates.

The subject compounds were alkali dibenzoylmethides (I) and dipivaloylmethides (II).



I, R = C_6H_5
II, R = *t*-butyl

In Table I are presented spectral and conductivity data in tetrahydrofuran (THF) and dimethyl sulfoxide (Me_2SO) as solvents showing the variation of these properties in response to change of cation (M^+) and anion (I and II). Clearly, all three properties are quite sensitive to changes of the ionic components in a manner which is reasonably relatable to positive charge density on the cation and to the ability of the anion to delocalize negative charge internally. All reported results for alkali salts vary linearly as reciprocal functions of their Pauling cation radii. Such a dependence has been noted previously[1-3] for ion-paired systems and is to be expected for variation of the Coulombic potential between charges.

Of particular interest are the sharp, cation-sensitive, far-infrared bands when THF is solvent. We assign these to cation–anion interactions. Edgell and coworkers[4] also observed bands in this solvent for several inorganic alkali metal salts. They attributed these to vibrations of solvated intimate ion pairs in which the cation–anion interaction was modulated by cation–solvent attraction. However, their frequencies are not related directly to $1/r_{\text{cation}}$ and have a much larger range than do ours. Recently, cation-sensitive bands in the carbonyl region of alkali metal manganese carbonylates have been reported.[5]

Popov[6] and co-workers reported broad bands between 100 and 430 cm^{-1} for alkali cation salts in Me_2SO and other solvents. These are anion independent and were assigned, by Popov, to cation–solvent interactions. We were unable to observe these bands for M^+I^- and M^+II^-, which suggests that the cations in our compounds are predominately anion bound at the concentrations of the infrared studies. Relatively low solubility limits in Me_2SO and strong absorption by this solvent in the working range prevented a search for the 300–450 cm^{-1} bands in this solvent, which we resolved in THF.

The position of the band for the Bu_4N^+ ion is somewhat surprising in view of its large size compared to unsolvated Na^+ and K^+. Other workers[7,8] have described cation–anion bands for tetraalkylammonium salts in the same region reported here.[9] Furthermore, Popov[6] found that the *cation–solvent* bands for Na^+ and NH_4^+ in Me_2SO were similar. Our ob-

Table I. Properties of Metal β-Ketoenolate at 25 °C

	Cation-sensitive IR band in THF, cm^{-1}		τ methide in Me_2SO, ppm rel to Me_4Si		Λ_0 in Me_2SO		$K_{\text{diss}} \times 10^4$ in Me_2SO	
M^+	I	II	I	II	I	II	I	II
H			7.32	5.86				
Li	433.71	426.73	6.48	5.36	N.C.[a]	N.C.[a]	N.C.[a]	N.C.[a]
Na	399.98	391.90	6.37	5.28	19.6	9.96	1.61	3.41
K	339.33	374.30	6.24	5.22	29.7	27.1	19.2	7.47
Cs	337.62	370.74	6.14	5.19	29.8	29.7	68.1	36.9
Bu_4N	351.00		6.29		30.8		61.6	
Instrument	Beckman IR-11, polyethylene cell		Varian A60-D		Leeds & Northrup #4866-60			
Exptl error	±0.50 cm^{-1}		±0.01 ppm		±5%			
Concn range	0.05–0.15 M		0.02–0.05 M		2×10^{-5}–4×10^{-3} M			

[a] Negligible conductance.

servations may be rationalized, if we assume reasonably that *cation-anion* bands follow the same pattern and that alkylation of the ammonium ion causes a shift to lower frequencies by increasing the cation mass and radius. We also realize that the effective radii of loosely solvated alkali cations are undoubtedly greater than their Pauling radii.[11]

The fact that Bu$_4$N$^+$ salts behave similarly to the alkali ones actually lends further support to the notion that the latter are ionic. For ion pairs there is no strict geometric requirement for binding the cations to particular regions of the anions, as is true in the transition metal chelates. Thus, the Bu$_4$N$^+$ cation might be oriented above the plane of a U-shaped β-ketonolate anion, while a smaller alkali cation might be accommodated better in the plane and between the oxygen atoms.

The pattern of methine shifts in Me$_2$SO is closely parallel (linear correlation coefficients = 0.966 (I), 0.985 (II)) to that of the far-infrared bands in THF, including the position of Bu$_4$N$^+$. The trend is reasonable, the greatest downfield shift being produced by Li$^+$ and the least by Cs$^+$.

Our conductance data also support the spectral picture of ion pairing and the effects of charge density and delocalization in cation and anion. Finally, our observations are consistent with a variety of other studies on related systems in which the presence of contact ion pairs has been inferred, from ultraviolet spectra,[3] infrared spectra,[12] NMR spectra,[13-15] conductance,[16] and kinetics.[16,17] House[18] and LeNoble[19] have provided extensive reviews of the ambident nucleophilicity of enolate anions. We will present our own observations on this question in subsequent articles.

Acknowledgment. We gratefully acknowledge support of this work by grants from N.S.F. Professor Foil Miller and Dr. William Elbert rendered invaluable assistance in the use of the infrared equipment.

References and Notes

(1) H. V. Carter, B. S. McClelland, and E. Warhurst, *Trans. Faraday Soc.*, **56**, 455 (1960).

(2) T. E. Hogen-Esch and J. Smid, *J. Am. Chem. Soc.*, **87**, 669 (1965).

(3) H. E. Zaugg and A. D. Schaefer, *J. Am. Chem. Soc.*, **87**, 1897 (1965).

(4) W. F. Edgell, A. T. Watts, J. Lyford, and W. M. Risen, *J. Am. Chem. Soc.*, **88**, 1815 (1966); **92**, 2240 (1970).

(5) M. Y. Darensbourg, D. J. Darensbourg, D. Burns, and D. A. Drew, *J. Am. Chem. Soc.*, **98**, 3127 (1976).

(6) A. I. Popov, *Pure Appl. Chem.*, **41**, 275 (1975); B. W. Maxey and A. I. Popov, *J. Am. Chem. Soc.*, **89**, 2230 (1967).

(7) J. C. Evans and G. Y-S Lo, *J. Phys. Chem.*, **69**, 3223 (1965).

(8) V. G. Pagarena and S. P. Apraksin, *Zh. Prikl. Spektrosk.*, **22**, 140 (1975).

(9) A referee has questioned our assignment of this band in view of the fact that tetrabutylammonium halides, whose anions are of lower mass and radius than those considered here, fall in the 50–150 cm^{-1} region in benzene.[7] As supportive, but admittedly inconclusive, evidence we note the sharp difference between the small dissociation constant, which we report in Table I, for Bu$_4$N$^+$ dibenzoylmethide and the complete dissociation[10] of tetrabutylammonium halides in Me$_2$SO. From this, we infer a higher force constant for the enolate ion pair relative to that for the halide one, and hence, a higher frequency.

(10) D. E. Arrington and E. Griswald, *J. Phys. Chem.*, **74**, 123 (1970); J. S. Jha, S. Singh, and R. Gopal, *Bull. Chem. Soc. Jpn.*, **48**, 2782 (1975).

(11) M. S. Goldenberg, P. Kruus, and S. K. F. Luk, *Can. J. Chem.*, **53**, 1007 (1975).

(12) R. D. Hancock and D. A. Thorton, *J. Mol. Struct.*, **4**, 337 (1969); *Theor. Chim. Acta*, **18**, 67 (1970).

(13) R. H. Holm and F. A. Cotton, *J. Am. Chem. Soc.*, **80**, 5658 (1958).

(14) H. O. House, A. V. Prabhu, and W. V. Phillips, *J. Org. Chem.*, **41**, 1209 (1976).

(15) M. E. H. Howden and M. Tyler, *Tetrahedron Lett.*, **24**, 1974 (1975).

(16) A. L. Kurts, A. Macias, I. P. Beletskaya, and O. A. Reutov, *Tetrahedron*, **27**, 4759 (1971).

(17) A. L. Kurts, S. M. Sakembaeva, I. P. Beletskaya, and O. A. Reutov, *Zh. Org. Khim.*, **9**, 553 (1973).

(18) H. O. House, "Modern Synthetic Reactions", 2d ed, W. A. Benjamin, Menlo Park, Calif., 1972, pp 492–623.

(19) W. J. LeNoble, *Synthesis*, 1, (1970).

Edward M. Arnett,* Vincent M. DePalma

Department of Chemistry, University of Pittsburgh
Pittsburgh, Pennsylvania 15260

Received July 13, 1976

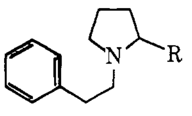
A High Yield Regiospecific Preparation of Iminium Salts

Sir:

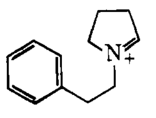
Iminium salts are highly versatile synthetic intermediates[1] since they present an extremely electrophilic carbon for nucleophilic attack. Their use, however, is often rendered unattractive because they are obtained in poor yield or as isomeric mixtures, or both. Currently, the most popular modes of preparing these salts involve (a) oxidation of a tertiary amine,[2] (b) condensation of a carbonyl component and a secondary amine,[3] and (c) addition to amides.[4] There are a number of specialized and limited methods[5] as well. These procedures sometimes produce adequate yields of iminium salts, but frequently suffer seriously from a lack of regiospecificity. We not report the development of a high yield, single-step, regiospecific method for preparing iminium salts from α-tertiary amino acids.

Our method is based on the frequently reported observation that acid chlorides of α-tertiary amino acids are unstable. These observations were first rationalized by Maksimov[6] who reported that activated acyl derivatives of α-tertiary amino acids were thermally decarbonylated, yielding in part a secondary amine and an aldehyde after decomposition with water. This instability, a drawback in utilization of the acyl derivatives, could become a virtue for the preparation of specific iminium salts if a convenient, high yielding procedure could be developed. Such a procedure is now at hand.

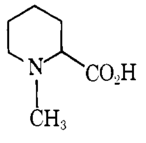
The iminium salts are obtained by briefly (3-5 min) heating the α-tertiary amino acids in phosphorus oxychloride. At this point, starting acid has been completely consumed, and a single product has been formed as demonstrated by thin layer chromatography. This organic product is iminium salt as shown in the infrared where the only absorption is between ~1670 and 1700 cm^{-1} and is due to the iminium ion. As an example, *N*-β-phenylethylproline hydrochloride (**1**, mp 186-189 °C)[7] was decarbonylated in this manner and, after adding the reaction mixture to water, the *N*-β-phenylethyl-Δ^1-pyrrolinium ion (**2**)



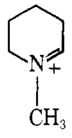
1, R = COOH
3, R = H



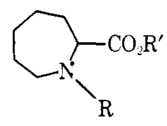
2



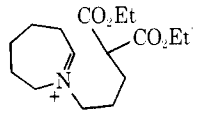
4



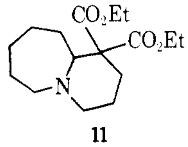
5



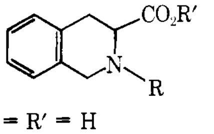
6, R = R′ = H
7, R = H; R′ = Bn
8, R = $(CH_2)_3CH(CO_2Et)_2$; R′ = Bn
9, R = $(CH_2)_3CH(CO_2Et)_2$; R′ = H



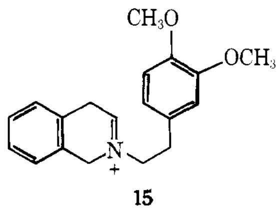
10



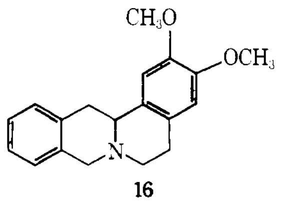
11



12, R = R′ = H
13, R = H; R′ = $CH(CH_3)_2$
14, R = $CH_2CH_2C_6H_3(OCH_3)_2$-3,4



15



16