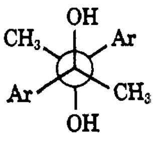
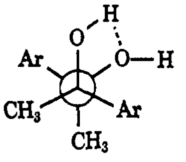
been reported by Heindel,[6] who has also pointed out[7] that the successful pinacolization of *para*-substituted acetophenones appeared to be limited to those with Hammett σ_p values between approximately $+0.25$ and -0.25. The corresponding value for the trifluoromethyl group[8] is $+0.55$.

The fact that several of the *para*-substituted acetophenones do not photopinacolize, or do so only in very low yield, may be attributed to a lower lying triplet π,π^* state which is resonance stabilized and is reached by an internal conversion process from the n,π^* triplet.[9,10] The differences, in electronic structure, between the π,π^* and n,π^* triplets are manifested in their chemical behavior. The localization of a nonbonded electron on the carbonyl oxygen in the n,π^* triplet allows H-atom abstraction and subsequent dimerization to the pinacol, whereas the delocalized electrons of the π,π^* triplet cause the carbonyl oxygen to be ineffective as an H-atom abstractor. The unique behavior of the trifluoromethyl group is quite likely due to its inability to participate in other than an inductive fashion.

It has been proposed previously[11] that the intermediate coupling ketyl radicals approach and bond formation take place either without hydrogen bonding (A, *meso* form results) or with such bonding (B, one of two possibilities, *dl* form results). The ratio for acetophenone provides a measure of the relative importance of these two pathways. Substitution on the phenyl ring with an electron-releasing group would be expected to enhance the electron availability or the bridging oxygen for the adjacent hydroxylic proton. This would make B more attractive relative to A and be reflected in an increase in the *dl*/*meso* ratio. Similarly, electron-withdrawing groups should decrease the electron availability on the bridging oxygen and produce a decrease in the *dl*/*meso* ratio. The observed results correlate well with this reasoning.



A, *meso*



B, *dl*

Experimental Section

The starting materials were commercially available research grade chemicals and were used as received. Sample preparation and the apparatus have been previously described.[1] After irradiation, the reaction mixture was added to 100 ml of ether, washed with 50 ml of Na_2CO_3 solution and two 50-ml portions of water, and then dried over anhydrous magnesium sulfate. A suitable aliquot of the ether solution was evaporated to dryness and dissolved in $CDCl_3$, from which solution the nmr spectra were then obtained.

***meso*-2,3-Di(*p*-trifluoromethylphenyl)-2,3-butanediol**, mp 119–120°, was isolated by concentration of the reaction mixture to an oil and subsequent crystallization from hot heptane. It was identified by its infrared (characteristic CF_3 bands between 1065 and 1180 cm^{-1}) and nmr spectra.

Anal. Calcd for $C_{18}H_{16}O_2F_6$: C, 57.14; H, 4.27. Found: C, 56.98; H, 3.98.

Registry No.—*meso*-2,3-Di(*p*-trifluoromethylphenyl)-2,3-butanediol, 14734-18-0.

Acknowledgment.—Financial support of this research under Atomic Energy Commission Contract No. At-(40-1)-2833 (ORO-2833-14) is gratefully acknowledged. The nmr instrument employed, an A-60 (Varian Corp.), was awarded to Louisiana State University in New Orleans by the National Science Foundation under GP-3674.

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[6] N. D. Heindel, Ph.D. Thesis, University of Delaware, 1963; University Microfilms, Inc., Ann Arbor, Mich., 64-2206, p 100.

[7] See ref 6, p 118.

[8] H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

[9] J. N. Pitts, Jr., H. W. Johnson, Jr., and T. Kuwana, *J. Phys. Chem.*, **66**, 2456 (1962).

[10] N. D. Heindel, *J. Heterocyclic Chem.*, **3**, 379 (1966).

[11] For considerably greater detail than presented here, *cf.* ref 2.

The Nuclear Magnetic Resonance and Ultraviolet Spectra of Some Neutral and Protonated Cyclohexadienones

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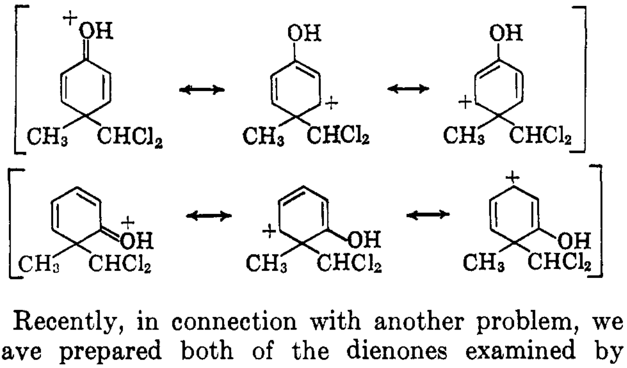
Received June 28, 1967

In 1960, Budzikiewicz[1] reported that the simple "Abnormal Reimer–Tiemann" cyclohexadienones, 4-methyl-4-dichloromethylcyclohexa-2,5-dienone (I) and 6-methyl-6-dichloromethylcyclohexa-2,4-dienone (IV), could be dissolved in concentrated sulfuric acid and recovered quantitatively by dilution with water. The ultraviolet spectra of these dienones in sulfuric acid were interpreted as indicating the formation of "delocalized ions." These must be oxygen-protonated species with structures which may be represented as hybrids of the resonance forms shown.



Recently, in connection with another problem, we have prepared both of the dienones examined by Budzikiewicz as well as all of their possible monomethylated derivatives. We now wish to report an investigation of the ultraviolet and nuclear magnetic resonance spectra of these dienones both in neutral solvents and in concentrated sulfuric acid. This was done in an attempt to learn more about the structures and charge distribution of the delocalized ions formed in sulfuric acid from the dienones.

The simple dienones (I and IV) needed for this study were prepared by method III of von Auwers and Keil[2] which involves the slow addition at reflux temperatures of 45% aqueous sodium hydroxide to a

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[1] H. Budzikiewicz, *Tetrahedron Letters*, 12 (1960).

[2] K. von Auwers and G. Keil, *Ber.*, **35**, 4207 (1902).

TABLE I
THE YIELDS, PHYSICAL PROPERTIES, ULTRAVIOLET MAXIMA, AND CARBONYL STRETCHING FREQUENCIES OF SOME CYCLOHEXADIENONES

Dienone	Isolated yield, %	Mp, °C	Bp, °C (mm)	$n^{20}D$	λ_{max}, mμ (ϵ_{max}) Abs ethanol	Concd H_2SO_4	>C=O str, cm^{-1}
4-Methyl-4-dichloromethylcyclohexa-2,5-dienone (I)	12	53–55	84–88 (0.25)	...	230 (15,200)	263 (12,800) 297 (3380)	1670^a
2,4-Dimethyl-4-dichloromethylcyclohexa-2,5-dienone (II)	27	55.5–57.5	80–85 (0.20)	...	233 (12,600) 263 (2560)	267 (11,700) 315 (3710)	1670^a
3,4-Dimethyl-4-dichloromethylcyclohexa-2,5-dienone (III)	25	98–100	...	...	231 (15,300) 263 (4040)	260 (13,000) 310 (5370)	1670^a
6-Methyl-6-dichloromethylcyclohexa-2,4-dienone (IV)	10	29–31	62–67 (0.50)	1.5398	301 (4750)	251 (2680) 370 (5880)	1670^a
2,6-Dimethyl-6-dichloromethylcyclohexa-2,4-dienone (V)	18	...	61–62 (0.35)	1.5342	308 (5080)	252 (2720) 385 (6000)	1665^b
3,6-Dimethyl-6-dichloromethylcyclohexa-2,4-dienone (VI)	6	22–24	65–67 (0.30)	1.5384	301 (4920)	252 (6930) 360 (6340)	1670^b
4,6-Dimethyl-6-dichloromethylcyclohexa-2,4-dienone (VII)	6	...	63–64 (0.25)	1.5346	311 (4200)	253 (2900) 393 (6100) 237 (3460)	1675^b
5,6-Dimethyl-6-dichloromethylcyclohexa-2,4-dienone (VIII)	10	...	71–73 (0.60)	1.5509	317 (5320)	275 (1270) 397 (8100)	1670^b

^{a} Nujol mull. ^{b} Neat.

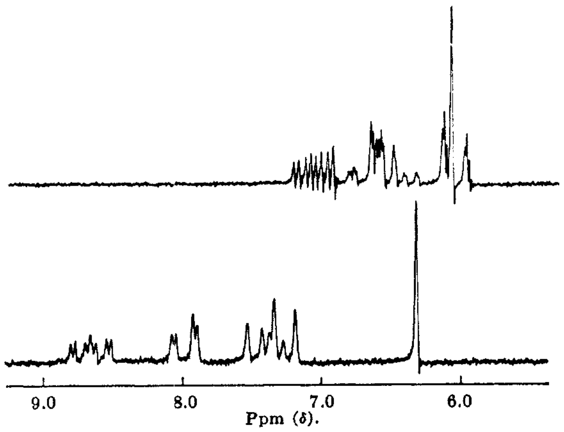

Figure 1.—The low-field portions of the 60-Mc nuclear magnetic resonance spectra of 6-methyl-6-dichloromethylcyclohexa-2,4-dienone (IV) in carbon tetrachloride solvent (top) and in concentrated sulfuric acid solvent (bottom).

solution of the cresol in chloroform. The methylated cyclohexadienones were prepared by method IV of von Auwers and Keil[2] which involves the slow addition of chloroform to a solution of the xylenol in excess 10% sodium hydroxide followed by heating for 4 hr under reflux. In both cases, the work-up procedures of von Auwers and Keil were modified slightly. These modifications are illustrated by the examples given in the Experimental Section. For each of the products, except III, final purification was accomplished by vacuum distillation followed in certain cases by recrystallization. The isolated yields, physical properties, and infrared carbonyl stretching frequencies observed by us for each of the cyclohexadienones are given in Table I. They agree closely with those reported by von Auwers and co-workers for I,[3] II,[4] III,[4] IV,[2] and VII.[4] Dienones V, VI, and VIII are reported here for the first time.

The ultraviolet absorption maxima for each of the dienones in absolute ethanol solvent were observed to be consistent with their structures[5] and are listed in Table I. Their spectra in concentrated sulfuric acid, also given in Table I, showed considerable changes which can all be interpreted[6] as resulting from the formation of delocalized ion species. The three cross-conjugated 2,5-dienones exhibited their major absorption maxima at 260–267 mμ and also possessed a less intense absorption at 297–315 mμ. The linearly conjugated 2,4-dienones, on the other hand, showed major absorptions at from 360 to 397 mμ and all except VIII also possessed a less intense absorption at 251–253 mμ. The sulfuric acid solutions of the cross-conjugated dienones I, II, and III and of the linearly conjugated dienones IV and VI were quite stable and showed little evidence of decomposition even after standing for 8 hr at room temperature. Solutions of the dienones V and VIII, however, showed some decomposition and of VII showed extensive decomposition even after 1 hr standing at room temperature, as evidenced by the appearance of a very intense (ϵ *ca.* 20,000) absorption in the range of 305–315 mμ. Thus, special care had to be taken to measure the sulfuric acid spectra of the latter materials immediately after solution was accomplished.

The nmr spectra of the dienones both in carbon tetrachloride solvent and in concentrated sulfuric acid were clean and well resolved as is shown by the example given in Figure 1. The proton chemical shifts and coupling patterns in each of the solvents are listed in Table II and are consistent with the structures for the dienones and oxygen-protonated dienones, respectively. A summary of the nmr proton coupling constants observed in each solvent is given in Table III. The large shifts of each of the methyl group and ring protons to lower field in the sulfuric acid solvent are indicative of the formation of delocalized carbonium ion species from each dienone examined. The nmr spectra of these species are very similar to those reported for the ring-protonated conjugate acids

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(3) K. von Auwers and F. Winternitz, *Ber.*, **35**, 465 (1902).

(4) K. von Auwers and K. Ziegler, *Ann.*, **425**, 243 (1921).

(5) J. DerKosch and W. Kaltenegger, *Monatsh. Chem.*, **88**, 778 (1957).

(6) N. C. Deno, *Progr. Phys. Org. Chem.*, **2**, 153 (1964).

TABLE II

NMR PROTON CHEMICAL SHIFTS[a,b]

Dienone	H^2	H^3	H^4	H^5	H^6	CH_3^2	CH_3^3	CH_3^4	CH_3^5	CH_3^6	$CHCl_2^4$	$CHCl_2^6$
					In Carbon Tetrachloride							
I	6.35 (d)	6.85 (d)		6.85 (d)	6.35 (d)			1.50 (s)			5.86 (s)	
II	...	6.67 (m)		6.83 (q)	6.34 (d)	1.92 (d)		1.46 (s)			5.82 (s)	
III	6.09 (m)	...		6.97 (d)	6.38 (q)		2.03 (d)	1.46 (s)			5.97 (s)	
IV	6.02 (q)	7.04 (o)	6.47 (q)	6.61 (m)						1.30 (s)		6.05 (s)
V	...	6.80 (m)	6.41 (q)	6.47 (q)		1.89 (d)				1.26 (s)		6.02 (s)
VI	5.89 (bs)	...	6.39 (q)	6.56 (d)			2.12 (d)			1.26 (s)		6.03 (s)
VII	6.02 (d)	6.81 (q)	...	6.30 (bs)				2.07 (d)		1.25 (s)		5.99 (s)
VIII	6.00 (d)	6.92 (q)	6.28 (bd)	...					2.22 (d)	1.35 (s)		6.22 (s)
					In Concentrated Sulfuric Acid[c]							
I	7.39 (d)	8.42 (d)		8.42 (d)	7.39 (d)			1.75 (s)			6.16 (s)	
II	...	8.20 (m)		8.40 (q)	7.43 (d)	2.35 (s)		1.73 (s)			6.13 (s)	
III	7.15 (m)	...		8.53 (d)	7.38 (q)		2.62 (s)	1.70 (s)			6.21 (s)	
IV	7.25 (d)	8.60 (h)	7.37 (q)	7.87 (q)						1.82 (s)		6.29 (s)
V	...	8.50 (bd)	7.37 (q)	7.84 (q)		2.42 (s)				1.83 (s)		6.34 (s)
VI	7.09 (s)	...	7.35 (d)	7.79 (d)			2.82 (s)			1.80 (s)		6.25 (s)
VII	7.27 (d)	8.51 (q)	...	7.69 (bs)				2.42 (s)		1.80 (s)		6.26 (s)
VIII	7.14 (d)	8.57 (q)	7.25 (d)	...					2.72 (s)	1.87 (s)		6.44 (s)

[a] Reported in parts per million (δ) downfield from TMS; Varian A-60A instrument. [b] s = singlet, d = doublet, q = quartet, h = heptet, o = octet, m = multiplet, b = broad. [c] TMS sealed in a capillary tube.

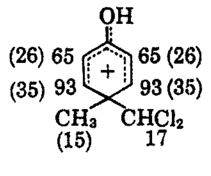
TABLE III

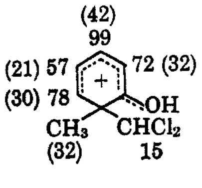
NMR PROTON COUPLING CONSTANTS

Coupling	In CCl_4	In H_2SO_4
4-Methyl-4-dichloromethylcyclohexa-2,5-dienones		
$J_{2,3}$ and $J_{5,6}$	10.0–10.5	9.5–10.0
$J_{2,6}$ and $J_{3,5}$	2.0–3.0	2.0–2.5
$J_{CH_3^n,H^{n\pm1}}$	1.5	*Ca.* 0
6-Methyl-6-dichloromethylcyclohexa-2,4-dienones		
$J_{2,3}$	9.0–10.0	9.0
$J_{2,4}$	1.0–1.5	*Ca.* 0
$J_{3,4}$	5.0–6.0	6.0–7.0
$J_{3,5}$	2.0–2.5	1.5–2.0
$J_{4,5}$	8.0–9.0	9.0
$J_{CH_3^n,H^{n\pm1}}$	1.0–2.0	*Ca.* 0

of anisole and phenol in fluorosulfuric acid solvent[7] and for several dimethylanisoles in HF solvent.[8]

The figures shown below summarize the deshielding in cycles per second at 60 Mc observed by us for each of the methyl groups (in parentheses) and ring protons in the cyclohexadienones on going from carbon tetrachloride to concentrated sulfuric acid solvent. Although nothing quantitative may properly be concluded from the nmr data regarding the charge distribution at each of the ring carbons in the protonated cyclohexadienones, it is apparent from the magnitudes of both the ring proton and methyl group deshielding values that the greatest electron deficiency (*i.e.*, greatest deshielding) in both the cross-conjugated and linearly conjugated dienones is located at the 3 and 5 positions. This is in accord with theory[9] and may readily be seen by examination of the three possible resonance forms shown earlier for each of these ions.





Experimental Section

Melting points and boiling points are uncorrected. Ultraviolet spectra were recorded on a Beckman DB instrument and infrared spectra were taken with a Perkin-Elmer Model 237B instrument. Nuclear magnetic resonance spectra were obtained using a Varian Associates Model A-60A instrument. Microanalyses were performed by Mr. V. Tashinian and Associates, Berkeley, Calif.

2,6-Dimethyl-6-dichloromethylcyclohexa-2,4-dienone (V).—To a well-stirred solution of 100 g of 2,6-dimethylphenol in 2000 ml of water containing 200 g of sodium hydroxide was added dropwise 240 g of chloroform over a period of 1.5 hr. The resulting beet red solution was then heated at reflux on a steam bath for 4 hr. After cooling to room temperature, the reaction mixture was worked up by extracting with three 200-ml portions of ether. The combined ether extracts were washed with 100 ml of water, six 80-ml portions of 10% sodium hydroxide, three 100-ml portions of water, and dried over anhydrous magnesium sulfate. Removal of the ether solvent on a rotary vacuum evaporator gave 54.5 g of a yellow oil. This oil was distilled under vacuum through a 60-cm tantalum spiral column to obtain 30.6 g (18% yield) of V as a light yellow oil: bp 61–62° (0.35 mm), $n^{20}D$ 1.5342.

Anal. Calcd for $C_9H_{10}OCl_2$: C, 52.68; H, 4.88. Found: C, 52.91; H, 4.94.

3,6-Dimethyl-6-dichloromethylcyclohexa-2,4-dienone (VI).—A solution of 100 g of 2,5-dimethylphenol and 200 g of sodium hydroxide was prepared in 2000 ml of water. To this solution was added dropwise over a period of 2 hr, while stirring vigorously, 240 g of chloroform. The resulting mixture was then heated at reflux on a steam bath for 4 hr, cooled to room temperature, and extracted with three 200-ml portions of ether. The combined ether extracts were washed with one 100-ml portion of water, six 80-ml portions of 10% sodium hydroxide, three 100-ml portions of water, and dried over anhydrous magnesium sulfate. Concentration of the ether solution on a rotary vacuum evaporator gave 21.5 g of a red oil. This oil was distilled under vacuum through a 60-cm tantalum spiral column to give 10.2 g (6% yield) of VI as a yellow oil, bp 65–67° (0.30 mm), $n^{20}D$ 1.5384, which solidified on standing in the refrigerator, mp 22–24°.

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(7) T. Birchall, A. N. Bourns, R. J. Gillespie, and P. J. Smith, *Can. J. Chem.*, **42**, 1433 (1964).

(8) D. M. Brouwer, E. L. Mackor, and C. MacLean, *Rec. Trav. Chim.*, **85**, 114 (1966).

(9) J. P. Colpa, C. MacLean, and E. L. Mackor, *Tetrahedron Suppl.*, **2**, 65 (1963).

Anal. Calcd for $C_9H_{10}OCl_2$: C, 52.68; H, 4.88. Found: C, 52.50; H, 4.95.

5,6-Dimethyl-6-dichloromethylcyclohexa-2,4-dienone (VIII).—To a well-stirred solution of 100 g of 2,3-dimethylphenol and 200 g of sodium hydroxide in 2000 ml of water was added dropwise 240 g of chloroform over a period of 2 hr. The resulting mixture was allowed to stir without heating for 1 additional hr and was then heated under reflux on a steam bath for 3 hr. After cooling to room temperature, the mixture was extracted with two 250-ml portions of ether. The combined ether extracts were washed with two 100-ml portions of water, four 100-ml portions of 10% sodium hydroxide, three 100-ml portions of water, and dried over anhydrous magnesium sulfate. The 28.3 g of red oil remaining after removal of the solvent ether on a rotary vacuum evaporator was distilled through a 60-cm tantalum spiral column to give 17.0 g (10% yield) of VIII as a light yellow oil: bp 71–73° (0.60 mm), $n^{20}D$ 1.5509.

Anal. Calcd for $C_9H_{10}OCl_2$: C, 52.68; H, 4.88. Found: C, 52.89; H, 5.00.

Registry No.—I, 6611-78-5; II, 14789-73-2; III, 14789-74-3; IV, 14789-75-4; V, 14789-76-5; VI, 14789-77-6; VII, 14789-78-7; VIII, 14789-79-8.

Acknowledgment.—The author is indebted to the University of California, Davis, for receipt of a Faculty Fellowship for the summer of 1966.

The Effect of Ground-State Solvation on the n → π* Transition of Ethyl Acetate[1a,b]

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The availability of partial molal heats of solution ($\Delta\bar{H}_S$) of ethyl acetate in several ethanol–water mixtures[2] made it of interest to compare this ground-state solvation effect with the solvent effect on the n → π* transition of the ester in the same solvents. Formally, as discussed by Arnett and co-workers,[3] one may estimate the solvent effect on the heat of solution of the excited state, $\delta_M\Delta\bar{H}_S^{EX}$, by the expression

$$\delta_M\Delta\bar{H}_S^{EX} = \delta_M E_T + \delta_M\Delta\bar{H}_S^{g}$$

where $\delta_M E_T$ is the solvent effect on the transition energy and $\delta_M\Delta\bar{H}_S^{g}$, the solvent effect on the heat of solution of the ground state. The $\Delta\bar{H}_S$ data of Arnett and coworkers[2] and the spectroscopic data for the n → π* transition of ethyl acetate in ethanol–water solutions are presented in Table I. In Table II are presented the solvent-effect data, using pure water as reference solvent. Whereas the n → π* transition of ethyl acetate is, of course, a rather broad (but symmetrical) band, and the value of λ_{max} corresponds only to the most probable transition energy, the great similarity of shape and height (note the λ_{max} values in Table I) of the band from one solvent mixture to another implies that the entire band envelope is being shifted smoothly, and that it is meaningful to examine the variation of E_T based on the value of λ_{max}.

TABLE I

HEATS OF SOLUTION AND SPECTROSCOPIC DATA FOR ETHYL ACETATE IN AQUEOUS ETHANOL

Mole fraction of H_2O	$\Delta\bar{H}_S$[a]	λ_{max}, A[b]	ϵ_{max}	E_T, kcal/mole	Z[c]
1.000	−2.36	2041	58	140.1	94.6
0.929	+0.23	2043	58	139.9	93.4
0.906	1.12	2045	58	139.8	92.9
0.884	1.78	2047	59	139.7	92.5
0.857	2.08	2048	57	139.6	91.7
0.830	2.14	2052	58	139.3	90.8
0.798	1.94	2057	59	139.0	90.2
0.765	1.97	2058	58	138.9	89.3
0.726	1.62	2060	59	138.8	89.7
0.684	1.56	2062	59	138.7	88.0
0.582	1.25	2066	58	138.4	86.6
0.000		2083	59	137.3	79.6

[a] Data from ref 2, in kcal/mole. [b] Precision of measurement is at least ±3 A, corresponding to about 0.2 kcal/mole in transition energy (E_T). [c] Values of Z, the solvent polarity parameter, either are from ref 6c or were calculated from the relationship $Y = 0.35338Z - 29.946$ and the known Y values, from ref 11 or A. H. Fainberg and S. Winstein, *J. Am. Chem. Soc.*, **78**, 2770 (1956).

TABLE II

SOLVENT EFFECTS ON TRANSITION ENERGIES AND HEATS OF SOLUTION OF ETHYL ACETATE IN AQUEOUS ETHANOL[a]

Mole fraction of H_2O	$\delta_M E_T$	$\delta_M\Delta\bar{H}_S^{g}$	$\delta_M\Delta\bar{H}_S^{EX}$
1.000	0	0	0
0.929	−0.2	2.59	2.4
0.906	−0.3	3.48	3.2
0.884	−0.4	4.14	3.7
0.857	−0.5	4.44	3.9
0.830	−0.8	4.50	3.7
0.798	−1.1	4.30	3.2
0.765	−1.2	4.33	3.1
0.726	−1.3	3.98	2.7
0.684	−1.4	3.92	2.5
0.582	−1.7	3.61	1.9

[a] Calculated from the data in Table I, and relative to pure water solvent. Symbols are explained in text, energies are in kcal/mole.

On examination of Table II, it can be seen that in solvents of high water content there is little difference in solvent effect on the heats of solution of ground and excited states. Thus, in a region of solvent composition where the ground state goes through rather large changes of energy (note the $\Delta\bar{H}_S$ values in Table I) the transition energy varies only slightly, continuing its slow, steady increase with increasing water content that it exhibits across the entire solvent composition range. In particular, there is no reversible solvatochromic shift associated with the endothermic maxima of $\Delta\bar{H}_S^{g}$ (near 0.85 mole fraction of water) similar to that observed by Arnett and coworkers[3,4] for several aromatic compounds in aqueous *t*-butyl alcohol solvents. While at the low-water end of the solvent range there does appear to be a modest ground-state solvation contribution to the spectral shift, the data suggest that the bulk of the solvent–solute interaction changes very little between ground and excited states in very polar solvents.

Actually, the n → π* transition of carboxylic acid esters is quite sensitive to solvent polarity,[5] the transi-

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(1) (a) The Electronic Absorption Spectra of Carboxylate Derivatives. V. For part IV see W. D. Closson, P. J. Orenski, and B. M. Goldschmidt, *J. Org. Chem.*, **32**, 3160 (1967). (b) Supported in part by the National Science Foundation. (c) To whom correspondence should be addressed: Department of Chemistry, State University of New York at Albany, Albany, N. Y. 12203. (d) National Institutes of Health Predoctoral Fellow, 1965–1967.

(2) E. M. Arnett, W. G. Bentrude, J. J. Burke, and P. McC. Duggleby, *J. Am. Chem. Soc.*, **87**, 1541 (1965).

(3) E. M. Arnett, D. Hufford, and D. R. McKelvey, *ibid.*, **88**, 3142 (1966).

(4) E. M. Arnett and D. Hufford, *ibid.*, **88**, 3140 (1966).

(5) (a) W. D. Closson and P. Haug, *ibid.*, **86**, 2384 (1964); (b) W. D. Closson, S. F. Brady, and P. J. Orenski, *J. Org. Chem.*, **30**, 4026 (1965).