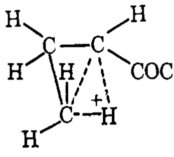
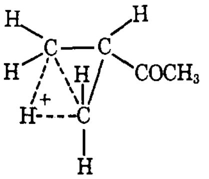
Table I. Cyclopropane Acylation with Added Chloro Ketones or Acetycyclopropane

Cyclopropane, mole	Solvent	Added reactant, mole	Products	Normal acylation, %	Expected, %	Obsd, %
0.010	CCl_4	I, 0.0044	I	35	55	57
			II	41	28	24
			III	20	14	16
			IV	4	3	3
0.005	CCl_4	II, 0.0017	I	35	26	28
			II	41	56	48
			III	20	15	20
			IV	4	3	4
0.010	CH_2Cl_2	IV, 0.0077	I	24	14	16
			II	56	32	28
			III	16	9	11
			IV	4	46	45
0.05	CH_2Cl_2	V, 0.05	I	24	12	11
			II	56	28	32
			III	16	8	7
			IV	4	2	2
			V		50	48

propane ring, as in VII. VII may react with a nucleophile (*i.e.*, $AlCl_4^-$) to give I or IV or may, by a process similar to those described by Baird and Aboderin,[8] isomerize to VIII. VIII should be more stable than VII, since the positive charge is further from the carbonyl group. VIII may react with nucleophile to give II or may lose the proton α to the carbonyl group, giving III.



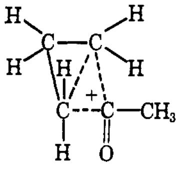
VII



VIII

One might expect that if the nucleophile concentration were kept low to allow time for the conversion VII → VIII, most of the product would be derived from VIII. Inverse addition gave results in accord with this hypothesis. The yields of II and III were increased at the expense of I and IV. For example, in CH_2Cl_2 the yields of I–IV were changed from 24, 56, 16, and 4% to 4, 74, 20, and 2%, respectively, by inverse addition.

Acetylcyclopropane does not give the observed chloro ketones because it is probably first protonated on oxygen.[9] Because of the retarding effect of electron-withdrawing substituents on the rate of cyclopropane acylation,[2] we regard the formation of VII or its probable immediate precursor IX as rate determining, and subsequent steps as fast.



IX

We believe intermediates similar to VII–IX will be important in the attack of other electrophiles on cyclopropanes[10] and are continuing our studies.[11]

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[8] R. L. Baird and A. A. Aboderin, *J. Am. Chem. Soc.*, **86**, 252 (1964); A. A. Aboderin and R. L. Baird, *ibid.*, **86**, 2300 (1964).

[9] VII or VIII might possibly lose the bridged proton. Experiments using various nonnucleophilic bases in the acylating mixture have thus far not yielded any acetylcyclopropane.

(10) N. C. Deno and D. N. Lincoln have obtained similar results in the addition of bromine to cyclopropane (private communication from Professor Deno).

(11) We are grateful to the National Science Foundation (GP-71) and the National Institutes of Health (GM 11775) for partial financial support of this work.

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A Large Enhancement of Solvation Enthalpy by the Reduction of Temperature[1,2]

Sir:

Recently we reported[3] a very large (about 17 kcal/mole) change in the partial molal heat of solution, $\Delta\bar{H}_s$, of sodium tetraphenylboride produced on going from pure water to water containing 0.04 mole fraction of *t*-butyl alcohol. That experiment was tried because a variety of evidence[3] suggested that very large changes in thermodynamic properties related to the structuredness of water would be found using that binary solvent system and that solute.[4] One test of our interpretation of these phenomena[3,5] would be to see if the inflection in $\Delta\bar{H}_s$ would be further amplified by cooling since the structuredness of water is very sensitive to temperature change. The results displayed in Table I[6] and Figure 1 indicate that, in fact, there is a considerable increase in the endothermic maximum so that *the change in* $\Delta\bar{H}_s$ *on going from*

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(1) Solvent Effects in Organic Chemistry. XI.

(2) This work was made possible by grants from the National Science Foundation (NSF-GP-2014) and the Health Research and Services Foundation of Pittsburgh.

(3) E. M. Arnett and D. R. McKelvey, *J. Am. Chem. Soc.*, **87**, 1393 (1965).

(4) See the recent ultrasonic studies of M. J. Blandamer, M. J. Foster, N. J. Hidden, and M. C. R. Symons, *Chem. Commun.*, 62 (1966), for support of this interpretation.

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

(6) A preliminary, and less accurate, examination of this phenomenon was made in our laboratory by Dr. George Mach and reported at the Symposium on Physico-Chemical Process in Aqueous Solvents held at Bradford, England, in May 1966, which is to be published.

Table I. Heats of Solutions at 25 and 4° and the Derived Heat Capacities

X_{H_2O}	Vol. % H_2O	$\Delta\bar{H}_s$,[a] kcal mole^{-1} 25°	$\Delta\bar{H}_s$,[a] kcal mole^{-1} 4°	$\Delta\bar{C}_{p_s}$,[b] cal deg^{-1} mole^{-1}
1	100	-4.77 ± 0.10	-7.43 ± 0.14	127
0.979	90	-0.25 ± 0.41		
0.955	80	11.62 ± 0.30	6.58 ± 0.16	240
0.949	78	12.15 ± 0.39	11.15 ± 0.45	48
0.941	75	10.73 ± 0.34	17.41 ± 0.39	−318
0.925	70	6.41 ± 0.22	14.04 ± 0.36	−363
0.888	60	1.91 ± 0.36	4.47 ± 0.23	−122
0.841	50	-0.57 ± 0.30		
0.779	40	-1.33 ± 0.24		
0.694	30	-2.36 ± 0.33	-1.93 ± 0.14	−20

[a] Errors are expressed as confidence limits at the 95% level. [b] $\Delta\bar{C}_{p_s}$ values were calculated from $[\Delta\bar{H}_s(25°) - \Delta\bar{H}_s(4°)]/21$, and the errors are estimated to be on the order of ±30 cal mole^{-1} deg^{-1}.

pure water to water containing 0.06 mole fraction of t-butyl alcohol is over 24 kcal/mole!

This result is in conformity with the temperature behavior of a number of other properties of highly aqueous alcohol solutions which Franks and Ives have reviewed recently[7] and related to the structure of highly aqueous solutions.

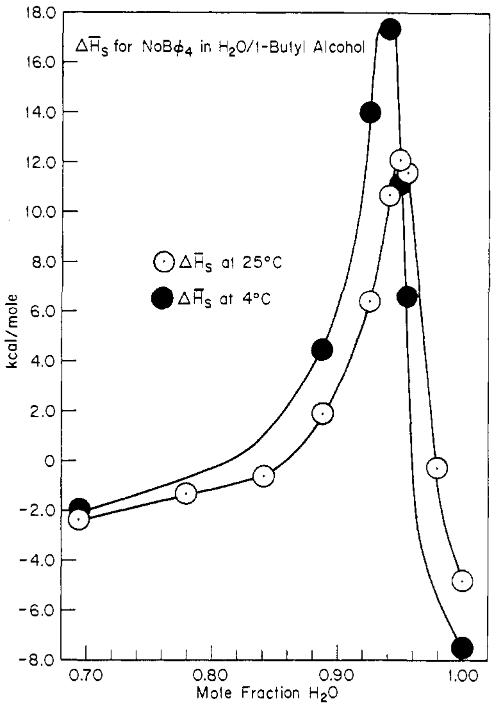

Figure 1. Partial molal heats of solution ($\Delta\bar{H}_s$) of sodium tetraphenylboron in aqueous *t*-butyl alcohol solutions at 4 and 25°.

The enormous energy changes of the kind we have described[3,5,6] are indeed quite peculiar to aqueous binaries[6,8] and are not related to conventional bulk solvent properties. It would be surprising if they were not implicated in a number of phenomena involving the reactivity of large molecules in highly aqueous solution[9] of relevance to many fields of chemistry.

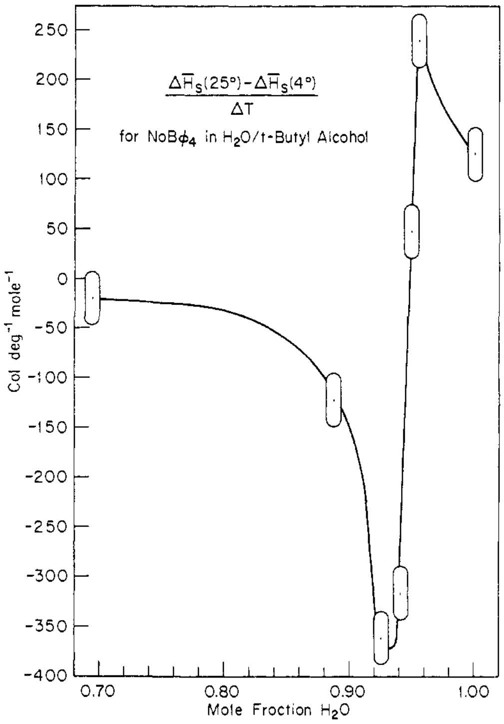

Figure 2. Variation of the partial molal heat capacity of solution ΔC_{p_s} of sodium tetraphenylboron in aqueous *t*-butyl alcohol solutions.

The present results may be used to estimate the solvent effects (δ_M) on the partial molal heat capacity of solution ($\Delta\bar{C}_{p_s}$) of sodium tetraphenylboron in this solvent system and are presented in this way in Table I and Figure 2. They are based on only two temperatures and probably represent average $\Delta\bar{C}_{p_s}$ values from 4 to 25° unless (as seems unlikely) the $\Delta\bar{C}_{p_s}$ values are constant. Detailed interpretation of such a complicated double perturbation function as $\delta_M\Delta\bar{C}_{p_s}$ would be rash.[7] It is worth noting, however, that the enormous inflection in $\Delta\bar{C}_{p_s}$ *amounting to a 600 cal/mole deg variation with a 0.03 mole fraction composition change* is caused by a small shift of the $\Delta\bar{H}_s$ profile toward a higher mole fraction of *t*-butyl alcohol as the temperature is lowered. This would be the expected result if the reduction in temperature stabilized the structure of the aqueous binary so that it could tolerate a slightly greater concentra-

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(7) F. Franks and D. J. G. Ives, *Quart. Rev.* (London), **20**, 1 (1966).

(8) D. R. McKelvey, unpublished report.

(9) For an example of the use of this approach for the control of light absorption, see E. M. Arnett and D. Hufford, *J. Am. Chem. Soc.*, **88**, 3140 (1966). The experiment presented here suggests that even larger spectral shifts would be found at lower temperature in the system described there.

tion of nonaqueous component before "falling apart." This is in keeping with our previously stated hypothesis[5] of the origin of the extrema.

Although a number of $\Delta\bar{C}_{p_s}$ measurements have been reported for electrolytes[10,11] and a few nonelectrolytes[12] in water, we are aware of no previous study of a medium effect on heat capacity. The results described here suggest that solvent–temperature studies of heats of solution, activation, and reaction may be a useful specialized tool for the study of reactions.[9]

Measurements of $\Delta\bar{H}_s$ at 4° were made in a calorimeter such as we have described previously.[5] The entire calorimeter apparatus was enveloped in a metal casing and held conveniently at 4° by immersion in an ice–water slush. We attach no unique significance to results obtained at this temperature.

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(10) "Thermal Properties of Aqueous Uni-Univalent Electrolytes," National Bureau of Standards Annual Report, NSRDS-NBS-2, U. S. Government Printing Office, Washington, D. C., 1965.

(11) G. N. Lewis and M. Randall, "Thermodynamics," 2nd ed, revised by K. S. Pitzer and L. Brewer, McGraw-Hill Book Co., Inc., New York, N. Y., 1961, p 379.

(12) G. Némethy and H. A. Scheraga, *J. Chem. Phys.*, **36**, 3382, 3401 (1962).

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Nuclear Magnetic Resonance Evidence for a Three-Well Torsional Potential in Vinylcyclopropane

Sir:

We have observed the nmr spectrum of vinylcyclopropane as a function of temperature from −60° to +76°, in *ca.* 10% v/v solutions, using a Varian HA-100 spectrometer. The four-spin system of the vinyl and adjacent ring protons (Figure 1) was analyzed using the computer program TWOSUM,[1] a development of the program NMRIT described by Ferguson and Marquardt.[2] A method of analysis was adopted which treats the other ring protons as a first-order perturbation. Only three parameters, τ_2, τ_4, and J_{12}, are strongly temperature dependent; these are presented in Table I. A downfield shift of approximately 0.02 ppm on going from CS_2 to CCl_4 at constant temperature was observed for all protons.

Table I. Spectral Parameters

Solvent	Temp, °C	τ_2, ppm	τ_4, ppm	J_{12}, cps
CS_2	−60	4.944	5.017	9.64
CS_2	−30	4.873	5.027	9.13
CS_2	0	4.809	5.035	8.73
CS_2	+31	4.745	5.045	8.34
CCl_4	−30	4.850	5.004	9.10
CCl_4	+31	4.729	5.029	8.38
CCl_4	+53	4.691	5.036	8.16
CCl_4	+76	4.655	5.042	7.94

The uncertainty of each coupling presented is less than 0.1 cps; that of each shielding is less than 0.001 ppm.

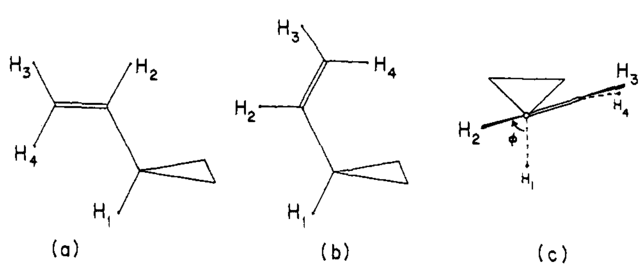

Figure 1. Conformations of vinylcyclopropane.

Chemical shifts in a large number of cyclopropyl derivatives have been interpreted in terms of the anisotropic diamagnetic polarizability of the ring,[3] with the larger component of $\Delta\chi$ normal to the ring. The linear dependence of both proton shifts τ_2 and τ_4 on the coupling J_{12} supports the hypothesis that all of these depend on the same mechanism, a thermal redistribution among conformers related by rotation about the C–C single bond. In this and related systems the low-energy conformer appears to be the *s-trans* form,[4] in which the dihedral angle relating H_1 and H_2 is 180° (Figure 1a). The abnormally high shielding of H_2 at low temperatures would thus reflect its location near the symmetry axis of the ring polarizability tensor.

The relative magnitudes of the H_2 and H_4 shielding shifts, $\Delta\sigma_2$ and $\Delta\sigma_4$, are sensitive to the dihedral angle, ϕ (Figure 1c), of the high-energy conformer or conformers (for dihedral angles other than 0 and 180° these must occur in symmetrically related pairs). Using the point-dipole ring-current approximation we have computed the reduced shieldings, $\sigma_2/\Delta\chi$ and $\sigma_4/\Delta\chi$, and the ratio of their shifts, $\Delta\sigma_4/\Delta\sigma_2$, which is independent of the magnitude of the anisotropy. These values are plotted as a function of the dihedral angle of the upper state, ϕ, in Figure 2.

A graph of τ_4 *vs.* τ_2 should give a straight line whose slope is $\Delta\sigma_4/\Delta\sigma_2$. Our shielding data give two well-defined straight lines, one for each solvent. Their slopes differ significantly, being −0.197 in CCl_4 and −0.138 in CS_2, suggesting upper-state dihedral angles (see Figure 2) of 79 and 86°, respectively. These compare to electron-diffraction values of *ca.* 40° for bicyclopropyl[5] and 0° (the *s-cis* form) for cyclopropylaldehyde.[6] Note that if the upper state of vinylcyclopropane were the *s-cis* form, the shift ratio (Figure 2) would be *ca.* −1.2, an order of magnitude larger than that observed, because of the high shielding of H_4 in that conformer (Figure 1b). The predicted values of the shift ratio do not involve any assumption about the magnitude of the anisotropy, nor would a more refined geometric model (*e.g.*, treating the polarization as a current loop[7]) significantly alter these conclusions.

If the coupling between protons 1 and 2 takes the value J_l in the lower energy conformer and J_u in each

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(1) G. R. De Maré, F. W. Birss, and J. S. Martin, submitted for publication.

(2) R. C. Ferguson and D. W. Marquardt, *J. Chem. Phys.*, **41**, 2087 (1964).

(3) K. Tori and K. Kitahonki, *J. Am. Chem. Soc.*, **87**, 386 (1965); T. Norin and K. Forsen, *Tetrahedron Letters*, **39**, 2845 (1964); D. J. Patel, M. E. Howden, and J. D. Roberts, *J. Am. Chem. Soc.*, **85**, 3218 (1963).

(4) W. Lüttke and A. de Meijere, *Angew. Chem. Intern. Ed. Engl.*, **5**, 521 (1966).

(5) O. Bastiansen and A. de Meijere, *ibid.*, **5**, 124 (1966).

(6) L. S. Bartell and J. P. Guillory, *J. Chem. Phys.*, 43, 647 (1965).

(7) G. L. Closs and H. B. Klinger, *J. Am. Chem. Soc.*, **87**, 3265 (1965).