The rearrangements of monobromide **4** and dibromide **6** are without precedent. Nevertheless, the importance of these experiments is their relevance to organic photochemistry.

Both sets of reaction conditions were designed to afford a Favorskii-like species, the bromo enolate **7**, and thence to give mesoionic zwitterion[6] **2** proposed[2] for the type A dienone photochemical rearrangement (see Chart I). That the bromo enolate **7** was reached is confirmed by the different reactions giving the same product.

It is, of course, possible that the bromo enolate **7** rearranges to photoketone **3** concertedly with the loss of bromide; this would not change the fundamental argument, for then one would be dealing with an incipient zwitterion. However, since the ground-state reaction affords the same product (**3**) as the photochemical dienone reaction which has no bromide to depart, we have suggestive evidence in favor of bromide departing prior to rearrangement.

One final relevant point is that the photochemical intermediate showed a strong preference for proceeding onward to photoketone **3** although reversion to dienone is an *a priori* possibility.[7] The same preference is found in the ground-state reactions presently described supporting the view that the same intermediate is involved.

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(6) For the Favorskii rearrangement similar zwitterions have been considered in the literature. For discussions concerning the validity of assuming such intermediates *cf.* H. O. House and W. F. Gilmore, *J. Am. Chem. Soc.*, **83**, 3972, 3980 (1961); E. E. Smissman, T. L. Lemke, and O. Kristiansen, *ibid.*, **88**, 334 (1966).

(7) This is evidenced by the high quantum yield for dienone to photoketone rearrangement. This point will be discussed in detail: H. E. Zimmerman and J. S. Swenton, to be published.

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Solvent Structure and Solvolysis in Ethanol–Water Mixtures

Sir:

Arnett and co-workers have shown[1] that there are striking similarities between the changes in the heat of solution (ΔH_S) of neutral molecules through a series of alcohol–water mixtures and the corresponding changes in the enthalpy of activation ($\Delta H^{\neq}$) for the hydrolysis of *t*-butyl chloride, as reported earlier by Winstein and Fainberg[2] and by Tommila and coworkers,[3] and for the solvolysis of benzyl chloride.[4] Since the heats of solution of salt (and, by inference, a salt-like transition state) did not show similar sensitivity to solvent compositions,[5] there seemed good reason to believe that the changes in ΔH_S and in $\Delta H^{\neq}$ were both related to the same kind of changes in solvent structure with changing composition.

Since $\Delta C_p^{\neq}$ for hydrolysis in water had already been attributed in part to the changes in the structural stability of the initial-state solvation shell with temperature,[6] it was an easy deduction from Arnett's findings to expect remarkable changes in this parameter ($\Delta C_p^{\neq}$) for the hydrolysis of *t*-butyl chloride across a similar series of ethanol–water mixtures. The value of $\Delta C_p^{\neq}$ for hydrolysis of *t*-butyl chloride in water was known to be -83 cal/mole deg,[7] while Hakka, Queen, and Robertson[8] confirmed the earlier report of Kohnstam[9] that the value of $\Delta C_p^{\neq}$ in 50:50 (v/v) ethanol–water was about -30 cal/mol deg. We report here values of $\Delta C_p^{\neq}$ for solvolysis of *t*-butyl chloride for two intermediate ethanol–water concentrations (Table I).

Table I. Enthalpy and Heat Capacity of Activation for the Solvolysis of *t*-Butyl Chloride in a Series of Ethanol–Water Mixtures

Solvent, v/v	Mole fraction of H_2O	$\Delta C_p^{\neq}$, cal/mol deg	$\Delta H^{\neq}$, cal/mole	Ref
Water	1.0	−83	23,830	7
27:73	0.89	−116	21,200	This work
37:63	0.85	−49	20,080	This work
50:50	0.75	−34	21,550	8

Evidence derived from changes in the partial molar volume of the alcohol,[10] viscosity,[11] spin–lattice relaxation time,[12] and sound absorption[13] supports the conclusion that the addition of ethanol to water enhances those characteristics normally considered to reflect three-dimensional structural stability in the water-rich concentration range. Obviously these new hybrid structures are not equivalent to water structure, one indication of this being that the solution of the third component (*e.g.*, *t*-butyl chloride) is endothermic[1] rather than exothermic.[14] The qualitative description in terms of a three-dimensional structure, however, still seems appropriate.

Whatever the detailed mechanism of hydrolysis and solvent reorganization attending activation, it is apparent from Table I that $-\Delta C_p^{\neq}$ passes through a sharp maximum in the same composition range where other tests indicate extreme behavior which could be attributed to a rapid change in structural stability with composition. For any given composition, the tendency of the solvent mixture to maintain preferred structural configuration will be opposed by thermal

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agitation; hence the average initial state "stability" will decrease as the temperature increases—the greater the complexity of structural interactions, the more sensitive the solvent shell to temperature. It is such changes with temperature summed over a number of solvent interaction terms which we believe are observed when $\Delta C_p^{\ddagger}$ changes with composition. Were this the only factor involved in the activation process, it is a corollary that $\Delta H^{\ddagger}$ would increase through the concentration range where structural stability appears to increase. This does not happen, but it is significant that the maxima in $-\Delta C_p^{\ddagger}$ appear to lie at about the same ethanol–water concentration as that for maxima in Walden products and $d\eta/dx_2$.[11] Since the former reflects the effect of ions on the structure and the latter is related to structural stability, it is probably no coincidence that the breakdown of structure as a consequence of charge development in the activation process should show similar sensitivity to solvent change.

t-Butyl chloride had been purified for previous study[7] and was passed through Al_2O_3 prior to use. Alcohol–water mixtures were made up from purified solvents in sufficient quantity for a $\Delta C_p^{\ddagger}$ determination, and the final concentration was determined by density. Rate determinations were by the conductance method previously reported,[7] and calculation of constants followed previous work.

(15) National Research Council of Canada summer student, 1965.

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Nickel Carbonyl Complexes with Bifunctional Nonchelate Ligands[1]

Sir:

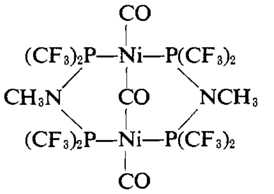
Bifunctional phosphines of the type represented by $(CF_3)_2POP(CF_3)_2$,[2] $(CF_3)_2PSP(CF_3)_2$,[3] and $(CF_3)_2P(NCH_3)P(CF_3)_2$[4] are not expected to be effective chelating ligands on account of unfavorable bond angles at O, S, or N. Accordingly, their reactions with nickel carbonyl lead to polynuclear complexes.

The Aminobisphosphine Product. Equimolar quantities of $Ni(CO)_4$ and $(CF_3)_2P(NCH_3)P(CF_3)_2$ (ligand Ln), in hexane at 25°, liberated one CO in 35 min, after which a bright yellow precipitate began to form as more CO was removed by the automatic Sprengel pump. More than 24 hr was required to approach the limit indicated by the following equation with millimole stoichiometry.

$$\begin{array}{llll} 2\mathrm{Ln} + & 2\mathrm{Ni(CO)_4} \longrightarrow & 5\mathrm{CO} + & \mathrm{Ln_2Ni_2(CO)_3} \\ 1.678 & 1.64 & 3.957 & 0.811 \\ \underline{-0.064} & & (2.45\times\mathrm{Ln}) & \\ 1.614 & & & \end{array}$$

The air-stable yellow product (weighed after evaporation of the hexane) could be recrystallized from CCl_4, $HCCl_3$, acetone, or ether. It could be sublimed *in vacuo* at 90° without change but lost CO during melting near 150°. Its molecular weight in ether (by means of the differential tensimeter at 23.5°) was 922 *vs.* 935 calculated for the formula as written. Heated in a stream of CO, it liberated at least 82% of the original ligand, showing that this bisphosphine had not been disrupted in forming the complex.

The infrared spectrum of this sesquicarbonyl as a vapor at low pressure showed peaks at 2083, 2072, and 1917.5 cm^{-1} (or 2074.5, 2052, and 1912.5 cm^{-1} in Nujol *vs.* 2075.5, 2062, and 1905.5 cm^{-1} in CCl_4), clearly demonstrating both terminal and bridging C–O groups.[5] In view of its stability, it is reasonable to suggest a compact bicyclic structure such as



in which the hexatomic rings could well have the cyclohexane chair configuration.

The Thiobisphosphine Product. The action of $(CF_3)_2PSP(CF_3)_2$ (ligand Ls) upon $Ni(CO)_4$ was much like that of Ln, always forming a sesquicarbonyl despite a considerable variation of the reactant ratio. In this case, however, a volatile red product (very unstable) appeared in the early stages, and the final air-stable yellow product contained a nonvolatile red impurity, removable by washing with hexane. With equimolar reactants, the usual limit was represented by 2.5CO evolved.

Again the infrared spectrum of the yellow precipitate (Nujol mull) showed terminal and bridging C=O stretching, at 2088, 2075, and 1894 cm^{-1}. Analysis by iodine in CCl_4 gave 8.88% CO, 12.8% Ni, and (by difference) 78.3% Ls; calculated for $Ls_2Ni_2(CO)_3$, 8.92, 12.5, and 78.6%, respectively. However, the molecular weight remains unknown because of instability in any effective solvent. For example, in CCl_4 the C=O frequencies at 2090, 2075, and 1915 cm^{-1} lost intensity with time as new peaks at 2110 and 2050 cm^{-1} replaced them.

Thermal decomposition of pure $Ls_2Ni_2(CO)_3$ at 80° led to the recovery of 48% of the expected Ls, from the rest of which some $P_2(CF_3)_4$ was formed while the nickel ended as a black solid having the X-ray powder pattern of Ni_3S_2. However, on heating in a stream of CO, this sesquicarbonyl was dissociated and partly re-formed, giving the appearance of sublimation.

Possibly $Ls_2Ni_2(CO)_3$ is only a less stable example of the $Ln_2Ni_2(CO)_3$ structural type, but a decision will await the results of X-ray studies which have been initiated.

The Diphosphoxane Product. The action of $(CF_3)_2POP(CF_3)_2$ (ligand Lo) upon equimolar $Ni(CO)_4$ is different, forming a slightly volatile, hexane-soluble white solid having the molecular formula $Lo_2Ni_2(CO)_4$ and showing only terminal C=O stretching, at 2100

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