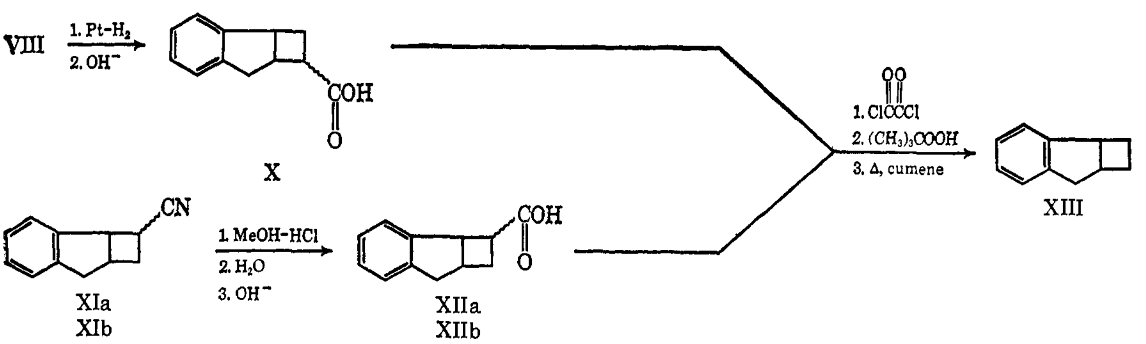
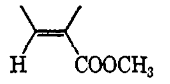
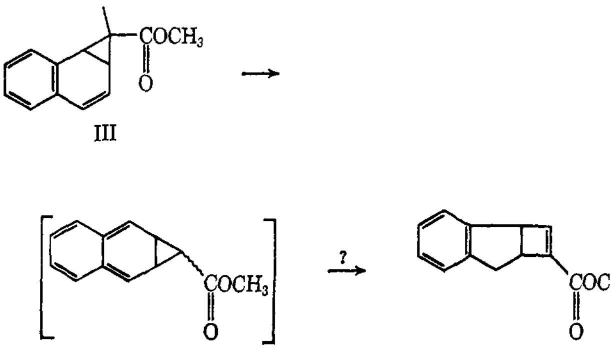


XIIa or XIIb and the requirement of the



linkage establishes the photoisomer as VIII.

The photofragmentation of I to naphthalene and carbomethoxycarbene has much analogy in earlier work.[1,2] Although processes analogous to the formation of esters VI and VII have not been reported,[1,2] they are easily understood by breakage of the external bond of the cyclopropane ring followed by a 1,2-hydrogen shift.[7] The intriguing transformation of III → VIII appears to be without precedent in these systems. Most mechanisms which can be written involve stable ground-state precursors which have not been detected in our studies. It is apparent that either carbomethoxy migration has occurred or else an intermediate having the symmetry of XIV is involved in this rearrangement. We are pursuing experiments



aimed at establishing the mechanism of this interesting and unusual transformation.

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[7] D. I. Schuster and I. S. Krull, *J. Am. Chem. Soc.*, **88**, 3456 (1966).

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Enthalpies of Transfer of S$_N$2 and S$_N$Ar Transition States from a Protic to a Dipolar Aprotic Solvent

Sir:

The much faster rates and lower activation enthalpies of S$_N$2 and S$_N$Ar reactions in dipolar aprotic solvents relative to polar protic solvents have been the subject of much recent study and speculation.[1] This effect can be attributed to enhanced solvation of the nucleophiles in the protic solvent or to greater solvation of the transition states in the dipolar aprotic solvent. Recently we were able to show[2] that the effect on the enthalpy of activation in the case of an S$_N$2 reaction involving an *uncharged nucleophile* (pyridine) was caused entirely by increased solvation of the transition state in the dipolar aprotic solvent (dimethylformamide) and not by increased solvation of the reactants in the protic solvent (methanol). We now present data showing that a similar conclusion holds for a representative sample of S$_N$2 and S$_N$Ar reactions involving *charged nucleophiles.*

The enthalpy of transfer of a transition state from one solvent to another, δH^t, is obtained from the relation: $\delta H^t = \delta\Delta H_s + \delta\Delta H^{\ddagger}$, where $\delta\Delta H_s$ is the enthalpy of transfer of the reactants from one solvent to the other and $\delta\Delta H^{\ddagger}$ is the difference in the enthalpies of activation of the reaction in the two solvents. Table I shows the results of our calorimetric measurements of the heats of solution, ΔH_s, in methanol and DMF of a number of reagents of interest. Making the assumption that tetrabutylammonium ion and tetrabutylboride ion have the same enthalpies of transfer[3] we can then calculate the single ion enthalpies of transfer for the nucleophiles of interest listed in Table II.

Table III compares the $\delta\Delta H_s$ values for the reactants in three S$_N$2 reactions and four S$_N$Ar reactions with their respective $\delta\Delta H^{\ddagger}$ values, from which are calculated the δH^t values for these reactions. As can be seen, in all cases the enthalpy of transfer of the transition state from methanol to DMF is exothermic. In all but one case, the enthalpies of transfer of the reactants are also exothermic!

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[1] For a recent discussion and references see R. Alexander, E. C. F. Ko, A. J. Parker, and T. J. Broxton, *J. Amer. Chem. Soc.*, 90, 5049 (1968).

[2] P. Haberfield, A. Nudelman, A. Bloom, R. Romm, H. Ginzberg, and P. Steinhertz, *Chem. Commun.*, 194 (1968).

[3] Similar assumptions had been made by E. M. Arnett and D. R. McKelvie, *J. Amer. Chem. Soc.*, **88**, 2598 (1966); O. Popovych, *Anal. Chem.*, **38**, 558 (1966).

Table I. Heats of Solution in Methanol and Dimethylformamide

Compound	ΔH_s (CH_3OH), kcal/mol	ΔH_s (DMF), kcal/mol
CH_3I	0.49 ± 0.01	−0.16 ± 0.01
4-Nitroiodobenzene	6.42 ± 0.24	4.62 ± 0.03
4-Nitrofluorobenzene (l)	1.02 ± 0.01	−0.37 ± 0.01
2,4-Dinitroiodobenzene	5.16 ± 0.25	1.71 ± 0.14
2,4-Dinitrochlorobenzene	5.57 ± 0.03	3.66 ± 0.04
NaSCN	−4.08 ± 0.14	−8.68 ± 0.09
Sodium 2,4-dinitrophenoxide	−2.13 ± 0.02	−3.42 ± 0.01
Sodium 4-nitrophenoxide	−6.34 ± 0.06	−3.35 ± 0.08
NaN_3	−1.08 ± 0.03	−1.89 ± 0.01
$(n\text{-}C_4H_9)_4NB(n\text{-}C_4H_9)_4$	6.99 ± 0.02	5.97 ± 0.06
$(n\text{-}C_4H_9)_4N(4\text{-}NO_2C_6H_4O)$	3.87 ± 0.10	7.60 ± 0.02

Table II. Single Ion Enthalpies of Transfer from Methanol to Dimethylformamide

Ion	SCN^-	2,4-Dinitrophenoxide	N_3^-	4-Nitrophenoxide
$\delta\Delta H_s$, kcal/mol	−3.35	−0.04	0.44	4.24

Table III. Enthalpies of Transfer (δH^t) of the Transition States of SN2 and SNAr Reactions from Methanol to Dimethylformamide

Reaction	$\delta\Delta H_s$, kcal/mol	$\delta\Delta H^{\ddagger}$, kcal/mol	δH^t, kcal/mol
$SCN^- + CH_3I$	−4.00	−4.3[a]	−8.3
2,4-Dinitrophenoxide + CH_3I	−0.69	−6.4[b]	−7.1
4-Nitrophenoxide + CH_3I	3.59	−7.7[b]	−4.1
SCN^- + 2,4-dinitroiodobenzene	−6.80	− .45[a]	−7.25
SCN^- + 2,4-dinitrochlorobenzene	−5.26	−3.08[a]	−8.34
N_3^- + 4-nitroiodobenzene	−1.36	−5.6[a]	−7.0
N_3^- + 4-nitrofluorobenzene	−0.95	−4.8[a]	−5.8

[a] B. O. Coniglio, D. E. Giles, W. R. McDonald, and A. J. Parker, *J. Chem. Soc.*, *B*, 152 (1966). [b] D. Cook, I. P. Evans, E. C. F. Ko, and A. J. Parker, *ibid.*, 404 (1966).

On examining the three SN2 reactions we see that for the case of the most basic nucleophile (4-nitrophenoxide ion) increased solvation of the transition state and decreased solvation of the nucleophile in the polar aprotic solvent contribute about equally to the large value of $\delta\Delta H^{\ddagger}$. For the weaker base, 2,4-dinitrophenoxide ion, solvation of the transition state is the major factor. In the case of the weakest base (SCN^-) we see that both the nucleophile and the transition state are more highly solvated in DMF. However, this effect is much greater for the transition state than for the nucleophile, thus still resulting in a lower activation enthalpy in DMF (negative $\delta\Delta H^{\ddagger}$).

Turning to the four SNAr reactions we see that although the $\delta\Delta H^{\ddagger}$ values vary considerably, the enthalpies of transfer of the transition states are more uniform and are all highly exothermic. The similarity in the enthalpies of transfer of SN2 and SNAr transition states is very striking. In both cases it appears that hydrogen bonding to the nucleophile and to the leaving group making up the transition state is less important than dipole–dipole interactions between the transition state and solvent molecules. The most interesting conclusion, however, is that a change in the enthalpy of solvation of nucleophiles on going from a polar protic to a dipolar aprotic solvent is not always the primary factor in determining the much smaller activation enthalpies of SN2 and SNAr reactions in dipolar aprotic solvents.[4] In fact, in some cases, the solvation enthalpy change of the nucleophile is negligible compared to the contribution from the transition state.

Acknowledgments. We thank Mr. D. Kurnit for performing some preliminary measurements and the National Science Foundation for support under its Undergraduate Science Education Program.

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[4] Indeed, the same may probably be said of the effect of dipolar aprotic solvent on the *rates* of these reactions. From the work of Alexander, *et al.*,[1] it appears that "protic–dipolar aprotic solvent effects are usually reflected much more strongly in the enthalpy rather than in the entropy of activation."

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Book Reviews

Dreiringe mit zwei Heteroatomen. Oxaziridine, Diaziridine, Cyclische Diazoverbindungen. By ERNST SCHMITZ. Springer-Verlag, Heidelberger Platz 3, Berlin-Wilmersdorf, Germany. 1967. xi + 179 pp. 16 × 23.5 cm. $14.50.

Inasmuch as authentic three-ring heterocyclic compounds with two heteroatoms in the three-rings were unknown prior to 1950, it is possible for Dr. Schmitz to provide in 170 pages a very thorough and pleasantly readable review of the chemistry of the presently known members of this series, the oxaziridines, the diaziridines, and the diazirines. Freed from the necessity of being as selective as authors attempting to review the chemistry of the more common heterocycles and bolstered by knowledge gained through his own research on each of the three heterocyclic systems, Dr. Schmitz has written an unusually informative description of the synthesis, reactions, reaction mechanisms, and physical properties of each ring system. From the reader's point of view the best reviews are those in which the reviewer serves not only as an efficient reporter but also as a commentator who amplifies or clarifies the results, concepts, or speculation presented more tersely in the original literature. By this measure, Dr. Schmitz's book is among the best monographs now available on the many heterocyclic systems.

Coverage of the literature appears to terminate somewhat before the end of 1966. This is the book's principal weakness, but one to be expected in a review of an active and rapidly developing field. There are already in print or in press papers carrying the known chemistry of three-rings with two heteroatoms well beyond the limits of the book. Furthermore, the last two and one-half pages of this fine little book are devoted to describing briefly other three-ring systems with two heteroatoms now known principally as hypothetical intermediates in organic reactions. This description will probably catalyze an effort to make this section rapidly obsolete.

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