

Assigning values for phenyl inductive retardation, steric acceleration, and steric inhibition to solvation calculated from V, VI, and VII,¹² respectively, we predicted a relative rate for VIII of 0.029. The actual rate was found to be 0.0078, which is *ca.* one-fourth the rate calculated. Since such calculations ignore the fact that transition states in *exo*- and *endo*-norbornyl systems differ, one might say that "the results of the calculations are better than we had a right to expect." Particularly noteworthy is the fact that the rate of VIII is slightly slower than that of VI.

Thus far we have identified most of the products from the acetolyses of V, VI, and VII in the presence of excess sodium acetate. From V and VII after lithium aluminum hydride reduction, we have obtained, in order of elution from chromatography over alumina, 3-phenyl-norbornene, 7-*syn*-phenyl-2-*exo*-norbornanol, 3-*endo*-phenyl-2-*exo*-norbornanol (I), 7-*anti*-phenyl-2-*exo*-norbornanol, and small amounts of an alcohol or alcohols of unknown structure. From VI we have obtained the same products as from V and VII, along with some 2-phenylnorbornene and 2-*endo*-phenyl-2-*exo*-norbornanol.

We plan on determining the rates of acetolysis of the four possible 7-*syn*- and 7-*anti*-phenyl-2-norbornyl tosylates to gain further insight on the magnitudes of the steric factors presented in this communication.

Acknowledgment. We are grateful to Mr. Louis Joris for performing the hydrogen-bonding measurements.

(12) This was done by multiplying 0.31 (from V) \times 2.4/0.31 (from VI) \times 0.0038/0.31 (from VII).

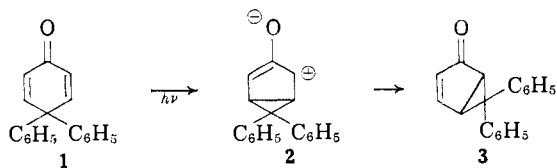
Donald C. Kleinfelter, Earl S. Trent
James E. Mallory, Terrell E. Dye
Department of Chemistry, University of Tennessee
Knoxville, Tennessee 37916

Received July 13, 1966

The Generation of Photochemical Intermediates without Light. Mechanistic Organic Photochemistry. XX¹

Sir:

In our mechanistic studies we have proposed mesoionic zwitterions as intermediates responsible for a large fraction of dienone photochemistry.² Thus in the reaction of 4,4-diphenylcyclohexadienone, zwitterion 2 was suggested as being formed by β,β bonding of the $n-\pi^*$ triplet of 1 and subsequent electron demotion. The formation of the observed 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one ("photoketone") (3) then was pictured as arising from rearrangement of zwitterion 2.^{2b,c,3}



type a dienone rearrangement

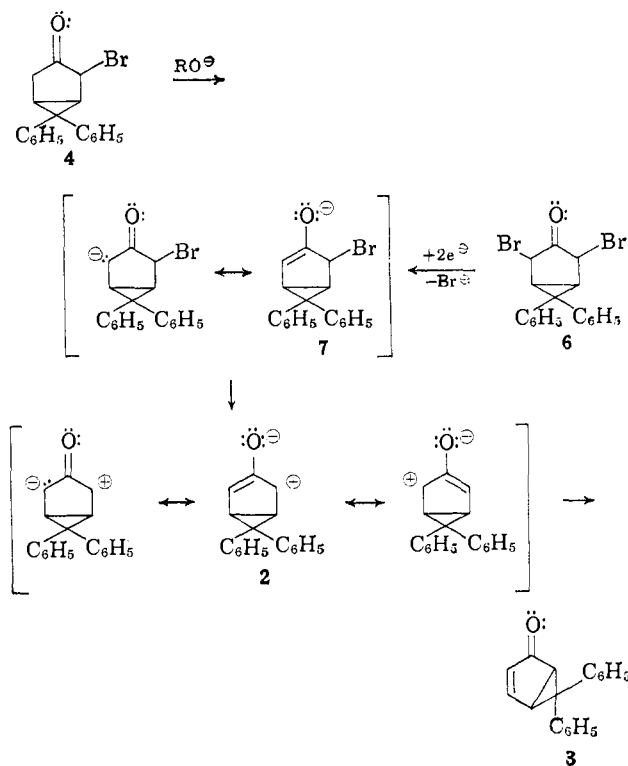
(1) For paper XIX see H. E. Zimmerman, *Science*, **153**, 837 (1966); paper XVIII: H. E. Zimmerman and D. J. Sam, *J. Am. Chem. Soc.*, **88**, 4905 (1966).

(2) (a) H. E. Zimmerman, 17th National Organic Chemistry Symposium, Bloomington, Ind., June 1961, Abstracts, p 31. (b) H. E. Zimmerman and D. I. Schuster, *J. Am. Chem. Soc.*, **83**, 4486 (1961); (c) *ibid.*, **84**, 4527 (1962).

The present study reports the ground-state generation of zwitterion 2 by two independent means and shows the behavior of the zwitterion to be the same as is observed in the type A photochemical rearrangement. This provides reasonable evidence that such mesoionic zwitterions are real intermediates rather than merely convenient devices.

Treating 2-bromo-6,6-diphenylbicyclo[3.1.0]hexan-3-one⁴ (4) with 1 equiv of potassium *t*-butoxide in *t*-butyl alcohol for 7 min at 40° afforded a 74% yield of 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one (3) (see Chart I). That the 2-bromo-6,6-diphenylbicyclo[3.1.0]hexan-3-one (4) indeed had the skeleton assumed was demonstrated

Chart I



by treating 4 with dilute hydrogen iodide in acetone;⁵ this afforded 6,6-diphenylbicyclo[3.1.0]hexan-3-one⁴ (5), the synthetic precursor of 4 and 6.

In parallel experiments 2,4-dibromo-6,6-diphenylbicyclo[3.1.0]hexan-3-one⁴ (6) was treated with zinc in dry refluxing dioxane to give 74% of photoketone 3. Similarly, the dibromide 6 gave 26% of photoketone 3 on treatment with calcium in THF at -70° and 14% of 3 when sodium amalgam in benzene at room temperature was employed. Again, the dibromo ketone 6 was shown to be unrearranged by dilute hydrogen iodide debromination⁵ to 5.

(3) H. E. Zimmerman and J. S. Swenton, *ibid.*, **86**, 1436 (1964).

(4) (a) Satisfactory analyses were obtained on all compounds. (b) Diphenyldiazomethane was added to cyclopentadiene to give 6,6-diphenylbicyclo[3.1.0]hex-2-ene which was subjected to hydroboration and oxidative work-up to afford 6,6-diphenylbicyclo[3.1.0]hexan-2-ol and -3-ol. Each alcohol was oxidized and the 3-one mono- and dibrominated. The synthesis of the monoene was first carried out by Dr. R. Keese in these laboratories. Details will be given in our full paper.

(5) Room temperature, 10 min; this reagent provides a mild method of debromination *via* the enol. Cf. H. E. Zimmerman, *J. Org. Chem.*, **20**, 549 (1955). Additional support was found in the nmr of the dibromide 6 and hydrogenation of photoketone 3 to give 6,6-diphenylbicyclo[3.1.0]hexan-2-one.

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 zwitterion⁶ **2** proposed² 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.

Acknowledgment Support of this research by National Institute of Health Grant GM 07487 and by the National Science Foundation is gratefully acknowledged. D. D. is indebted to the Deutsche Forschungsgemeinschaft for a travel grant.

(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. Smisson, 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.

Howard E. Zimmerman, Dietrich Döpp, Paul S. Huyffer
Chemistry Department, University of Wisconsin
Madison, Wisconsin 53706

Received September 9, 1966

Solvent Structure and Solvolysis in Ethanol-Water Mixtures

Sir:

Arnett and co-workers have shown¹ 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 (ΔH^\ddagger) for the hydrolysis of *t*-butyl chloride, as reported earlier by Winstein and Fainberg² and by Tommila and co-workers,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

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

(2) S. Winstein and A. H. Fainberg, *ibid.*, **79**, 5937 (1957).

(3) E. Tommila, E. Paakkala, U. Virtanen, A. Erva, and S. Varila, *Ann. Acad. Sci. Fennicae*, **A11**, 91 (1959).

(4) J. B. Hyne, R. Wills, and R. E. Wonkka, *J. Am. Chem. Soc.*, **84**, 2914 (1962).

reason to believe that the changes in ΔH_s and in ΔH^\ddagger were both related to the same kind of changes in solvent structure with changing composition.

Since ΔC_p^\ddagger 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 (ΔC_p^\ddagger) for the hydrolysis of *t*-butyl chloride across a similar series of ethanol-water mixtures. The value of ΔC_p^\ddagger for hydrolysis of *t*-butyl chloride in water was known to be -83 cal/mole deg,⁷ while Hakka, Queen, and Robertson⁸ confirmed the earlier report of Kohnstam⁹ that the value of ΔC_p^\ddagger in 50:50 (v/v) ethanol-water was about -30 cal/mol deg. We report here values of ΔC_p^\ddagger 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 ₂ O	ΔC_p^\ddagger , cal/mol deg	ΔH^\ddagger , 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 absorption¹³ 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 endothermic¹ 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 $-\Delta C_p^\ddagger$ 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

(5) We exclude here those salts having large organic cations, since these would reflect the solvation characteristics of neutral molecules: E. M. Arnett and D. R. McKelvey, *J. Am. Chem. Soc.*, **87**, 1393 (1965).

(6) R. E. Robertson, *Can. J. Chem.*, **42**, 1707 (1964).

(7) E. A. Moelwyn Hughes, R. E. Robertson, and S. E. Sugamori, *J. Chem. Soc.*, 1965 (1965).

(8) L. Hakka, A. Queen, and R. E. Robertson, *J. Am. Chem. Soc.*, **87**, 161 (1965).

(9) G. Kohnstam, "Transition State," Special Publication No. 16, The Chemical Society, London, 1962, p 179.

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

(11) Reference 10, pp 41-42.

(12) I. V. Malyash and V. I. Yashkichev, *Zh. Strukt. Khim.*, **5**, 13 (1964).

(13) C. J. Burton, *J. Acoust. Soc. Am.*, **20**, 186 (1948).

(14) H. S. Frank and M. W. Evans, *J. Chem. Phys.*, **13**, 507 (1945).