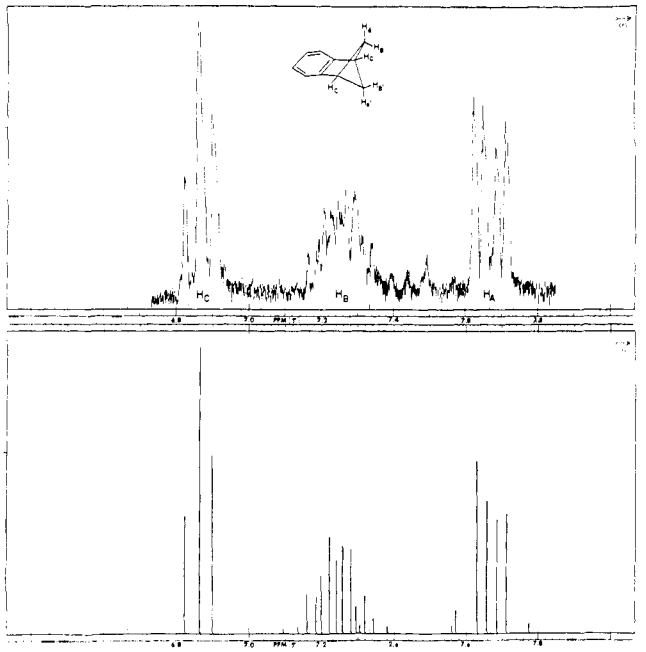
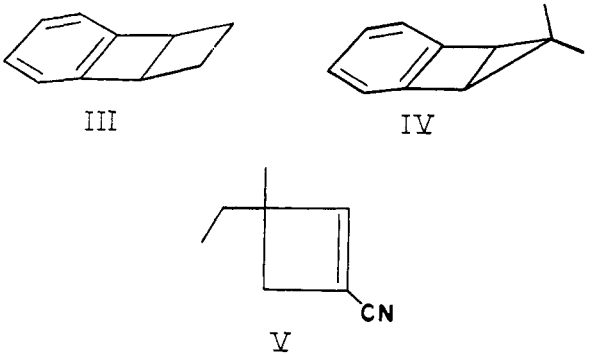


Figure 1. Observed and calculated nmr spectra of benzobicyclo-[2.1.1]hexene.

J_{BC} = 2.4 cps, J_{AB} = 4.9 cps, $J_{AA'}$ = 5.4 cps, and $J_{AC} = J_{BB'} = J_{AB'} = 0$ cps. The B hydrogens were assumed to be 25.6 cps and the C hydrogens 48.4 cps downfield from the A hydrogens. This spectrum is consistent, therefore, with the spectra of other bicyclo-[2.1.1]hexane derivatives reported by Wiberg.[12] He found that for bicyclo[2.1.1]hexane J_{AB} = 5.4 cps and $J_{AA'}$ = 6.7 cps, and for other derivatives, where nmr analysis was possible, J_{BC} varied, in most cases, between 2.6 and 3.0 cps. All other coupling constants (involving hydrogens of the A, B, and C type) were found to be zero.[13,13a]

The nmr spectrum is, therefore, unique and inconsistent with all other possible structures for the adduct. The observation that this adduct (II) is stable at 100° for 6 hr also rules out structure III since compound IV, a molecule with strain comparable to that of III,



apparently rearranges rapidly below 55° to the corresponding isoindene.[4]

(12) K. B. Wiberg, B. R. Lowry, and B. J. Nist, *J. Am. Chem. Soc.*, 84, 1594 (1962).

(13) Since Wiberg's compounds[12] and our compound all have a plane of symmetry the spectra are independent of J_{CC} and therefore a value for this coupling constant could not be determined.

(13a) NOTE ADDED IN PROOF. The nmr spectrum of methyl benzobicyclo[2.1.1]hexene-*endo*-5-carboxylate recently reported [H. Tanida and Y. Hata, *J. Am. Chem. Soc.*, **88**, 4289 (1966)] agrees extremely well with that of II.

The reaction of benzyne with bicyclobutane is thus quite analagous to its reaction with olefins, consistent with the proposed electronic formulation.[1]

We cannot, at this time, speculate about the mechanism of formation of the cycloadduct, benzobicyclo-[2.1.1]hexene. It should be pointed out, however, that 1-methyl-3-cyanobicyclobutane reacts with various olefins to give cycloadducts, apparently through an intermediate diradical.[14]

The major product, 3-phenylcyclobutene, arises from a reaction that is most simply rationalized as analagous to an Alder "ene" synthesis. Reaction of 1-methyl-3-cyanobicyclobutane with ethylene has been shown to give V, the "ene" synthesis product; however, a diradical mechanism was postulated for its formation.[15] We feel that, because of the electronic resemblance of the 1,3 bond in bicyclobutane and an olefinic π bond, the mechanism for the formation of I, and probably V, is most likely similar to that for the normal "ene" synthesis. It is generally thought that the "ene" synthesis is concerted although this has not been rigorously proven.[17]

Acknowledgment. We wish to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We also wish to thank Professor Donald Whitman for very helpful discussions concerning the nmr spectrum of compound II and for the use of his computer program for calculating nmr spectra.

(14) A. Cairncross and E. P. Blanchard, Jr., *J. Am. Chem. Soc.*, **88**, 496 (1966).

(15) The reaction of 1-methyl-3-cyanobicyclobutane with hexafluoroacetone and bis(trifluoromethyl)dicyanoethylene gives, formally, "ene" synthesis products.[16] The highly polar nature of the reactants makes a concerted "ene" synthesis mechanism less attractive.

(16) E. P. Blanchard, Jr., and A. Cairncross, *J. Am. Chem. Soc.*, **88**, 487 (1966).

(17) J. A. Berson, R. G. Wall, and H. D. Perlmutter, *ibid.*, **88**, 187 (1966).

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Received August 15, 1966

Acetolysis of the 3-Phenyl-2-norbornyl Tosylates[1]

Sir:

A priori we expected that if the intimate environment of a 2-*endo*-tosyl group in the bicyclo[2.2.1]heptane system were unchanged by substitution, then its solvolysis rate should also be unchanged relative to the parent compound. Winstein and co-workers[2] have found that the solvolysis rates of *endo*-brosylates unsubstituted at the 3 position differ from one another by a factor of less than two. However, 3,3-dimethyl substitution in *endo*-camphenyl and α-fenchyl brosylates causes rate retardations of 0.12 and 0.15, respectively. Schleyer and co-workers[3] have recently shown that 6,6-dimethyl substitution also markedly retards the acetolysis rate of a 2-norbornyl tosylate. Herein we

(1) This research was supported in part by a grant from the National Science Foundation.

(2) A. Colter, E. C. Friedrich, N. J. Holness, and S. Winstein, *J. Am. Chem. Soc.*, **87**, 378 (1965).

(3) P. von R. Schleyer, M. M. Donaldson, and W. E. Watts, *ibid.*, 87, 375 (1965).

Table I. Nuclear Magnetic Resonance Data for the 2- and 3-Hydrogens of Tosylates

Compound, mp, °C	δ, ppm	J, cps[a]	Spectra type
V, 95–96	4.68 (2n)	2n, 3x = 3.4 2n, 7a = 1.2	Doublet pair[b]
	3.08 (3x)	3x, 4 ≃ 3.6	Triplet
VI, 111–112	5.08 (2x)	1, 2x = 4.6 2x, 3x = 10.2	Doublet pair[c]
	3.12 (3x)	3x, 4 = 3.8	Doublet pair[c]
VII, 96–97	4.82 (2x)	1, 2x ≃ 4.0 2x, 3n = 3.8	Triplet
	2.52 (3n)	3n, 7a = 2.4	Doublet pair[b]
VIII, 102–103	4.74 (2n)	2n, 3n = 7.3 1, 2n = 2n, 7a = 1.2	Triplet pair
	2.86 (3n)	3n, 4 ≃ 0.5 3n, 7a = 1.1	Two doublet pairs

[a] Coupling constants are correct to ±0.1 cps unless indicated by ≃, which are correct to ±0.2 cps; x refers to an *exo* position, n is *endo*, and a is axial. [b] Difficultly resolved perhaps due to some finer splitting of 2n with 1. [c] Additional finer splitting of each line detectable, probably $J_{2x,6x}$ and $J_{3x,5x}$ (F. A. L. Anet, *Can. J. Chem.*, **39**, 789 (1961)).

Table II. Relative Acetolysis Rates of 2-Norbornyl Tosylates[a]

Tosylate	Rel rate at 25.0°	ΔH*, kcal/mole	ΔS*, eu
endo-Norbornyl[a,b]	1.0	25.8	−4.4
VI	2.4	25.6	−3.3
VII	0.0038	29.5	−3.0
1-Phenyl-2-*endo*-norbornyl[f]	0.68	25.1	−7.7
exo-Norbornyl[a,c]	1.0	21.6	−7.2
V[d]	0.31	23.0	−3.9
VIII[e]	0.0078	25.5	−3.8
1-Phenyl-2-*exo*-norbornyl[f]	4.1	22.8	−0.33

[a] V–VII run at least twice at three temperatures, VIII twice at two temperatures. All showed a normal salt effect when acetolyzed in 0.04 *M* $LiClO_4$. [b] $k_1 = 6.23 \times 10^{-8}$ sec^{-1}, calcd for 25.0°. [c] $k_1 = 2.33 \pm 0.09 \times 10^{-5}$ sec^{-1}, 25.0°. [d] That isomerization of V to the 7-*anti*-phenyl-2-*exo* isomer occurs has been shown by interrupting the acetolysis after *ca.* 30% reaction at *ca.* 70°, an equimolar mixture of the two tosylates resulting. Recent experiments have shown the isomerization to be an irreversible one. The relative rate reported is for the indicated tosylate. [e] Isomerization of VIII to the 7-*syn*-phenyl-2-*exo* isomer is nondetectable after *ca.* 25% reaction at *ca.* 70°. [f] D. C. Kleinfelter, Ph.D. Thesis, Princeton University, 1960.

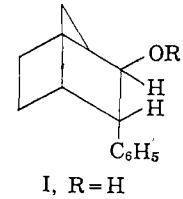
report the effects of 3-phenyl substitution on 2-norbornyl tosylate acetolyses.

All four isomeric 3-phenyl-2-norbornanols and their tosylates and *p*-nitrobenzoates have been prepared and characterized by infrared and nmr analyses. As previously reported, 3-*endo*-phenyl-2-*exo*-norbornanol (I), mp 52–53°, was prepared by hydroboration of 2-phenylnorbornene,[4] and 3-*endo*-phenyl-2-*endo*-norbornanol (II), mp 71–72°, by hydride reduction of 3-*endo*-phenyl-2-norbornanone.[5,6] The two 3-*exo*-phenyl alcohols III, mp 42.5–43.5°, and IV, an uncrystallizable oil, were prepared by hydride reduction of 3-*exo*-phenyl-2-norbornanone obtained from the Nef reaction on 3-*exo*-phenyl-2-*endo*-nitronorbornane.[7] Chromatography over alumina afforded alcohols III and IV in ratios of 3–4:1.

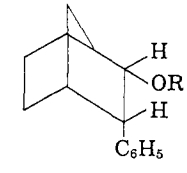
Table I lists the pertinent nmr data for the tosylates, which allows us to assign the indicated structures. Values of coupling constants are in line with those reported by Davis and Van Auken[8] and references therein. Alcohols II and IV showed OH···π hydrogen bonding in the infrared with Δν values of 10 and 36 cm^{-1}, respectively, while I and III showed no such bonding.[9]

Since the H–C–C–H dihedral angle in V is *ca.* 120° no effect from the *endo*-3-phenyl group would be expected other than the rate-retarding inductive effect,[10] and consequently the relative rate of 0.31 is not unexpected. In VI the H–C–C–H dihedral angle is *ca.* 0° and the relative rate of 2.4 must be due to a combination of steric acceleration and phenyl inductive retardation. Apparently steric hindrance to ionization[11] is unimportant here.

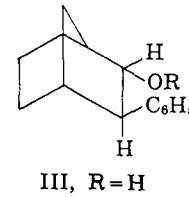
The H–C–C–H dihedral angle in VII approximates that in V, and one would probably expect no effect from the *exo*-3-phenyl other than the rate-retarding inductive effect. However, the actual rate is $^1/_{260}$ the rate of *endo*-norbornyl tosylate. We suggest that another effect may be in operation in the acetolyses of VII and VIII. Carbonium ions owe a measure of their inherent stability to stabilization by solvation. Carbonium ions in the bicyclo[2.2.1]heptane system are stabilized by solvent preferentially from the *exo* side. The 3-*exo*-phenyl group may be sterically inhibiting solvation of the developing positive charge in the transition state, thus raising the activation energy sufficiently to account for the extra rate retardation.



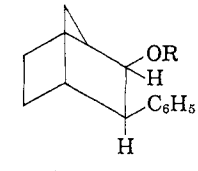
I, R = H
V, R = Ts



II, R = H
VI, R = Ts



III, R = H
VII, R = Ts



IV, R = H
VIII, R = Ts

(4) C. J. Collins, Z. K. Cheema, R. G. Werth, and B. M. Benjamin, *J. Am. Chem. Soc.*, **86**, 4913 (1964).
(5) B. M. Benjamin and C. J. Collins, *ibid.*, **88**, 1556 (1966).
(6) D. C. Kleinfelter and T. E. Dye, *ibid.*, **88**, 3174 (1966).
(7) W. C. Wildman and C. H. Hemminger, *J. Org. Chem.*, **17**, 1641 (1952).
(8) J. C. Davis, Jr., and T. V. Van Auken, *J. Am. Chem. Soc.*, **87**, 3900 (1965).
(9) All the alcohols and derivatives gave satisfactory elemental analyses.
(10) V may be expected to show some steric acceleration due to partial relief of unfavorable interactions between an *o*-phenyl hydrogen and the *endo*-5-hydrogen. Since the acetolysis rates of V and the 7-*anti*-phenyl-2-*exo* isomer differ by only a factor of *ca.* 1.2, and since acetolysis presumably proceeds to a common intermediate, we feel that such steric acceleration will contribute only a small amount to the acetolysis rate of V. If the plane of the benzene ring is rotated out of the plane of the *endo*-6-hydrogen, steric interactions can be minimized. Analysis of the infrared and nmr data for our 3-*endo*-phenyl-2-norbornyl compounds suggests this effect to be in operation.
(11) H. C. Brown, *Chem. Brit.*, 199 (1966).

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-phenylnortricyclene, 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) × 2.4/0.31 (from VI) × 0.0038/0.31 (from VII).

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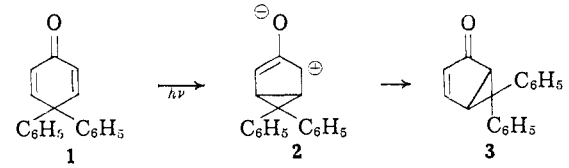
The Generation of Photochemical Intermediates without Light. Mechanistic Organic Photochemistry. XX[1]

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]

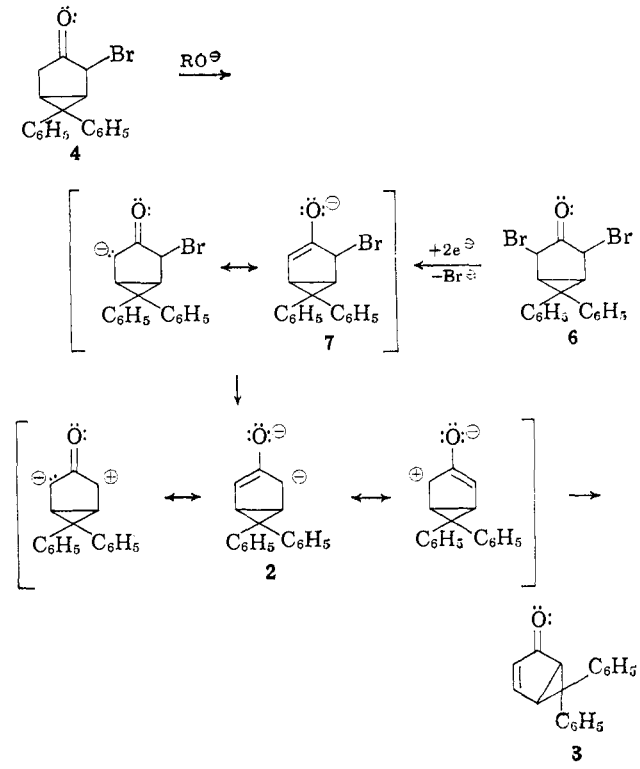


type a dienone rearrangement

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-one[4] (**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-one[4] (**5**), the synthetic precursor of **4** and **6**.

In parallel experiments 2,4-dibromo-6,6-diphenylbicyclo[3.1.0]hexan-3-one[4] (**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 debromination[5] to **5**.

(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).

(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[3.10]-hexan-2-one.