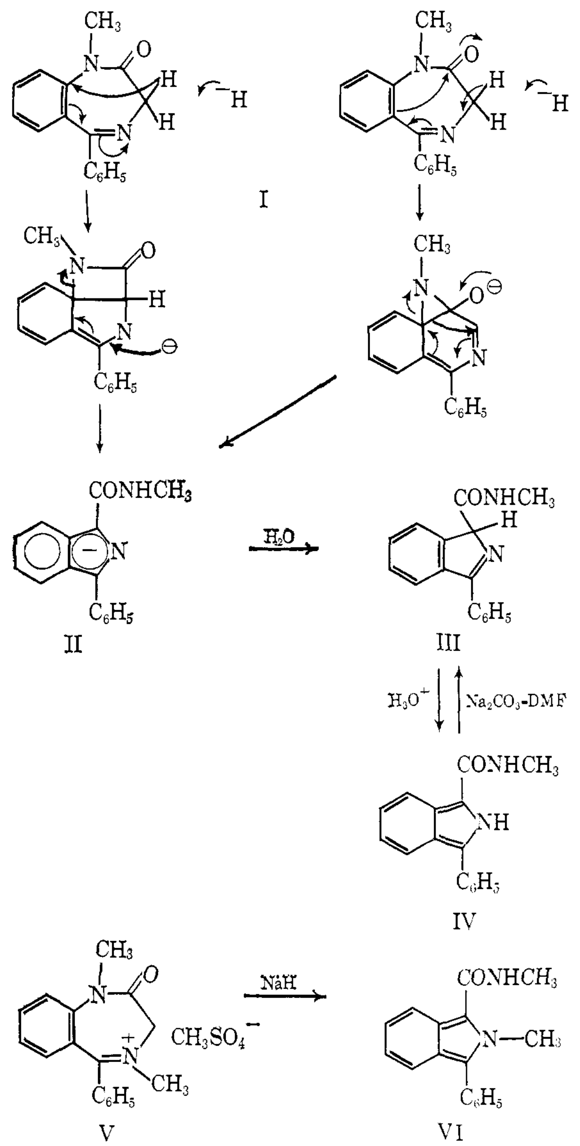

223–228°, mmp with IV 190–202°; $\nu_{NH}^{CHCl_3}$ 3410 cm^{-1}; $\nu_{C=O}^{CHCl_3}$ 1680 and 1530 cm^{-1}; nmr spectrum (CDCl$_3$) NHCH$_3$, three-proton doublet centered at δ 2.65 (J = 5 cps), NH δ 6.55, 10 protons in aromatic region (band) centered at δ 7.5; λ_{max} (2-propanol) 253 mμ (ϵ 13,700). *Anal.* Calcd for $C_{16}H_{14}N_2O$: C, 76.78; H, 5.64. Found: C, 76.79; H, 5.34.

The isoindolenine III could be reconverted quantitatively to the thermodynamically more stable isoindole IV simply by treatment with dilute acid or strong aqueous base.

The mechanism of the rearrangement can be explained by an initial attack of hydride ion at the 3 position of the benzodiazepinone nucleus (removal of one of the acidic protons) followed by a ring contraction to give either of the tricyclic intermediates as shown. Either intermediate would then undergo further rearrangement to give the salt of the isoindole carboanion II.

The 1,4-dimethyl-2-oxo-1,4-benzodiazepinium salt V could also, by treatment with sodium hydride, be rearranged to the corresponding 2,N-dimethyl-3-phenyl-1-isoindolecarboxamide (VI), mp 185–188°; $\nu_{NH}^{CHCl_3}$ 3460 cm^{-1}; $\nu_{C=O}^{CHCl_3}$ 1640 and 1530 cm^{-1}; nmr spectrum (CDCl$_3$) N–CH$_3$, δ 4.08; NHCH$_3$, three-proton doublet centered at δ 3.05 (J = 5 cps); λ_{max} (2-propanol) 222 (ϵ 23,200), 260 (ϵ 25,750), 298 (ϵ 5000), 306 (ϵ 5050), and 356 mμ (ϵ 19,000). *Anal.* Calcd for $C_{17}H_{16}N_2O$: C, 77.25; H, 6.10. Found: C, 77.59; H, 5.85. The isoindole structure of VI was proved by comparison with an authentic specimen, prepared from the known 2-methyl-1-phenylisoindole and methyl isocyanate.[4]

A detailed account of this investigation will be the subject of a forthcoming publication.

Acknowledgment. We wish to thank Professor G. Büchi for many helpful suggestions and his valuable advice.

pound IV. These shifts indicate that the CONHCH$_3$ group is attached to a saturated center on the isoindolenine nucleus.

(4) W. Theilacker and O. R. Leichtle, *Ann.*, **572**, 124 (1951).

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The Pinacol Rearrangement of 2-*p*-Anisylnorbornane-2,3-*cis*,*exo*-diol[1]

Sir:

Collins, *et al.*[2] have aptly demonstrated that the rearrangement of 2-phenylnorbornane-2,3-*cis*,*exo*-diol (I) in concentrated sulfuric acid at 0° takes place with rearrangement of the norbornane carbon skeleton *via* a hydride shift from the 6 to the 1 position,[3] accompanied by an intramolecular migration of hydrogen from C-3 to C-2 to give 3-*endo*-phenyl-2-norbornanone (II). Roberts[4] has suggested that the 2,4-dimethoxy analog of I could give *endo*-3-hydrogen migration during the pinacol rearrangement, as it is conceivable that the two methoxy groups could stabilize the tertiary classical open carbonium ion III at the expense of the bridged ion IV.

In connection with another study in the norbornane system we had prepared 2-*p*-anisylnorbornane-2,3-*cis*,*exo*-diol (V) and have carried out its rearrangement in concentrated sulfuric acid at 0°. While some sulfonation did take place, the only nonacidic compound isolable was 3-*endo*-*p*-anisyl-2-norbornanone (VI) in *ca.* 50% yield. The preparations of the compounds involved in this study and their structural assignments are as follows.

Peracetic acid oxidation of 2-*p*-anisylnorbornene followed by lithium aluminum hydride reduction gave the diol V. The performic acid oxidation procedure which previously afforded I[5] proved unsatisfactory as a pathway to V, apparently due to the more rapid alkene dimerization reaction.[6]

The structure of V was confirmed by comparison with I in the 3-μ region of the infrared, where both showed strong intramolecular OH···O hydrogen bonds,[7] and

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[1] This work was supported by a research grant from the National Science Foundation.

[2] C. J. Collins, Z. K. Cheema, R. G. Werth, and B. M. Benjamin, *J. Am. Chem. Soc.*, **86**, 4913 (1964); B. M. Benjamin and C. J. Collins, *ibid.*, **88**, 1556 (1966).

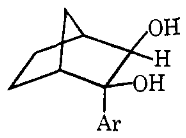
[3] If one renumbers the carbon atoms after the initial Wagner–Meerwein rearrangement, it is apparent that a 6,1-hydride shift becomes a classical 6,2-hydride shift.

[4] See ref 2, p 4915.

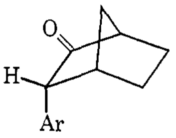
[5] D. C. Kleinfelter and P. von R. Schleyer, *J. Am. Chem. Soc.*, **83**, 2329 (1961).

[6] D. C. Kleinfelter and P. von R. Schleyer, *J. Org. Chem.*, **26**, 3740 (1961).

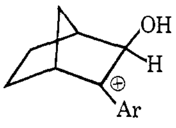
[7] L. P. Kuhn, *J. Am. Chem. Soc.*, **74**, 2492 (1952); **76**, 4323 (1954); **80**, 5950 (1958).



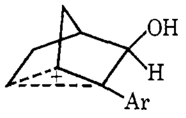
I, Ar = phenyl
V, Ar = *p*-anisyl



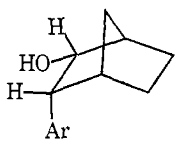
II, Ar = phenyl
VI, Ar = *p*-anisyl



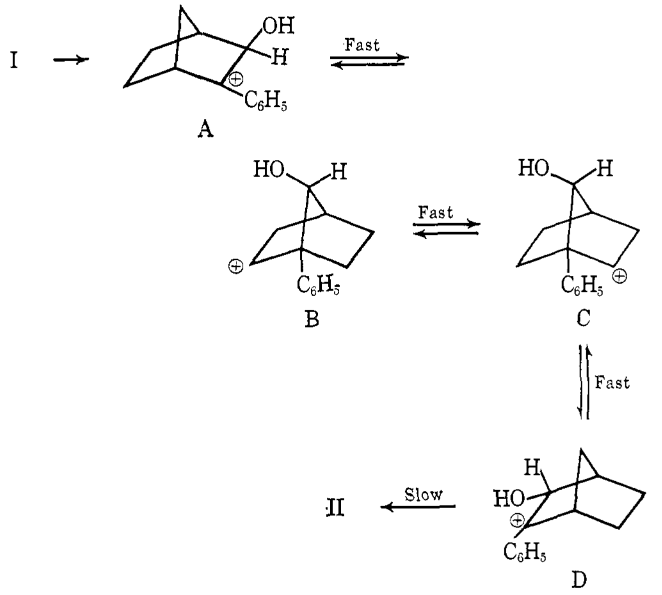
III

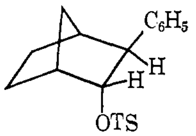


IV

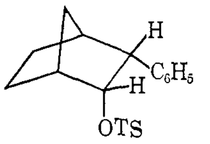


VII, Ar = phenyl
VIII, Ar = *p*-anisyl

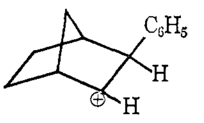




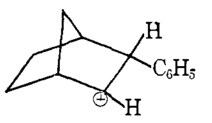
IX



X



XI



XII

in the 4.0-ppm region of the nmr spectrum, where both showed a doublet at 3.98 ppm ($J_{3n,7a} = 1.6$ cps) corresponding to the *endo*-3-hydrogen being split by the *anti*-7-hydrogen.[8]

Ketone VI showed an *exo*-3-hydrogen doublet at 3.30 ppm ($J_{3x,4} = 4.4$ cps), while II exhibited the corresponding doublet at 3.32 ppm ($J_{3x,4} = 4.2$ cps). The values of the coupling constants agree favorably with those tabulated by Davis and Van Auken.[9] Both ketones were reduced with lithium aluminum hydride to give 3-*endo*-aryl-2-*endo*-norbornanols, which showed intramolecular hydrogen bonding, OH···π type, in the infrared with $\Delta\nu = 10$ and 13 cm^{-1} for the phenyl VII and *p*-anisyl VIII compounds, respectively, relative to 2-*endo*-norbornanol. The nmr spectra of VII and VIII showed quartets for both the *exo*-2- and *exo*-3-hydrogens. Both showed signals for their *exo*-2-hydrogens at 4.16 ppm with $J_{2x,3x} = 9.8$; $J_{1,2x} = 4.5$ cps for VII, and $J_{2x,3x} = 9.8$, $J_{1,2x} = 4.4$ cps for VIII. Alcohol VII showed its *exo*-3-hydrogen signal at 2.93 ppm with $J_{2x,3x} = 9.8$, $J_{3x,4} = 3.7$ cps, while VIII's *exo*-3-hydrogen fell at 2.90 ppm with $J_{2x,3x} = 9.8$, $J_{3x,4} = 3.8$ cps. Once again the coupling constants agree favorably with values previously recorded.[9]

Rearrangement of V to VI serves to further emphasize the apparent resistance of an *endo*-3 substituent, even hydrogen, to migration in the rearrangement of a norbornyl compound.[10] One could interpret our results as evidence that a *p*-methoxy group does not exert a sufficient influence to stabilize the tertiary, classical open carbonium ion III at the expense of the bridged ion IV. However, alternate explanations for the results communicated herein as well as those previously reported for I should be considered.

For simplicity we are considering these pinacol rearrangements as proceeding through classical carbonium ion intermediates.[11] The removal of water from I or V to form ion A should be extremely rapid in concentrated sulfuric acid. If one assumes that the subsequential steps, A → B → C → D, occur more rapidly than any *endo*-3 shift of hydrogen (which is apparently the case), then all that remains is to offer sufficient reason for the preference of ion D over ion A. Saunders, Schleyer, and Olah[12] by an nmr study of the norbornyl cation in mixed SbF_5–SO_2–SO_2F_2 solvent have calculated that at $-120°$ the 3,2-hydride shift is slower than the 6,2-hydride shift and the Wagner–Meerwein rearrangement by a minimum of $10^{8.8}$. Hence, we would expect that the change of one 2-arylnorbornyl cation A to another 2-arylnorbornyl cation D could occur much more rapidly than any 3,2-hydride shift, whether *endo* or *exo*, regardless of the effect of the aryl group in stabilizing the initially formed ion.

It is possible that ion D (*endo*-OH) is more stable than ion A (*exo*-OH) due to the steric inhibition to solvation of ion A caused by the *exo*-3-hydroxy group.

We have observed that 3-*exo*-phenyl-2-*endo*-norbornyl tosylate (IX) acetolyzes at a rate 262 times slower than *endo*-norbornyl tosylate, while the rate of the epimeric 3-*endo*-phenyl-2-*endo*-norbornyl tosylate (X) is 2.42 times faster than *endo*-norbornyl tosylate.[13] Thus, the effect of the *endo*-3-phenyl *vs.* the *exo*-3-phenyl results in a *ca.* 636-fold difference in reaction rates.[14] This, in effect, may be considered a quantitative measure of the relative stabilities of the ions XI and XII, or of the transition states leading to the ions.

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(8) J. Meinwald and Y. Meinwald, *J. Am. Chem. Soc.*, **85**, 2514 (1963).

(9) J. C. Davis, Jr., and T. Van Auken, *ibid.*, **87**, 3900 (1965).

(10) J. Berson in "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, Chapter, 3, p 159.

(11) P. von R. Schleyer, D. C. Kleinfelter, and H. G. Richey, Jr., *J. Am. Chem. Soc.*, **85**, 479 (1963), have shown that 1,2-diarylnorbornyl cations possess rapidly equilibrating classical ion structures. The present authors see no reason to abandon this assignment for the monoaryl analogs.

(12) M. Saunders, P. von R. Schleyer, and G. Olah, *ibid.*, **86**, 5680 (1964).

(13) D. C. Kleinfelter, E. S. Trent, J. E. Mallory, and T. E. Dye, Abstracts, Southeast-Southwest Joint Regional Meeting, American Chemical Society, Memphis, Tenn., Dec. 1965, p 71. Rate data are extrapolated to 25°. The details of this work will be the subject of a future communication.

(14) Steric acceleration may account for some of the rate increase of X over *endo*-norbornyl tosylate.

Normally, *exo* substituents are preferred over *endo* substituents for steric reasons.[15] However, solvent will stabilize the carbonium ion intermediates in these reactions preferentially from the *exo* side. Obviously there are no substituents (other than hydrogen) to inhibit this in ions D and XII, while the *exo*-3-OH and *exo*-3-phenyl in ions A and XI can both inhibit carbonium ion solvation.

We are currently directing our efforts toward the synthesis of appropriately substituted diols which might afford pinacol rearrangement products *via endo*-3-hydrogen migration. We also plan to determine the rates of hydrolysis of the 3-*exo*- and 3-*endo*-hydroxy-2-phenyl-2-norbornyl chlorides, which should give a quantitative measure of the relative stabilities of ions A and D.

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

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[15] For references, see P. von R. Schleyer and M. M. Donaldson, *J. Am. Chem. Soc.*, **82**, 4645 (1960).

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Photochemistry of Adsorbed Organic Molecules. III. The Photosensitized *cis–trans* Isomerization of Piperylene in Silica Gel–Benzene Matrices

Sir:

Recently we have been investigating aspects of the physical adsorption of organic molecules and the proposed resulting electronic perturbations.[1,2] Specifically, we have been examining the electronic configurations of relatively polar molecules "bound" to the adsorbing surface of finely powdered activated silica gel in solvent matrices. Obviously these electronic configurations on silica gel vary to a substantial degree from the "normal" or "free" species in solution. Corresponding disturbances therefore should be expected in the photochemical behavior of a molecule in these differing surroundings, purely from environmental considerations.

The data thus far reported from these laboratories have concerned spectral shifts in ultraviolet and visible absorption of "bound" molecules,[1] as well as photodecomposition product and reaction rate variations due to the effect of the matrix.[2] We now wish to report the effect of a benzene–silica gel matrix on the vertical triplet excitation donating ability of three carefully chosen donors to the acceptor piperylene (1,3-pentadiene). The polarity of the sensitizers used in this study is far greater than that of the piperylene (as, for that matter, is the benzene solvent to a smaller degree), and thus we have reason to believe that a silica gel–solvent matrix will produce adsorption effects primarily upon the electronic configuration of the sensitizers, leaving the piperylene relatively unaffected. This fact is born out by the very small ($\sim$50 A) red shift of the spectrum of piperylene in a cyclohexane–silica gel matrix alone.

Table I[a]

Sensitizer	Triplet energy,[b] kcal	% *trans* from *cis*	% *trans* from *trans*
Benzophenone	68 (n,π^*)		
Matrix		59	58
Solution		59	58
Solution (lit.)[c]		57	56
2-Acetonaphthone	59 (π,π^*)		
Matrix		71	71
Solution		75	76
Solution (lit.)[c]		72	72
Biacetyl	55 (n,π^*)		
Matrix		73	73
Solution		80	80
Solution (lit.)[c]		77	77

[a] Solutions were 0.1 *M* in sensitizer and 0.2 *M* in piperylene. Irradiation was at 3660 A using a Hanovia 450-w lamp. Analyses were carried out on a 12-ft β,β'-oxydipropionitrile column at 60°. [b] Values from W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Am. Chem. Soc.*, **86**, 4537 (1964). [c] Values from G. S. Hammond, J. Saltiel, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *ibid.*, **86**, 3197 (1964). The discrepency between our solution values and those of Hammond is due to the fact that we measured vpc peak *areas*, whereas in Hammond's data most measurements were based on peak heights.

The donors selected were benzophenone, 2-acetonaphthone, and biacetyl. Table I lists the sensitizers, their triplet energies, and the values for the *cis–trans* photostationary states of piperylene in benzene solution and in a benzene–silica gel matrix. Results in solution are compared with literature values.

The trend in the data, in view of our previous experience with the matrices and in view of the dependence of photostationary states on triplet energy of sensitizer,[3] is both interesting and reasonable. The triplet n,π^* state of benzophenone in the matrix should be at higher energy[1] than in solution, but "*high-energy*" *sensitizers all give the same photostationary state*;[3] thus we see no effect of the matrix. "Low-energy" sensitizers, on the other hand, show a high preponderance of *trans* over *cis* at the photostationary state, and small (3–4 kcal) energy differences affect the ratio markedly, lower energy favoring *trans*. Biacetyl has as its lowest triplet the n,π^* configuration; the effect of the matrix would be to substantially raise the energy and lower the *trans/cis* ratio. This is clearly what is observed, with the per cent *trans* changing from 80 to 73. To round out the study, another low-energy sensitizer, acetonaphthone, with a lowest π,π^* triplet, was investigated. According to our predictions[1] the excited-state energy should be very slightly lowered in this case, thus, if anything, *increasing* slightly the ratio of *trans*. This, however, was *not* observed, the per cent *trans* lowering from 75 to 71. Thus it appears that the lowest π,π^* triplet of this particular molecule is less polar, rather than more polar, than the ground-state molecule. This is perhaps not too surprising since we have recently observed in absorption spectroscopy (singlet–singlet) in the matrix some π–π^* transitions in certain molecules are blue shifted rather than red shifted (azulene being a notable example).[4] Obviously, theoretical and experimental calculations of dipole moments of excited states of a great many molecules

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[1] P. A. Leermakers and H. T. Thomas, *J. Am. Chem. Soc.*, **87**, 1620 (1965).

[2] P. A. Leermakers, L. D. Weis, and H. T. Thomas, *ibid.*, **87**, 4403 (1965).

[3] G. S. Hammond, N. J. Turro, and P. A. Leermakers, *J. Phys. Chem.*, **66**, 1144 (1962).

[4] P. A. Leermakers and L. D. Weis, unpublished results.