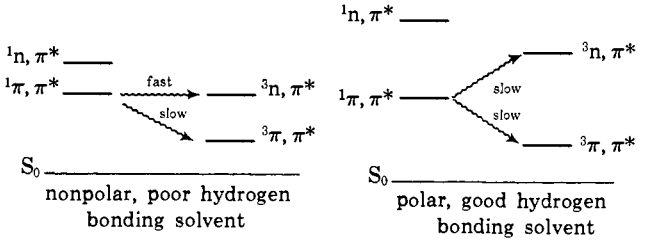
Scheme I



the energy of the $^3n,\pi^*$ state (T_2) will become greater than that of the $^1\pi,\pi^*$ state (S_1) meaning that intersystem crossing from S_1 to T_2 will require a larger activation energy and will become slower. The greater the solvent polarity or hydrogen bonding ability, the larger the energy difference between T_2 and S_1, the greater the activation energy and the lower the rate constant for intersystem crossing from S_1 to T_2 will be. This predicts that the intersystem crossing rate will decrease continuously as a function of increasing solvent polarity or hydrogen-bonding ability, until only the slow intersystem crossing from S_1 (π,π^*) to T_1 (π,π^*) remains.[14] In solvents of intermediate polarity and hydrogen bonding ability, the observed intersystem crossing rate will equal the sum of the rates of intersystem crossing to T_2 and T_1. (The solvent effect of k_{st} can also be explained by an analogous argument involving the extent of mixing of n,π^* character into the vibrationally excited level of the π,π^* triplet isoenergetic with the π,π^* singlet.)

The explanation given above for the enormous effect of solvent on the Φ_f^{rel} values also accounts for the solvent effect on $\lambda^{fl}{}_{max}$. Since the S_1 state is π,π^*, presumably with substantial amounts of intramolecular charge transfer character,[15] its energy should decrease in going to solvents of greater polarity or hydrogen-bonding ability causing $\lambda^{fl}{}_{max}$ to red shift, as is observed. If the lowest singlet of thioxanthone in nonpolar solvents were the n,π^* singlet, then increasing solvent hydrogen-bonding ability would be expected to cause an initial blue shift in $\lambda^{fl}{}_{max}$. The absence of such a blue shift suggests that S_1 is π,π^* in all solvents.

In summary, we have observed substantial solvent effects on the fluorescence efficiency and lifetime and the position of the fluorescence maximum of thioxanthone. The Φ_f^{rel} and τ_f changes are attributed to solvent effects on the rate of intersystem crossing caused by changes in relative energies of the $^1\pi,\pi^*$ (S_1) state and $^3n,\pi^*$ (T_2) state. The sensitivity of $\lambda^{fl}{}_{max}$ to solvent character may make thioxanthone useful in fluorescence labeling experiments as a probe for molecular environment.[16]

Acknowledgment. We would like to thank Dr. William H. Saunders Jr. for helpful assistance with this research.

(14) A similar explanation has been suggested for the stronger fluorescence of acridone in alcohol relative to hexane and solvent effects on fluorenone fluorescence lifetimes and efficiencies. See (a) ref 8a; (b) L. A. Singer, *Tetrahedron Lett.*, 923 (1969); (c) R. A. Caldwell, *ibid.*, 2121 (1969); (d) B. M. Monroe and R. P. Groff, *ibid.*, 3955 (1973).

(15) V.-K. H. Giovanelli, J. Dehler, and G. Hohlneicher, *Ber. Bunsenges. Phys. Chem.*, 75, 864 (1971).

(16) For a recent review of an application of fluorescence probes, see G. M. Edelman and W. O. McClure, *Accounts Chem. Res.*, 1, 65 (1968).

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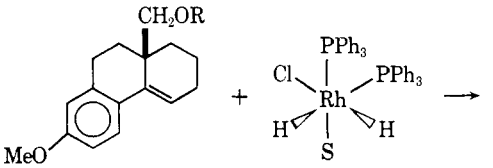
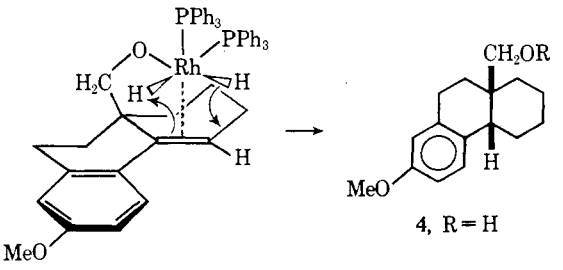
Control of Hydrogenation Stereochemistry by Intramolecular Anionic Coordination to Homogeneous Catalysts[1]

Sir:

Hydrogenation of olefins in the presence of homogeneous catalysts[2] holds potential for stereochemical control of the reduction process through coordination to the catalyst by polar functional groups within the molecule.[1b] This potential has so far remained unrealized,[3] in part because instances to which this idea might be applied usually involve alkenes whose degree of substitution would be expected to depress their rates of reduction severely.[4] However, several entries in the literature of this subject suggest that reduction of olefins may be accelerated by an assisting coordination to the catalyst of certain very polar functional groups within the molecule,[5-7] and that increasing the electron density on such a functional group may further favor this coordination.[6a,c]





We have applied the above principles to the reduction of compound **1**, which can serve as a model precursor for many polycyclic systems of interest. The trisubstituted styrene bond of **1** is expectedly unreactive[2c,4] toward hydrogenation with $(Ph_3P)_3RhCl$ at atmospheric pressure and room temperature, and even at 100 psi and 50°. However, treatment of alkali metal salts of **1** in benzene with hydrogen and 0.036 equiv of $(Ph_3P)_3RhCl$ under the latter conditions, leads to olefin

(1) (a) Part IV in the series Stereochemical Control of Reductions. (b) Part III: H. W. Thompson and R. E. Naipawer, *J. Amer. Chem. Soc.*, 95, 6379 (1973).

(2) (a) R. E. Harmon, S. K. Gupta, and D. J. Brown, *Chem. Rev.*, 73, 21 (1973); (b) F. J. McQuillin, *Progr. Org. Chem.*, 8, 314 (1972); (c) J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc. A*, 1711 (1966); (d) S. Montelatici, A. van der Ent, J. A. Osborn, and G. Wilkinson, *ibid.*, 1054 (1968).

(3) (a) *Cf.* A. J. Birch and K. A. M. Walker, *J. Chem. Soc. C*, 1894 (1966); Y. K. Sawa, N. Tsuji, K. Okabe, and T. Miyamoto, *Tetrahedron*, 21, 1121 (1965); (b) *cf.* H. J. Brodie, C. E. Hay, and T. A. Wittstruck, *J. Org. Chem.*, 37, 3361 (1972); (c) *cf.* Y. J. Abul-Hajj, *Steroids*, 18, 281 (1971).

(4) A. S. Hussey and Y. Takeuchi, *J. Amer. Chem. Soc.*, 91, 672 (1969); *J. Org. Chem.*, 35, 643 (1970).

(5) R. E. Harmon, J. L. Parsons, D. W. Cooke, S. K. Gupta, and J. Schoolenberg, *J. Org. Chem.*, 34, 3684 (1969).

(6) (a) W. S. Knowles, M. J. Sabacky, and B. D. Vineyard, *Ann. N. Y. Acad. Sci.*, 172, 232 (1970); (b) W. S. Knowles and M. J. Sabacky, *Chem. Commun.*, 1445 (1968); (c) T. P. Dang and H. B. Kogan, *Chem. Commun.*, 481 (1971); (d) J. D. Morrison, R. E. Burnett, A. M. Aguiar, C. J. Morrow, and C. Phillips, *J. Amer. Chem. Soc.*, 93, 1301 (1971).

(7) F. H. Jardine, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc. A*, 1574 (1967); S. Siegel and D. W. Ohrt, *Tetrahedron Lett.*, 5155 (1972).

saturation *with exclusive production of the cis-isomer* **4**, in conversions ranging from 7 to 68%, depending on the alkali metal used (K > Na > Li). This is to be contrasted with hydrogenations of **1** and its salts over heterogeneous palladium and platinum catalysts, which invariably lead to mixtures containing appreciable quantities of the trans isomer.[8]

We propose that these homogeneous reactions proceed by way of a complex resembling **3**, in which not only a solvent molecule but the anionic species as well, chloride in this instance, has been displaced. This corresponds closely to the type of complexing suggested to operate in reduction of certain acrylates and cinnamates.[6a] We believe that the principles exemplified in the reduction of the salts of **1** offer valuable possibilities for haptophilic[1b] stereochemical control of olefin reduction in a wide variety of chemical species and situations.

Acknowledgments. Support from the Rutgers Research Council and helpful consultations with G. L. Spoog are gratefully acknowledged.

(8) H. W. Thompson and E. McPherson, unpublished results.

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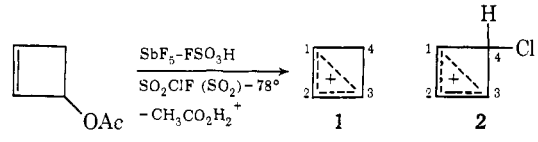
Novel Aromatic Systems. I. The Homocyclopropenyl Cation, the Simplest 2π Homoaromatic System

Sir:

In 1956 Applequist and Roberts[1a] predicted the existence of the homocyclopropenyl cation, the simplest possible homoaromatic species, resembling in its aromatic stabilization the cyclopropenium ion, but involving cyclic electron delocalization of the 2π system through an intervening sp^3 hybridized carbon. Subsequently, homoaromatic systems including the homotropylium ion and related analogs were studied in detail, most notably by Winstein.[1b] Although some information concerning the homoaromatic nature of cyclobutenyl cations has been provided over the past 2 decades through experimental study of substituted analogs[2,3] showing some degree of 1,3-overlap, conclusive evidence for a truly homoaromatic cyclobutenyl cation, such as expected in the case of the parent homocyclopropenyl cation, has thus far not been obtained.

We now wish to report the preparation and characterization (by ^1H and ^{13}C nmr) of the till now elusive parent cyclobutenyl cation **1** showing it to be the true homocylcopropenyl cation.

The homocyclopropenyl cation was prepared (after many inconclusive attempts) from 3-acetoxycyclobutene[4] in FSO_3H–SbF_5 (Magic Acid)–SO_2ClF (or SO_2) solution at −78°.[5] The pmr spectrum (100 MHz) of the solution of ion **1** at −60° (Figure 1B) shows three



absorptions at δ 4.53, 7.95, and 9.72 with relative peak intensities of 2:2:1 (Table I), respectively. The pmr spectrum of **1** remained unchanged upon warming the solution to 20°. Below −60° ion **1** shows temperature-dependent behavior. Within the temperature range studied (−60 to −110°) the two most deshielded absorptions remained unchanged, while the more shielded methylene signal gradually became broadened and finally merged into the baseline as the temperature was lowered to −110°. The process is reversible and raising the temperature of the sample to −60° regenerated the original spectrum. We attribute this temperature-

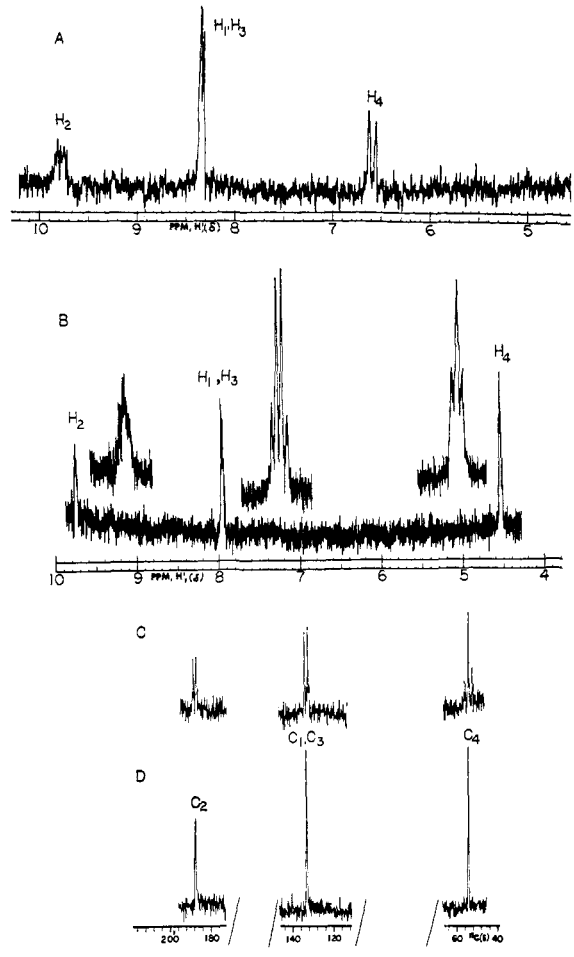


Figure 1. (A) The 60-MHz pmr spectrum of **2** at −60°. (B) The 100-MHz pmr spectrum of **1** at −40°. (C) and (D) off-resonance and noise decoupled cmr spectra of **1** at −60°.

(1) (a) D. E. Applequist and J. D. Roberts, *J. Amer. Chem. Soc.*, 78, 4012 (1956); (b) For a review on homoaromaticity, see S. Winstein, *Quart. Rev., Chem. Soc.*, 23, 141 (1969).

(2) (a) T. J. Katz and E. H. Gold, *J. Amer. Chem. Soc.*, 86, 1600 (1964); (b) T. J. Katz, J. R. Hall, and W. C. Neikam, *ibid.*, 84, 3199 (1962); (c) E. F. Kiefer and J. D. Roberts, *ibid.*, 84, 784 (1962); (d) S. L. Manatt, M. Vogel, D. Knutson, and J. D. Roberts, *ibid.*, 86, 2645 (1964); (e) I. A. Shleider, I. S. Isaer, and V. A. Koptyug, *Zh. Org. Khim.*, 8, 1337 (1972).

(3) G. A. Olah, P. R. Clifford, Y. Halpern, and R. G. Johanson, *J. Amer. Chem. Soc.*, 93, 4219 (1971), and references therein.

(4) K. B. Wiberg, V. Z. Williams, Jr., and N. E. Friedrich, *J. Amer. Chem. Soc.*, 92, 564 (1970).

(5) Ionization of 3-acetoxycyclobutene gives, beside the formation of **1**, also protonated acetic acid, acetylium ion, some polymeric material, protonated crotonaldehyde, and fluorosulfonates. The formation of crotonaldehyde is believed to result from the ring opening protolysis of 3-acetoxycyclobutene. Attempts to ionize 3-acetoxycyclobutene at −120° did not eliminate the formation of protonated crotonaldehyde.