appear to be stable indefinitely. When the solution was buffered with K_2HPO_4, oxidation to 9,10-diethyl-3,6-phenanthrenediol (**6**) was negligible, even in samples open to the atmosphere. However, **6** was the only product obtained from photolyses carried out in acidic media.[7,8]

Elemental analysis of the yellow crystals was consistent with formula **5**. The ir spectrum indicated absence of hydroxyl and presence of highly conjugated carbonyl (1651 cm^{-1}). The electronic absorption in methanol showed λ_{max}, mμ (ϵ, l./mol cm) at 406 (19,600), 287 (23,600), and 221 (8900). The extended unsaturated diketone system of **5** seems without close analogy in the literature; however, adaptation of Woodward's rules[9] predicts absorption in the 400–450-mμ range, as observed.

In addition to characteristic ethyl groups (10 H), the nmr spectrum of **5** showed a doublet pair (4 H) at 6.1 and 7.6 ppm, assigned to the vinyl protons, and a complex multiplet (6 H) in the 2–3-ppm region, partially obscured by the methylene quartet of the ethyl groups. The mass spectrum obtained by direct inlet at 195° gave a base peak at the parent *m/e* 268, as well as prominent peaks at *m/e* 239, 211, 183, and 115 attributable to successive losses of ethyl, ethene, and two carbon monoxide fragments, respectively.

Exchange of the active protons α to the carbonyl groups for deuterium was readily achieved by stirring **5** in $NaOCH_3$–CH_3OD at room temperature for 3 hr. The deuterated product exhibited a mass spectrum similar to that of **5** except that most major peaks were shifted higher by 4 *m/e* units. In addition, loss of 42 *m/e* units (ketene) from fragments of **5** was replaced by a corresponding decrease of 44 *m/e* units in the spectrum of **5**-d_4.[10] The 6 H multiplet at 2–3 ppm in the nmr spectrum of **5** became a 2 H singlet at 2.3 ppm in the spectrum of **5**-d_4, as expected for the now unsplit signal of the 4a and 4b protons. New bands were observed in the ir spectrum at 2211 and 2131 cm^{-1} (C–D stretch).

These results are all in excellent agreement with structure **5**.

Changes in the uv-visible absorption spectrum of dilute (3×10^{-5} *M*) solutions of diethylstilbestrol upon successive short irradiations at 254 mμ indicated efficient and virtually quantitative[11] conversion to **5**. The presence of an isosbestic point at 267 mμ in these consecutive-spectra diagrams testified to the constant molar relationship between product and reactant and to the absence of either dark or photochemical side reactions. The thermal stability of **5**, both toward oxidation to **6** and reversion to **2**, was shown by the absence of change in the electronic spectra of photolyzed solutions stored in the dark for several months. On the other hand, irradiation of **5** in the visible (~400 mμ) or near-uv (366 mμ) caused partial return to **2** or **3**.

As with other stilbenes, the **3** → **5** photocyclization did not proceed in the presence of sensitizers with lowest triplet in proper energetic relationship with that of **3**. Therefore the assignment of either excited singlet[12] or hot ground level[13] as the reacting state seems to hold for stilbene **3** as well.

On the basis of bond energies, the stabilization of diketone **5** relative to its enolic tautomer **4** is estimated to be 37 kcal/mol. When one compares this value with the 39 kcal/mol calculated by Mallory[12] for the expected difference in stability between *trans*-stilbene and unsubstituted DHP, one easily understands why ketoform DHP **5** is isolable, whereas all other reported attempts to isolate a DHP have been fruitless.

There has been uncertainty concerning the geometry of the 4a and 4b hydrogens. Assuming a concerted reaction in a first excited state, the Woodward–Hoffmann orbital symmetry rules[14] predict a conrotatory cyclization with consequent trans configuration for the 4a and 4b hydrogens of **4** and **5**. Steric restraints in the formation of substituted dihydrophenanthrenes also favor trans geometry.[3,15] However, reaction from a hot ground state suggested by quantum mechanical calculations[13] would result in cis configuration. Since *cis*-DHP would undergo facile exothermic elimination of molecular hydrogen,[12] the fact that the mass spectrum of **5** showed only a minor peak (1.3% of M^+) at $M^+ - 2$ provides strong experimental support for the trans configuration.

(7) Isolation of phenol **6** without detection of **5** on photolysis of **2** in acetic acid was reported previously by P. Hugelshofer, J. Kalvoda, and K. Schaffner, *Helv. Chim. Acta*, **43**, 1322 (1960).

(8) Phenanthrene **6** has also been synthesized by an alternative route: D. J. Collins and J. J. Hobbs, *Aust. J. Chem.*, **20**, 1905 (1967). A sample kindly sent us by D. J. C. was identical with our material.

(9) L. F. Fieser and M. Fieser, "Steroids," Reinhold, New York, N. Y., 1959, p 15.

(10) This is a well-known fragmentation: H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Interpretation of Mass Spectra of Organic Compounds," Holden-Day, San Francisco, Calif., 1964, p 155.

(11) In fact, production of **5** is the basis of a quantitative assay procedure for drug **2**: (a) D. Banes, *J. Ass. Offic. Agr. Chem.*, **43**, 248 (1960); (b) United States Pharmacopeia, 16th rev, Mack Publishing Co., Easton, Pa., 1960, p 217; 18th rev, 1970, p 187.

(12) F. B. Mallory, C. S. Wood, and J. T. Gordon, *J. Amer. Chem. Soc.*, **86**, 3094 (1964).

(13) H. Guesten and L. Klasnic, *Tetrahedron*, **24**, 5499 (1968).

(14) R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 395 (1965).

(15) C. E. Ramey and V. Boekelheide, *ibid.*, **92**, 3681 (1970).

(16) From work done in partial fulfillment of requirements for the Ph.D. degree at The George Washington University.

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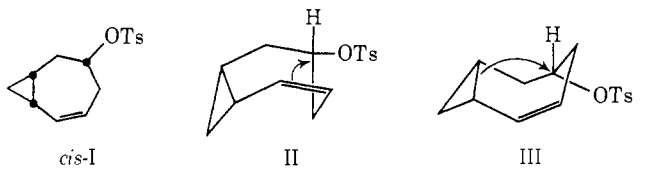
Competitive Homoconjugation between Conformationally Related Species

Sir:

cis-Bicyclo[5.1.0]oct-5-en-3-yl tosylate (*cis*-I-OTs) offers structural features for internal competition between



cis-I II III

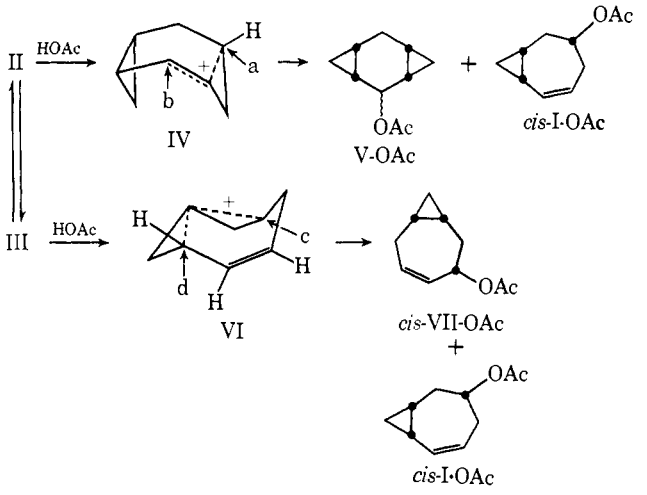
two types of homoconjugation. The molecule can exist in two conformations (II and III). In II, the double bond is best oriented for participation; in III, the cyclopropane ring. Although II and III may interconvert, the ions they produce, as will be seen, do not.

Therefore II yields only products of double-bond participation and III of cyclopropane participation. If the barrier to interconversion of II and III is considerably less than the activation energy for solvolysis, product analysis will furnish a direct measure of the contributions from the two types of participation. We wish to report by this method that participation from the double bond is dominant under these competitive conditions.

The synthesis of *cis*-I-OH was accomplished by the cyclopropanation of 3,5-cycloheptadienol,[1] and the structure and stereochemistry were proved by hydrogenation to the known *cis*-bicyclo[5.1.0]octanol.[2] It was considered necessary first to establish the presence of participation. The rate of reaction in acetic acid–sodium acetate ($k_{25} = 6.57 \times 10^{-6}$ sec^{-1}) indicates a modest anchimeric acceleration (10^2–10^3) by the Schleyer–Foote correlation[3] ($\nu_{CO} = 1713$ cm^{-1}). Despite the presence of the inductively retarding double bond and cyclopropane ring, *cis*-I-OTs acetolyzes more rapidly than cycloheptyl tosylate.[4] Although the kinetics establish the existence of participation, they give no information concerning the structural source (double bond or cyclopropane ring).

The activation energy to acetolysis was found to be 22.5 kcal/mol, whereas the barrier to ring interconversion (II $\rightleftharpoons$ III) is probably in the range 6–10 kcal/mol.[5] By the Curtin–Hammett principle, the product distribution should therefore reflect the relative energies of the transition states from II and III, and not the ground-state energies. The ions and expected products are depicted in Scheme I. From conformer II (double-bond participation), the first-formed ion IV may suffer attack at position a or b to give esters I or V. From conformer III (cyclopropane participation), the first-formed ion VI may suffer solvent attack at c or d to give esters I or VII. In an initial and somewhat simplistic analysis, V will therefore indicate double bond participation, VII cyclopropane participation, and I either mode.

Scheme I



(1) D. I. Schuster, J. M. Palmer, and S. C. Dickerman, *J. Org. Chem.*, **31**, 4281 (1966); H. E. Simmons and R. D. Smith, *J. Amer. Chem. Soc.*, **81**, 4256 (1959).

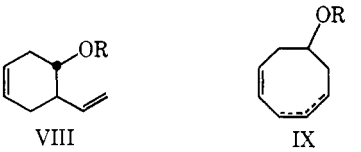
(2) A. C. Cope, S. Moon, and C. H. Park, *ibid.*, **84**, 4843 (1962).

(3) C. S. Foote, *ibid.*, **86**, 1853 (1964); P. von R. Schleyer, *ibid.*, **86**, 1854, 1856 (1964).

(4) H. C. Brown and G. Ham, *ibid.*, **78**, 2735 (1956).

(5) G. Binsch, *Top. Stereochem.*, **3**, 97 (1968).

The products from solvolysis of *cis*-I-OTs were isolated after 5 half-lives (45°, 14 hr). The structure and stereochemistry were proved rigorously by isolation and comparison with authentic materials, or by degradation to known substances. The products and percentages for buffered acetolysis and formolysis, respectively, are



cis-I (41, 48), V (0, 0), *cis*-VII (22, 16), *trans*-VII (10, 14), VIII (12, 11), and IX (15, 11). All the products, including V-OR, were subjected to the reaction conditions and found to be stable. Before proceeding to the discussion of the relative proportions of participation, we should call attention to the large amount of I-OR with the retained cis stereochemistry. There can thus be little or no direct nucleophilic substitution. Furthermore, reduction of the ketone that corresponds to I [LiAl(O-*tert*-Bu)$_3$H, $LiAlH_4$, $NaBH_4$] gives only *cis*-I-OH, *i.e.*, hydride enters from the side opposite to the cyclopropane ring. In the solvolysis, solvent therefore enters from the more hindered side in order to effect a backside attack on the partial bonds of IV or VI.

Because of the large amount of hydride-shift product and of *cis*-I, which do not give immediate information concerning their participative source, we sought additional insight from the solvolytic behavior of *cis,cis*-V-OR and *cis*-VII-OR, which can enter the ionic manifold (Scheme I) at different, but well-defined conformational points. These experiments not only demonstrated the predominance of double bond participation, but furthermore proved that ionic equilibration between the two manifolds does not occur (IV $\rightleftharpoons$ VI).

Solvolysis of *cis,cis*-V-OPNB[6] produces by cyclopropylcarbinyl participation an ion that is closely similar to IV. The products of the solvolysis of *cis,cis*-V can thus be related on a one-to-one basis to the products of double bond participation in conformer II of *cis*-I. Compound *cis,cis*-V-OH was prepared by a modification of the Winstein–Sims procedure.[7] Formolysis of the *p*-nitrobenzoate at 25° for either 5 min or 4 hr yielded *cis*-I (33%), V (0), *cis*-VII (0), *trans*-VII (14), VIII (21), IX (32), and *trans*-I (0). The significant observation is that the reaction mixture from *cis,cis*-V is nearly identical with that from *cis*-I, with the exception that the cyclopropane-participation product *cis*-VII is totally absent.[8] The somewhat higher proportion of hydride-shift products at the expense of *cis*-I may be due to a slightly longer lived species from *cis,cis*-V-OPNB than from *cis*-I-OTs, and a resultant greater opportunity for secondary reactions. The absence of *cis*-VII shows that ion IV is not in equilibrium with ion VI. It should be noted that formolysis of *cis,cis*-V-OPNB produces no *cis,cis*-V-OF. Ironically, the absence of *cis,cis*-V as a product does not indicate the absence of double bond participation in formolysis

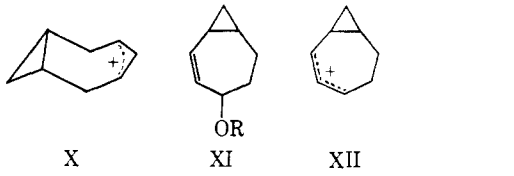
(6) The tosylate proved to be too reactive.

(7) T. Hanafusa, L. Birladeanu, and S. Winstein, *J. Amer. Chem. Soc.*, **87**, 3510 (1965); J. H. Sims, *ibid.*, **87**, 3511 (1965).

(8) The presence of *trans*-VII is not contradictory, since only *cis*-VII is expected from the delocalized ion VI (Scheme I). In fact, *trans*-VII may result from a hydride-shift process.

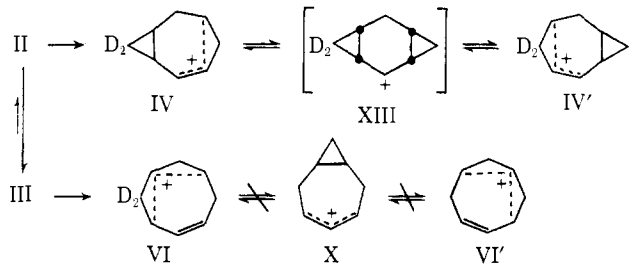
since it is not produced from the ion IV. At this point in the analysis, it appears that 16–22% (*cis*-VII) of the reaction products can be attributed to cyclopropane participation, and the remainder are adequately accounted for by double bond participation.

We prepared *cis*-VII-OH from bicyclo[5.1.0]octan-4-one[2] by the method of Gore,[9] and solvolyzed the corresponding tosylate. It should be noted that the allylic ion X produced from *cis*-VII-OTs is quite different from ion VI, so the system is a poor model for cyclopropane participation. In fact, *cis*-VII-OTs on acetolysis produces only XI-OAc, which is not present in the mixture from either *cis*-I-OTs or *cis,cis*-V-OPNB. Apparently X prefers the hydride-shift path leading to the more stable allylic ion XII. These results prove that ion X is not in equilibrium with the ion(s) produced from *cis*-I-OTs or *cis,cis*-V-OPNB (IV, VI). It follows that ion VI can therefore never equilibrate with its mirror image VI′, since the intermediacy of X would be required for such a process (Scheme II). Also, *cis*-VII-OAc must come directly from VI, rather than from X. On the other hand, ion IV is expected to equilibrate rapidly with its mirror image, since ion XIII is unstable with respect to IV. A simple deuterium labeling experiment can therefore substantiate that the product *cis*-I comes only from double bond participation. If *cis*-I-OTs labeled with deuterium in the cyclopropane ring as in Scheme II were solvolyzed, product *cis*-I from double bond participation should have deuterium scrambled between positions across the ring (IV $\rightleftharpoons$ IV′), whereas *cis*-I from cyclopropane participation must have the deuterium only in the initially labeled position (VI $\not\rightleftharpoons$ VI′). Since formolysis did yield scrambling of the label, the product *cis*-I must come only from IV. Considerable internal reorganization of the molecule has thus occurred before it is regenerated with high stereoselectivity.



X XI XII

Scheme II



In conclusion, the solvolytic reactivity of *cis*-I-OTs is partitioned into contributions from double bond and cyclopropane participation. About 80% of the products are derived from the former mode and 20% from the latter. The transition state from II must therefore be about 0.8 kcal/mol lower than that from III. Since the ground-state structure II is 2–4 kcal/mol higher in energy than III because of "prow–prow" buttressing, the energy of activation for double bond participation in II must be 3–5 kcal/mol smaller than that for cyclopropane participation in III.

Acknowledgment. This work was supported by the Petroleum Research Fund, administered by the American Chemical Society (Grant No. 2970-A4,5), and by the National Science Foundation (Grant No. GP-9257).

(9) J. Gore, J. P. Drouet, and J. J. Barieux, *Tetrahedron Lett.*, 9 (1969).

(10) (a) Alfred P. Sloan Foundation Fellow, 1968–1970; to whom correspondence should be addressed; (b) NDEA Fellow, 1967–1969; (c) NIH Predoctoral Fellow, 1968–1970; (d) NDEA Fellow, 1969; (e) National Science Foundation Undergraduate Research Participant, 1966.

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The Photochemistry of 1,2-Bis(dimethylamino)-1,2-diphenyldiborane(4). An Isoelectronic Heteroatom Analog of Dienes

Sir:

We wish to record the discovery of a new primary photoprocess operative in organoboron chemistry which may have mechanistic implications in the photochemistry of dienes, azines, and related compounds. Olefins, dienes, and many of their heteroatom analogs have been the objects of extensive photochemical investigation.[1] Yet, one of the most intriguing groups of analogs—the B–N "double bonds" of aminoboranes and related compounds—has remained virtually unexplored,[2] although their isoelectronic and nearly isosteric[3] relationship to olefins makes the aminoboranes and homologous chromophores uniquely adapted to studies of electronegativity effects in the photochemistry of π systems. It is apparent that the differing electronegativities of boron and nitrogen cause important differences in the ground-state chemistry of olefins and B–N analogs, and even simple quantum-mechanical considerations suggest that the excited states of aminoboranes and homologs may also behave quite differently from olefins and dienes.[4]

We report here the preliminary results of our investigation of the photochemistry of 1,2-bis(dimethylamino)-1,2-diphenyldiborane(4) (**1**), a boron–nitrogen analog of conjugated dienes chosen partly for its structural and electronic similarity to the previously studied 2,3-diphenyl-1,3-butadiene[5] and benzalazine.[6]

(1) R. O. Kan, "Organic Photochemistry," McGraw-Hill, New York, N. Y., 1966; E. V. Blackburn and C. J. Timmons, *Quart. Rev., Chem. Soc.*, 23, 482 (1969); D. Bryce-Smith, A. Gilbert, W. M. Horspool, and D. Phillips, "Photochemistry," Vol. 1, The Chemical Society, London, 1970.

(2) Exceptions known to us are the recent reports by (a) P. J. Grisdale and J. L. R. Williams, *J. Org. Chem.*, 34, 1765 (1969), and (b) M. Oertel and R. F. Porter, *Inorg. Chem.*, 9, 904 (1970), and earlier papers cited therein.

(3) G. J. Bullen and N. H. Clark, *J. Chem. Soc. A*, 992 (1970).

(4) (a) R. Hoffmann, *J. Chem. Phys.*, 40, 2474 (1964); (b) D. R. Armstrong, B. J. Duke, and P. G. Perkins, *J. Chem. Soc. A*, 2566 (1969).

(5) E. H. White and J. P. Anhalt, *Tetrahedron Lett.*, 3937 (1965).

(6) R. W. Binkley, *J. Org. Chem.*, 33, 2311 (1968); *ibid.*, 34, 931, 3218 (1969).[7]

(7) Nitrogen–nitrogen cleavage products were also found in the photochemistry of acetaldazine: R. K. Brinton, *J. Amer. Chem. Soc.*, 77, 842 (1955).