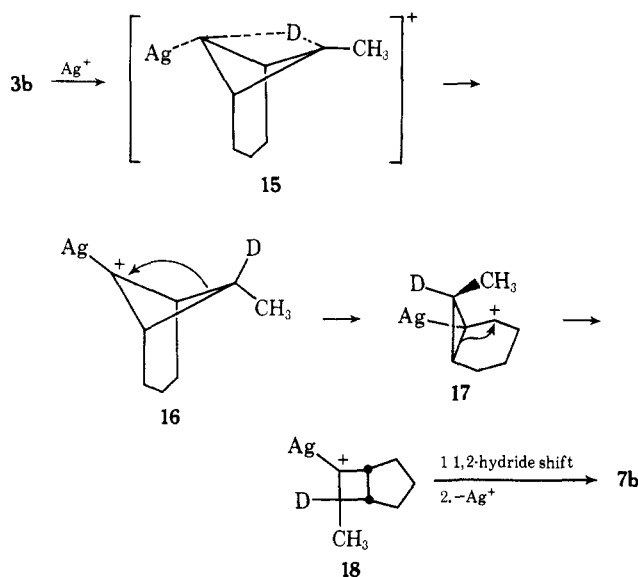


a somewhat remote cationic site. Rather, the result is in keeping with a hyperconjugative effect at a highly developed electrophilic center. Simultaneous edge and central bond cleavage is therefore proposed. Because transition state **13** resembles tertiary argento carbonium ion **14** structurally, substantial positive character should reside on the carbon bearing the CD_3 (CH_3) substituent. This mechanism bears many similarities to a reverse carbenoid addition to a double bond. The fractionation factor exhibited by **4b** and **5b** (0.95) is likewise in accord with Scheme II. Since only one deuterium atom is involved, the total observable impact of the effect of isotopic substitution should understandably be less than that experienced by **2b**.

Lastly, we address ourselves to the primary isotope effect experienced by **7**. The magnitude of this effect (1.74) indicates that the bridgehead C-H or C-D bond is either weakly or extensively stretched at the transition state. In view of the very small fractionation factor shown by **7'** (1.03), the latter alternative appears uniquely reasonable (*cf.* **15**, Scheme III). Furthermore,

Scheme III



the geometry associated with this 1,3-hydride shift is sufficiently nonlinear that only a low $k_{\text{H}}/k_{\text{D}}$ value can be expected on the basis of recent theoretical calculations.⁷ The driving force for the deuteride (hydride) shift can be thought of as being due principally to the generation of argento carbonium ion **16**. Rearrangement of **16** to **17** appears to be followed by internal cyclopropyl bond migration (rather than cleavage) because of the compensating gain in stabilization derivable from newly generated bicyclic argento carbonium ion **18**. The conversion of **18** to **7** follows a well-recognized pathway. Additional ramifications of this novel kinetically controlled hydrogen transfer are being sought.

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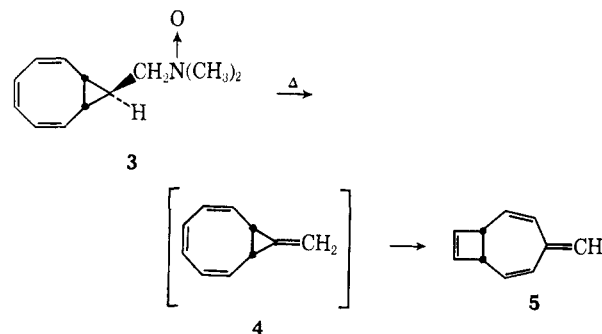
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The *cis*-Bicyclo[5.2.0]nona-2,5,8-triene to *cis*-Bicyclo[6.1.0]nona-2,4,6-triene Rearrangement. Elucidation of the Relative Efficiencies of Syn-Disposed Cyclopropane and Cyclobutene Ring Cleavages during Azo Decomposition

Sir:

The mechanisms by which *cis*-bicyclo[6.1.0]nona-2,4,6-trienes (**1**) undergo thermal rearrangement to 8,9-dihydroindenes have been the object of much discussion in the current literature.¹ Several groups have recently considered the possibility that such bond reorganizations may be triggered in certain instances by initial [3,3] sigmatropic rearrangement to *cis*-bicyclo[5.2.0]nona-2,5,8-trienes (**2**).² Despite the fact that there exists some evidence that the bicyclo[6.1.0]-nonatriene ring system may be capable of kinetically controlled Cope rearrangement to a [5.2.0]bicyclo counterpart,³ the behavior of **4** (not interceptable) is likely to be atypical because of the destabilization accorded this triene by the exocyclic methylene group.⁴



To the present time, **5** represents the only known derivative of **2**. In an attempt to remove this hiatus and simultaneously obtain evidence on the chemical behavior of this novel polyenic system, a synthesis of the 2,6-diphenyl derivative **9** has been developed. The route of **9** is of interest because it also provides unequivocal demonstration of the fact that cleavage of a cyclopropyl bond is kinetically preferred to that of an internal cyclobutene σ bond when both rings are aligned syn to departing nitrogen in a tetracyclic azo compound **8**.

Ceric ion oxidation of cyclobutadieneiron tricarbonyl (**7**)⁵ in the presence of 2,5-diphenyl-3,4-diazanorcaradiene (**9**)⁶ has been developed.

(1) J. C. Barborak, T.-M. Su, P. v. R. Schleyer, G. Boche, and G. Schneider, *J. Amer. Chem. Soc.*, **93**, 279 (1971), and references cited therein.

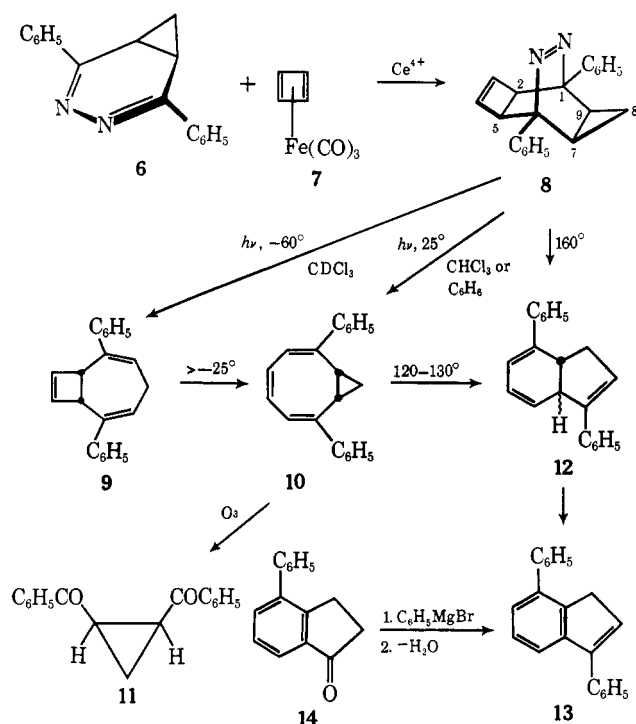
(2) (a) P. Radlick and W. Fenical, *ibid.*, **91**, 1560 (1969); (b) A. G. Anastassiou and R. C. Griffith, *ibid.*, **93**, 3083 (1971).

(3) P. Radlick, W. Fenical, and G. Alford, *Tetrahedron Lett.*, 2707 (1970).

(4) The estimated strain-energy difference between methylene-cyclopropane (41.7 kcal/mol) and cyclobutene (30.6 kcal/mol) reflects the magnitude of this effect (*ca.* 11.1 kcal/mol): P. v. R. Schleyer, J. E. Williams, and K. L. Blanchard, *J. Amer. Chem. Soc.*, **92**, 2377 (1970).

(7) R. A. More O'Ferrall, *J. Chem. Soc. B*, 785 (1970).

diene (6)⁶ afforded diazo derivative 8: mp 170–172°;⁷ 36% yield; $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 7.20–8.00 (m, 10, aryl), 6.04 (s, 2, olefinic), 3.56 (s, 2, allylic), 1.53–1.80 (m, 2, H₇ and H₉), and 0.15–0.68 (m, 2, H₈). The stereochemical



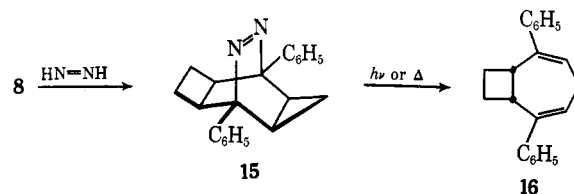
assignment to 8 is supported by two lines of evidence: (a) irradiation of the two-proton singlet at δ 3.56 causes an increase in the integral intensity of the δ 1.53–1.80 signal, thereby indicating the spatial proximity of H₂ and H₅ to H₇ and H₉; (b) addition of 0.25 mol equiv of Eu(DPM)₃ to a CDCl₃ solution of 8 results in the following lanthanide-induced shifts (LIS, in parts per million): syn H₈ = −1.1, H₇ and H₉ = −0.7, allylic = −0.7, and olefinic = −0.3. The large LIS for syn H₈ establishes the juxtaposition of this proton and the site of metal ion coordination (azo linkage). When 8 was irradiated (200-W Hanovia mercury arc) in CDCl₃ solution at −60°, nitrogen extrusion proceeded readily with exclusive formation of 9. The structure of 9 was assigned on the basis of its nmr spectrum [δ 7.38 (m, 10, aryl), 6.29 (t, J = 7 Hz, 2, olefinic), 6.15 (s, 2, cyclobutene), 4.48 (br, s, 2, cyclobutane), and *ca.* 3.1 (m, 2, allylic)] and its facile [3,3] sigmatropic shift to 10 at temperatures above −25°. The first-order rate constants for the conversion of 9 to 10 in CDCl₃ measured at −6, −18, and −25° were found to be 1.38×10^{-3} , 3.83×10^{-4} , and 1.84×10^{-4} sec^{−1}, respectively. The activation parameters, ΔH^\ddagger = 13.6 kcal/mol, ΔG^\ddagger = 19.7 kcal/mol, and ΔS^\ddagger = −20.4 eu, follow directly from these data.

One interesting feature of this Cope rearrangement is its moderate ΔG^\ddagger . Although the free energy of activation for 9 is appreciably higher than those associated with cis-locked divinylcyclopropanes such as octameth-

ylsemibullvalene (6.4 kcal/mol),^{8a} barbaralane (7.8 kcal/mol)^{8b} and bullvalene (12.8 kcal/mol),^{8c} it is lower than the value measured for *cis*-1,2-divinylcyclobutane (26.6 kcal/mol).^{8d} Rather it is roughly comparable to the ΔG^\ddagger for the degenerate rearrangement of 1,3,5,7-tetramethylbicyclo[5.1.0]octa-2,5-diene (13.6 kcal/mol);^{8e} not unlike this latter hydrocarbon, 9 may exist in either cisoid or transoid conformations, but probably rearranges *via* the less stable cis-like transition state.⁹

Understandably, when 8 was irradiated (CHCl₃ or C₆H₆ solutions) at 25°, bicyclo[6.1.0]nonatriene (10) was the only product obtained. This substance was a very insoluble solid: mp 162–164°;⁷ *m/e* 270; $\lambda_{\text{max}}^{\text{C}_2\text{H}_5\text{OH}}$ 254 (ϵ 22,600) and 305 nm (9600). Ozonolysis of 10 gave *cis*-dibenzoylcyclopropane, identical in all respects with an authentic sample.¹⁰ Thermal rearrangement of 10 at 120–130° in Cl₂C=CCl₂ or pyridine resulted in conversion to 8,9-dihydroindene 12 [viscous pale yellow oil;⁷ $\lambda_{\text{max}}^{\text{isooctane}}$ 234 (ϵ 15,000) and 305 nm (6900), stereochemistry not elucidated] which upon treatment with H₂NCH₂CH₂NHNa in ethylenediamine¹¹ afforded diphenylindene 13, mp 112–114°. Unequivocal synthesis of 13 was achieved by addition of phenylmagnesium bromide to known indanone 14¹² and subsequent dehydration.

Diimide reduction of 8 gave rise conveniently to 15, mp 173–175°, which when photolyzed as above at −60 or +25° afforded 16, mp 53–55°, as the sole product. In its electronic spectrum (isooctane solution), 16 displays a maximum at 243 nm (ϵ 15,000), whereas its nmr spectrum (in CDCl₃) consists of an aryl multiplet of area 10 at δ 7.18, a two-proton olefinic triplet (J = 6.5 Hz) centered at 6.00, and multiplets at



3.83, 3.04, and 2.02 due to doubly allylic (2 H), allylic (2 H), and cyclobutyl (4 H) protons, respectively. Diene 16 can be heated at 135° for at least 1 hr with no visible change; at 160°, however, slow polymerization was encountered, during which time no new nmr signals appeared.

In a preliminary study, thermolysis of 15 in Cl₂C=CCl₂ solution at 135° (sealed nmr tubes) was found to proceed readily ($t_{1/2}$ \approx 20 min). Again, 16 was produced exclusively. By comparison, the half-life for the thermal extrusion of nitrogen from 8 at 132° under

(8) (a) F. A. L. Anet and G. E. Schenck, *Tetrahedron Lett.*, 4237 (1970); (b) W. von E. Doering, B. M. Ferrier, E. T. Fossel, J. H. Hartenstein, M. Jones, Jr., G. Klumpp, R. M. Rubin, and M. Saunders, *Tetrahedron*, 23, 3943 (1967); (c) A. Allerhand and H. S. Gutowsky, *J. Amer. Chem. Soc.*, 87, 4092 (1965); (d) G. S. Hammond and C. D. DeBoer, *ibid.*, 86, 899 (1964); (e) L. Birladeanu, D. L. Harris, and S. Winstein, *ibid.*, 92, 6387 (1970).

(9) Nmr evidence on this point was not obtainable. However, note the magnitude of the ΔS^\ddagger term.

(10) G. W. Griffin, E. J. O'Connell, and H. A. Hammond, *J. Amer. Chem. Soc.*, 85, 1001 (1963). We thank Professor Griffin for the requisite sample.

(11) L. Reggel, S. Friedman, and I. Wender, *J. Org. Chem.*, 23, 1136 (1958).

(12) J. W. Cook, G. T. Dickson, J. Jack, J. D. Loudon, J. McKeown, J. Macmillan, and W. F. Williamson, *J. Chem. Soc.*, 139 (1950).

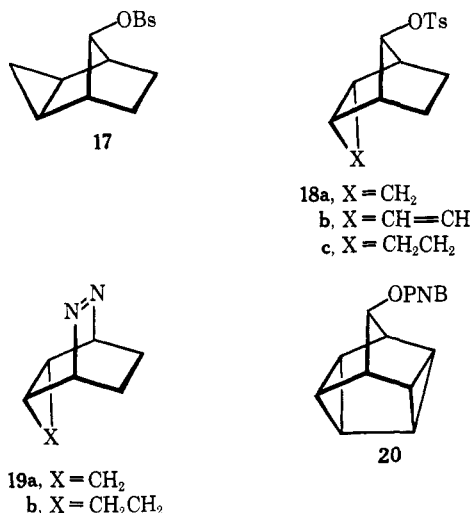
(5) (a) L. A. Paquette and L. D. Wise, *J. Amer. Chem. Soc.*, 89, 6659 (1967); (b) L. Watts, J. D. Fitzpatrick, and R. Pettit, *ibid.*, 87, 3253 (1965).

(6) (a) R. G. Amiet and R. B. Johns, *Aust. J. Chem.*, 21, 1279 (1968); (b) G. Maier, *Chem. Ber.*, 98, 2438, 2446 (1965).

(7) Satisfactory elemental analyses ($\pm 0.3\%$) were obtained for all stable new compounds.

comparable conditions was >90 min. At 160°, **8** is essentially quantitatively transformed into dihydroindene **12** at a convenient rate.

As regards neighboring group reactivity of edge-fused three- and four-membered carbocyclic rings proximately disposed to developing cationic centers, recent investigations have established not only the necessity of proper stereochemical orientation but also a marked dependence on ring size. For example, whereas the solvolytic rate constant for **17** is merely comparable to that of the 7-norbornyl derivative, tosylate **18a** exhibits a rate acceleration of 10^{14} .¹³ Anchimeric assistance by cyclobutene (**18b**, $k_{\text{rel}} =$



$10^{5.8}$) and cyclobutane rings (**18c**, $k_{\text{rel}} = 10^{4.3}$) positioned endo on the norbornyl framework is seen to be only a small fraction of that provided by the cyclopropyl group.¹⁴ In related azo systems, **19a** suffers loss of nitrogen 10^{17} times faster than 2,3-diazabicyclo[2.2.2]oct-2-ene while **19b** is only 10^4 times more reactive.¹⁵ These effects appear not to arise from factors associated with strain release. This conclusion is supported by the behavior of **20** whose large solvolytic rate ($k_{\text{rel}} = 10^{12}$) cannot be attributed to overall relief of strain since the major solvolysis product is structurally identical by virtue of a triply degenerate rearrangement.¹⁶

In the case of **8** and **15**, the small rings are exo fused. As a result, the bent bonds are not favorably oriented for overlap as C-N cleavage begins. Accordingly, concerted loss of nitrogen is not possible. Nevertheless, the data require that production of the transient 1,4 diradicals from **8** and **15** be followed by cleavage of that adjacent C-C linkage endowed with the greatest "bent-bond" character.¹⁷ In other words, despite geometrically enforced inoperability of synchronous

reactions in exo-fused systems, the relative efficiencies of strained bond cleavage reactions are also dictated chiefly by bond hybridization factors.

Irrespective of the stereochemistry of **12**, it must be appreciated that the degree of substitution on **10** does not permit the present work to contribute substantially toward the mechanistic solution of the bicyclo[6.1.0]nonatriene to 8,9-dihydroindene rearrangement. The presence of the two phenyl groups is perhaps too great a complication of the molecule for the results to be directly applicable to ultimate clarification of that particular problem.

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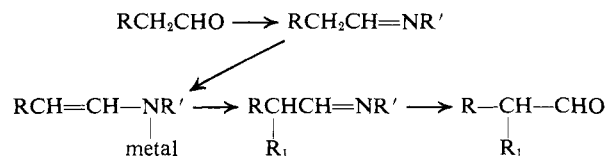
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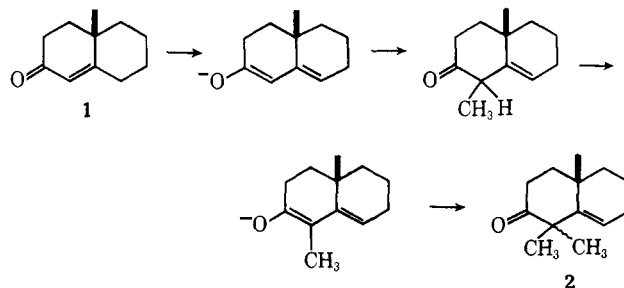
Monoalkylation of α,β -Unsaturated Ketones via Metalloenamines

Sir:

We demonstrated a few years ago¹ that aldehydes and ketones can be monoalkylated by making use of the metalloenamines derived by the treatment of the corresponding *N*-alkylimines with strong bases, such as Grignard reagents.



It was tempting to see if the very troublesome problem of the monoalkylation of α,β -unsaturated ketones² might be resolvable in the same manner. This was particularly interesting as all attempts to stop dialkylation, at least with small molecules like methyl iodide, have uniformly led to variable amounts of dialkylated material, presumably because of very rapid proton transfer in the intermediate β,γ -unsaturated ketone (cf. **1** \rightarrow **2**).



(1) G. Stork and S. Dowd, *J. Amer. Chem. Soc.*, **85**, 2178 (1963).

(2) Such a monoalkylation can sometimes be effected with the corresponding enamines (cf. G. Stork and G. Birnbaum, *Tetrahedron Lett.*, 313 (1961)) but the method is generally not applicable when C-alkylation is attempted with systems having an axial substituent in a 1,3 relationship, as in the cases illustrated here.

(13) (a) H. Tanida, T. Tsuji, and T. Irie, *J. Amer. Chem. Soc.*, **89**, 1953 (1967); (b) M. A. Battiste, C. L. Deyrup, R. E. Pincock, and J. Haywood-Farmer, *ibid.*, **89**, 1954 (1967); (c) J. Haywood-Farmer and R. E. Pincock, *ibid.*, **91**, 3020 (1969).

(14) (a) M. Sakai, A. Diaz, and S. Winstein, *ibid.*, **92**, 4452 (1970); (b) M. A. Battiste and J. W. Nebzydoski, *ibid.*, **92**, 4450 (1970).

(15) E. L. Allred and J. C. Hinshaw, *Chem. Commun.*, 1021 (1969).

(16) R. M. Coates and J. L. Kirkpatrick, *J. Amer. Chem. Soc.*, **90**, 4162 (1968); **92**, 4883 (1970).

(17) The calculated degree of "bent bonding" for cyclobutane is about one-third that calculated for cyclopropane: C. A. Coulson and T. H. Goodwin, *J. Chem. Soc.*, 2851 (1962); 3161 (1963). On the other hand, strain estimates⁴ show cyclobutene to be 2.5 kcal/mol more strained than cyclopropane.