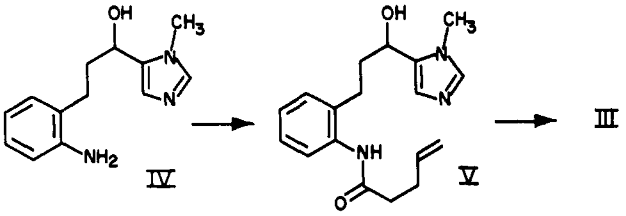

foam, in 59.5% yield.[4] Upon oxidation of V with CrO_3 in aqueous pyridine (Cornforth's reagent[5]) overnight at ambient temperature, III, the desired precursor to isolongistrobine, was obtained in 52% yield, as white crystals (CH_2Cl_2–hexane), mp 105.5–107°.[6]

Oxidative cleavage of the vinyl group of III to the aldehyde equivalent to II was accomplished by means of 2 equiv of sodium periodate and a catalytic amount of osmium tetroxide in 10:3 dioxane-water at ambient temperature[7] for 1.5 hr. Compound II, obtained in 85% yield[8] (mp 134–139°, lit.[2] mp 132–136°), was identical in all respects (ir, uv, nmr, and mass spectra) with natural isolongistrobine.[9]

On the basis of this work a 4-acyl-1-methylimidazole structure, analogous to II, can be inferred for longistrobine.

Acknowledgments. M. A. W. thanks Professor R. B. Woodward for a Research Assistantship (1971–1973). Thanks are also due to Mr. W. J. Pegg for mass spectra and to Dr. P. Balaram and Dr. G. Dudek for nmr spectra. Elemental analyses were performed by Scandinavian Microanalytical Laboratories, Herlev, Denmark.

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[4] Physical data for V: ir (NaCl plate) 3300 (broad), 1660, and 1530 cm^{-1}; mass spectrum (70 eV) *m/e* 111, 125, 213, 295, and 313 (parent).

[5] R. H. Cornforth, J. W. Cornforth, and G. Popják, *Tetrahedron*, **18**, 1351 (1962).

[6] Physical data for III: ir (KBr) 3400, 1670, 1685, and 1540 cm^{-1}; uv (MeOH) λ_{max} 255 nm (ϵ 11,000) shifted to 232 nm (ϵ 11,400) in acid; nmr ($CDCl_3$, 100 MHz) δ 2.60 (4 H, br s), 2.95 (2 H, t, J = 6 Hz), 3.26 (2 H, t, J = 6 Hz), 3.89 (3 H, s), 4.9–5.3 (2 H, m), 5.6–6.2 (1 H, m), 7.0–7.9 (6 H, m), and 8.95 (1 H, br s) ppm; mass spectrum (70 eV) *m/e* 82, 109, 202, 213, 256, and 311 (parent). *Anal.* Calcd for $C_{18}H_{21}N_3O_2$: C, 69.43; H, 6.80; N, 13.50. Found: C, 69.25; H, 6.82; N, 13.51.

[7] R. Pappo, D. S. Allen, Jr., R. U. Lemieux, and W. S. Johnson, *J. Org. Chem.*, **21**, 478 (1956).

[8] *Anal.* Calcd for $C_{17}H_{19}N_3O_3$: C, 65.16; H, 6.11; N, 13.41. Found: C, 65.12; H, 6.22; N, 13.28.

[9] We are indebted to Dr. A. Jordaan for a sample of isolongistrobine from natural sources.

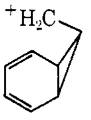
Mark A. Wuonola, R. B. Woodward*
Converse Memorial Laboratories
Department of Chemistry, Harvard University
Cambridge, Massachusetts 02138

Received April 2, 1973

A Norcaradienylcarbinyl Cation. Effective π Participation in a σ-Delocalized Cyclopropylcarbinyl System. The Magnitude of the Norcaradiene–Cycloheptatriene Energy Gap[1]

Sir:

The question of the precise nature of the interactions which occur in norcaradienylcarbinyl cations has taken on increased importance since Sargent[2] originally suggested their intermediacy in the solvolysis of cycloheptatrienylcarbinyl 3,5-dinitrobenzoate. Subsequently, Hoffmann[3] pointed out that electron donation from cyclopropane to an adjacent (partially) positively charged center could be a prime factor in determining certain norcaradiene–cycloheptatriene equilibria (*e.g.*, that of 7,7-dicyanonorcaradiene[4]). Although Hoffmann did not consider the stereochemistry of the norcaradiene, it is apparent that, in the syn orientation (**1**), the symmetry of the orbitals is such that the diene could donate electron density directly (through space) to the positive center (stereochemically impossible for the anti analog **2**, however).



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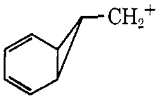
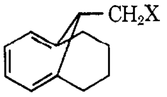
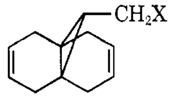


2

3-*syn*-



3-*anti*-



4

Recently, Wilcox[5] has seemingly eliminated the possibility that the double bonds of **1** or **2** could stabilize the positive center *via* π conjugation, by elegantly demonstrating the lack of such participation in other cyclopropylcarbinyl systems. In apparent accord with this, Paquette[6] has just reported that solvolysis of the epimers of **3**, thought to proceed *via* the intermediacy of norcaradienes, is unaccelerated relative to suitable models (*e.g.*, **4**). However, no firm conclusions can be drawn from studies of **3**, since the solvolyses are dependent upon preequilibria (introducing K_{eq} values of unknown magnitude). Nevertheless, Paquette concludes that conformational factors (*i.e.*, **1** *vs.* **2**) play an insignificant role in solvolyses where such ions intervene.

Clearly, direct evidence on the nature of ions such as **1** and **2** can only be obtained from an investigation of compounds whose ground-state structure is of the norcaradiene type.[7] We herein report such a study. The compounds chosen were derivatives of the tricyclo[4.3.1.0^{1,6}]decane series, the diene of which has been shown, by Vogel,[8] to exist "exclusively" in the norcaradiene form. All syntheses proceeded normally.[9] The vital distinction of stereochemistry was unambiguously made *via* iodolactonization of a precursor to the syn isomer, **9** (separations were made at this point[9]). Table I summarizes the kinetic solvolysis data obtained in 70% (v/v) acetone–water.[10]

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[1] We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work.

[2] G. D. Sargent, N. Lowry, and S. D. Reich, *J. Amer. Chem. Soc.*, **89**, 4085 (1967).

[3] R. Hoffmann, *Tetrahedron Lett.*, 2907 (1970).

[4] E. Ciganek, *J. Amer. Chem. Soc.*, **87**, 652 (1965).

[5] C. F. Wilcox, Jr., and H. D. Banks, *ibid.*, **94**, 8232 (1972).

[6] L. A. Paquette and G. L. Thompson, *ibid.*, **95**, 2364 (1973).

[7] For a review of the norcaradiene–cycloheptatriene equilibrium problem, see G. Maier, *Angew. Chem., Int. Ed. Engl.*, **6**, 402 (1967).

[8] E. Vogel, W. Wiedemann, H. Kiefer, and W. Harrison, *Tetrahedron Lett.*, 673 (1963).

[9] Details of our synthetic approaches will appear in the full paper on the subject. Complete characterization (nmr, ir, mass spectra, analyses) of all key intermediates and products (except for 10-OH, which was not obtained pure) was obtained.

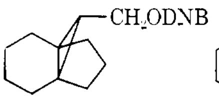
0) (1Product studies on **7** and **10** in both unbuffered and urea-buffered 70% aqueous acetone showed 4-vinylindan to be the only identifiable product ($\geq$80% yield). Also, 7-OH was shown to be stable under even the unbuffered conditions. Therefore, we are confident of the absence of acyl-oxygen cleavage. The 4-vinylindan formed is completely analogous to Paquette's results,[6,11] and presumably arises *via* the same mechanism.[11] With respect to **5**, **6**, **8**, and **9**, the products are exclusively of the allylcarbinyl variety.

[11] In footnote 8 of ref 6, Paquette reports formation of 1-vinyltetralin. However, from the context, this clearly should be 5-vinyltetralin.

Table I. Solvolysis Data for 3,5-Dinitrobenzoates in 70:30 Acetone–Water

Compd	T, °C	k, sec$^{-1\,a}$	Rel rate
5	70	$(21.7 \pm 0.9) \times 10^{-6}$	8.58
6	70	$(5.18 \pm 0.44) \times 10^{-6}$	2.05
7	70	$(203 \pm 7) \times 10^{-6}$	80.2
8	70	$(10.4 \pm 0.2) \times 10^{-6}$	4.11
9	70	$(3.04 \pm 0.30) \times 10^{-6}$	1.20
10	70	$(2.53 \pm 0.13) \times 10^{-6}$	1.00

[a] Average values for duplicate runs with error limits the average deviations; good first-order kinetics were observed in every case.



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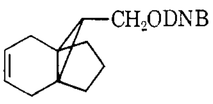

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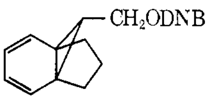

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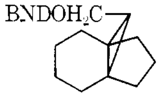

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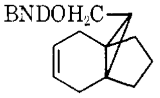

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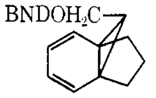

10

The prime conclusion is that a significant reactivity difference exists between the epimers **7** and **10**. Although we would forestall discussion of the origin of this difference (it clearly is not a positive through-space effect), it is seen that **7** is unusually reactive, while **10** is "normal." Comparison of **7** with **5** and **6** shows that steric crowding in the anti series is not the source of the high reactivity of **7** (a factor of *ca.* 2 appears attributable to steric factors). Thus, it seems inevitable that acceleration is due to conjugative factors, which is in disaccord with Wilcox's findings.[5] What is the "real" acceleration in **7** (*i.e.*, after factoring out inductive effects)? A factor of at least 160 seems probable; this point is being investigated further.

From a consideration of our data, some important conclusions may be drawn regarding the cycloheptatriene–norcaradiene preequilibria encountered by Sargent[2] and Paquette.[6] Let us assume their[2,6] mechanism, as shown in eq 1. A steady-state treatment of

$$\text{cycloheptatriene derivative} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{norcaradiene derivative} \xrightarrow{k_2} \text{products} \qquad (1)$$

[norcaradiene derivative] gives eq 2. Fortunately, the

$$k_1/k_{-1} = K_{eq} = k_{solv}/k_2 + k_{solv}/k_{-1} \qquad (2)$$

k_{solv}/k_{-1} term can be neglected, since k_{-1} is undoubtedly much larger than k_2.[12] The determination of k_2 may be done only in a relative fashion;[14] thus, k_7/k_5 = 9.3 (see Table I) gives a k_2^{rel} which can be used only since the same relative models are available from the work of Sargent[2] and Paquette.[6] Additionally, k_7/k_6 = 39.1 (see Table I) gives an independent k_2^{rel}.[15] Applying these numbers first to the monosubstituted cycloheptatriene studied by Sargent, we find $K_{eq}^{100°}$ = 2.9 × 10^{-3} and 4.4 × 10^{-3}, respectively; this gives ΔF = 4.4 and 4.1 kcal/mol.[14-16] This value is approximately 2–2.5 kcal/mol lower than that found by Huisgen[13] for the cyclooctatetraene–bicyclooctatriene valence isomerization. However, considering our uncertainties,[14,15] and the 1 kcal/mol less strain in cyclopropane (compared to cyclobutene), these appear as quite reasonable values. Clearly, the cycloheptatriene–norcaradiene energy gap is much smaller than has commonly been thought.[17]

When comparing our data with Paquette's,[6,14] only k_7/k_5 (and the corresponding k_{10}/k_8 = 0.24) may be used. So doing, we find $K_{eq}^{100°}$ = 4.4 × 10^{-2} for the anti isomer (*anti*-**3**) and $K_{eq}^{100°}$ = 0.5 for the syn isomer (*syn*-**3**). Interestingly, this latter value is almost identical with the one found for 7-cyano-7-trifluoromethylcycloheptatriene,[18] whereby it is suggested that both norcaradiene and cycloheptatriene forms perhaps could be observed, in the case of *syn*-**3**, by low-temperature nmr spectroscopy.[19]

Acknowledgment. We are grateful for helpful discussions with Professors Jerome Berson, Stuart Staley, Walter Trahanovsky, and Kenneth Wiberg.

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[12] In the cyclooctatetraene–bicyclooctatriene valence isomerization studied by Huisgen,[13] the analogous k_{-1} = 5.4 sec^{-1} was obtained. All logic suggests the two valence isomerizations are similar (*vide infra*). However, an error of 10^3 in k_{-1} would not invalidate our premise ($k_{-1} \gg k_2$).

[13] (a) R. Huisgen and F. Mietzsch, *Angew. Chem., Int. Ed. Engl.*, 3, 83 (1964); (b) R. Huisgen, F. Mietzsch, G. Boche, and H. Seidl, *Chem. Soc., Spec. Publ.*, No. **19**, 3 (1964).

[14] We must assume that the preferred conformation of the $-CH_2X$ group in **5**, **6**, and **7** is the same as in the bicyclic compounds of Sargent[2] and the tricyclic ones of Paquette.[6] There is the possibility that our systems prefer a conformation roughly 1–2 kcal/mol below the ideal solvolytic conformation. If so, our estimates for the energy gap between norcaradiene and cycloheptatriene may be *low* by that amount.

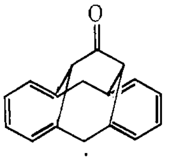
[15] In both cases, we are introducing some error by assuming that the relative rates stay constant between 70° (our temperature) and 100° (Sargent's[2] and Paquette's[6] temperature). From Paquette's[6] work, it seems that we may be, at most, 0.3–0.4 kcal/mol *low* in our estimates of ΔF, due to this factor.

[16] We assume solvolysis occurs, in this case, *via* the anti arrangement (**2**).

[17] (a) Compare the widely quoted 11–14 kcal/mol: W. von E. Doering and M. R. Wilcott, III, unpublished calculations; M. R. Wilcott, III, Ph.D. Dissertation, Yale University, New Haven, Conn., 1963. (b) T. Tsuji, S. Teratake, and H. Tanida, *Bull. Chem. Soc. Jap.*, **42**, 2033 (1969), have studied the norcaradiene–cycloheptatriene equilibrium dilatometrically. One possible conclusion, from their data (although not preferred by these authors), is that the norcaradiene–cycloheptatriene energy gap is 4.0–4.5 kcal/mol. (c) By studying various 7-substituted 2,5-diphenylcycloheptatrienes, Dr. Allan Cairncross (Dupont) has found an energy gap similar to ours for the norcaradiene–cycloheptatriene equilibrium. We thank Dr. Cairncross for this information prior to publication.

[18] E. Ciganek, *J. Amer. Chem. Soc.*, **87**, 1149 (1965).

[19] Recently [H. Günther, H. Schmickler, H. Königshofen, K. Recker, and E. Vogel, *Angew. Chem., Int. Ed. Engl.*, **12**, 243 (1973)] it has been shown that i exists in valence-tautomeric equilibrium with the norcaradiene form.



i

Philip Warner,* Shih-Lai Lu
Department of Chemistry, Iowa State University
Ames, Iowa 50010

Received May 14, 1973

Solution Phase Photochemistry of 2-Methylenebenznorbornene. An Apparent Diversion of the Di-π-methane Reaction[1,2]

Sir:

We have recently reported on the photochemical and photophysical properties of two nonconjugated aryl

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[1] Organic Photochemistry. XXV. Part XXIV is F. Scully and H. Morrison, *J. Chem. Soc., Chem. Commun.*, in press.

[2] Presented at the 165th National Meeting of the American Chemical Society, Dallas, Tex., April 9–13, 1973.