

Instead, irradiation of **1** in cyclohexane leads to cyclometalation, producing **5a**, isolated by low-temperature chromatography in 31% yield and fully characterized.⁷

The reluctance of reactive intermediate **4a** to react with secondary C-H bonds provided, for the first time, a readily available hydrocarbon which could be used as an inert solvent for carrying out intermolecular C-H activation of materials that are difficult to liquefy under ambient conditions. Thus, upon photolysis of **1** in cyclohexane under CH₄ (25 atm)⁸ or ethylene (25 atm), significant quantities of hydrido methyl complex **9a** (42% isolated yield) and hydrido vinyl complex **10a** (42% NMR yield) are formed, respectively. Compound **9a** was isolated and fully characterized; NMR evidence supports the assignment of **10a**.

In the pentamethylcyclopentadienyl series, irradiation of dicarbonyl complex **2** results in loss of CO, and irradiation of bis(phosphine) complex **3** results in loss of phosphine;⁹ thus both systems lead to the same carbonyl(phosphine)rhenium intermediate **4b**. Irradiation in benzene leads to **7b** and in cyclopropane **8b** is formed; both can be observed by NMR but were too sensitive to isolate. Further photolysis of phenyl hydride **7b**, particularly in the presence of added PMe₃, provided the corresponding bis(phosphine) complex **7c**. This material was much more amenable to purification: chromatography at 15 °C on alumina III under air-free conditions provided **7c** (64%), which was fully characterized.

No intermolecular C-H activation products are formed directly from **2** or **3** in the presence of larger cycloalkanes, *n*-alkanes, or methane (however, certain ones can be obtained from cyclometalated products **5**; see below). Cyclometalation is the favored process under these conditions, and complex **5b** is formed (ca. 20% yield from **2** by ¹H NMR). Treatment of **5b** with iodoform led to the corresponding iodide **6b**; it was isolated in 18% yield based on **2** and fully characterized. Exhaustive photolysis of **2** at low concentration (10⁻⁴ M) in alkanes such as *n*-hexane and cyclohexane in the presence of added PMe₃ leads to cyclometalated bis(phosphine) complex **5c** (>20% yield by NMR). Although thermally stable (up to 125 °C in *n*-hexane), this material proved difficult to purify fully even by chromatography at -110 °C; it was characterized by ¹H, ¹³C, and ³¹P NMR and high-resolution MS.¹⁰

In both the parent Cp and C₅Me₅ series, many of the hydrido(alkyl)rhenium complexes, including the cyclometalated products **5**, react with benzene (and certain other hydrocarbons) to give intermolecular C-H insertion products, as illustrated in Scheme I. This provides evidence that these materials form small amounts of the corresponding coordinatively unsaturated reductive elimination products **4** at room temperature. The half-lives of the elimination reactions correlate with expected relative strengths of the metal-carbon bonds in these complexes.^{8b,11}

This propensity for reductive elimination was utilized in the C₅Me₅ series, with the cyclometalated complex **5c** being the most useful precursor to the bis(phosphine) C-H insertion products. However, the relative stabilities of starting material and product here are nearly comparable. Thus equilibrating mixtures of cyclometalated complex **5c** and hydridocyclopropylrhenium complex

8c, and **5c** and hydridomethylrhenium complex **9c**, are observed by NMR spectroscopy.¹² Optimum conversion of **5c** to **8c** was 33% at 45 °C with cyclopropane as solvent, and of **5c** to **9c** was 20% at 70 °C under 82 atm of CH₄ in hexane (Parr bomb), as measured by ¹H NMR spectroscopy. Hydrido cyclopropyl complex **8c** was partially purified by fast chromatography at 15 °C on alumina III, whereas **9c** required chromatography at -100 °C. Samples providing satisfactory elemental analysis could not be obtained, but both complexes were characterized fully by spectroscopy, including high-resolution MS.

In summary, cyclopentadienyl- and pentamethylcyclopentadienylrhenium complexes are capable of both intra- and intermolecular C-H activation if appropriate electron-donating ligands are attached to the metal center. The highly chemoselective behavior of these rhenium systems should allow one to activate small amounts of important hydrocarbons, such as methane, in the presence of large quantities of higher hydrocarbons. By further exploring the effect of the ancillary ligands on reactivity, we hope to find systems in which these ligands can participate in the functionalization of the activated alkanes.

Acknowledgment. We are grateful to Profs. W. A. G. Graham and W. D. Jones for helpful discussions and to the National Science Foundation for a predoctoral fellowship award to P.F.S. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract DE-AC03-76SF00098.

Registry No. **1**, 96760-24-6; **2**, 96791-01-4; **3**, 96760-25-7; **4a**, 96760-26-8; **4b**, 96760-27-9; **4c**, 96760-28-0; **5a**, 96760-29-1; **5b**, 96760-30-4; **5c**, 96760-31-5; **6b**, 96760-32-6; **7a**, 96791-02-5; **7b**, 96760-33-7; **7c**, 96760-34-8; **8a**, 96791-03-6; **8b**, 96760-35-9; **8c**, 96760-36-0; **9a**, 96760-37-1; **9c**, 96760-38-2; **10a**, 96760-39-3; **12a**, 96760-40-6; (C₅Me₅)Re(CO)₂, 12130-88-0; ReCl₃(PMe₃)₃, 96760-41-7; CH₄, 74-82-8; benzene, 71-43-2; cyclopropane, 75-19-4; *n*-hexane, 110-54-3; cyclohexane, 110-82-7; ethylene, 74-85-1; iodoform, 75-47-8.

Supplementary Material Available: Spectral and analytical data for the compounds illustrated in Scheme I (8 pages). Ordering information is given on any current masthead page.

(12) Incorporation of gaseous methane was confirmed by showing that the use of ¹³CH₄ resulted in a strongly enhanced Re-CH₃ resonance in the ¹³C{¹H} NMR spectrum.

Synthetic and Mechanistic Studies of the Retro-Claisen Rearrangement: An Example of Cation Acceleration of a [3,3]-Sigmatropic Rearrangement

Robert K. Boeckman, Jr.,* Christopher J. Flann, and Kathleen M. Poss

Department of Chemistry, University of Rochester
Rochester, New York 14627

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The Claisen rearrangement and its variants have proven to have wide generality and utility for the construction of unsaturated ketones and aldehydes with a high degree of regiochemical and stereochemical control.¹ As a member of the general class of [3,3]-sigmatropic rearrangements, the reaction is under thermodynamic control with respect to reactants and products. This fact is easily overlooked, since the Claisen rearrangement generally

(7) Intramolecular metalation of trimethylphosphine without competing intermolecular C-H activation has been observed before in several systems; for specific examples involving rhenium, see ref 2 and: Chiu, K. W.; Wong, W.-K.; Wilkinson, G. *J. Chem. Soc., Chem. Commun.* **1981**, 451. We cannot, of course, rule out the reversible formation of a very unstable hydridocyclohexylrhenium complex during this reaction.

(8) For results on oxidative addition of iridium into methane C-H bonds, see: (a) Hoyano, J. K.; McMaster, A. D.; Graham, W. A. G. *J. Am. Chem. Soc.* **1983**, *105*, 7190. (b) Wax, M. J.; Stryker, J. M.; Buchanan, J. M.; Kovac, C. A.; Bergman, R. G. *Ibid.* **1984**, *106*, 1121.

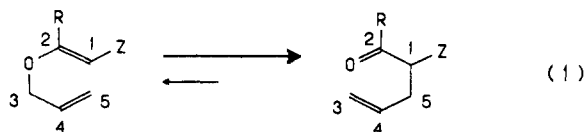
(9) We have also confirmed, as reported earlier by Graham and co-workers, that only rhenium dimers are formed on irradiation of CpRe(CO)₃ and (C₅Me₅)Re(CO)₃; cf.: (a) Foust, A. S.; Hoyano, J. K.; Graham, W. A. G. *J. Organomet. Chem.* **1971**, *32*, C65. (b) Hoyano, J. K.; Graham, W. A. G. *J. Chem. Soc., Chem. Commun.* **1982**, 27. Insertion into silane C-H bonds has been observed: Dong, D. F.; Hoyano, J. K.; Graham, W. A. G. *Can. J. Chem.* **1981**, *59*, 1455.

(10) Conversion of **5c** to the corresponding iodide does not occur upon treatment with iodoform.

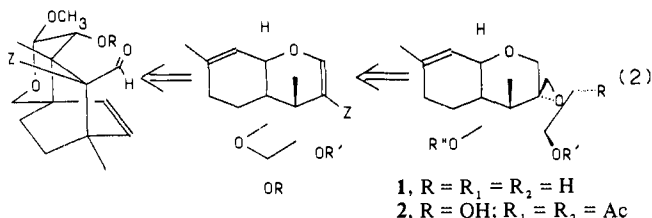
(11) Buchanan, J. M.; Bergman, R. G., manuscript in preparation.

(1) For reviews of the Cope and Claisen rearrangements, see: Rhodes, S. J.; Raulins, N. R. *Org. React.* **1975**, *22*, 1. Ziegler, F. E. *Acc. Chem. Res.* **1977**, *10*, 227. Bennett, G. B. *Synthesis* **1977**, 589. Ziegler, F. E.; Piwinski, J. J. *J. Am. Chem. Soc.* **1982**, *104*, 7181 and references cited therein.

proceeds, apparently irreversibly, to the carbonyl-containing products due to their normally greater thermodynamic stability (eq 1).²

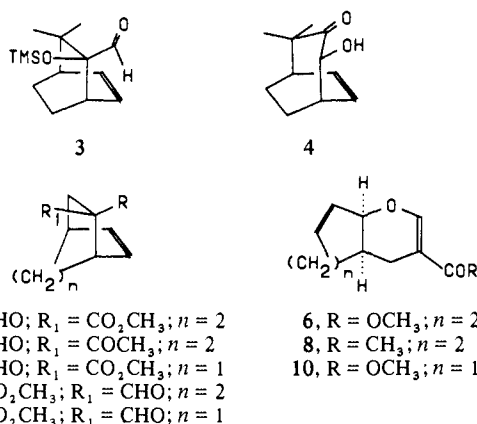


We became interested in identifying the structural features that would reverse the normal situation and permit conversion of the carbonyl-containing substance to the vinyl ether. This process appeared to possess significant potential as a protocol for the synthesis of the *cis*-oxadecalin systems present in the trichothecin class of antitumor substances (e.g., verrucarol (1)³ or anguidine (2)⁴) as shown in eq 2. In particular, the presence of substituents



at position 1 (eq 1) were expected to have a significant impact on both the activation energy and the position of the equilibrium as predicted by the theoretical treatment of Carpenter.⁵

Preliminary experiments rapidly established that electron-releasing groups (e.g., OSiMe₃) and H were not suitable. In the former case, aldehyde 3 upon heating at 200 °C underwent the silyl analogue of the α -ketol rearrangement to afford the ring-expanded ketone 4.⁶ This outcome was interpreted to be the result



of an unfavorable equilibrium constant for the retro-Claisen rearrangement, thus an electron-withdrawing group was substituted for OSiMe₃ in an effort to further stabilize the product.⁷ Ester 5 upon heating at 110 °C for 4 h in toluene (HOAc (catalytic)) afforded a near quantitative recovery of a mixture of 5 and the desired retro-Claisen rearrangement product 6 (89:11).⁸ The

purified ester 6, upon reexposure to the reaction conditions, was reconverted to the equilibrium mixture of 5 and 6 (~90:10) confirming that this interconversion was under thermodynamic control. Thus, the presence of conjugation from the ester altered the equilibrium in a favorable direction by stabilization of the product but insufficiently to be of practical value. The magnitude of the change is dependent on the extent of conjugation in the product since rearrangement of ketoaldehyde 7 proceeds to a 1:1 mixture of 7 and 8 (BF₃-Et₂O) after 2 h at room temperature. Ring strain present in the ring system also plays a major role as was evidenced by the thermal rearrangement of bicycloheptene analogue 9 quantitatively to 10 at room temperature over ~24 h.⁹ Estimates from molecular mechanics (MM2) calculations placed $\Delta H_f^\circ(6) - \Delta H_f^\circ(5) = \sim 2$ kcal/mol.¹⁰

Since relief of nonbonded repulsions was also expected to contribute significantly to the energetics which determine the position of the equilibrium in the rearrangement, we utilized MM2 calculations as a guide, to screen various substitution patterns in the bicyclo[2.2.2]octane series. These computations suggested that the presence of bridgehead substituents would be expected to shift the position of the equilibrium toward the retro-Claisen isomer as the result of relief of strain due to the presence of vicinal quaternary carbon centers in the bicyclic isomer ($\Delta\Delta H = \sim 2$ -3 kcal/mol).¹⁰ We were indeed gratified to observe the aldehyde 11 upon exposure to HOAc (catalytic) in toluene (4 h/110 °C) was essentially completely converted to 12 (~98% by NMR), which was isolated in 72% yield.⁸ Other substituents appear to affect the equilibrium constant only if they develop substantial nonbonded interactions in either the reactant or product or alter the stability of the product by reducing stabilization by conjugation. For example 13, bearing an additional quaternary center, rearranges smoothly (79% yield) to 14 (HOAc (catalytic)/toluene/ Δ /4 h) but in the case of 15, the rearrangement proceeds only to the extent of ~5%, apparently due to a 1,3 interaction which develops in the product 16.¹¹ In the case of nitrile 17 rearrangement proceeds only to the extent of ~60% as a result of diminished conjugation in the product 18.¹²

The most striking observation is the marked acceleration of the above rearrangements when conducted in the presence of a catalytic amount (0.1 equiv) of Lewis acid (BF₃-Et₂O).¹³⁻¹⁶ In

(8) The required bicyclic compounds (e.g., 5 and 13) were prepared by the general sequence involving Diels-Alder reaction of the appropriate diene with methyl acrylate followed by formylation of the ester enolate generated with LDA/THF (hindered cases required use of KDA). Where ever possible, epimeric starting bicyclic isomers were separated chromatographically prior to rearrangement. All new compounds exhibit satisfactory spectral data and either combustion or high-resolution exact mass analytical data. Partial NMR data (in δ at 400 MHz): 5, 9.45 (s, 1 H), 6.63 (t, $J = 7.1$ Hz, 1 H), 6.14 (t, $J = 7.1$ Hz, 1 H), 3.77 (s, 3 H), 3.23 (d, $J = 3.0$ Hz, 1 H), 2.68 (s(br), 1 H), 2.21 (dd, $J_1 = 11.0$, $J_2 = 1.1$ Hz, 1 H), 1.97 (d, $J = 11.0$ Hz, 1 H), 1.61 (m, 2 H), 1.29 (m, 2 H); 6, 7.56 (s, 1 H), 5.96 (s(br), 1 H), 5.82 (s(br), 1 H), 4.40 (s, 1 H), 3.71 (s, 3 H), 2.43 (ddd, $J_1 = 16.9$, $J_2 = 6.2$, $J_3 = 1.3$ Hz, 1 H), 2.12 (dd, $J_1 = 16.9$, $J_2 = 6.2$ Hz, 1 H), 2.30-2.10 (m, 3 H), 1.66-1.54 (m, 2 H); 11, 9.66 (s, 1 H), 6.34 (t, $J = 7.8$ Hz, 1 H), 5.89 (d, $J = 8.0$ Hz, 1 H), 3.76 (s, 3 H), 2.66 (s(br), 1 H), 2.10-1.00 (m, 3 H), 1.39 (s, 3 H); 12, 7.53 (s, 1 H), 5.59 (s(br), 1 H), 4.33 (s(br), 1 H), 3.70 (s, 3 H), 2.45 (ddd, $J_1 = 14.1$, $J_2 = 6.7$, $J_3 = 1.6$ Hz, 1 H), 2.14 (dd, $J_1 = 14.1$, $J_2 = 2.8$ Hz, 1 H), 2.09-1.98 (m, 3 H), 1.73 (s, 3 H), 1.74-1.52 (m, 2 H); 21, 6.19 (m, 1 H), 5.96 (d, $J = 5.5$ Hz, 1 H), 5.59 (s, 1 H), 5.42 (s, 1 H), 3.68 (s, 3 H), 3.32 (d, $J = 14.7$ Hz, 1 H), 3.02 (d, $J = 14.7$ Hz, 1 H), 2.84 (s, 1 H), 2.30-2.00 (m, 4 H), 2.10 (s, 3 H); 22, 5.70 (s, 1 H), 5.64 (s, 1 H), 5.51 (s, 1 H), 5.00 (d, $J = 6.7$ Hz), 3.70 (s, 3 H), 3.25 (s, 2 H), 2.70 (m, 1 H), 2.52 (m, 2 H), 2.25 (s, 3 H).

(9) After these studies were under way, the rearrangement of 9 to 10 was reported: Oppolzer, W.; Francotte, E.; Battig, K. *Helv. Chim. Acta* 1981, 64, 478 ref 6.

(10) The use of MM2 calculations to compare the rearrangement partners (e.g. 5 and 6) apparently results in a systematic overestimate of the energy of the bicyclic isomer (~10 kcal/mol) due to the lack of adequate correction in our force field for the heats of formation of the quaternary carbon centers. The ΔH values cited are corrected for this systematic error.

(11) The exact position of the equilibrium was difficult to establish in this case, since the rearrangement product underwent irreversible conversion to a mixture of olefins by rupture of the 3° allylic ether linkage under the acidic reaction conditions.

(12) The cyano group provides ~2.5 kcal/mol less stabilization than ester in this system (11 vs. 17), thus neither steric nor electronic effects alone are sufficient to assure complete rearrangement.

(2) Metzner, P.; Pham, T. N.; Vialle, J. *Nouv. J. Chim.* 1978, 2, 179 and references cited therein. Beslin, P.; Lagain, D.; Vialle, J. *J. Org. Chem.* 1980, 45, 2517. See also ref 9 and 10 of ref 16.

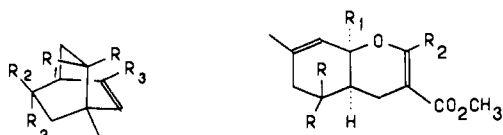
(3) For recent syntheses, see: Schlessinger, R. H.; Nugent, R. A. *J. Am. Chem. Soc.* 1982, 104, 1116. Trost, B. M.; McDougal, P. G. *J. Am. Chem. Soc.* 1982, 104, 6110. Roush, W. R.; D'Ambra, T. E. *J. Am. Chem. Soc.* 1983, 105, 1058 and references cited therein.

(4) Brooks, D. W.; Grothaus, P. G.; Mazdiziyani, H. *J. Am. Chem. Soc.* 1983, 105, 4472.

(5) Carpenter, B. K. *Tetrahedron* 1978, 34, 1877. Burrows, C. J.; Carpenter, B. K. *J. Am. Chem. Soc.* 1981, 103, 6983, 6984.

(6) Fry, A. *Mech. Mol. Migr.* 1971, 4, 113.

(7) This result could also arise as the result of kinetic control due to a low activation barrier for the formation of 4.



11, R = CHO; R₁ = CO₂CH₃;
R₂ = R₃ = H

13, R = CHO; R₁ = CO₂CH₃;
R₂ = CH₃; R₃ = H

15, R = CHO; R₁ = CO₂CH₃;
R₂ = R₃ = CH₃

17, R = CHO; R₁ = CN; R₂ =
R₃ = H

23, R = COCH₃; R₁ = CO₂CH₃;
R₂ = R₃ = H

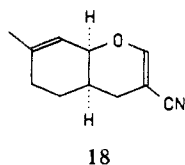
26, R = CO₂CH₃; R₁ = CHO; R₂ =
R₃ = H

12, R = R₁ = R₂ = H

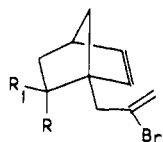
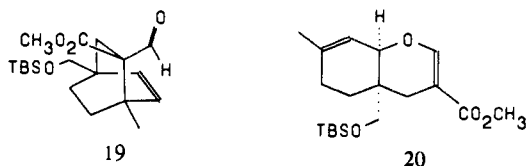
14, R = CH₃; R₁ = R₂ = H

16, R = R₁ = CH₃; R₂ = H

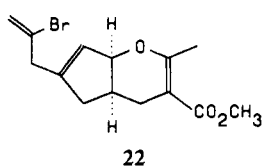
24, R = R₁ = H; R₂ = CH₃



favorable cases such as **11** → **12**, **13** → **14**, and **19** → **20**, the



21, R = COCH₃; R₁ = CO₂CH₃
28, R = CO₂CH₃; R₁ = COCH₃



rearrangement proceeds slowly as low as -78 °C, and rapidly at 0 °C (1 h). Based upon approximate half-life data for **13**, the magnitude of the acceleration can be estimated to be $\geq 10^9$.¹⁷ In cases where the ring system is more strained, such as **21**, the rate acceleration is further enhanced as judged by the near instantaneous rearrangement **21** → **22** at -78 °C (0.5 h).^{8,18-20} However,

(13) For an excellent review of catalysis of Cope and Claisen rearrangements, see: Lutz, R. P. *Chem. Rev.* **1984**, *84*, 205.

(14) For two notable examples of Lewis acid acceleration of Cope rearrangements see: Yates, P.; Eaton, P. E. *Tetrahedron* **1961**, *12*, 13. Breslow, R.; Hoffman, J. M., Jr. *J. Am. Chem. Soc.* **1972**, *94*, 2111.

(15) Evans, D. A.; Nelson, J. V. *J. Am. Chem. Soc.* **1980**, *102*, 774 and references cited therein.

(16) Denmark, S. E.; Harmata, M. A. *Tetrahedron Lett.* **1984**, *25*, 1543 and references cited therein.

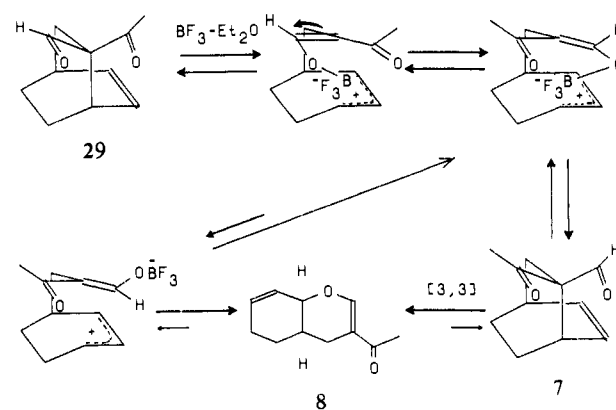
(17) The rearrangements occur thermally with half-lives of about 0.5 h at 135 °C except for the bicyclo[2.2.1]heptene derivatives which rearrange at or below room temperature.

(18) Intermediates **21** (and **28**) were prepared from the epimeric mixture of Diels-Alder adducts obtained from 1-(2-bromo-2-propenyl)cyclopentadiene and methyl acrylate by the sequence: (1) LDA/CH₃CHO/THF/-78 °C; (2) (COCl)₂/Me₂SO/Et₃N/-78 °C. Due to the sensitivity of **21** and **28**, the rearrangement was conducted on the mixture of isomers. The regioisomeric adducts were also present; however, they were demonstrated to be inert to the reaction conditions in control experiments.

(19) Corey, E. J.; Munroe, J. E. *J. Am. Chem. Soc.* **1982**, *104*, 6129.

(20) The facility of this rearrangement under the reaction conditions utilized by Corey and Munroe¹⁹ to prepare **22** may require reinterpretation of the mode of formation of **22** cited by these authors. However, at present it is not possible to exclude the direct production of **22** in a single-step cycloaddition. This type of retro-Claisen process is general and must be considered whenever contiguous quaternary centers would be formed in such a Lewis acid catalyzed cycloaddition. Additional experiments are under way to attempt to resolve the remaining questions.

Scheme 1



the rearrangement **23** → **24** is $\sim 7\times$ slower than **11** → **12**.²¹

There are at least two plausible mechanistic hypotheses that could account for the foregoing observations, a sigmatropic rearrangement pathway and a pathway involving the intermediacy of one or more carbonium ions. Since the aldehydes **25** and **26** (isomeric with **5** and **11**) were recovered unchanged after exposure to the identical reaction conditions, the former hypothesis appears valid for examples such as **5** and **11**.²² In the case of aldehydes **27** and **28** (isomeric with **9** and **21**) which were converted to **10** and **22**, respectively, under BF₃-Et₂O catalysis, and keto aldehyde **7** which afforded a minor amount of **29** (in addition to **8**) in the presence of BF₃-Et₂O (room temperature/2 h), the intervention of some type of carbonium ion intermediate seems to be required.²³ However, it is not necessary to invoke the intervention of carbonium ion intermediates for these cases except to permit interconversion of the epimeric substrates. Indeed, the fact that the epimeric substrates rearrange at appreciably different rates (e.g., **7** → **8** \gg **29** → **8**) is fully accounted for by the mechanistic scheme shown below (Scheme I).

In this formulation, the rearrangement is postulated to occur by the [3,3]-sigmatropic pathway for both isomers. If one makes the plausible assumptions that the rate of carbonium ion formation ought not differ markedly in the two epimers and that keto-enol interconversion is not rate limiting, a common carbonium ion intermediate is precluded since the ion derived from **29** cannot undergo direct collapse to product but direct collapse to product is possible for the ion derived from **7**. However, if a common carbonium ion intermediate were involved, both epimers would be expected to rearrange at comparable rates.²⁴

The observed acceleration presumably arises via complexation of the Lewis acid at the distal carbonyl group, developing electron deficiency at the α carbon (to position 1) which is properly situated to stabilize the transition state relative to starting material (cf. **30**) as described by the Carpenter model.⁵ The 7-fold slower rearrangement of **23** relative to **11** (vide supra) further supports the validity of this rationale since the presence of donor substituents at position 2 (eq 1) should result in a retardation of the rate.⁵

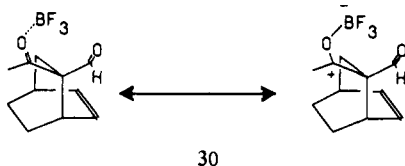
We are further examining the scope and mechanistic details of these processes as well as the aforementioned applications to

(21) Differing behavior depending upon substrate stereochemistry is characteristic of processes that occur by a [3,3]-sigmatropic rearrangement pathway, cf. ref 15.

(22) The geometric requirements of the [3,3] rearrangement preclude a single-step concerted rearrangement for cases such as these, since a bond rotation leading to effective epimerization of the quaternary center must occur at some point along the reaction coordinate in order for the observed products to form.

(23) The intervention of carbonium ion intermediates must occur in this case as is discussed; however, the higher activation barrier for **29** is suggestive that a sigmatropic rearrangement pathway is still operable for the actual rearrangement step.

(24) The retro-Claisen rearrangement must be analyzed at the level of the Carpenter treatment as a Cope rearrangement. At the 1-position, any charge buildup (+ or -) would be expected to accelerate the rearrangement according to the model. Whereas, the conjugating substituent would be expected to retard the reverse reaction (Claisen rearrangement).



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the synthesis of trichothecins. The results of these studies will be reported in due course.

Acknowledgment. We thank the National Cancer Institute of the National Institutes of Health for a research grant (CA-29108) in support of these studies.

Ab Initio Study of 1,2,4,5-Tetramethylenebenzene: A Disjoint Non-Kekulé Molecule with a Possible Singlet Ground State

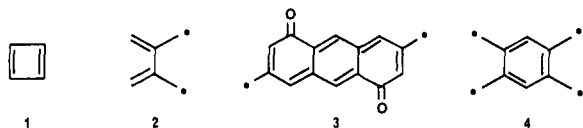
Paul M. Lahti,¹ Angelo Rossi,^{*2} and Jerome A. Berson^{*1}

Departments of Chemistry, Yale University
New Haven, Connecticut 06511

University of Connecticut, Storrs, Connecticut 06268

Received September 17, 1984

The application³ of Hund's first rule, not only to its original domain in atomic spectroscopy⁴ but also to conjugated non-Kekulé molecules, has been discussed widely.⁵⁻⁷ Hückel⁶ was the first to point out that a violation might occur in the specific case of the Schlenk-Brauns hydrocarbon, because theory then available showed the singlet and triplet states to be of nearly equal energy. Borden and Davidson⁷ later discerned theoretically that this property should inhere in the whole class of "disjoint" biradicals, of which an important subgroup comprises alternant systems with equal numbers of starred and unstarred π -centers.^{7,8} Higher level ab initio SCF-MO-CI calculations confirm this idea by predicting singlet ground states for two disjoint systems, square cyclobutadiene (1)^{5d,h,9} and tetramethyleneethane (2).^{7,10} However,



the only available experimental test shows the disjoint non-Kekulé molecule 3 to have a triplet ground state,¹¹ and, although an ab initio calculation currently is not practical, INDO/S-CI calcu-

Table I. CI Results for 1,2,4,5-Tetramethylenebenzene

state	UHF optimized ^{a,b}	ROHF optimized ^{a,c}
	SD-CI/STO-3G ^e	
³ B _{1u}	-379.773 01	-379.826 71
¹ A _g	-379.783 08	-379.778 38
⁵ A _g	-379.760 39	
state	SDTQ-CI energy ^d	rel energy ^d
	SDTQ-CI/STO-3G ^e	
¹ A _g	-379.863 47	0.0
³ B _{1u}	-379.851 72	7.4
⁵ A _g	-379.773 90	56.2
	SDTQ-CI[4s,2p] ^f	
¹ A _g	-384.366 65	0.0
³ B _{1u}	-384.341 94	15.5

^aEnergy in hartrees. ^bSD-CI energy at STO-3G UHF optimized geometry. The ¹A_g calculation uses a two-configuration reference state. ^cSD-CI energy at STO-3G ROHF/TCSCF optimized geometry. The ¹A_g calculation was done as in footnote b. ^dEnergy relative to ¹A_g state in kcal/mol at SDTQ-CI level. ^eSTO-3G basis set at STO-3G optimized geometry, using UHF geometry for ¹A_g and ROHF geometry for ³B_{1u} (see text). ^fDunning-Huzinaga (9s,5p)[4s,2p] basis set at STO-3G optimized geometry.

lations do concur with the experimental finding.¹² In order to explore further the consequences of disjoint character, we have undertaken an ab initio study of a disjoint system of intermediate size, 1,2,4,5-tetramethylenebenzene (4). INDO/S-CI calculations¹² predict a singlet ground state by 9 kcal/mol. So far, this is the largest system for which our previously reliable semiempirical method¹² has been tested against higher level theory.

Geometry optimization of 4 was carried out using restricted open-shell Hartree-Fock (ROHF) and unrestricted Hartree-Fock (UHF) wave functions for the ³B_{1u} state, two-configuration SCF (TSCF) wave functions for the ¹A_g state, and UHF wave functions for the ⁵A_g state; the STO-3G basis set¹³ was used to optimize the geometries to less than 2.0 millihartrees/bohr using the program GAMESS.¹⁴ Planarity was imposed during the optimization since our objective was to examine disjoint character. The final geometries are shown in the supplementary material. Only the ⁵A_g state has an "aromatic" geometry. The geometries of the ¹A_g TCSCF and ³B_{1u} ROHF states, as expected,^{15,16} are essentially identical and resemble partially localized pentadienyl radicals joined at inactive sites. The ³B_{1u} UHF geometry has longer exocyclic methylene bond lengths than does the triplet ROHF geometry, but the UHF geometry is still approximately that of joined pentadienyl radicals. UHF wave functions are known to give variationally better geometries than ROHF wave functions for many open-shell species, due to the better correlation in UHF wave functions,¹⁵ which helps to avoid doublet instability in the triplet wavefunction.^{5b} However, the UHF/STO-3G-optimized ³B_{1u} state of 4 has a spin-squared expectation value ($\langle S^2 \rangle$) of 3.14, indicating substantial spin contamination, since a pure triplet should have $\langle S^2 \rangle = 2.00$. As a result, the UHF geometry presumably reflects the optimum for some mixture of spin states, not for the "pure" ³B_{1u} state. Therefore both UHF and ROHF geometries were used in configuration interaction (CI) calculations described below. The geometry of lowest CI energy would under these circumstances be variationally preferable, though probably not optimal due to the approximate nature of the wave functions used for optimization.

CI calculations were then carried out on the appropriate geometries for the states of 4, using STO-3G (spin-pure) ROHF MO's for multiplet states and TCSCF MO's for ¹A_g. We carried

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- (2) University of Connecticut.
- (3) For a particularly relevant example, see Hund, F., as cited by Müller, E.; Bunge, W. *Ber.* **1936**, *69*, 2168.
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