was, therefore, useful for quantitative analyses near equilibrium or qualitative assessments when the system was far from equilibrium. To make quantification possible under the latter conditions, we developed an HPLC technique using a column with a polar bonded phase and a mixed fluorocarbon solvent system to separate S_6, S_7, and S_8 without detectable decomposition.[13] This allowed the determination that our preparations[4] of reference samples of S_6 and S_7 yielded products with <1% S_8 as an impurity. The HPLC procedures now available[6,13] yield information on elemental sulfur systems that was not previously accessible.

The allotropic composition of elemental sulfur is perturbed by light. S_8, irradiated with a sunlamp, is converted to a reactive form of sulfur.[14] Irradiation of S_6, S_8, or S_{10} in various solvents is reported to produce S_7.[15] We find that prolonged irradiation of S_8 in methanol at 2537 Å yields mixtures with S_6 and S_7 considerably in excess of the amounts achieved by equilibrations of samples in the dark, sugggesting that a photostationary state can be significantly displaced from the thermal equilibrium. At concentrations of $\sim 10^{-5}$ M, S_6 may be ~40% and S_7 ~20% of total sulfur. The quantities of the less stable S_6 and S_7 in methanol–cyclohexane are also enhanced by heating, as expected. Because of the sensitivity of the system to light and temperature, the data used for establishing the existence of the equilibrium discussed above were obtained with solutions kept in the dark at temperatures near 22 °C.

The presence of S_6 and S_7 in sulfur melts[16] and in gaseous sulfur at high temperatures[17] is well documented. Extrapolations of these measurements to the quite different temperatures and concentrations of the above solutions indicate that in "nonpolar" environments the equilibrium concentrations of $S_6 + S_7$ may be similar to those in polar solvents. In this case, solvent polarity may not drastically shift the position of equilibrium but may increase the rates of interconversion. The possibility that rates in polar solvents are affected by small amounts of impurities[8] is being investigated. An equilibrium position independent of solvent is compatible with S_6 and S_8 having no permanent dipoles while the small moment of S_7 may be further reduced by rapid pseudorotation.[18] Near the completion of this study, a communication by Steudel and Strauss appeared reporting the equilibrium of Se_6, Se_7, and Se_8 in carbon disulfide.[19]

The solvent effects noted above may signal the presence of polar intermediates in the interconversion processes. The intermediates could be structurally related to the ions generated by dissolution of sulfur in polar media[20] or to S_7 ring compounds isolated from oxidations of S_8 in polar solvents,[21] e.g., S_7O.[21c] Extended Hückel calculations indicate that a polar S_7S is only 5–10 kcal above S_8 in energy.[22] The exo sulfur might be transferred to other sulfur rings. Mechanistic studies are underway to elucidate these and related points.

Acknowledgment. We thank Dr. D. J. Sam for a series of useful technical discussions and prescient comments on the probability of a significant solvent effect in this system. We also gratefully acknowledge the skilled experimental assistance of R. J. Young and E. B. Holler and the useful discussions and mass spectroscopy determinations from Dr. C. N. McEwen and his co-workers.

Note Added in Proof. A wide-ranging article by R. Steudel has appeared in *Topics in Current Chemistry*. Among other subjects it reports the formation of S_6 and S_7 on ultraviolet irradiation of S_8 solutions and the thermal approach to equilibrium of the three rings in CS_2 at 130–150°. We are grateful to Professor Steudel for a preprint of his manuscript.

Registry No. S_6, 13798-23-7; S_7, 21459-04-1; S_8, 10544-50-0.

---

(13) Hayman, A. C., to be submitted for publication.

(14) Bartlett, P. D.; Meguerian, G. *J. Am. Chem. Soc.* **1956**, *78*, 3710–3715.

(15) Steudel, R.; Steidel, J.; Pickardt, J.; Schuster, F. *Z. Naturforsch., B* **1980**, *35B*, 1378–1383.

(16) See: (a) Harris, R. E. *J. Phys. Chem.* **1970**, *74*, 3102–3111. (b) Mansle, H. J.; Steudel, R. *Z. Anorg. Allg. Chem.* **1981**, *478*, 177–190. Extrapolation of Harris' data from the melt to room temperature and correction for the difference in concentration between the melt and 10^{-4} M solutions lead to ~1% $S_6 + S_7$ (the main components of his S_π).

(17) (a) Berkowitz, J. In "Elemental Sulfur"; Meyer, B., Ed.; Interscience: New York, 1965; Chapter 7. Extrapolation of the vapor-phase data to 20 °C and 10^{-4} M sulfur leads to S_6 and S_7 concentrations within factors of 3 of those found in methanol solutions. Thus a large dependence of the equilibrium composition on solvent is not predicted: (b) Drowart, J.; Goldfinger, P.; Detry, D.; Rickert, H.; Keller, H. *Adv. Mass Spectrom.* **1968**, *4*, 499–509.

(18) Steudel, R.; Schuster, F. *J. Mol. Struct.* **1978**, *44*, 143–157.

(19) Steudel, R.; Strauss, E. M. *Z. Naturforsch., B* **1981**, *36B*, 1085–1088.

(20) Chivers, T.; Lau, C. *Inorg. Chem.* **1982**, *21*, 453–455.

(21) (a) Burns, R. C.; Gillespie, R. J.; Sawyer, J. F. *Inorg. Chem.* **1980**, *19*, 1423–1432. (b) Passmore, J.; Sutherland, G.; Taylor, P.; Whidden, T. K.; White, P. S. *Ibid.* **1981**, *20*, 3839–3845. (c) Steudel, R.; Shandow, T. *Angew. Chem.* **1978**, *80*, 644–645.

(22) Wasserman, Z. R., unpublished results.

Carbanion-Accelerated Claisen Rearrangements

S. E. Denmark* and M. A. Harmata†

Roger Adams Laboratory, School of Chemical Sciences
University of Illinois, Urbana, Illinois 61801

Received April 30, 1982

The [3,3] sigmatropic rearrangement of allyl vinyl ethers (Claisen rearrangement,[1] Scheme I) has enjoyed widespread application in many facets of organic synthesis over the past 20 years.[1e] It has proved no less attractive to physical and theoretical organic chemists[2] who have contributed greatly to understanding mechanism and energetics of the rearrangement. Modern variants[3] that employ ketene acetal tautomers of carboxylic acid derivatives provide the corresponding amide,[3a–d] ester,[3e,f] acid[3g–i] or thioester[3j,k] upon rearrangement. The increasingly mild conditions required for these variants (Scheme I) amplifies their value as synthetic methods. *We report a new variant of the Claisen rearrangement that is mild and regioselective and produces γ,δ-unsaturated ketones as rearrangement products.*[4]

Our strategy was based on the empirical observation that π-electron donating groups at the 2-position of an allyl vinyl ether accelerate the reaction;[5] cf. Scheme I. We therefore reasoned that the greatest acceleration should be observed with the most powerful π-donor, i.e., a carbanion.[6] Initial experiments involving lithium salts of cyano- and carboethoxy-stabilized anions (Z =

---

† Eastman Kodak Graduate Fellow, 1981–1984.

(1) Reviews: (a) Tarbell, D. S. *Chem. Rev.* **1940**, *27*, 495. (b) Tarbell, D. S. *Org. React.* **1944**, *2*, 1. (c) Rhoads, S. J.; Raulins, R. N. *Ibid.* **1975**, *22*, 1. (d) Ziegler, F. E. *Acc. Chem. Res.* **1977**, *10*, 227. (e) Bennett, G. B. *Synthesis* **1977**, 589.

(2) (a) Rhoads, S. J. In "Molecular Rearrangements"; deMayo, P., Ed.; Interscience: New York, 1963; Part 1, pp 655–684. (b) Hansen, H. J. In "Mechanism of Molecular Migration"; Thyagarajan, B. S., Ed.; Wiley-Interscience: New York, 1971; Vol. 3, pp 177–236. (c) McMichael, K. C.; Korver, G. L. *J. Am. Chem. Soc.* **1978**, *100*, 2746. (d) Gajewski, J. J.; Conrad, N. D. *Ibid.* **1978**, *100*, 2747. (e) Gajewski, J. J. *Acc. Chem. Res.* **1980**, *13*, 142. (f) Carpenter, B. K.; Burrows, C. J. *J. Am. Chem. Soc.* **1981**, *103*, 6983, 6984.

(3) (a) Wick, A. E.; Felix, D.; Steen, K.; Eschenmoser, A. *Helv. Chim. Acta* **1964**, *47*, 2425. (b) Felix, D.; Gschwend-Steen, D.; Wick, A. E.; Eschenmoser, A. *Ibid.* **1969**, *52*, 1030. (c) Ficini, J.; Barbara, C. *Tetrahedron Lett.* **1966**, 6425. (d) Bartlett, P. A.; Hahne, W. F. *J. Org. Chem.* **1979**, *44*, 882. (e) Johnson, W. S.; Wethermann, L.; Bartlett, W. R.; Brocksom, T. J.; Li, T.; Faulkner, D. J.; Peterson, M. R. *J. Am. Chem. Soc.* **1970**, *92*, 741. (f) Faulkner, D. J.; Peterson, M. R. *Ibid.* **1973**, *95*, 553. (g) Arnold, R. T.; Searles, S. *Ibid.* **1949**, *71*, 1150. (h) Ireland, R. E.; Mueller, R. H. *Ibid.* **1972**, *94*, 5897. (i) Ireland, R. E.; Mueller, R. H.; Willard, A. K. *Ibid.* **1976**, *98*, 2868. (j) Malherbe, R.; Bellus, D. *Helv. Chim. Acta* **1978**, *61*, 295. (k) Rosini, G.; Spineti, G. G.; Foresti, E.; Pradella, G. *J. Org. Chem.* **1981**, *46*, 2228.

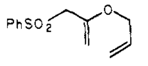
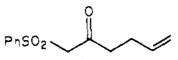
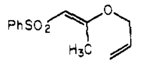
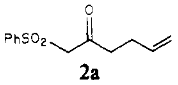
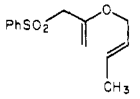
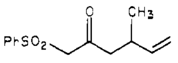
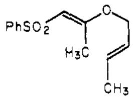
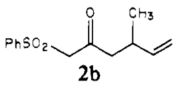
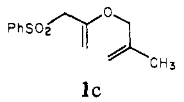
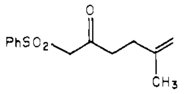
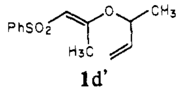
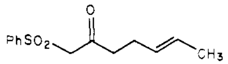
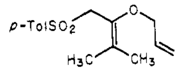
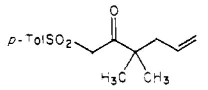
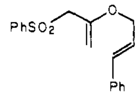
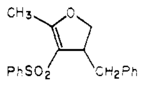
(4) The Carroll modification of the Claisen rearrangement also affords γ,δ-unsaturated ketones. (a) Carroll, M. F. *J. Chem. Soc.* **1940**, 704, 1266; **1941**, 507. (b) Kimel, W.; Cope, A. C. *J. Am. Chem. Soc.* **1943**, *65*, 1992.

(5) This purely intuitive analysis has received qualitative theoretical support recently from Carpenter.[2f] See also: Carpenter, B. K. *Tetrahedron* **1978**, *34*, 1877.

(6) The accelerating effect of a carbanion in the electrocyclic opening of benzocyclobutenes has been documented: Kametani, T.; Tsubuki, M.; Nemoto, H.; Suzuki, K. *J. Am. Chem. Soc.* **1981**, *103*, 1256.

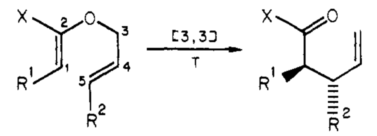
0002-7863/82/1504-4972$01.25/0 © 1982 American Chemical Society

Table I. Carbanion-Accelerated Claisen Rearrangements[a]

expt	substrate[10]	temp,[b] °C	time, h	product[10]	yield,[c] %
1	 **1a**	50	4	 **2a**	78
2	 **1a'**	50	4	 **2a**	76
3	 **1b**	50	4.5	 **2b**	71 (64)
4	 **1b'**	50	5	 **2b**	69 (54)
5	 **1c**	50 → 62	4.5 → 2.25	 **2c**	71
6 7	 **1d'**	50 20	0.5 4	 **2d**[d,e]	89 82
8	 **1e**	20	0.25	 **2e**	91
9	 **1f**	20	0.5	 **3**	63

[a] All reactions were done under the rigorous exclusion of moisture and oxygen in 3:1 HMPA/THF at ca. 0.13 M concentration. The anion was formed at 20 °C and the reaction monitored at the indicated temperature by TLC until complete and worked up by aqueous extraction in the usual way. The products were purified by flash chromatography on silica gel. [b] Temperature given is ±2 °C. [c] Yields refer to chromatographically homogeneous materials. [d] The assignment of *E* geometry to the double bond was supported by a 15-Hz vicinal coupling constant in the proton-decoupled 360-MHz NMR spectrum. [e] 8% of regioisomer 2d' was also formed.

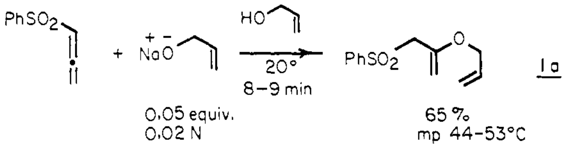
Scheme I



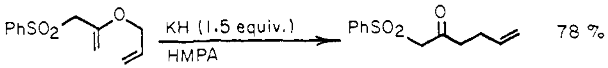
X	*T*, °C
H, alkyl	160–200
OR^3	135
$NR^3{}_2$	110–140
OLi, $OSiMe_3$	25–67
ZCH^-	?

CN, CO_2Et; Scheme I) were unsuccessful, most likely due to extensive delocalization of charge and the highly covalent nature of the anions. Thus we directed our efforts at inductively stabilized α-sulfonyl carbanions.[7] Further, to maximize charge on the X substituent, Scheme I, we changed to potassium salts, recalling the strong counterion dependence observed by Evans in the anionic oxy–Cope rearrangement.[8,9]

The parent system **1a**[10] was prepared by modification of Stirling's[11] procedure, eq 1. Treatment of **1a** with 1.5 equiv of

 (1)

oil-free potassium hydride and 1.5 equiv of 18-crown-6 in refluxing THF (1.5 h) produced the rearrangement product **2a**[10,12] in 40% yield along with phenylsulfonyl acetone (11%). The reaction temperature could be lowered (50 °C) and the yield markedly improved (78%) by using neat HMPA as solvent (eq 2). Apparently ion-pair dissociation is necessary to achieve rate enhancement. Control experiments (no KH) resulted in >97% recovery of **1a** unchanged, proving that anions are responsible for

 (2)

---

[7] For a recent review on the chemistry of α-sulfonyl carbanions see: Block, E. "Reactions of Organosulfur Compounds"; Academic Press: New York, 1978; Chapter 2.

[8] (a) Evans, D. E.; Golob, A. M. *J. Am. Chem. Soc.* **1975**, *97*, 4765. (b) Evans, D. A.; Baillargeon, D. J.; Nelson, J. V. *Ibid.* **1978**, *100*, 2242. (c) Evans, D. A.; Nelson, J. V. *Ibid.* **1980**, *102*, 774.

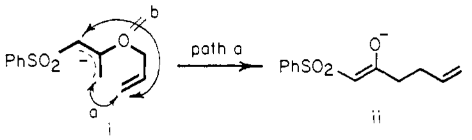
[9] We have observed little counterion effect in preliminary experiments with lithium and sodium salts of sulfones. This will be elaborated in the full paper.

[10] This compound has been fully characterized by ^1H NMR (220 or 360 MHz), IR, and mass spectra as well as satisfactory combustion data.

[11] Stirling, C. J. M. *J. Chem. Soc.* **1964**, 5863.

[12] Spectral data for **2a**: ^1H NMR ($CDCl_3$, Me_4Si) δ 7.97–7.73 (2 H, m), 7.73–7.43 (3 H, m), 5.9–5.48 (1 H, m), 5.13–4.86 (2 H, m), 4.16 (2 H, s), 2.79 (2 H, t, *J* = 7 Hz), 2.27 (2 H, q, *J* = 7 Hz); IR (neat) ν 3090, 2995, 1720, 1650, 1445, 1310, 1152 cm^{-1}; MS *m/e* (rel intensity) 238 (0.63), 141 (37), 96 (100), 77 (91), 56 (53).

the observed rearrangements.[13,14] It is noteworthy that none of the regioisomeric rearrangement product (arrow b, eq 3) was



(3)

observed. This probably derives from the fact that the primary product of rearrangement, path a, is a β-keto sulfone anion, ii, while the product of path b would be a simple ketone enolate.[15,16] The direct formation of stabilized enolates of the type ii has obvious implications for organic synthesis.

We have examined the effects of methyl substitution and double-bond position in the allyl vinyl ether system on the regioselectivity and rate of the rearrangement. Those results are shown in Table I.[17] Experiments 2 and 4 demonstrate that the high regioselectivity of the anionic rearrangements was in *no way affected by the position of double bond in the vinyl ether portion.*[18] This lends further support to the intervention of allylic anions as the rearranging species. We have observed an interesting dependence of the reaction rate on the position of methyl substitution. Substrates **1b** and **1c** (experiments 3 and 5), derived from crotyl and methallyl alcohol, rearranged more slowly than **1a**, with the effect being greater for **1c**, which required heating to 62 °C for complete reaction. The yields were not seriously affected, and the regioselectivity was still very high. The yields of β-keto sulfones **2b** (experiments 3 and 4) have been corrected for minor amounts of phenylsulfonyl acetone (actual yields in parentheses), which were formed by a competing reaction[19] from **1b** (**1b′**). Contrariwise, **1d′** (derived from 3-buten-2-ol) rearranged much faster and in higher yield than any of the previous substrates. While the total yield was very good, we did isolate 3% of the regioisomeric β-keto sulfone **2d′**.[20] The potassium salt of **1d′** rearranges even at *room temperature* in comparable yield. HPLC analysis of the reaction product again showed ca. 8% of **2d′**. While still only a minor component, a regioisomer formed exclusively from **1d′** is intriguing. Experiments are in progress to determine the importance of steric effects in this side reaction. Substitution on the *vinyl unit* is apparently of no consequence in controlling the regioselectivity but has a remarkable accelerating effect on the rate of the rearrangement. The potassium salt of **1e** spontaneously rearranged at room temperature in excellent yield (experiment 8). Finally, the only structural limitation we have found thus far is the incompatibility of phenyl substituents as shown in experiment 9. Substrate **1f** produced dihydrofuran **3**, which is not derived from a rearrangement but rather is an addition to the styryl double bond followed by a series of proton shifts.

The effects of methyl substitution on the rates of these reactions are qualitatively similar to those effects observed by Ireland[3h,i] in the ester enolate Claisen rearrangement. Further, if one considers methyl groups to be π donors, then there is again qualitative agreement with Carpenter's predictions.[2f]

In summary, we have documented that first examples of a carbanion-accelerated Claisen rearrangement[21] that occurs under mild conditions (50 °C or less) in good yield (69–91%) and with excellent regioselectivity to produce β-keto sulfones. We are currently investigating (1) other carbanion stabilizing substituents (phenylsulfinyl, phenylsulfenyl), (2) relative and absolute stereochemical control, and (3) general methods for the preparation of precursors.

Acknowledgment. We thank the Research Corp. for financial support. This work was in part supported by the University of Illinois NSF Regional Instrumentation Facility (NSF CHE 79-16100) and the University of Illinois Mass Spectrometry Laboratory (NIH PHS HHS GM 27029). M.A.H. thanks the Campbell Soup Co., the University of Illinois, and the Eastman Kodak Company for fellowships.

Registry No. 1a·K, 82352-25-8; **1a′**, 82352-26-9; **1b**·K, 82352-27-0; **1b′**, 82352-28-1; **1c**·K, 82352-29-2; **1d′**·K, 82352-30-5; **1e**·K, 82352-31-6; **1f**, 82352-32-7; **2a**, 80945-31-9; **2b**, 82352-33-8; **2c**, 82352-34-9; **2d**, 82352-35-0; **2e**, 82352-36-1; **3**, 82352-37-2; ii, 82352-38-3; $PhSO_2CH{=}C{=}CH_2$, 2525-42-0; $PhSO_2CH_2C{\equiv}CH$, 2525-40-8; *p*-Tol-$SO_2CH{=}C{=}C(CH_3)_2$, 82352-39-4; 2-propen-1-ol sodium salt, 20907-32-8; phenylsulfonylacetone, 5000-44-2; crotyl alcohol, 6117-91-5; methyallyl alcohol, 513-42-8; 3-buten-2-ol, 598-32-3.

---

(13) The potassium salt of **1a** is soluble in HMPA, and the reaction is homogeneous throughout, excluding surface-catalyzed processes.

(14) Accurate kinetic measurements are in progress to determine the factor of acceleration.

(15) Based on pK_a values *alone* there is a ca. 20 kcal/mol advantage (at 50 °C) for the formation of β-keto sulfone anions compared to ketone enolates. Compare, e.g., pk_a's: acetone[15a] (26.5) vs. phenylsulfonyl acetone[15b] (12.5). (a) Matthews, W. D.; Bartmess, J. E.; Bordwell, F. G.; Cornforth, F. J.; Drucker, G. E.; Margolin, Z.; McCallum, R. J.; McCollum, G. J.; Vanier, N. R. *J. Am. Chem. Soc.* **1975**, *97*, 7006. (b) Bordwell, F. G.; Van der Puy, M.; Vanier, N. R. *J. Org. Chem.* **1976**, *41*, 1883.

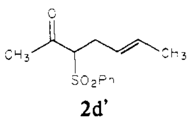
(16) This is, obviously, a product-side, ground-state argument. It remains to be seen if frontier molecular orbital coefficients in the HOMO of the (phenylsulfonyl)allyl anion would predict the same result.

(17) The starting sulfones are new compounds[10] and were prepared by one of the following routes: (a) **1** (a–c, f), alumina-catalyzed addition of the appropriate allylic alcohol to $PhSO_2CH{=}C{=}CH_2$; (b) **1** (a, b, d), addition of the sodium or potassium salt of the appropriate allylic alcohol to $PhSO_2CH_2C{\equiv}CH$; (c) **1e**, same as method b but with *p*-Tol-$SO_2CH{=}C{=}C(CH_3)_2$.

(18) This is in contrast to the behavior of the related α,β- and β,γ-unsaturated sulfoxides. Cookson, R. C.; Gopalan, R. *J. Chem. Soc., Chem. Commun.* **1978**, 608.

(19) The origin of the phenylsulfonyl acetone is still unclear. Control experiments showed that it was not arising in the workup.

(20) The structure of **2d′** is supported by its ^1H NMR (220 MHz) spectrum.



2d′

(21) For other examples of anionically accelerated Claisen rearrangements see (a) Frihard, C. R.; Leonard, N. J. *J. Am. Chem. Soc.* **1973**, *95*, 7174; **1974**, *96*, 5874. (b) Schultz, A. G.; Napier, J. *J. Chem. Soc., Chem. Commun.* **1981**, 224.

Origin of Huisgen's Factor "*x*": Staggering of Allylic Bonds Promotes Anomalously Rapid Exo Attack on Norbornenes

Nelson G. Rondan, Michael N. Paddon-Row,[1a]
Pierluigi Caramella,[1b] Jiri Mareda, Paul H. Mueller, and
K. N. Houk*

Department of Chemistry, University of Pittsburgh
Pittsburgh, Pennsylvania 15260

Received April 15, 1982

Norbornene and many derivatives are attacked by a variety of reagents preferentially from the exo face of the double bond.[2–5] Preferred exo attack has been attributed variously to steric effects,[2] torsional effects,[6] or to "nonequivalent orbital extension".[7] The

---

(1) Present addresses: (a) New South Wales Institute of Technology, Sydney, Australia; (b) University of Catania, Catania, Italy.

(2) Brown, H. C.; Hammar, W. J.; Kawakami, J. H.; Rothberg, I.; Van der Jugt, D. L. *J. Am. Chem. Soc.* **1967**, *89*, 6381. Brown, H. C.; Kawakami, J. H.; Liu, K.-T. *Ibid.* **1973**, *95*, 2209.

(3) Electrophiles and cycloaddends: Freeman, F. *Chem. Rev.* **1975**, *75*, 439. Allen, A. D.; Tidwell, T. T. *J. Am. Chem. Soc.* **1982**, *104*. 3145.

(4) Nucleophiles: Richey, H. G., Jr.; et al. *J. Org. Chem.* **1980**, *45*, 5027, 5042. See also: Corey, E. J.; Shibasaki, M.; Nicolau, K. C.; Malmstein, C. L.; Samuelson, B. *Tetrahedron Lett.* **1976**, 737. Baldwin, S. W.; Tomesch, J. C. *J. Org. Chem.* **1974**, *39*, 2382.

(5) Radicals: Davies, D. I.; Parrot, M. J. *Tetrahedron Lett.* **1972**, *2719* references therein.

(6) Schleyer, P. v. R. *J. Am. Chem. Soc.* **1967**, *89*, 701.

(7) Inagaki, S.; Fujimoto, H.; Fukui, K. *J. Am. Chem. Soc.* **1976**, *98*, 4054.

0002-7863/82/1504-4974$01.25/0