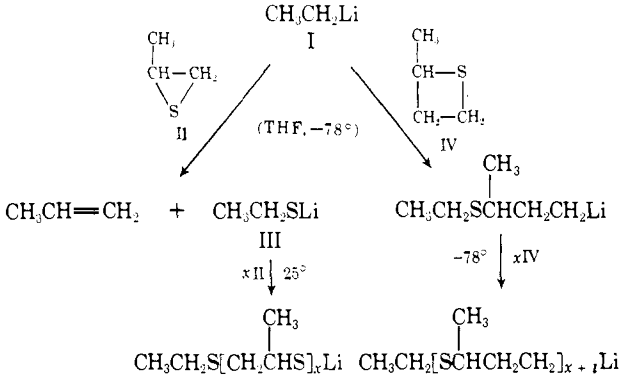
solution, and maintained at a temperature of −78°. In order to assure the absence of oxygen and moisture, all operations were carried out under high vacuum conditions. The resultant reaction products, after acid hydrolysis, were analyzed by gas-vapor chromatography and were found to be exclusively propylene and ethanethiol. The fact that the sulfur atom of the heterocyclic was found with the organic moiety of the alkyllithium leads to the conclusion that the sulfur atom was the site of attack by the carbanion. Lithium ethanethiolate, III, formed in this reaction, is capable of reacting with excess II at room temperature to a quantitative yield of a linear polymer possessing a carbon–carbon–sulfur backbone.

The reaction products of four-membered heterocyclic sulfur compounds with ethyllithium were analyzed *in situ* by high-resolution nmr. Under reaction conditions identical with those employed for the three-membered ring compound, 2-methylthiacyclobutane,[5] IV, and thiacyclobutane, V, yielded products which would be expected from an attack of a carbanion at the sulfur atom and subsequent ring opening with formation of a new carbanion species.



The new carbanion species appears in the nmr spectrum as a triplet (τ 10.95, J = 8.5 cps) which is clearly distinguishable from the quartet (τ 11.05, J = 8.4 cps) originating from ethyllithium. No elimination products such as cyclopropane or methylcyclopropane were observed. The newly formed carbanion species is capable of reacting in a repetitive process with excess IV or V to a quantitative yield of a linear polymer. This polymer–lithium species readily initiates the polymerization of vinyl compounds such as styrene, which is further evidence for the carbanionic nature of the propagating chain end. In contrast to thiacyclopropanes, the four-membered cyclic sulfides did not react with authentic III under comparable experimental conditions.

The higher rings, thiacyclopentane and thiacycloheptane, failed to undergo reaction with either I or III at −78 or 25°, respectively. From thermodynamic considerations[6] thiacyclopentane is not expected to polymerize, while thiacycloheptane should undergo ring opening. The ring strain in the seven-membered ring compound, however, arises mainly from hydrogen atom crowding brought about by eclipsed conformations, rather than bond angle distortions as is the case in rings of smaller size. Nucleophilic attack at bivalent sulfur, flanked by two carbon atoms, appears therefore to be restricted to valence states arising from severe bond angle distortions around the sulfur atom.

Acknowledgment. Acknowledgment is made to the Phillips Petroleum Company, Bartlesville, Okla., for partial support of this work.

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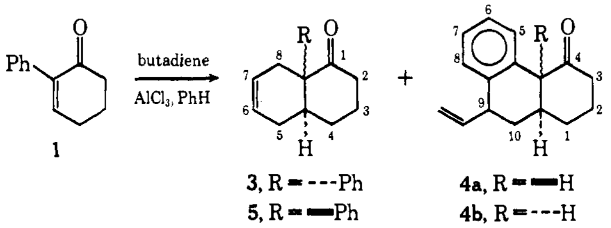
[5] Synthesized according to the procedure of S. Searles, H. R. Hays, and E. F. Lutz, *J. Org. Chem.*, 27, 2828 (1962).

[6] F. S. Dainton and K. J. Ivin, *Quart. Rev.*, 12, 61 (1958).

The Mechanism of the Catalyzed Diels–Alder Reaction

Sir:

Evidence has long been available that in Diels–Alder reactions employing strongly electrophilic dienophiles rates may be increased by addition of proton[1] and Lewis acids.[2] Recently additional findings concerning isomer distribution,[3] reaction rates,[3b,c] and spectra of presumed intermediates[4] have prompted the postulation of mechanisms for the Lewis acid catalyzed version which incorporate initial coordination of the catalyst with the dienophile's electron-withdrawing function[3a,c,4] and a two-step ring formation with a very short-lived zwitterionic intermediate.[3c] We have succeeded in trapping internally an intermediate of the postulated type by a catalyzed reaction between butadiene and 2-phenyl-2-cyclohexen-1-one (**1**). This is the first instance of which we are aware of the isolation of isomeric products derived from such intermediates in a catalyzed Diels–Alder reaction, and our results, as well as strongly supporting the suggested mechanism, demonstrate that the intermediates may have appreciable lifetimes.



Although the uncatalyzed reaction failed to proceed even at 200°, when the reaction was carried out by bubbling butadiene through a solution of **1** and *ca.* 0.5 equiv of aluminum chloride in benzene at 50–60°, loss of starting material was complete in about 1.5 hr. The product was a complex mixture containing components with a wide range of vpc retention times; however when the nonpolar polymers and solvent-condensation products were removed by column chromatography, the remaining material contained only four compounds whose vpc retention values were consistent with 1:1 adduct structures. These compounds, **3**, **4a**, **4b**, and **5**, were present in a ratio of 13:6 (both **4a** and **4b**):1 and in a combined absolute yield of about 65%. They

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[1] A. Wasserman, *J. Chem. Soc.*, 828 (1935); A. Wasserman, *ibid.*, 3046 (1949); A. Rodgman and G. F. Wright, *J. Org. Chem.*, **18**, 465 (1953).

[2] P. Yates and P. Eaton, *J. Amer. Chem. Soc.*, **82**, 4436 (1960); G. I. Fray and R. Robinson, *ibid.*, **83**, 249 (1961).

[3] (a) E. F. Lutz and G. M. Bailey, *ibid.*, **86**, 3899 (1964); (b) J. Sauer, D. Lang, and H. Wiest, *Ber.*, **97**, 3208 (1964); (c) T. Inukai and T. Kojima, *J. Org. Chem.*, **31**, 1121, 2032 (1966).

[4] J. Sauer and J. Kredel, *Tetrahedron Lett.*, 731 (1966).

were isolated as pure solids by repeated chromatography and fractional crystallization and provided spectral, chemical, and physical evidence[5] in agreement with structures **3**, **4**, and **5**.

The infrared spectra of **3**–**5** display absorptions consistent with the assigned structures in the regions characteristic for ketone carbonyl, monosubstituted phenyl, *cis*-disubstituted alkene, and monosubstituted vinyl groups.

The nmr spectra of **3** and **5** are similar and unremarkable except for the presence in the spectrum of **5** of a one-hydrogen quartet at δ 3.7 due to the axial hydrogen at C-2, deshielded by the phenyl[6] in the *trans* but not in the *cis* compound. The nmr spectra of both isomers of **4** contain separated absorptions representing four aromatic, three vinylic, two benzylic, and nine aliphatic hydrogens.

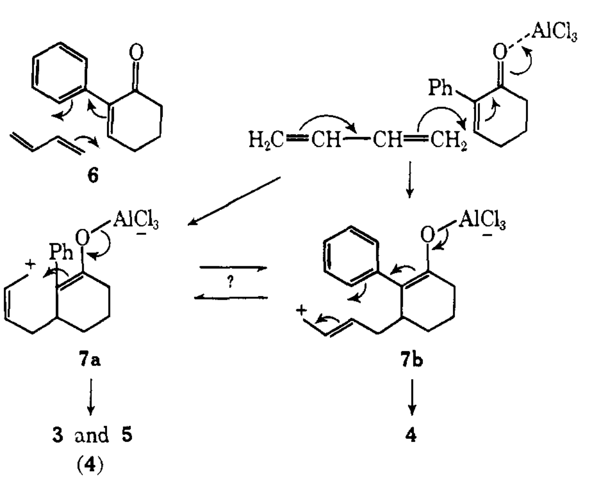
The mass spectra of **3**–**5** all have strong molecular ion peaks at m/e 226 (80–100% of base). In addition the spectra of **3** and **5** both have strong peaks for m/e 77 and 91 (50–80%) but these peaks are weak (<35%) in the spectra of **4a** and **4b**, which lack monosubstituted phenyl. When molecular ion intensity is computed as a percentage of total ion intensity for **3** *vs.* **5** and **4a** *vs.* **4b**, significant differences are observed indicating that the stabler isomers are **3** and **4a**, in agreement with the assignments.[7]

Catalytic hydrogenation of **3** produced *cis*-9-phenyl-1-decalone,[5] identical with material from two independent sources.[8]

There are several possible explanations for the appearance of compounds **4** and **5**, which would not be produced by a classical Diels–Alder reaction. The most obvious, that **4** and **5** are secondary products derived from the normal one (**3**) by Lewis acid catalyzed isomerization, has been disposed of by demonstrating that **3** is not converted to **4** or **5** at an appreciable rate under the conditions of the reaction.

A second possibility is that **4** and **5** simply arise by aberrant Diels–Alder mechanisms: it is theoretically and may be physically possible to arrange the atoms and orbitals involved in the conformations required to produce what has been categorized as a *trans–trans* cycloaddition,[9] leading to **5**, while **4** might be derived from the bizarre but not totally unprecedented[10] mechanism represented in **6**.

However in addition to being implausible, these mechanisms fail to provide any specific explanation for the effect of aluminum chloride. The simpler, more reasonable explanation, below, provides a common precursor for **3**, **4**, and **5** and does explain the role of the catalyst.



Several aspects of this mechanism deserve comment. Since allylic carbonium ions have been shown to have a high degree of configurational stability[11] up to at least 50°,[11d] it might be supposed that configurations like **7a** and **7b** are not interconvertible but must have arisen separately from *s-cis-* and *s-trans*-butadiene. If this were so, **3** and **5** would be derived only from *s-cis*-butadiene, while **4** might arise from either **7a** or **7b**. However, regardless of whether **3** and **4** arise from different, identical, or interconvertible configurations and conformations of the zwitterionic intermediate, an appreciable lifetime is required for the intermediate leading to **5**, since **5** can be formed in this mechanism only by considerable rotation around one or more of the appropriate bonds in **7**.

In addition to taking the paths shown, **7a** and **7b** might also close to vinylcyclobutanes such as have been found in certain uncatalyzed Diels–Alder reactions.[12] Whether such compounds could survive the reaction conditions employed here is dubious. We have no information either favoring or disfavoring their involvement.

Since **7a** and **7b** could *each* close to **4** by way of two different conformations leading to opposite relationships for the 9 and 10a hydrogens, this stereochemistry in **4**, concerning which we have no evidence, is not clearly predicted by the mechanism. The proposed mechanism, however, does suggest that the stereochemistry at the enolizable ring juncture in **4** is established last, perhaps only on work-up, and that it might be either kinetically or thermodynamically controlled depending on reaction and work-up conditions. It is probable that the observed ratio of **4a** to **4b** (*ca.* 2:1) is the result of equilibrium control, since we have produced approximately the same ratio of **4a** to **4b** by equilibrating[7c] pure samples of each. This constitutes proof of the epimeric relationship of **4a** and **4b**, and the position of their equilibrium is the principal basis for their stereochemical assignments, since the *trans* isomer is expected[7d,e] to predominate by close to this amount.

We believe that the foregoing evidence firmly establishes the validity of the proposed mechanism and makes it clear that, while the products of such catalyzed reac-

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[5] Satisfactory combustion analyses have been obtained for all new compounds reported.

[6] This phenomenon has been observed in other *trans*-9-substituted-1-decalone systems: see H. O. House and H. W. Thompson, *J. Org. Chem.*, **28**, 164 (1963), footnote 17, and H. O. House and G. A. Frank, *ibid.*, **30**, 2948 (1965), footnote 28.

[7] (a) N. L. Allinger and J. L. Coke, *J. Amer. Chem. Soc.*, **81**, 4080 (1959); (b) N. L. Allinger and J. L. Coke, *J. Org. Chem.*, **26**, 2096 (1961); (c) H. O. House and G. H. Rasmusson, *ibid.*, **28**, 31 (1963); (d) S. K. Balasubramanian, *Tetrahedron*, **12**, 196 (1961); (e) J. A. Barltrop and A. C. Day, *ibid.*, **14**, 310 (1961).

[8] H. W. Thompson and R. R. Muccino, unpublished results.

[9] R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968).

[10] M. C. Kloetzel, *Org. React.*, **4**, 1 (1948); E. LeGoff and R. B. Lacount, *J. Org. Chem.*, **33**, 2529 (1968); S. Wawzonek, G. R. Hansen, and A. R. Zigman, *Chem. Commun.*, 6 (1969).

[11] (a) W. G. Young, S. H. Sharman, and S. Winstein, *J. Amer. Chem. Soc.*, **82**, 1376 (1960); (b) P. D. Sleezer, S. Winstein, and W. G. Young, *ibid.*, **85**, 1890 (1963); (c) J. H. Brewster and H. O. Bayer, *J. Org. Chem.*, **29**, 105 (1964); (d) W. G. Young and J. S. Franklin, *J. Amer. Chem. Soc.*, **88**, 785 (1966).

[12] J. C. Little, *ibid.*, **87**, 4020 (1965).

tions often coincide with those from the uncatalyzed Diels–Alder reaction, mechanistically the two reactions may be largely unrelated,[13] the catalyzed version being more reasonably classifiable as a vinylogous variant of the Friedel–Crafts acylation of olefins.

Acknowledgment. Support from the National Science Foundation and the donors of the Petroleum Research Fund, administered the American Chemical Society is gratefully acknowledged.

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(13) For leading references to discussions of the mechanism of the normal Diels–Alder reaction, see ref 12.

(14) Summer 1969, National Science Foundation Undergraduate Research Participant.

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Vinylic Cations from Solvolysis. III. Solvolysis of Triarylvinyl Arylsulfonates in Aqueous Acetone

Sir:

Evidence for intermediate vinyl cations in solvolysis of vinyl sulfonates and halides activated by aryl group,[1] cyclopropyl ring,[2] double bond,[3] and alkyl groups[1k,4] is increasing. The possibility of sulfur–oxygen cleavage was discussed for vinyl triflates,[11] although attack of base on sulfur occurs with phenyl[5] and vinyl tosylates.[6] We now report the reactivity of several trianisylvinyl arylsulfonates and relevant solvent effects, which give additional evidence for vinyl-cationic transition states *via* carbon–oxygen cleavage.

Trianisylvinyl arylsulfonates were prepared by the reaction of trianisylvinyl bromide with silver arylsulfonates in dry acetonitrile.[7] Their solvolysis rate at 0.002–0.008 M concentrations in 70% acetone (containing 0.004–0.02 M 2,6-lutidine) was followed conductometrically (Table I). For all compounds $\Delta H^{\ddagger} = 25\text{–}27$ kcal/mol and $\Delta S^{\ddagger} = -5$ to -1 eu, and the product is 1,2,2-trianisylethanone.[8] For trianisylvinyl bromide, $k_1 = 2.52 \times 10^{-6}$ sec^{-1} at 75° (extrapolated value), $\Delta H^{\ddagger} = 26$ kcal/mol, $\Delta S^{\ddagger} = -10$ eu. A 4.2- and a 5.7-fold increase in the lutidine concentration caused a 13 and 8% decrease in k_1 for the tosylate and for the bromide, respectively. From Table I Hammett's ρ at 75° for changes in the leaving group is 1.67 (correlation coefficient 0.997).[9] Triphenylvinyl tosylate is 830-fold less reactive than 1-anisyl-2,2-diphenylvinyl tosylate at 120°.

Table I. Rates of Solvolysis of Triarylvinyl Arylsulfonates[a]

Ar^1 [b]	Ar^2 [b]	X	$10^5 k_1$, sec^{-1}
An	Ph	*p*-Me	2.72 ± 0.08
An	An	*p*-MeO	4.95 ± 0.18
An	An	*p*-Me	8.10 ± 0.60
An	An	H	14.1 ± 0.70
An	An	*p*-Br	35.5 ± 1.7
An[c]	An	*p*-NO_2	335.0 ± 11.2[d]
An[e]	An	*o*-NO_2	678.0 ± 10.0[d,f]

[a] $Ar_2{}^2C{=}C(Ar^1)OSO_2C_6H_4X$ in 70% acetone at 75°; [RX] = 0.008 M, [lutidine] = 1.6–1.7 × 10^{-2} M. [b] An = anisyl. [c] [RX] = 0.002 M, [lutidine] = 0.004 M. [d] Extrapolated from data in 90% acetone, assuming $m = 0.41$ as found for the tosylate (Table II). [e] [RX] = 0.005 M, [lutidine] = 0.02 M. [f] Extrapolated from data at lower temperatures.

In the solvolysis of trianisylvinyl tosylate in aqueous acetone k_1 increases with the water content (Table II) and a plot of log k *vs.* Grunwald–Winstein's Y[10] is linear, $m = 0.41$ (correlation coefficient 0.997). Solvolysis of 0.02 M tosylate in 70% acetone in the presence of 0.38 M Bu_4NBr gave over 95% of trianisylvinyl bromide.

Table II. Rates of Solvolysis of Trianisylvinyl Tosylate in Acetone-Water Mixtures at 75°[a]

Solvent, v/v	Y[b]	$10^5 k_1$, sec^{-1}
90% acetone	−1.86	1.23 ± 0.07
80% acetone	−0.67	4.43 ± 0.20
70% acetone	0.13	8.10 ± 0.60
60% acetone	0.80	15.1 ± 0.60

[a] [ROTs] = 0.008 M, [lutidine] = 0.016 M. [b] From ref 10b.

A rate-determining electrophilic "addition–elimination" of a proton from the water to the double bond (transition state **1**) is rejected since it requires a negative ρ value for substitution in the leaving group.[11] Attack on sulfur by hydroxide ion, formed by the reaction of lutidine with water, should be sensitive to the lutidine concentration and be slower on increasing the dielectric constant,[12] contrary to what was found. However, an O–S cleavage by water (transition state **2**) will show the same substituent and solvent effects as the rate-determining C–O cleavage (transition state **3**), since **2** is dipolar. The inertness of phenyl tosylate toward water,[5] the tosylate–bromide exchange, the lower reactivity of the β,β-diphenyl compared to the β,β-dianisyl derivative as found for the corresponding bromides,[1j,13] and the much higher reactivity of the α-anisyl compared to the α-phenyl group are compatible only with the vinyl-cationic transition state **3**.[14]

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(1) (a) C. A. Grob and G. Cseh, *Helv. Chim. Acta*, **47**, 194 (1964); (b) C. A. Grob, J. Csapilla, and G. Cseh, *ibid.*, **47**, 1590 (1964); (c) G. Modena and U. Tonellato, *Chem. Commun.*, 1363 (1968); (d) G. Modena, U. Tonellato, and F. Naso, *ibid.*, 1676 (1968); (e) G. Capozzi, G. Melloni, G. Modena, and M. Piscitelli, *Tetrahedron Lett.*, 4039 (1968); (f) Z. Rappoport, A. Gal, and Y. Apeloig, *Israel J. Chem. Proc.*, 16p (1968); (g) S. J. Huang and M. V. Lessard, *J. Amer. Chem. Soc.*, **90**, 2432 (1968); (i) W. M. Jones and D. D. Maness, *ibid.*, **91**, 4134 (1969); (j) Z. Rappoport and A. Gal, *ibid.*, **91**, 5246 (1969); (k) P. E. Peterson and J. M. Indelicato, *ibid.*, **91**, 6194 (1969); (l) Z. Rappoport and Y. Apeloig, *ibid.*, **91**, 6734 (1969); *Israel J. Chem. Proc.*, **7**, 34p (1969).

(2) (a) S. A. Sherrod and R. G. Bergman, *J. Amer. Chem. Soc.*, **91**, 2115 (1969); (b) M. Hanack and T. Bassler, *ibid.*, **91**, 2117 (1969); (c) D. R. Kelsey and R. G. Bergman, *ibid.*, **92**, 228 (1970).

(3) C. A. Grob and R. Spaar, *Tetrahedron Lett.*, 1439 (1969).

(4) P. J. Stang and R. Summerville, *J. Amer. Chem. Soc.*, **91**, 2117 (1969).

(5) C. A. Bunton and Y. H. Frei, *J. Chem. Soc.*, 1872 (1951).

(6) N. Frydman, R. Bixon, M. Sprecher, and Y. Mazur, *Chem. Commun.*, 1044 (1969).

(7) All new compounds reported here gave satisfactory analyses and showed spectral properties in agreement with the assigned structures.

(8) The compound was obtained only as an oil. See footnote 20 of ref 1j on this point.

(9) σ values given by H. H. Jaffé (*Chem. Rev.*, **53**, 191 (1951)) were used.

(10) (a) E. Grunwald and S. Winstein, *J. Amer. Chem. Soc.*, **70**, 846 (1948); (b) A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2770 (1956).

(11) P. E. Peterson and J. M. Indelicato (*ibid.*, **90**, 6516 (1968)) used a similar argument to show that in formic acid several vinyl arylsulfonates solvolyze by the electrophilic addition–elimination route.

(12) K. B. Wiberg, "Physical Organic Chemistry," Wiley, New York, N. Y., 1963, p 388.

(13) Z. Rappoport and A. Gal, unpublished results. The threefold rate difference between the β,β-dianisyl and the β,β-diphenyl derivatives points also to the absence of β-anisyl participation.

(14) A referee suggested that enough protons may be formed by the dissociation of the lutidinium ion, so that the addition–elimination forming the $AnCX^+\text{–}CHAn_2$ cation contributes to the reaction. This is in contradiction to several of the criteria discussed above. Moreover,