

**Table I.** Relative Rate Constants for the Addition of Cycloheptatrienyliene to Substituted Styrenes,  $\text{XC}_6\text{H}_4\text{CH}=\text{CH}_2$ 

X in $\text{XC}_6\text{H}_4\text{CHCH}_2$	$k_X/k_H^a$
4-OCH <sub>3</sub>	0.51
4-CH <sub>3</sub>	0.57
H	1.00
4-Cl	1.59 <sup>b</sup>
4-Br	1.68
3-Br	2.22

<sup>a</sup> Average of two glpc determinations. <sup>b</sup> Nmr analysis of the mixture of the original adducts gave  $k_X/k_H = 1.61$ .

reaction conditions. Both points were confirmed by removal of aliquots from the reaction mixture of *p*-bromostyrene vs. styrene at 2.5, 3.5, and 4.5 hr and observing that the relative ratio of styrenes and products did not change with time. Most of the spirononatrienes were not amenable to direct analysis and were therefore quantitatively reduced with hydrogen using a platinum/charcoal catalyst to give the substituted spirononanes which could be quantitatively analyzed by glpc.<sup>7,8</sup> Control experiments with the *p*-chloro adduct established that reduction and work-up procedures did not alter the relative ratio of products. The spirononatriene structures assigned to the adducts were further supported by independent synthesis of their reduction products from the reaction of the sodium salt of cycloheptanone tosylhydrazone with styrenes.<sup>9</sup> The relative rate constant data correlate well with the Hammett equation using primary  $\sigma$  values (Figure 1). The  $\rho$  value was computed by a least-squares analysis to be  $+1.05 \pm 0.05$  with a correlation coefficient of 0.982. This positive  $\rho$  value provides the first quantitative demonstration of the nucleophilicity of a carbocyclic aromatic carbene. It is interesting to compare this  $\rho$  value with  $\rho$  values reported in the literature for other carbenes. In similar competitive experiments the  $\rho$  value for dichlorocarbene was reported to be  $-0.619^{10}$  at 80° and independently determined to be  $-0.378^{11}$  at 0°. The  $\rho$  value for carboxycarbene has been reported as  $-0.38$  at 129°.<sup>12</sup> The change in sign in going from a typical electrophilic carbene such as dichlorocarbene to a perturbed carbene such as cycloheptatrienyliene requires a transition state **1** with charge distribution opposite to that of normal carbenes. Furthermore, the linear Hammett relationship, even with electron donating groups, suggests a change in the mode of addition with contribution of resonance form **2** (in contrast to simple inductive effects) in the transition state. Extension of this study to other model carbenes, which should allow separation of resonance and inductive effects and which hopefully will provide a firm

(7) The arylspirononatrienes were unstable to glpc analysis and unresolvable by 60 MHz nmr with the exception of the 4-Cl-4-H reaction mixture which could be analyzed directly by nmr giving a value for  $k_{rel}$  in excellent agreement (see Table I) with the reduction-glpc analysis sequence.

(8) All spirononanes gave ir, nmr, and mass spectra consistent with the assigned structure and satisfactory elemental analyses. Analyses by glpc were carried out with an analytical P1200 Varian Aerograph using a 15% SE-30 on Chromosorb W column.

(9) We are indebted to Dr. Karl Untch for prior communication of his work on the reaction of this salt with other double bonds.

(10) D. Seyferth, J. Y.-P. Mui, and R. Damrauer, *J. Amer. Chem. Soc.*, **90**, 6182 (1968).

(11) J. H. Sadler, *J. Chem. Soc. B*, 1024 (1969).

(12) J. E. Baldwin and R. A. Smith, *J. Amer. Chem. Soc.*, **89**, 1886 (1967).

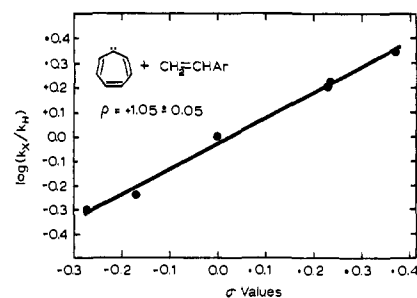
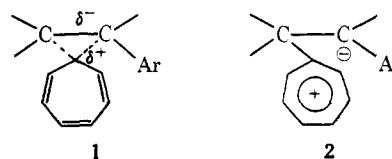


Figure 1. Log  $k_X/k_H$  vs.  $\sigma$  values for the reaction of 2,4,6-cycloheptatrienone *p*-toluenesulfonylhydrazone sodium salt derived cycloheptatrienyliene with substituted styrenes.

basis on which to make judgments concerning the nucleophilicities of carbenes, is now under intensive investigation.



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### Ion-Pair $\text{S}_{\text{N}}2$ Reactions at a Tertiary Center

Sir:

Second-order nucleophilic substitutions ( $\text{S}_{\text{N}}2$  reactions) at tertiary centers are rare. Reactions of nucleophiles with tertiary halides in protic solvents often give substitution products, but detailed examination has generally shown that the rate of formation of such products is independent of the nucleophile concentration, except for salt effects.<sup>1</sup> Reactions of *tert*-BuBr with LiCl or LiBr in acetone, which at one time were claimed to proceed by  $\text{S}_{\text{N}}2$  mechanisms, later were shown to be elimination-addition reactions, the supposed second-order component being a positive salt effect on the elimination reaction.<sup>2</sup> Substitution reactions have been observed recently for the reaction of nucleophiles with *p*-nitrocumyl halides, and related systems, but these have been shown to occur by radical-anion processes rather than by  $\text{S}_{\text{N}}2$  mechanisms.<sup>3</sup> The only ex-

(1) (a) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," 2nd ed, Cornell University Press, Ithaca, N. Y., 1969, Chapter VII; (b) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962; (c) C. A. Bunton, "Nucleophilic Substitution at the Saturated Carbon Atom," E. D. Hughes, Ed., Elsevier, New York, N. Y., 1963.

(2) S. Winstein, S. Smith, and D. Darwish, *Tetrahedron Lett.*, **16**, 24 (1959).

(3) See N. Kornblum and F. W. Stuchal, *J. Amer. Chem. Soc.*, **92**, 1804 (1970), and references cited therein.

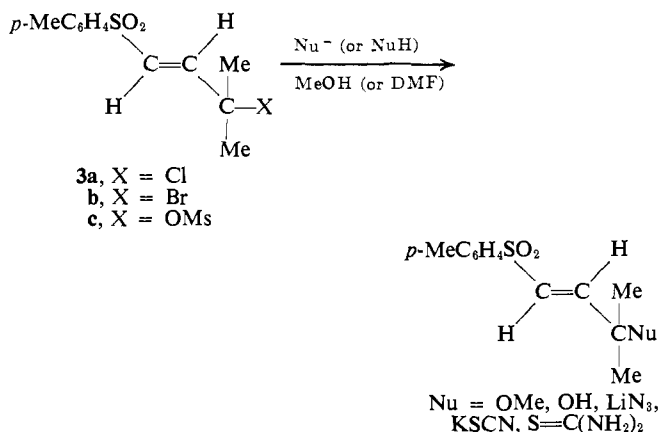
Table I. Comparisons of SN2 Reactions at a Primary and a Tertiary Center

No.	Mechanistic probe	Relative response to mechanistic probe	
		Of RCH <sub>2</sub> X <sup>a,b</sup>	Of ArSO <sub>2</sub> CH=CHCMe <sub>2</sub> X <sup>b</sup>
1	$k^{rel}$ (LiN <sub>3</sub> in MeOH)	29 <sup>c</sup>	1.0
2	$k_{N_3^-}^{-60\% MeOH}/k_{N_3^-}^{-MeOH}$	1.7	6.9
3	Kinetic salt effect on $k_{N_3^-}$ (LiClO <sub>4</sub> in MeOH or 60% MeOH)	Negative <sup>d</sup>	Positive
4	$k_{N_3^-}^{-OMs}/k_{N_3^-}^{-Br}$ (in MeOH)	Ca. 0.2 <sup>d,e</sup>	260
5	$k_{N_3^-}/k_{S=C(NH_2)_2}$ (in 60% MeOH)	0.67	51
6	$k_{N_3^-}/k_{SCN^-}$ (in MeOH)	0.16 <sup>f</sup>	10 <sup>g</sup>
7	Product with KSCN (in MeOH) (in acetone)	>98% RSCN >98% RSCN Negligible <sup>i</sup>	[RSCN]:[RNCS] = 1.3:1.0 <sup>h</sup> [RSCN]:[RNCS] = 1.3:1.0 1.22-fold retardation per CD <sub>3</sub> group <sup>h</sup>
8	$\beta$ -Deuterium isotope effect <sup>i</sup> (LiN <sub>3</sub> in 60% MeOH)		
9	$\beta$ -Deuterium isotope effect <sup>i</sup> (solvolysis in 60% MeOH)	1.02 <sup>i</sup>	1.37 <sup>m</sup>
10	$k^{OMs}/k^{Br}$ (in 60% MeOH)	11 <sup>n</sup>	12,600 <sup>o</sup>

<sup>a</sup> R = C<sub>6</sub>H<sub>5</sub>SO<sub>2</sub>CH=CH (i.e., RCH<sub>2</sub>X = 1) unless otherwise noted. <sup>b</sup> X = Br unless otherwise noted. <sup>c</sup> The rate for the corresponding secondary bromide 2 is 2.9 times slower; for 3b,  $k = 9.0 \times 10^{-4} M^{-1} sec^{-1}$  at 50°. <sup>d</sup> Typical of a primary bromide. <sup>e</sup> Based on the behavior of 1 with PhNH<sub>2</sub> and S=C(NH<sub>2</sub>)<sub>2</sub>. <sup>f</sup> For MeBr in H<sub>2</sub>O; for MeI in MeOH the value is 0.15 [see R. G. Pearson, H. Sobel, and J. Songstad, *J. Amer. Chem. Soc.*, **90**, 319 (1968)]. <sup>g</sup> Based on product analysis [>98% RN<sub>3</sub> plus <2% ROME as compared to 43% RSCN (and RNCS) plus 57% ROME]. <sup>h</sup> X = OMs. <sup>i</sup> We are indebted to Dr. P. F. Wiley for the preparation of deuterated sample. <sup>j</sup> Expected for a primary bromide. <sup>k</sup> In MeOH the effect is 1.10 per CD<sub>3</sub>. <sup>l</sup> EtBr in H<sub>2</sub>O. <sup>m</sup> For mesylate 3c the value is 1.33 ± 0.01 in MeOH and 1.34 ± 0.01 in 80% MeOH. <sup>n</sup> MeX in 80% EtOH. <sup>o</sup>  $k^{Br} = 1.03 \times 10^{-4} sec^{-1}$  at 50°.

ample of a second-order reaction at a tertiary center to give a good yield of substitution product that has come to our attention is that of tris(*p*-nitrophenyl)methyl chloride with azide ion or (radioactive) chloride ion;<sup>4</sup> here the structure of the halide precludes an E2 reaction.

In sharp contrast to the behavior of most tertiary systems we have found that the tertiary allylic chloride (3a), bromide (3b), and mesylate (3c) undergo substitu-



tion reactions, accompanied by only small amounts of elimination, with a variety of weakly basic nucleophiles in both protic and dipolar aprotic solvents. Furthermore, the reactions with LiN<sub>3</sub> (in MeOH and DMF), PhNH<sub>2</sub> (in MeOH), and S=C(NH<sub>2</sub>)<sub>2</sub> (in MeOH) are first order in substrate 3 and first order in nucleophile. Detailed studies involving comparisons with primary (and secondary) substrates corresponding to 3 in structure (1 and 2, respectively) have been made; these studies provide strong circumstantial evidence for ion-pair SN2, rather than classical SN2, mechanisms for these reactions of 3 (Table I).

The possible existence of a mechanism wherein the rate-limiting step is attack by a nucleophile on an ion pair, which is in equilibrium with the covalent sub-

(4) A. Miotti and A. Fava, *J. Amer. Chem. Soc.*, **88**, 4274 (1966).

strate, has been recognized for some time.<sup>5</sup> Although circumstantial evidence has been presented for the operation of this ion-pair SN2 mechanism in a number of systems,<sup>6</sup> even a detailed kinetic analysis<sup>6</sup> has failed to distinguish between this and a classical SN2 mechanism involving the covalent substrate.<sup>7,8</sup> Our evidence for this mechanistic assignment for 3 reacting with various nucleophiles, particularly azide ion, in protic solvents is based on: (1) an appreciable increase in rate with increased solvent ionizing power (Table I, probe 2), (2) a positive salt effect (probe 3) (this is atypical of an SN2 mechanism), (3) a  $k^{OMs}/k^{Br}$  leaving ratio > 1 (probe 4) (this is the reverse of that for the SN2 mechanisms),<sup>9</sup> (4) a greater reactivity of 3b toward the negatively charged azide ion than toward S=C(NH<sub>2</sub>)<sub>2</sub> (probe 5) (this is opposite to the behavior of primary halides), (5) a greater reactivity of 3b toward N<sub>3</sub><sup>-</sup> than toward SCN<sup>-</sup> (probe 6), (6) formation of appreciable amounts of RNCS products from the reaction of 3b (or 3c) with KSCN under conditions where product formation is kinetically controlled (probe 7),<sup>10</sup> and (7) an appreciable  $\beta$ -deuterium isotope effect in 60% MeOH (probe 8). A more detailed analysis, which will be given in the full paper, indicates that the reactions of bromide 3b with nucleophiles may involve principally intimate ion pairs and, to some extent, the covalent bromide, whereas the reactions of mesylate 3c may involve principally sol-

(5) (a) S. Winstein, A. Ledwith, and M. Hojo, *Tetrahedron Lett.*, 341 (1961); (b) J. Hine, "Physical Organic Chemistry," McGraw-Hill, New York, N. Y., 1963, p 138.

(6) See R. A. Snee and J. W. Larsen, *J. Amer. Chem. Soc.*, **91**, 362 (1969), and references cited therein.

(7) B. J. Gregory, G. Kohnstam, M. Paddon-Row, and A. Queen, *Chem. Commun.*, 1032 (1970).

(8) D. J. Raber, J. M. Harris, R. E. Hall, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **93**, 4821 (1971).

(9) H. M. R. Hoffmann, *J. Chem. Soc.*, 6753 (1965).

(10) Primary halides give essentially 100% RSCN.<sup>11</sup> On the other hand, *tert*-BuCl reacting with KSCN in water at 38° gave [RSCN]:[RNCS] = 2.5:1.0.<sup>12</sup>

(11) A. Fava, A. Illiceto, A. Ceccan, and P. Kock, *J. Amer. Chem. Soc.*, **87**, 1045 (1965), and references cited therein.

(12) L. G. Cannell and R. W. Taft, Jr., Abstracts, 129th National Meeting of the American Chemical Society, Dallas, Tex., April, 1956, p 46N.

vent-separated ion pairs and, to some extent, free ions.<sup>13</sup>

If one accepts the ion-pair SN2 mechanism for the reactions of **3** with weakly basic nucleophiles in protic solvents, one would expect that solvolyses of **3** would also occur *via* ion pairs. This view is supported by the observation that changing the solvent for the reaction of bromide **3b** with LiN<sub>3</sub> from MeOH to 60% MeOH changed the kinetic order from second order to mixed order. For the reaction in 60% MeOH a plot of the pseudo-first-order rate constant  $k_{\text{obsd}}$  vs. [N<sub>3</sub><sup>-</sup>] was linear, as expected for a reaction where the azide and solvolysis products are derived from a common precursor.<sup>6</sup> From the kinetic analysis,  $k_N/k_S = 2180$ , which compared well with the value of 2150 derived from a product analysis. In MeOH,  $k_N/k_S \cong 6000$  for **3b** and *ca.* 120 for mesylate **3c**. The view that the common precursors for the azide and solvolysis products are ion pairs was given strong support by the observation of a large  $\beta$ -deuterium isotope effect<sup>14</sup> and a large  $k^{\text{OMs}}/k^{\text{Br}}$  leaving group effect<sup>9</sup> for solvolyses in 60% MeOH (probes 9 and 10, respectively).

The success of the tertiary allylic system **3** in evoking ion-pair SN2 mechanisms, relative to *tert*-alkyl systems, probably depends on: (a) the electron-withdrawing effect of the C<sub>7</sub>H<sub>7</sub>SO<sub>2</sub> group, which is sufficient to inhibit ion-pair dissociation, but not ion-pair formation, (b) the delocalizing effect of the vinyl group, which decreases the positive charge on the protons of the methyl groups in **3**, and thus decreases the tendency toward elimination, and (c) the smaller steric effect resulting from replacement of an alkyl group by a vinyl group, which facilitates nucleophilic attack on the cation and may inhibit elimination.<sup>15</sup>

**Acknowledgment.** We are grateful to Professor V. J. Shiner, Jr., for a number of helpful discussions.

(13) The Winstein ionization scheme is assumed. See V. J. Shiner, Jr., and R. D. Fisher, *J. Amer. Chem. Soc.*, **93**, 2553 (1971), for a recent elaboration of this scheme.

(14) This value is close to that observed for near Lim solvolyses (*e.g.*, for *tert*-BuCl in water the value is 1.37 per CD<sub>3</sub>). See E. R. Thornton, "Solvolysis Mechanisms," Ronald Press, New York, N. Y., 1964, for a discussion.

(15) As a corollary it should be noted that the elimination reactions which accompany these ion-pair SN2 reactions no doubt occur by ion-pair E2 mechanisms. In our opinion, ion-pair E2 mechanisms, rather than concerted E2 mechanisms, are responsible for the second-order components which commonly appear in the rate expressions when high concentrations of lyate ion are introduced into solvolysis reactions of tertiary halide (or like) substrates.

(16) National Institutes of Health Predoctoral Fellow, 1958–1971.

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## A Novel Antiferromagnetic Oxo-Bridged Manganese Complex

Sir:

An insight into antiferromagnetic interactions is provided by our study of the novel complex di- $\mu$ -oxo-tetrakis(2,2'-bipyridine)dimanganese(III,IV) perchlorate trihydrate. This unusual complex contains two manganese atoms in different oxidation states bridged by two oxygen atoms; one of the manganese atoms is subject to "Jahn-Teller distortions." Thus, a unique labeling of one manganese atom gives results that pro-

