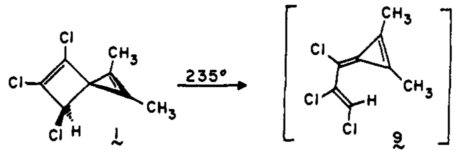
to an exceedingly labile substance which polymerizes on the cold collector surface as an amorphous, insoluble solid. The product expected from cyclobutene ring opening is 3-(1,2,3-trichloro-2-propenylidene)-1,2-dimethylcycloprop-1-ene (**9**), which, if formed during pyrolysis, must be very sensitive toward self-polymerization. A few stabilized derivatives of methylenecyclopropene have been isolated,[5] but a propensity toward self-condensation is not surprising for a relatively simple derivative such as **9**. In an nmr sample tube (CCl_4), the spirodiene **1** disappears with a half-life of 17 hr/25° (10 min/70°). During the initial stages of the reaction, transient singlets appear in the ^1H nmr spectrum at δ 6.25 (1 H) and 2.33 (6 H), each somewhat broadened, consistent with structure **9**. However, as the concentration of the new product rises, its rate of disappearance increases; after 40 min at 75°, the ^1H nmr spectrum shows no signals attributable to **1** or **9**. The final product is nonvolatile and could not be characterized.



The significantly lower temperature required for rearrangement of **3** compared to **2** is consistent with a concerted opening of the cyclobutene ring in the symmetry-allowed conrotatory fashion. Spirocycle **2** has two distinct transition states for conrotatory opening; in one case (leading to **10a**) the *gem*-dimethyl groups and the methine hydrogen at C-6 are involved in an unfavorable steric interaction, while in the alternative (leading to **10b**), the chlorine at C-6 and the cyclopropylmethylene group interact. However, the temperature necessary to cause ring opening of **2** is high enough to bring about rapid rearrangement of the intermediate **10**, probably *via* the trimethylenemethane diradical[7] **11**. Further reaction can occur from either of two conformations of the diradicals **11a** and **11b**,[14] one leading to **5** and the other leading to an isomeric methylenecyclopentene (**12**) which loses hydrogen chloride spontaneously during pyrolysis to give **4**.

Spirocycle **3**, on the other hand, can undergo concerted ring opening *via* a transition state with small steric interaction of the C-6 hydrogen and the cyclopropylmethylene group, and thus rearranges to **8** at modest temperature. Higher temperatures convert **8** to the diradical **11c**, which, in light of the observed products **4** and **5**, must equilibrate with **11a** at a rate faster than the rate of ring closure.[13]

Low-temperature matrix isolation techniques are expected to allow characterization of **9** and provide the first study of a methylenecyclopropene with simple substituents.

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(14) Additional geometrical isomers of **11** are also possible intermediates, arising through cis–trans isomerization of either of the double bonds. In the delocalized diradical **11**, the double bonds have bond order considerably less than two and rapid rotation at the pyrolysis temperature would not be unexpected.

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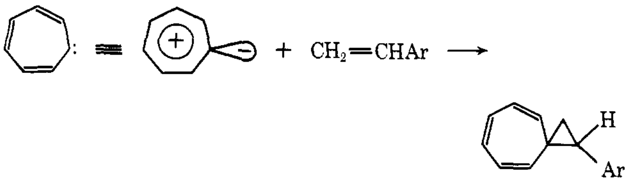
Reactivity of Cycloheptatrienylidene with Substituted Styrenes

Sir:

Suppression of the electrophilic character of a carbene with enhancement of its nucleophilic properties is expected if the vacant p orbital, which is presumed to initiate "electrophilic" attack on multiple bonds,[1] is incorporated into a ring in such a way as to make it an integral part of a "$4n + 2$" π-electron system.[2] Two examples of such carbocyclic aromatic carbenes, diphenylcyclopropenylidene and cycloheptatrienylidene, have been generated in this laboratory[3] and in each case have been found to show low reactivity with normal double bonds. Although suppression of reactivity with typical double bonds has been qualitatively identified[3,4] with nucleophilicity of carbenes, a more quantitative determination of charge distribution in the transition states of reactions of this type was certainly desirable.

With the recent discovery[5] that cycloheptatrienylidene adds to styrene, a Hammett study of the addition to double bonds became possible. At this time we report the results of such a study. The relative reactivities were determined by a competitive method in which two styrenes were allowed to compete for a limited amount of the carbene. In a typical run, the sodium salt of 2,4,6-cycloheptatrienone *p*-toluenesulfonylhydrazone was added slowly to an eight- to tenfold excess of the mixture of styrenes in dry THF while being photolyzed with a 550-W Hanovia lamp through a Pyrex filter.



The relative reactivities of the styrenes were then calculated by the equation[6]

$$k_{\text{rel}} = \frac{k_X}{k_H} = \frac{P_X I_H}{P_H I_X}$$

where P_X and P_H are the moles of product derived from styrene X and H, respectively, and I_X and I_H are the initial moles of substituted and unsubstituted styrenes. The validity of this equation depends on maintaining an essentially constant ratio of the olefins and preclusion of subsequent reaction of the adducts under the

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(1) P. S. Skell and A. Y. Garner, *J. Amer. Chem. Soc.*, **78**, 5430 (1956); J. Hine, "Divalent Carbon," The Ronald Press, New York, N. Y., 1964, p 43; W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964, p 164; R. Hoffmann, *J. Amer. Chem. Soc.*, **90**, 1475 (1968).

(2) For a theoretical treatment of the nucleophilicity of this type of carbene, see R. Gleiter and R. Hoffmann, *ibid.*, **90**, 5457 (1968).

(3) W. M. Jones, M. E. Stowe, E. E. Wells, Jr., and E. W. Lester, *ibid.*, **90**, 1849 (1968); W. M. Jones and C. L. Ennis, *ibid.*, **91**, 6391 (1969), and references cited therein.

(4) D. M. Lemal, E. P. Grosselink, and S. D. McGregor, *ibid.*, **88**, 582 (1966); H. Quast and S. Hunig, *Chem. Ber.*, **99**, 2017 (1966); A. G. Brook, H. W. Kucera, and R. Pearce, *Can. J. Chem.*, **49**, 1618 (1971).

(5) Unpublished work of K. Untch, Syntex Corp., and E. Waali, University of Florida. We are indebted to Dr. Untch for communicating his results prior to publication.

(6) W. von E. Doering and W. A. Henderson, *J. Amer. Chem. Soc.*, **80**, 5274 (1958).

Table I. Relative Rate Constants for the Addition of Cycloheptatrienylidene to Substituted Styrenes, $XC_6H_4CH{=}CH_2$

X in $XC_6H_4CHCH_2$	k_X/k_H[a]
4-OCH_3	0.51
4-CH_3	0.57
H	1.00
4-Cl	1.59[b]
4-Br	1.68
3-Br	2.22

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

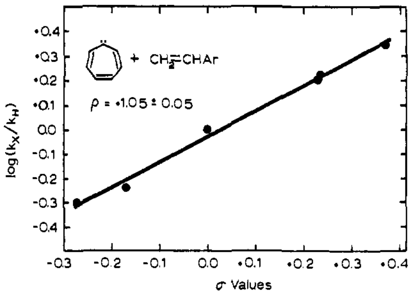
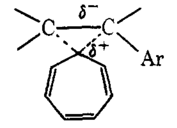


Figure 1. Log k_X/k_H *vs.* σ values for the reaction of 2,4,6-cycloheptatrienone *p*-toluenesulfonylhydrazone sodium salt derived cycloheptatrienylidene with substituted styrenes.

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.[7,8] 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.[9] The relative rate constant data correlate well with the Hammett equation using primary σ values (Figure 1). The ρ value was computed by a least-squares analysis to be $+1.05 \pm 0.05$ with a correlation coefficient of 0.982. This positive ρ value provides the first quantitative demonstration of the nucleophilicity of a carbocyclic aromatic carbene. It is interesting to compare this ρ value with ρ values reported in the literature for other carbenes. In similar competitive experiments the ρ value for dichlorocarbene was reported to be -0.619[10] at 80° and independently determined to be -0.378[11] at 0°. The ρ value for carbethoxycarbene has been reported as -0.38 at 129°.[12] The change in sign in going from a typical electrophilic carbene such as dichlorocarbene to a perturbed carbene such as cycloheptatrienylidene 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 basis on which to make judgments concerning the nucleophilicities of carbenes, is now under intensive investigation.



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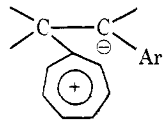

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Acknowledgment. The authors gratefully acknowledge the support of this work received from the National Science Foundation.

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[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).

[13] Participant in the NSF College Teachers Summer Research Participation Program.

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Ion-Pair SN2 Reactions at a Tertiary Center

Sir:

Second-order nucleophilic substitutions (SN2 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.[1] Reactions of *tert*-BuBr with LiCl or LiBr in acetone, which at one time were claimed to proceed by SN2 mechanisms, later were shown to be elimination–addition reactions, the supposed second-order component being a positive salt effect on the elimination reaction.[2] 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 SN2 mechanisms.[3] The only ex-

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[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.