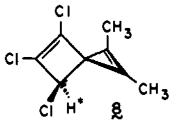
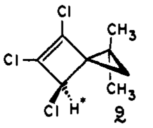
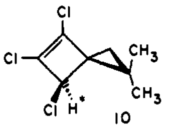
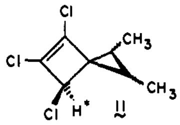
A more sensitive and proven method of measuring the rate of anion formation is the determination of kinetic acidity by base-catalyzed proton abstraction. In practice, a simple and accurate procedure involves measurement of the rate of loss of tritium from the carbon of interest in the presence of base.[8] For this experiment, a series of labeled spirocycles **8**–**11** were prepared by electrolytic replacement of chlorine with tritium-enriched hydrogen: **4** gave **8**, **5** gave **9** and **10** (separable by glpc), and **6** gave **11a** and **11b** (an inseparable mixture).[7] All were obtained with high specific activity, $>10^6$ cpm/mg (Packard Tri-Carb scintillation spectrometer).

The rates of tritium loss were determined on 5.0-μl samples (*ca.* 3×10^{-4} *M*) of the labeled spirocycles at 25° in homogeneous aqueous solution containing 0.20 *M* sodium hydroxide and 38 mol % dimethyl sulfoxide. The pseudo-first-order rate constants were calculated[9] and converted to second-order rate constants which are presented in Table I.

Table I

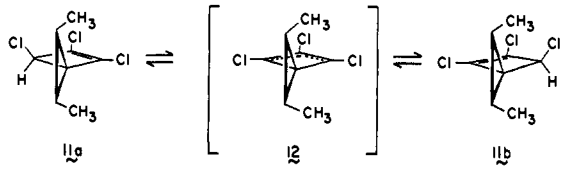
Spirocycle	Second-order rate constant (l. mol^{-1} sec^{-1}) $\times 10^5$
 **8**	4.6 ± 0.2[a]
 **9**	24.14 ± 0.05[b]
 **10**	2.03 ± 0.04[b]
 **11**	5.70 ± 0.05[c,d]
	H* is enriched in tritium

[a] The rate constant was extracted from six parallel kinetic runs. Data were collected for only 300 min due to the known (M. F. Semmelhack and R. J. DeFranco, *J. Amer. Chem. Soc.*, **94**, 2116 (1972)) thermal instability of **8**. [b] The rate constant was extracted from two parallel kinetic runs. Data were collected for 2000 min. [c] The rate constant was extracted from four parallel kinetic runs. Data were collected for 2000 min. [d] This entry represents an experiment using a mixture of the two *cis*-1,2-dimethyl isomers (75% **11a** and 25% **11b**).

The spiro[2.3]hex-4-enes (**9**–**11**), where spiroaromaticity is not possible, were studied to provide comparison with **8** and as probes of the steric effect of substituents on the cyclopropyl ring. The data show that the rate constants are relatively insensitive to steric factors; the largest difference, surprisingly between the epimers **9** and **10**, is a factor of only 12. Therefore, while proton abstraction from spiro[2.3]hexadiene **8** is certain to have steric interactions different from the same reaction of the spiro[2.3]hex-4-enes, we feel that the differences are likely to be small.

The data provide clear evidence that spiroaromaticity is *not* an important stabilizing factor in anion **7**. Among possible explanations are the following: (1) the anion derived from **8** is not planar so that spiro interaction is minimized; (2) the chlorine substituents interact strongly to stabilize the anion, decreasing the effect of spiroaromaticity; and (3) overlap of π-orbital ribbons in the spiro [2.3] rings is not significant—there is no spiroaromaticity.

The following experiment lends strong support to the supposition that the anions in these systems are indeed planar. A mixture of 40% **11a** and 60% **11b** (^{1}H nmr analysis[10]) was subjected to the basic medium (sodium hydroxide–water–dimethyl sulfoxide) used for kinetic runs for 30 hr at 25°. The spirocycles were recovered in 80% combined yield with the composition 75% **11a** and 25% **11b**; the isomers thus interconvert *via* an intermediate with the symmetry of anion **12**.


11a **12** **11b**

It is not now possible to provide definitive evidence concerning the effect of chlorine substituents in minimizing spiroaromatic stabilization. However, anion **7** is not a highly stabilized species—the pK_a of **8** is $\sim$32.[11] Propene, the simplest allylic system, has been estimated[12] to have a pK_a of 35.5. There are significant structural differences between the anion from propene and the anion **7**, but an estimated difference in pK_a of 3–4 units due to stabilization by the chlorine substituents is not unreasonable.

Acknowledgment. We are indebted to Professor F. A. Long for his cooperation with this work, and to the National Institutes of Health and the du Pont Company (Young Faculty Grant) for financial support.

---

[8] E. Halevi and F. A. Long, *J. Amer. Chem. Soc.*, **83**, 2809 (1961).

[9] A nonlinear least-squares program (MAXLIK) prepared by R. Williamson and modified by M. J. Goldstein was generously provided by Professor Goldstein. We are indebted to Professor Goldstein for his assistance with the calculations.

[10] The mixture was obtained from the reaction of 3*H*-pentachlorocyclobutene, *n*-butyllithium, and *cis*-2-butene.[7]

[11] Unpublished results of F. A. Long and Z. Margolin indicate that the rate constant for detritiation of $CHCl_3$ is faster than that of **8** by a factor of 10^8, in the same medium. Assuming that protonation of the anions is diffusion controlled, the pK_a values must also differ by eight units. The pK_a of chloroform is estimated by the same workers at $\sim$24, so the pK_a of **8** must be $\sim$32.

[12] D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965, p 19.

[13] Monsanto Summer Fellow, 1969; Shell Summer Fellow, 1970.

M. F. Semmelhack,* R. J. DeFranco,[13] Z. Margolin, J. Stock
Department of Chemistry, Cornell University
Ithaca, New York 14850

Received December 18, 1971

Thermal Rearrangements of Spiro[2.3]hex-4-enes and Spiro[2.3]hexadienes

Sir:

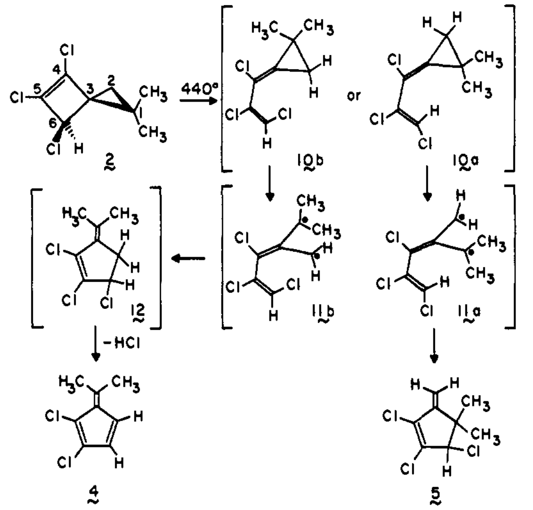
The thermal rearrangement properties of the spirocycles[1] **1**–**3** are of interest in several respects. They are

---

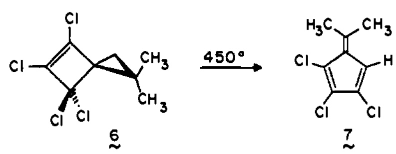
[1] M. F. Semmelhack, R. J. DeFranco, and J. Stock, submitted for publication elsewhere.

the only known unsaturated representatives of this ring system and contain 60–90 kcal/mol of bond angle strain energy,[2] with a symmetry-allowed concerted pathway to partial relief of strain *via* electrocyclic opening of the cyclobutene ring.[4] The products of ring opening would be a methylenecyclopropene (from **1**) and a propenylidenecyclopropane (from **2** and **3**), both of current interest.[5] Careful consideration of the thermal stability is also crucial to the study of the kinetic acidity of the spirocycles, which is reported in the accompanying communication.[8]

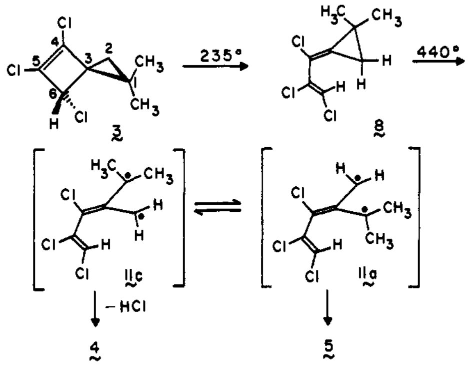
Pyrolyses were carried out in a gas-phase flow system consisting of a glass tube wrapped with Briskat heavy-duty heating tape and filled with glass helices. The sample was distilled through the hot tube at 0.01 Torr and the products were collected at −196° in a special apparatus that allows transfer to an nmr sample tube without exposure to air or warming to ambient temperature.



When samples of **2** were distilled through the pyrolysis apparatus at various temperatures, it was observed that 4,4-dimethyl-3-methylene-1,2,5-trichlorocyclopent-1-ene[9] (**5**) and 2,3-dichloro-6,6-dimethylfulvene (**4**) began to appear at 360°; conversion to the same two products (ratio **4**:**5** = 1:3.3) was complete at 440°. The structural assignments for **4** and **5** rest primarily on spectral data. The fulvene **4** is unstable toward air oxidation and self-polymerization;[10] ^{1}H nmr (CCl$_4$) δ 6.52 (d, 1 H, J = 6 Hz), 6.23 (d, 1 H, J = 6 Hz), 2.45 (s, 3 H), 2.23 (s, 3 H). For compound **5**, ^{1}H nmr (CCl$_4$) δ 5.35 (s, 1 H), 5.04 (s, 1 H), 4.61 (s, 1 H), 1.35 (s, 3 H), 1.28 (s, 3 H); uv max (isooctane) 247 nm (ε 15,000). The infrared spectrum shows the characteristic strong absorption of terminal methylene groups at 885 cm^{-1}. By the same technique, at 450°, 1,1-dimethyl-4,5,6,6-tetrachlorospiro[2.3]hex-4-ene[11] (**6**) gave only the corresponding fulvene (**7**, 40% yield), a relatively stable yellow solid[9] (mp 23–25° from *n*-pentane): ^{1}H nmr (CCl$_4$) δ 6.50 (s, 1 H), 2.45 (s, 3 H), 2.20 (s, 3 H); uv max (isooctane) 284 (ε 15,600), 291 (15,300), 303 sh (8350), and 378 nm (394).[12]



The spirocycle **3**, differing from **2** only in the configuration at C-6, rearranges at much lower temperature. Pyrolysis at 235° gives 50% conversion to 2,2-dimethyl-1-(1,2,3-trichloro-2-propenylidene)cyclopropane[9,13] (**8**): ^{1}H nmr (CCl$_4$) δ 7.06 (t, 1 H, J = 0.8 Hz), 1.32 (s, 6 H), 1.25 (d, 2 H, J = 0.8 Hz); uv max (isooctane) at 246 (ε 22,300), 253 sh, (18,300), and 239 nm sh (18,500). At higher temperature (440°), comparable to that necessary for rearrangement of **2**, a sample of **8** rearranges to give a mixture of **4** and **5** (1:3.5). As expected, **4** and **5** are produced directly from **3** at 435°.



The rearrangement **3** → **8** is also observed directly in solution. Spirocycle **3** has a half-life of 36 hr at 135° in carbon tetrachloride, monitored by ^{1}H nmr. The peaks characteristic of **8** grow into the spectrum reaching maximum intensity after 25 hr and then disappear with time to leave an intractable mixture, probably arising from polymerization of **4**.

The spirodiene **1** is even more labile. Flow pyrolysis at 225° (0.01 Torr) causes complete rearrangement of **1**

---

(2) Assuming additivity of strain effects, the minimum strain energy of 1 is about 73 kcal/mol (47 kcal/mol for 1,2-dimethylcyclopropene[3] and 26 kcal/mol for cyclobutene[3]). However, constraint of these two systems to a spiro arrangement would undoubtedly contribute additional strain; the observed strain energy of spiropentane is 61.4 kcal/mol compared to 55 kcal/mol for two isolated cyclopropane rings.[3]

(3) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1970, p 461.

(4) R. B. Woodward and R. Hoffmann, "Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1969, p 43.

(5) Derivatives of methylenecyclopropene are known with substituents capable of strong electronic interaction,[6] but no derivatives with relatively simple substituents have been isolated. Propenylidenecyclopropanes have been the subject of recent studies because of their facile thermal rearrangement.[7]

(6) For a number of examples, see (a) A. W. Krebs, *Angew. Chem., Int. Ed. Engl.*, **4**, 10 (1965); (b) E. D. Bergmann, *Chem. Rev.*, **68**, 41 (1968); (c) Z. Yoshida and Y. Tawara, *Tetrahedron Lett.*, 3613 (1971).

(7) W. R. Roth and Th. Schmidt, *ibid.*, 3639 (1971), and references therein.

(8) M. F. Semmelhack, R. J. DeFranco, Z. Margolin, and J. Stock, *J. Amer. Chem. Soc.*, **94**, 2115 (1972).

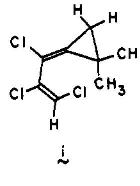
(9) The composition of this compound was verified by high-resolution mass spectrometry on an AEI Model MS-902 instrument.

(10) Due to the instability of 4, a pure sample could not be obtained. The spectral data were measured on a mixture of 4 and 5; pure 5 was isolated by preparative layer chromatography.

(11) M. F. Semmelhack and R. J. DeFranco, *Tetrahedron Lett.*, 1061 (1971).

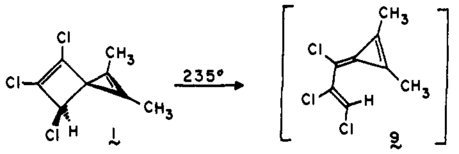
(12) The uv maxima are characteristic of fulvenes; *cf.* E. D. Bergmann, *Progr. Org. Chem.*, **3**, 81 (1955).

(13) An alternative product is i, consistent with conservation of orbital symmetry but arising *via* a more hindered transition state compared to that for 8, as detailed in the discussion of mechanism. No data have been obtained which distinguish 8 from i.



i

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 ^{1}H 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 ^{1}H 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.

[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.

[15] Monsanto Summer Fellow, 1969; Shell Summer Fellow, 1970.

[16] We are pleased to acknowledge financial support from the National Institutes of Health, Eli Lilly and Company, and the Merck Foundation.

M. F. Semmelhack,* R. J. DeFranco[15,16]
Department of Chemistry, Cornell University
Ithaca, New York 14850

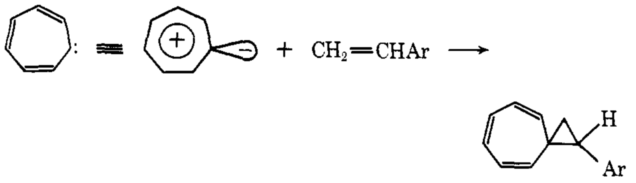
Received December 18, 1971

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

[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).