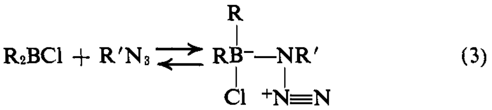
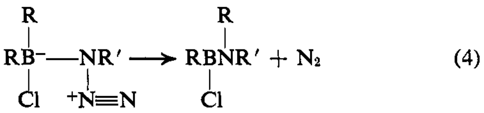
tained 6.2 g (74%) of cyclohexylcyclopentylamine: bp 83.0–83.5° (2.4 mm); $n^{20}D$ 1.4796 (lit.[7] bp 118–120° (17 mm)).

Primary dialkylchloroboranes and primary azides react smoothly at room temperature. Others require higher temperature. Addition of the azide at room temperature followed by distillation of the ether and slowly raising the temperature to refluxing toluene allows one to gradually increase the rate of reaction to bring it to completion.

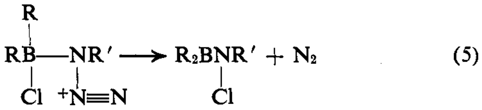
The increased reactivity of the dialkylchloroboranes may be attributed to the increased Lewis acidity. The reaction presumably involves reversible coordination of the azide with the borane (eq 3), followed by a transfer from boron to nitrogen. Whether there is alkyl group (eq 4) or chloride (eq 5) migration has not as yet been established. Chloride migration would produce an intermediate, which upon attack by a nucleophile, X^-, could undergo alkyl group migration (eq 6), as may occur in the reaction of trialkylboranes with chloramine.[8]



$$R_2BCl + R'N_3 \rightleftarrows \overset{R}{\underset{Cl}{RB^-}}\text{—}\underset{{}^+N\equiv N}{NR'} \qquad (3)$$



$$\overset{R}{\underset{Cl}{RB^-}}\text{—}\underset{{}^+N\equiv N}{NR'} \longrightarrow \overset{R}{\underset{Cl}{RB}}NR' + N_2 \qquad (4)$$



$$\overset{R}{\underset{Cl}{RB}}\text{—}\underset{{}^+N\equiv N}{NR'} \longrightarrow \underset{Cl}{R_2B}NR' + N_2 \qquad (5)$$

$$\underset{Cl}{R_2B}NR' + X^- \longrightarrow R\underset{X}{B}\underset{R}{N}R' + Cl^- \qquad (6)$$

Irrespective of the precise nature of the reaction mechanism, the dialkylchloroboranes provide a remarkably facile method of achieving reactions which are very sluggish with trialkylboranes. This increased reactivity suggests that it may be possible to achieve with dialkylchloroboranes many other types of reactions which have either been sluggish or have failed with trialkylboranes. We are continuing to explore these developments.

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(7) K. Jewers and J. McKenna, *J. Chem. Soc.*, 2209 (1958).

(8) H. C. Brown, W. R. Heydkamp, E. Breuer, and W. S. Murphy, *J. Amer. Chem. Soc.*, **86**, 3568 (1964).

(9) National Science Foundation Predoctoral Fellow.

(10) Postdoctorate research associate on Grant No. GM 10937 from the National Institutes of Health.

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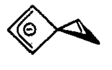
Received November 15, 1971

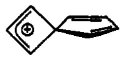
Kinetic Acidity as a Probe for Spiroaromaticity in a Spiro[2.3]hexadiene

Sir:

The electronic spectra of certain spirocycles[1] have been interpreted in terms of π-orbital interaction between the spiro-connected rings, an effect called spiroconjugation.[1] The ground states of particular spirocycles, called spirenes,[1b] with continuous ribbons of p orbitals in each ring,[2] are expected to be specially stabilized, a manifestation of spiroaromaticity. The effect should be noted in the stability of certain anions (*e.g.*, **1**), cations (*e.g.*, **2**), and diradicals (*e.g.*, **3**). Compared to the overlap of adjacent p orbitals in a benzene ring, the overlap between spirocyclic π systems is estimated at 20%.[1a,b] No previous study of spiroaromaticity in species **1–3** or related compounds has been reported.



1



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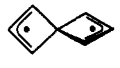
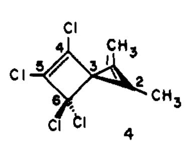


3

Part of the reason for the paucity of information is the absence of appropriate molecules from which to generate **1**, **2**, or **3**. We recently uncovered a simple route to the first examples of the spiro[2.3]hex-4-ene and spiro[2.3]hexadiene ring systems (*e.g.*, **4–6**)[3] and have therefore undertaken to test for spiroaromaticity in **7**, a derivative of anion **1**. Anion **7** is kinetically unstable, apparently undergoing α elimination of chloride anion and irreversible reaction of the resulting carbene,[4] which complicates the direct determination of the thermodynamic stability. Therefore, we studied the relative rates of formation of anion **7** and the corresponding anions of **5** and **6** where spiroaromaticity is not possible.



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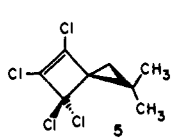

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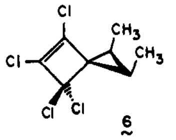

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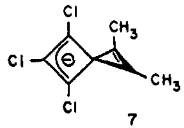

7

Polarographic half-wave potentials for reduction of carbon–halogen bonds have been related to the stability of the resulting carbanions,[5] although in the case of benzylic halides, the half-wave potential seems to reflect the stability of the carbon radical rather than the carbanion.[5b] In acetonitrile, with 0.1 *M* tetraethylammonium perchlorate, the spirocycles **4**, **5**, and **6** show similar two-electron reduction half-wave potentials (1.68 ± 0.03 for **4**, 1.58 ± 0.02 for **5**, and 1.62 ± 0.02 V for **6**, relative to the saturated calomel electrode).[6] Thus the spiroaromaticity of **7** is *not* a significant factor in the rate of electrolytic formation of **7**; in fact, the polarographic results suggest that anion **7** is less easily formed than the anions from **5** and **6**.

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(1) (a) H. E. Simmons and T. Fukunaga, *J. Amer. Chem. Soc.*, **89**, 5208 (1967); (b) R. Hoffmann, A. Imamura, and G. D. Zeiss, *ibid.*, **89**, 5219 (1967); (c) R. Boschi, A. Dreiding, and E. Heilbronner, *ibid.*, **92**, 123 (1970).

(2) M. J. Goldstein and R. Hoffmann, *ibid.*, **93**, 6193 (1971).

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

(4) Attempts to metalate **4** with *n*-butyllithium at −30 to 0° followed by quenching with water gave no trace of **4** or **8**.

(5) (a) P. Zuman, *Collect. Czech. Chem. Commun.*, **25**, 3225 (1960); (b) A. Streitwieser and C. Perrin, *J. Amer. Chem. Soc.*, **86**, 4938 (1964); (c) F. L. Lambert, *J. Org. Chem.*, **31**, 4184 (1966).

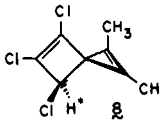
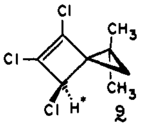
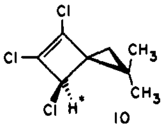
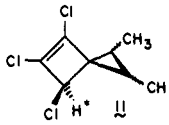
(6) Preparative-scale electrolyses in acetonitrile containing 0.1 *M* tetraethylammonium perchlorate under conditions parallel with the polarographic experiments afforded the series of spirocycles **8–11** as the only products; thus, the half-wave potentials correspond to reduction of one of the allylic chlorine atoms.[7]

(7) M. F. Semmelhack, R. DeFranco, and J. Stock, submitted for publication elsewhere.

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

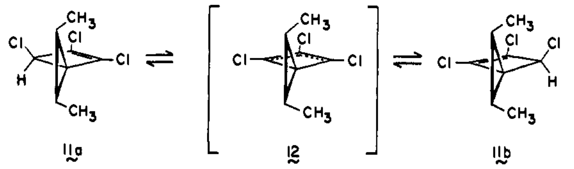
Spirocycle	Second-order rate constant (l. mol^{-1} sec^{-1}) $\times 10^5$
 **8**	4.6 ± 0.2^a
 **9**	24.14 ± 0.05^b
 **10**	2.03 ± 0.04^b
 **11**	$5.70 \pm 0.05^{c,d}$
	H* is enriched in tritium

[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**.



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 ~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.

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(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 ~24, so the pK_a of **8** must be ~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.

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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

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(1) M. F. Semmelhack, R. J. DeFranco, and J. Stock, submitted for publication elsewhere.