Table II. Ratio of Shifts of the $NH_2$ to NH Proton Resonance of Guanosine (0.1 *M*) in DMSO

| Cation | Chloride | Bromide | Iodide |
|---|---|---|---|
| Li | 1.05[a] | 3.1[a] | |
| Na | 1.05[a] | ~3[a] | |
| K | ~1[a] | ~3[a] | |
| Mg | 0.93[b] | | |
| Ca | 1.02[b] | 2.44 | ~8.8 |
| Sr | 0.99[b] | 1.27 | |
| Ba | 1.09[b] | ~3[a] | |
| Zn | 0.65[b] | 0.23 | 0.33 |
| Cd | 0.16 | 0.19 | 0.17 |
| Hg | 0.61[b] | | |
| $Et_4N$ | 1.09[a] | | ~4 |
| $Bu_4N$ | | 2.9[a] | |

[a] From ref 8. [b] From ref 7.

guanosine and contribute to the complex formation of guanosine with both anion and cation. In general, one must consider that both the cations and the anions affect the interaction between the metal salts and the nucleosides in a complicated way.

## References and Notes

(1) M. Cohn, *Biochemistry*, **2**, 623 (1963).
(2) S. Ebashi, *J. Biochem.*, **50**, 236 (1961).
(3) W. Hasselbach and M. Makinose, *Biochemistry*, **2**, 333, 518 (1961).
(4) K. Fuwa, W. E. C. Wacker, R. Druyan, A. F. Bartholomay, and B. L. Vallee, *Proc. Nat. Acad. Sci. U.S.A.*, **46**, 1298 (1960).
(5) J. Sohma, S. Shimokawa, and K. Hotta, "Recent Development of Magnetic Resonance in Biological Systems", S. Fujiwara and L. H. Piette, Ed., Hirokawa Publishing Co., Tokyo, 1968, p 57.
(6) T. Yokono, S. Shimokawa, H. Fukui, and J. Sohma, *J. Chem. Soc. Jpn., Chem. Ind. Chem.*, **2**, 201 (1973).
(7) S. Shimokawa, H. Fukui, J. Sohma, and K. Hotta, *J. Am. Chem. Soc.*, **95**, 1777 (1973).
(8) C. H. Chang and L. G. Marzilli, *J. Am. Chem. Soc.*, **96**, 3656 (1974).
(9) S. M. Wang and N. C. Li, *J. Am. Chem. Soc.*, **90**, 5069 (1968).
(10) L. S. Kan and N. C. Li, *J. Am. Chem. Soc.*, **92**, 4823 (1970).
(11) K. C. Tewari, J. Lee, and N. C. Li, *Trans. Faraday Soc.*, **66**, 2069 (1970).
(12) D. M. Grant et al., *J. Am. Chem. Soc.*, **93**, 1880, 1887 (1971); **92**, 2386 (1970).
(13) D. T. Clark and J. W. Emsley, *Mol. Phys.*, **12**, 365 (1967).
(14) J. E. Bloor and D. L. Breen, *J. Am. Chem. Soc.*, **89**, 6835 (1967).
(15) A. Allerhand and E. A. Trull, *Annu. Rev. Phys. Chem.*, **21**, 317 (1970).

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*Received February 10, 1975*

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## Stabilization of Cyclopropenium Ion by Nonbenzenoid Aromatics. Triferrocenylcyclopropenium Ion and Diferrocenylcyclopropenone

*Sir:*

Recent interest in cyclopropenium ion chemistry has focused on the stabilization of the "aromatic" but highly strained $2\pi 3C$ ring system by appropriate electron-donating substitutents, particularly heteroatoms.[1-3] In a search for alternative substituents which are capable of delocalizing the positive charge of the three-membered ring, we have considered the ferrocenyl group. The rationale underlying this approach was inherent in the unusual stabilization of carbenium ions adjacent to metallocenes.[4,5] We report straightforward syntheses and various properties of cyclopropenium ion and cyclopropenone *totally* substituted by ferrocenyl groups: triferrocenylcyclopropenium perchlorate (**1**) and diferrocenylcyclopropenone (**2**). We note the remarkable collective effect of the three ferrocenyl groups in stabilizing the $C_3^+$ ring in **1**. Ferrocenyldiphenylcyclopropenium tetrafluoroborate has previously been described, including its crystal and molecular structure.[6,7]

The synthetic route of choice was the electrophilic substitution of aromatic substrates by trichlorocyclopropenium salts (method of West and Tobey),[8-10] applied in dichloromethane. Treatment of $C_3Cl_3^+AlCl_4^-$ with ferrocene (2 mol equiv) in $CH_2Cl_2$ (5 hr at −70 to −80° and 30 min at 20°) gave a dark red complex which was decomposed (−60°) with aqueous acetone (20%). Purification by dry column chromatography (silica gel, ethyl acetate, $R_f$ = 0.25) and recrystallization (benzene–petroleum ether 40–60°) afforded **2** as dark red crystals, mp 181° dec (yield, 7%; yield prior to recrystallization, 18%). Elemental analysis and spectral properties were all consistent with the formulation of **2**. The mass spectrum revealed the fragmentation $M\cdot^+$ (*m/e* 422, 6%) → $[M - CO]\cdot^+$ (*m/e* 394, 100%) (substantiated by appropriate metastable transitions). Ir, $\nu_{max}$ (KBr) 3095 (w), 2920 (w), 1850 (vs), 1820 (m), 1612 (vs), 1475 (s), 1105 (s), 892 (m), 839 (s), 815 (s), 727 (m), 514 (m), 496 (s), and 482 (s) $cm^{-1}$. Noteworthy are the infrared bands at 1850, 1820, and 1612 $cm^{-1}$ which are diagnostic for the cyclopropenone nucleus.[10-12] Uv, $\lambda_{max}$ (EtOH) 243 (log $\epsilon$ 4.15), 275 (4.08), 300 (4.08), 348 (3.71), and 477 nm (3.33). NMR:[13] $\delta$ ($CDCl_3$) 4.23 (10 H, s, 1′-H), 4.56 (4 H, t, $J$ = 2 Hz, $\beta - H$), and 4.83 (4 H, t, $J$ = 2 Hz, $\alpha - H$); $\delta$ ($C_6D_6$) 3.94 (10 H, s), 4.13 (4 H, s, broad), and 4.60 (4 H, s, broad). $\delta(\alpha - H)$, $\delta(\beta - H)$, $\Delta\delta(\delta(\alpha - H) - \delta(\beta - H))$, the benzene induced solvent shifts, and the pattern of the NMR spectra closely resemble those of ferrocenecarboxaldehyde.[14] The shift of $\delta(\alpha - H)$ to lower field is due mainly to the anisotropy of the cyclopropenone system, including the diamagnetic anisotropy of the carbonyl group. The electric dipole moment of **2**, 5.37 D (benzene, 30°, $\alpha' = 41.60$, $\beta' = 3.09$, $MR_{calcd} = 109.56$ $cm^3$, $P_{2\infty} = 689.4$ $cm^3$) was only slightly higher than the corresponding moment of diphenylcyclopropenone[10] (5.08 D). A substantial displacement of the (modest) positive charge from the three-membered ring into the ferrocenyl moieties was not observed.

The analogous reaction of $C_3Cl_3^+AlCl_4^-$ with 3 mol equiv of ferrocene in $CH_2Cl_2$ (3 hr at −70°, 16 hr at 23°, 2 hr reflux, decomposition at −60° by aqueous acetone (20%)) followed by treatment with perchloric acid (70%) led to **1**. Purification by dry column chromatography (microcrystalline cellulose, $CH_2Cl_2$–petroleum ether 40–60°) and recrystallization ($CH_2Cl_2$–petroleum ether 40–60°) gave **1** as dark red crystals, mp 171° dec (explosive) (yield, 38%).[15] Uv, $\lambda_{max}$ ($CH_2Cl_2$) 309 (log $\epsilon$ 4.42), 363 (3.98), and 520 nm (3.85). Ir, $\nu_{max}$ (KBr) 3120 (w), 2930 (w), 1860 (w), 1494 (vs), 1412 (m), 1384 (s), 1359 (m), 1146 (m), 1120 (s), 1100 (vs), 1052 (m), 1030 (m), 1000 (m), 900 (m), 820 (m), 675 (w), 620 (m), 490 (s), and 478 $cm^{-1}$ (s). The very strong infrared band at 1494 $cm^{-1}$ is indicative of the cyclopropenium ion;[1,12,16] it is assigned to the unsymmetric degenerate stretching vibration (E′) of the $C_3^+$ ring.[1,16] The cyclopropenium structure of **1** was strikingly verified by the characteristic Raman absorption at 1860 $cm^{-1}$ due to the totally symmetric stretching vibration ($A_1{}^1$) of the aromatic $C_3^+$ ring.[1,12,16] NMR:[13] $\delta$ ($CDCl_3$) 4.38 (15 H, s, 1′ − H), and 5.13 (12 H, s, broad, $\alpha - H$, $\beta - H$); $\delta$ ($CD_3CN$) 4.35 (15 H, s, 1′ − H), 5.08 (6 H, s, broad, $\beta - H$ or $\alpha - H$), and 5.17 (6 H, s, broad, $\alpha - H$ or $\beta - H$). The collapse of $\Delta\delta$ (**1**) may reflect two opposing effects: as a ferrocenylcarbenium ion, $\Delta\delta$ should be negative,[5] while as a substituted cyclopropenium ion, $\Delta\delta$ should be positive.

Finally, the "aromatic" stabilization of **1** may be inferred from its high $pK_{R^+}$, >10 (potentiometric titration method,[17,18] 50% aqueous $CH_3CN$). The corresponding $pK_{R^+}$ values of triphenyl- and the triaminocyclopropenium ions are 3.1,[17] and >10,[1,16,18] respectively. These results clearly indicate the remarkable collective effect of the three ferrocenyl groups in delocalizing the positive charge of the three-membered ring of **1**.[19] The interaction between cyclopropenium ion and ferrocene, as illustrated in the present communication, results in a novel stabilization of one nonbenzenoid aromatic by another.

**Acknowledgment.** We thank Professor H. Selig and Dr. A. Loewenschuss of the Hebrew University of Jerusalem for the Raman spectra determinations.

## References and Notes

(1) Z. Yoshida, *Top. Curr. Chem.*, **40**, 47 (1973).
(2) E. V. Dehmlow, *Angew. Chem., Int. Ed. Engl.*, **13**, 209 (1974).
(3) Z. Yoshida, S. Araki, and H. Ogoshi, *Tetrahedron Lett.*, 19 (1975).
(4) M. Cais, *Jerusalem Symp. Quantum Chem. Biochem. III*, 96 (1971).
(5) S. Lupan, M. Kapon, M. Cais, and F. H. Herbstein, *Angew. Chem., Int. Ed. Engl.*, **11**, 1025 (1972).
(6) M. Cais and A. Eisenstadt, *J. Am. Chem. Soc.*, **89**, 5468 (1967).
(7) R. Lewin Sime and R. J. Sime, *J. Am. Chem. Soc.*, **96**, 892 (1974).
(8) S. W. Tobey and R. West, *J. Am. Chem. Soc.*, **86**, 4215 (1964).
(9) R. West, D. C. Zecher, and S. W. Tobey, *J. Am. Chem. Soc.*, **92**, 168 (1970).
(10) K. T. Potts and J. S. Baum, *Chem. Rev.*, **74**, 189 (1974).
(11) A. Krebs, B. Schrader, and F. Hoefler, *Tetrahedron Lett.*, 5935 (1968).
(12) B. Schrader, *Angew. Chem., Int. Ed. Engl.*, **12**, 884 (1973).
(13) The $^1$H NMR spectra were recorded at 100 MHz. $^1$H chemical shifts are reported in parts per million (ppm) downfield from $Me_4Si$.
(14) M. D. Rausch and A. Siegel, *J. Organomet. Chem.*, **17**, 117 (1969).
(15) Satisfactory elemental analysis was obtained for **1** as a monohydrate.
(16) Z. Yoshida, H. Ogoshi, and S. Hirota, *Tetrahedron Lett.*, 869 (1973).
(17) R. Breslow, *Pure Appl. Chem.*, **28**, 111 (1971).
(18) R. C. Kerber and C.-M. Hsu, *J. Am. Chem. Soc.*, **95**, 3239 (1973).
(19) Such an effect was not apparent in the ferrocenyldiphenylcyclopropenium ion, for which the corresponding p$K_{R^+}$ value is only 5.4.

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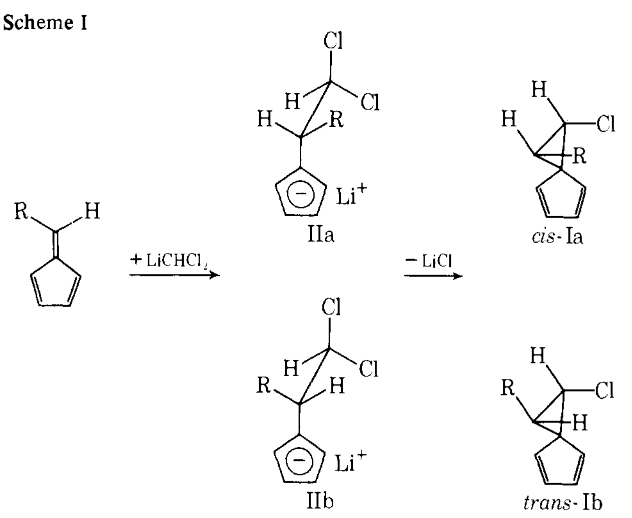
## A Novel Spirocyclization with Dihalomethyllithium Reagents

*Sir:*

Dichloromethyllithium, $LiCHCl_2$, has proved to be an extremely useful synthetic reagent.[1] Its synthesis has been of special importance in connection with the mechanism of the α-elimination of HCl from dichloromethane and the reactivity of the proposed chlorocarbene and dichloromethyllithium intermediates.[2] The reaction of chlorocarbene with alkenes leading to cyclopropanes is well documented. The alternative pathway to cyclopropanes, involving nucleophilic addition of dichloromethyllithium to olefins followed by an 1,3-elimination of lithium chloride has to our knowledge never been demonstrated nor ruled out.[3]

Scheme I



In connection with a project directed toward the synthesis of spiro[2.4]heptatriene, we investigated the reactions of dichloromethyllithium with fulvenes. Addition takes place at position 6 giving first an alkylated cyclopentadienide anion II; rapid 1,3-elimination of lithium chloride yields the chlorospiro[2.4]heptadienes(I) (Scheme I). The reaction was carried out by slowly adding the fulvene[4] to preformed dichloromethyllithium[1] at −95° in tetrahydrofuran-ether-pentane (8:1:1) and allowing the reaction mixture to warm to 0° over a period of 10–14 hours (method A). Alternatively lithium diisopropylamide[6] was added slowly to a mixture of the corresponding fulvene and dichloro- or dibromomethane in tetrahydrofuran at −75° followed by slow warming to 0° (method B). The compounds were isolated and purified by column chromatography (alumina III) and subsequent high vacuum distillation at room temperature. Purity and isomer ratios were determined using vapor phase chromatography (6 ft 0.25 in. OV-17 glass column, 90°) and NMR. The bromospiroheptadienes are thermally unstable. All pure materials had to be stored under argon below −25°.

The parent fulvene[4] and dichloromethyllithium gave in 56% yield (method A) the chlorospiro[2.4]heptadiene as a colorless homogeneous (GLPC, TLC) oil, bp$_{0.05}$ 19–21° (mass spectrum, $M^+ = m/e$ 126, 3%, $M - 35 = m/e$ 91, 100%; NMR spectrum, ABX $\delta$ 1.95 (2 H, AB, $J_{AX} = 8$ Hz, $J_{BX} = 6$ Hz, 3.90 (X part dd, $J_{AX} = 8$ Hz, $J_{BX} = 6$ Hz, $\delta$ 6 ppm (4 H m)). From 6,6-dimethylfulvene[7] the corresponding 1,1-dimethyl-2-chlorospiro[2.4]heptadiene was obtained in 80% yield as a colorless oil, bp$_{0.05}$ 32–35° (mass spectrum, $M^+ = m/e$ 154, 44%, $M - 35 = m/e$ 119, 93%, base peak $= m/e$ 91; NMR spectrum, $\delta$ 1.38 (s, 3 H), 1.50 (s, 3 H), 3.80 (s, 1 H), 6.2 ppm (m, 4 H)). Diphenylfulvene failed to react with dichloromethyllithium.

In position six monosubstituted fulvenes gave as expected the two isomeric *cis*- and *trans*-chlorospiro[2.4]heptadienes (Table I). Assignment of the cis and trans isomers was based upon the 1,2-proton coupling constants available from the characteristic X part of the observed NMR spec-

Table I. Yields and Isomer Ratios of the Halospiro [2.4] heptadienes

| | | Method A<br>X = Cl | | Method B | | | |
|---|---|---|---|---|---|---|---|
| | | | | X = Cl | | X = Br | |
| Fulvene | Spiro[2.4] heptadiene | *a* | *b* | *a* | *b* | *a* | *b* |
| Parent | Parent | 56 | | 37 | | | |
| 6-Methyl- | 1-Methyl- | 75 | 85:15 | 63 | 83:17 | 72 | 72:28 |
| 6-Phenyl- | 1-Phenyl- | 65 | 82:18 | 63 | 90:10 | | |
| 6-Isopropyl- | 1-Isopropyl- | 37 | 69:31 | 33 | 67:33 | 30 | 60:40 |
| 6-*tert*-Butyl- | 1-*tert*-Butyl- | 90 | 20:80 | 90 | 17:83 | 72 | 10:90 |
| 6,6-Dimethyl- | 1,1-Dimethyl- | 56 | | 80 | | 92 | |
| 6,6-Diphenyl- | No reaction | | | | | | |

[a] Yields in %; [b] Cis: trans ratios.