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.

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(19) Such an effect was not apparent in the ferrocenyldiphenylcyclopropenium ion, for which the corresponding pK_{R^+} value is only 5.4.

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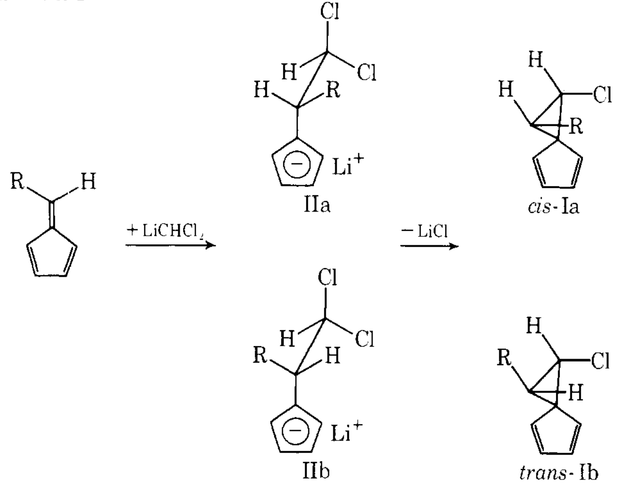
A Novel Spirocyclization with Dihalomethyllithium Reagents

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 δ 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, δ 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, δ 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 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.

trum.[8,13] The mass spectra of *cis*- and *trans*-1-methyl-2-chlorospiro[2.4]heptadienes are again remarkable; besides weak molecular ions at $M^+ = m/e$ 140, they exhibit a base peak of $M - 35 = m/e$ 105. This interesting loss of chlorine, also observed in the parent chlorospiro[2.4]heptadiene and in the 1,1-dimethyl derivative, appears to be very characteristic for this class of compounds.

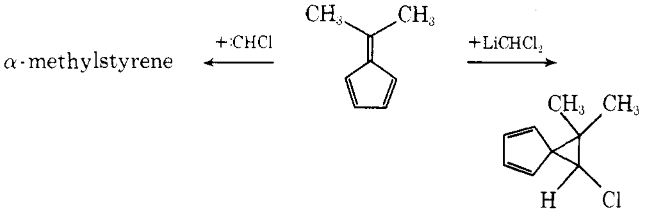
Most interesting are the observed isomer ratios for the spirocompounds obtained from monosubstituted fulvenes (Table I). Except for R = *tert*-butyl, the thermodynamically less favored cis isomer dominates. This corresponds to results obtained from the addition of chlorocarbene to *cis*-2-butene.[2] For the formation of the cis and trans isomers from monosubstituted fulvenes and dichloromethyllithium one can rationalize the mechanism shown in Scheme I. The relative conformational energies of the intermediates IIa and IIb determine the product ratio. According to Eliel[9] a gauche methyl–halogen attraction of unknown character would favor IIa for R = CH_3, isopropyl, and phenyl. For R = *tert*-butyl, van der Waals repulsion between the halogen and the *tert*-butyl group dominates, favoring IIb and leading to the trans isomer. For the bromo compounds there is a slight change in the isomer ratios in favor of the trans isomers owing to increased van der Waals repulsion between the substituents and the larger bromine.[9]

The structure of the chlorospiro[2.4]heptadienes was in one case confirmed by an independent synthesis. Photolysis of diazocyclopentadienes[10] in 1-chloropropene (cis:trans = 40:60) with a 450-W Hanovia lamp in a Pyrex tube under nitrogen at 20° gave besides polymers a mixture of several compounds. Repeated column chromatography separated in ca. 15% yield a fraction containing mainly a 40:60 mixture of the *cis*- and *trans*-1-methyl-2-chlorospiro[2.4]heptadienes, completely identical (GLPC, TLC, NMR) with the product obtained from methylfulvene and dichloromethyllithium.

We also investigated the reaction of chlorocarbene, generated from dichloromethane and methyllithium at −20° in ether,[11] with 6,6-dimethylfulvene. Under these conditions no dichloromethyllithium has ever been detected. Besides 58% unreacted dimethylfulvene, α-methylstyrene was isolated in 24% yield and identified by comparison (GLPC, NMR) with an authentic sample. Three minor still unidentified compounds were detected, but no trace of the 1,1-dimethyl-2-chlorospiro[2.4]heptadiene has been found. Furthermore the reaction of dimethylfulvene with dichloromethyllithium in tetrahydrofuran did not give any detectable amount of α-methylstyrene. This supports Closs' conclusion that under his conditions the species responsible for the formation of chlorocyclopropanes is the electrophilic chlorocarbene, different in reactivity from the intermediate leading to the chlorospiro[2.4]heptadienes. Based on the known reactivity of the fulvene system, this has to be the nucleophilic dichloromethyllithium (Scheme II).

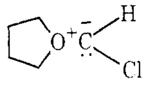
These results correspond to the work reported by Hart[12a] and Parham[12b] on the addition of dichlorocarbene to dimethyl- and diphenylfulvene. The fulvene system thus appears to be an ideal reactant to probe whether the formation of chlorocyclopropanes arises from a one-step electrophilic carbene addition or from a two-step nucleophilic attack by an α-halolithium reagent (a so-called carbenoid) followed by a fast 1,3-elimination of lithium halide.[2]

Scheme II



Our studies on the base catalyzed HX-elimination from the chloro- and bromospiro[2.4]heptadienes will be reported in a following communication.

Note: One referee suggested an interesting explanation for the different behavior of $LiCHCl_2$ in diethyl ether and in tetrahydrofuran. In the less nucleophilic solvent, diethyl ether, $LiCHCl_2$ reacts exclusively as electrophilic lithium chloride coordinated chlorocarbene, LiCl·CHCl. In the better solvating more nucleophilic solvent, tetrahydrofuran, on the other hand, it reacts as nucleophilic organolithium reagent $Li^+CHCl_2^-$. Alternatively, the formation of a relatively stable oxonium ylid, intermediate A, would account for the products observed. At the present time we have no data supporting either mechanistic alternative.



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Supplementary Material Available. Tables II (NMR data) and III (mass spectra) will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for \$4.00 for photocopy or \$2.50 for microfiche, referring to code number JACS-75-3830.

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(13) See paragraph at end of paper regarding supplementary material.
(14) Part of the Ph.D. Thesis of Alicia Amaro. Presented in part at the 167th National Meeting of the American Chemical Society, Spring 1974, Los Angeles, Calif.

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