purified by column chromatography, using a column of 32 × 3 cm packed with 100–200 mesh silica gel, and *n*-hexane as eluent: ir ν_{max}^{film} 3080, 2945, 1495, 758, 725, 700 cm^{-1}; nmr (100 MHz, CCl_4) δ 1.22 (d, *J* = 7.0 Hz, 3, CH_3), 1.35 (s, 3, CH_3), 1.59 and 1.72 (d, 1, CH), 2.04–2.13 (two sets of q, 1, CH), 2.50–2.88 and 3.10–3.33 (both m, 4, benzylic), and 6.64–7.27 ppm (m, 8, aromatic); mass spectrum *m/e* (rel intensity) 248 (100), 249 (24), 233 (70), 205 (27), 119 (26), 91 (9); mass, calcd for $C_{19}H_{20}$, 248.1565 (found, 248.1567).

Further Cyclodehydration Reaction of 4-Benzyl-1-tetralol (9).—(1) Water was distilled away from 3.0 ml of 85% phosphoric acid put into a small pear-shaped flask having a thermometer well, until the temperature rose to 240°. To this acid was then added 0.5 g of 4-benzyl-1-tetralol (**9**), and the temperature was kept at 230–240° for 20 min. Upon cooling, the reaction mixture was poured into a beaker of water. The organic layer was taken up in ether, washed, dried, and concentrated. Analysis by glpc, using a 10 ft × 0.125 in. column of Bentone-34 (5%) and SE-52 silicone gum rubber (5%) at 210° and nitrogen carrier gas at 60 psi, showed that the major product was **12**.

(2) A mixture of 1.0 g of 4-benzyl-1-tetralol (**9**) in 2.0 ml of 85% (by weight) H_2SO_4 was stirred magnetically at 105° for 3 hr. After working up, the same major product (**12**) was obtained by glpc analysis.

1-Benzyl-4,4-dimethyltetralin (30).—2-Methyl-5,6-diphenyl-2-hexanol (**29**) was first prepared by the Grignard reaction of methylmagnesium iodide with methyl γ,δ-diphenylvalerate, bp 130–132° (0.18 mm). Cyclodehydration of compound **29** gave 1-benzyl-4,4-dimethyltetralin (**30**): bp 109–110° (0.06 mm); $n^{23}D$ 1.5665; ir compatible with the structure; nmr (60 MHz, CCl_4) δ 1.20 (s, 3, CH_3), 1.31 (s, 3, CH_3), 1.52–1.88 (m, 4, CH_2CH_2), 2.51–3.11 (m, 3, benzylic), and 6.98–7.30 ppm (m, 9, aromatic); mass spectrum *m/e* (rel intensity) 251 (0.7), 250 (4), 182 (5), 159 (100), 145 (8), 117 (31), 91 (28); mass, calcd for $C_{19}H_{22}$, 250.1721 (found, 250.1722).

1-Benzyl-1-methyltetralin (32).—2-Methyl-1,5-diphenyl-2-pentanol (**31**), bp 110° (0.12 mm), was prepared by the reaction of 3-phenyl-*n*-propylmagnesium bromide with phenylacetone. Cyclodehydration[26] of compound **31** gave compound **32**: bp 84° (0.12 mm); ir compatible with the structure; nmr (60 MHz, $CDCl_3$) δ 1.21 (s, 3, CH_3), 1.32–1.85 (m, 4, CH_2CH_2), 2.50 (crude t, 2, ring benzylic), 2.82 (AB pattern, *J* = 12.0 Hz, 2, benzylic), and 6.85–7.25 ppm (m, 3, aromatic).

1,1-Dimethyl-4-phenyltetralin (34).—2-Methyl-5,5-diphenyl-2-pentanol (**33**), nmr (60 MHz, CCl_4) δ 1.05 (s, 6, CH_3), 2.00 (m, 2, CH_2), 2.50 (t, *J* = 7.2 Hz, 2, CH_2), 3.07 [s (broad), 1, OH], 3.75 (t, *J* = 7.2 Hz, 1, CH), 7.10 ppm (s, 10, aromatic), was first obtained by the Grignard reaction of CH_3MgI and methyl γ,γ-diphenylbutyrate: bp 188° (11 mm); nmr (60 MHz, neat) δ 2.15 (apparent t, *J* = 7.0 Hz, 2, CH_2), 2.52 (t, *J* = 7.0 Hz, 2, CH_2), 3.40 (s, 3, CH_3), 3.88 (t, *J* = 6.0 Hz, 1, CH), and 7.12 ppm (s, 10, aromatic). Cyclodehydration of **33** gave a 70% yield of **34**: ir compatible with the structure; nmr (60 MHz, $CDCl_3$) δ 1.28 (s, 3, CH_3), 1.32 (s, 3, CH_3), 1.52–2.10 (m, 4, CH_2CH_2), 4.02 (t, *J* = 6.5 Hz, 1, CH), and 6.76–7.38 ppm (m, 9, aromatic).[27]

1,1-Dimethyltetralin (36).—This compound was prepared by cyclodehydration[25] of 2-methyl-5-phenyl-2-pentanol (**35**), obtained by the Grignard reaction of methylmagnesium iodide with methyl 4-phenyl-*n*-butyrate. Compound **36** exhibited the following properties: bp 70° (6.0 mm) [lit.[28] bp 98° (10 mm)]; $n^{23}D$ 1.5255; ir compatible with the structure; nmr (60 MHz, $CDCl_3$) δ 1.22 (s, 6, 2 CH_3), 1.45–2.10 (m, 4, CH_2CH_2), 2.68 (t, *J* = 6.5 Hz, 2, benzylic), and 6.76–7.38 ppm (m, 4, aromatic).

Rearrangement of 2,3:6,7-Dibenzobicyclo[3.2.2]nona-2,6-diene (12) in $AlCl_3$.—The quantities of reactants employed and the methods used followed those of a reported procedure.[11] The results are recorded in Table I.

Registry No.—**9**, 38899-43-3; **10**, 38899-44-4; **11**, 38899-45-5; **12**, 23417-01-8; **13**, 31444-39-0; **14**, 38899-47-7; **16**, 38899-48-8; **23**, 38899-49-9; **29**, 38899-50-2; **30**, 38899-51-3; **31**, 34663-14-4; **32**, 38899-53-5; **33**, 38899-54-6; **34**, 13556-56-4; **35**, 2979-70-6; **36**, 1985-59-7; 4-benzyl-1-tetralone, 38899-63-7; 4-benzyl-2,2-dimethyl-1-tetralone, 38899-42-2; 4-benzyl-2-methyl-1-tetralone, 38899-65-9; methyl iodide, 74-88-4; methyl γ,δ-diphenylvalerate, 38899-66-0; 3-phenyl-*n*-propyl bromide, 637-59-2; phenylacetone, 103-79-7.

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Synthesis and Mass Spectral Behavior of Representative 1,1-Dichloro-2-phenylcyclopropanes and 1,1-Dichloro-2-ferrocenylcyclopropanes

GEORGE W. GOKEL, JAMES PETER SHEPHERD, AND WILLIAM P. WEBER*

Department of Chemistry, University of Southern California, Los Angeles, California 90007

HEINZ G. BOETTGER, JANN L. HOLWICK, AND DAVID J. MCADOO

Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California 91109

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1,1-Dichloro-2-ferrocenylcyclopropanes have been prepared in good yield by the addition of dichlorocarbene to vinylferrocenes under phase transfer catalysis conditions. The mass spectral fragmentation pattern of 1,1-dichloro-2-phenylcyclopropanes and of 1,1-dichloro-2-ferrocenylcyclopropanes are reported here and are found to be similar and quite simple.

1,1-Dichlorocyclopropanes have been of interest to organic chemists since Doering and Hoffmann's classic experiment.[1] Besides chloroform and base a variety of methods for generating dichlorocarbene have since been developed, including the decomposition of halomethylmercurials,[2] pyrolysis of trihaloacetate derivatives,[3] the base-induced decomposition of hexachloroacetone,[4,5] and others.[6,7]

The large number of dichlorocyclopropanes that have been synthesized notwithstanding, only a very limited amount of work has been reported on dichloro-

[1] W. von E. Doering and A. K. Hoffmann, *J. Amer. Chem. Soc.*, **76**, 6162 (1954).

[2] D. Seyferth, J. M. Burlitch, R. J. Minasz, J. Y. P. Mui, H. D. Simmons, Jr., A. J. H. Treibe, and S. R. Dowd, *J. Amer. Chem. Soc.*, **87**, 4259 (1965).

[3] W. M. Wagner, H. Kloosterziel, and S. van der Ven, *Recl. Trav. Chim. Pays-Bas*, **81**, 925, 933 (1961).

[4] P. K. Kadaba and J. O. Edwards, *J. Org. Chem.*, **25**, 1431 (1960).

[5] F. W. Grant and W. B. Cassie, *J. Org. Chem.*, **25**, 1433 (1960).

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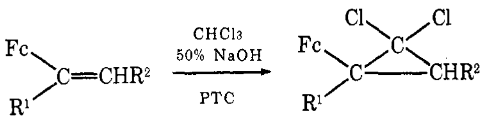
carbene adducts of vinylferrocenes. Such compounds are of interest, since it is well known that substituted ferrocene derivatives possessing a halogen or pseudohalogen α or β to the ferrocene nucleus are extremely labile.[8]

This property has made synthesis of these molecules both difficult and challenging. 1-Ferrocenylethyl chloride, for example, has been prepared only at low temperature, since it decomposes rapidly when warmed.[9] The even simpler compound ferrocenylmethyl chloride remains to be characterized, although it has been implicated in the synthesis of a ferrocenyl amino acid derivative.[10] Fitzgerald reported that 1,1-dichloro-2-ferrocenylcyclopropane was a notable exception to this instability–high reactivity pattern.[11] This is perhaps not surprising, since cyclopropyl halides are well known to solvolyze orders of magnitude more slowly than cyclohexyl halides.[12] This is due principally to two factors: the greater strength of the carbon–chlorine bond attributed to the greater s character of the carbon hybrid orbital forming the bond,[13,14] and strain developed in the ring (*"I"* stain) in going to a planar carbonium ion.[15,16]

Despite this unusual stability reported by Fitzgerald, the low yield (10%) he obtained[11] probably discouraged further work on these compounds. A communication by Horspool and Sutherland is the only other report of the preparation of 1,1-dichloro-2-ferrocencylcyclopropanes.[17] These workers used the thermal decomposition of sodium trichloroacetate in neutral solution to generate dichlorocarbene, which was trapped with vinylferrocenes in moderate (20–66%) yields.

We report here the high-yield synthesis of five representative 1,1-dichloro-2-ferrocenylcyclopropanes (eq 1) by the addition of dichlorocarbene generated by

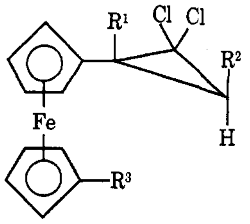


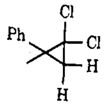
(1)

the phase transfer method to the corresponding vinylferrocenes (see Table I). Makosza and Wawrzyniewicz have shown that dichlorocarbene may be generated efficiently from chloroform and 50% aqueous sodium hydroxide in a heterogeneous system by use of the phase transfer catalyst (PTC) benzyltriethylammonium chloride (**1**), which is soluble in both the aqueous and organic phases.[18] Solution of **1** in the basic aqueous phase followed by anion exchange generates the benzyltriethylammonium hydroxide ion pair, which is soluble in the organic phase. Reaction of hydroxide ion with chloroform gives dichlorocarbene and regenerates **1**.[19] Similar results have been reported by Starks utilizing tetraalkylammonium salts[20] as well as by others.[21-23] We have utilized dichloromethane as a cosolvent to moderate the temperature of this highly exothermic reaction. The isolated yields of analytically pure recrystallized adducts were at least 70%. We believe that the lower temperature required to generate dichlorocarbene by the PTC method compared to those used to generate dichlorocarbene by sodium trichloroacetate pyrolysis[17] may explain our higher yields. In this connection, we have observed that 1,1-dichloro-*trans*-2-ferrocenyl-3-phenylcyclopropane is not stable even at 100° requiring care in recrystallization.

Table I

Synthesis of 1,1-Dichloro-2-ferrocenylcyclopropanes Utilizing the Phase Transfer Catalysis Method



Compd	R^1	R^2	R^3	Yield,[a] %
2	H	H	H	75
3	CH_3	H	H	75
4	Ph	H	H	70
5	H	Ph	H	97
6	Ph	H		71

[a] Yield of pure material.

A stringent test of the reaction's synthetic value was to use it on a diolefinic ferrocene. In this way, we have prepared 1,1′-bis(1-phenyl-2,2-dichlorocyclopropyl)ferrocene (**6**) from 1,1′-bis(α-styryl)ferrocene in 71% yield (after purification) by use of the PTC method.

Despite the broad interest in dichlorocarbene adducts, the only mass spectral data hitherto reported so far is for 1,1-dichloro-2-vinylcyclopropane.[24] We report here the mass spectra of a series of five 1,1-dichloro-2-ferrocenylcyclopropanes and compare them to the spectra of the corresponding 1,1-dichloro-2-phenylcyclopropanes.

The mass spectral fragmentation pattern of 1,1-dichloro-2-phenylcyclopropane (**7**) is outlined in Figure 1 (see Table II for supporting relative intensity and metastable data).[25] High-resolution data indicate that the elemental composition of the base

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(9) W. P. Fitzgerald and R. A. Benkeser, *J. Org. Chem.*, **26**, 4179 (1967).

(10) K. Schlögl, *Monatsh. Chem.*, **88**, 601 (1957).

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(20) C. M. Starks, *J. Amer. Chem. Soc.*, **93**, 195 (1971).

(21) G. C. Joshi, N. Singh, and L. M. Pande, *Tetrahedron Lett.*, 1461 (1972).

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(25) Complete mass spectral data has been submitted to the Mass Spectrometry Data Centre, Atomic Weapons Research Establishment, Aldermaston, Berkshire, England. Relative intensity data reported for peaks containing chlorine are the sum of the intensities of the P plus the P + 2 ions.

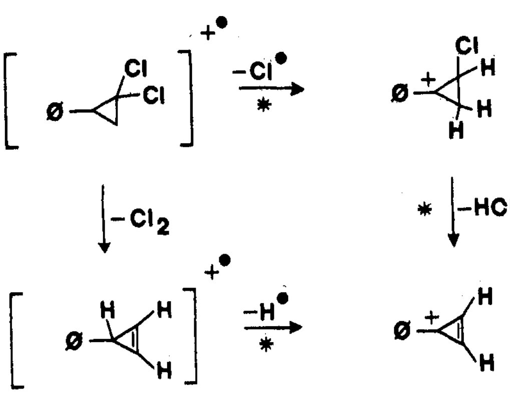

Figure 1.—Mass spectral fragmentation pattern of 1,1-dichloro-2-phenylcyclopropane.

TABLE II
MASS SPECTRAL DATA AT 70 eV FOR 1,1-DICHLOROPHENYLCYCLOPROPANES 7 AND 8

	1,1-Dichloro-2-phenylcyclopropane (7)		1,1-Dichloro-2-methyl-2-phenylcyclopropane (8)	
	Rel intensity	m*	Rel intensity	m*
Parent	47.3		37.0	
P − Cl	80.5	122.6	80.0	136.4
P − Cl_2	43.8		17.0	
[P − Cl] − CH_4			39.0	134.8
[P − Cl] − HCl	100.0	87.4	100.0	100.8 br

peak is C_9H_7.[26] It is not surprising that this peak at mass 115 is intense, since a possible structure for this ion is a phenyl-substituted cyclopropenium cation: a 2-π-electron system which is expected to be particularly stable from the known solution chemistry of these cations.[27-29]

The mass spectrum of 1,1-dichloro-2-methyl-2-phenylcyclopropane (8) is quite similar (see Table II). The base peak at mass 129 has an elemental composition of $C_{10}H_9$.[30] A possible structure for this ion is a cyclopropenium cation substituted by phenyl and methyl groups. One new fragmentation process is observed. Loss of CH_4 from the P − Cl ion leads to a pair of ions of mass 149 and 151. A possible structure for these ions is a cyclopropenium cation substituted by a chlorine atom and a phenyl group.

The mass spectrum of 1,1-dichloro-2,2-diphenylcyclopropane (9) is somewhat different (see Table III).

TABLE III
MASS SPECTRAL DATA AT 70 eV FOR 1,1-DICHLORODIPHENYLCYCLOPROPANES 9 AND 10

	1,1-Dichloro-2,2-diphenylcyclopropane (9)		1,1-Dichloro-*trans*-2,3-diphenylcyclopropane (10)	
	Rel intensity	m*	Rel intensity	m*
Parent	63.0		3.1	
P − Cl	100.0	196.6	31.7	196.6
P − Cl_2	31.8		23.5	
[P − Cl] − HCl	86.0	160.5	86.7	160.5
[P − Cl] − C_6H_6	85.4	98	100.0	98
[P − Cl − HCl] − H_2	18.3	187.2	29.4	187.2
[P − Cl − HCl] − C_2H_2	40.8	142.5	27.9	142.5

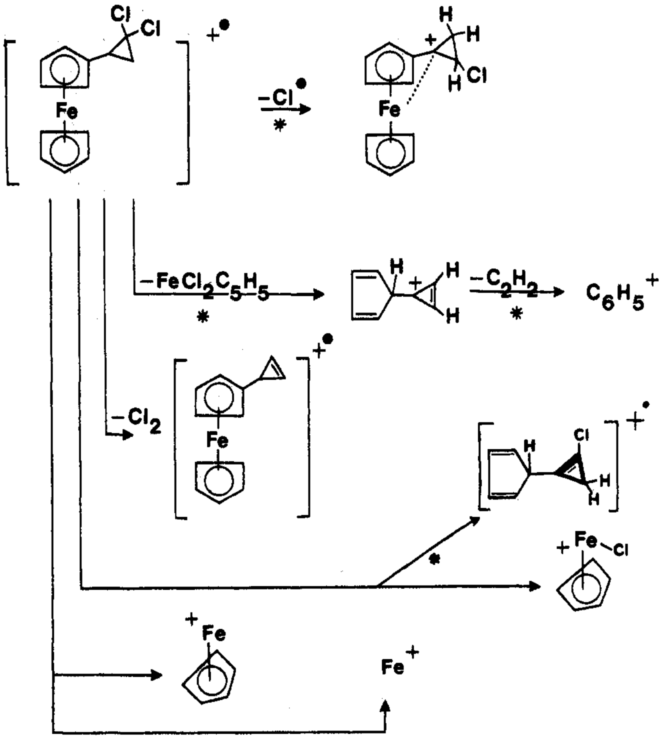

Figure 2.—Mass spectral fragmentation pattern of 1,1-dichloro-2-ferrocenylcyclopropane.

The P − Cl ion is the base peak. Loss of HCl from the P − Cl ion leads to an ion of mass 191 (elemental composition $C_{15}H_{11}$).[31] A possible structure for this ion is the diphenylcyclopropenium cation. The ion of mass 191 further fragments by loss of C_2H_2 to form an ion of mass 165. It also fragments by loss of H_2 to form an ion of mass 189. The P − Cl ion fragments by loss of C_6H_6 to form a pair of ions of mass 149 and 151 as in the spectrum of 8 above.

1,1-Dichloro-*trans*-2,3-diphenylcyclopropane (10) fragments in the mass spectrometer in essentially the same way. However, the relative intensities of various fragment ions are quite different. The pair of ions of mass 149 and 151 are the base peak as above.

The mass spectral fragmentation pattern of 1,1-dichloro-2-ferrocenylcyclopropane (2) is outlined in Figure 2 (see Table IV). In addition to the parent, P − Cl, and P − Cl_2 ions, fragmentation pathways characteristic of ferrocene compounds are observed,[32,33] including the ion at mass 56 due to Fe^+ and the iron cyclopentadienyl cation at mass 121.[34] Chloro iron cyclopentadienyl cations are observed as a pair at mass 156 and 158. A pair of related ions in which charge is retained by the cyclopropyl-substituted cyclopentadiene ring at mass 138 and 140 is observed (P − $FeClC_5H_5$). The base peak is found at mass 103 (elemental composition C_8H_7).[35] A possible structure for this ion is a cyclopentadiene-substituted cyclopropenium cation. A metastable peak indicates that it is formed directly from the parent ion by loss of $FeCl_2C_5H_5$.

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[26] Calculated for C_9H_7, 115.0546; observed, 115.0537.

[27] R. Breslow and H. Chang, *J. Amer. Chem. Soc.*, **83**, 2367 (1961).

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[30] Calculated for $C_{10}H_9$, 129.0702; observed, 129.076.

[31] Calculated for $C_{15}H_{11}$, 191.0858; observed, 191.0753.

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[34] H. Egger, *Monatsh. Chem.*, **97**, 602 (1966).

[35] Calculated for C_8H_7, 103.0546; observed, 103.0504.

TABLE IV

MASS SPECTRAL DATA AT 70 eV FOR 1,1-DICHLORO-2-FERROCENYLCYCLOPROPANES **2** AND **3**

	1,1-Dichloro-2-ferrocenylcyclopropane (**2**)		1,1-Dichloro-2-methyl-2-ferrocenylcyclopropane (**3**)	
	Rel intensity	m*	Rel intensity	m*
Parent	32.2		38.7	
P − Cl	6.1	228.2	3.0	
P − HCl			3.6	
P − Cl_2	8.2		11.3	
P − C_5H_5FeCl	4.9	64.9	18.3	75.0
P − $C_5H_5Cl_2Fe$	100.0	36.2	100.0	44.4
[P − $C_5H_5Cl_2Fe$] − C_2H_2	27.0	57.6	29.0	70.6
[P − $C_5H_5Cl_2Fe$] − H_2			58.0	113.0
C_5H_5FeCl	18.9		9.0	
C_5H_5Fe	6.7		15.3	
Fe	14.4		54.4	

The ion of mass 103 further fragments by loss of C_2H_2 to form an ion of mass 77.

The mass spectrum of 1,1-dichloro-2-methyl-2-ferrocenylcyclopropane (**3**) is similar (see Table IV) to the nonmethylated derivative discussed above. The base peak is observed at mass 117 (elemental composition C_9H_9).[36] A reasonable structure for this ion is a cyclopropenium cation substituted by methyl and cyclopentadiene residues. Loss of H_2 from the base peak leads to the ion of mass 115. The base peak also fragments by loss of C_2H_2 to form the ion of mass 91.

The mass spectrum of 1,1-dichloro-*trans*-2-phenyl-3-ferrocenylcyclopropane (**5**) is different (see Table V). In addition to the P − Cl, P − HCl, and P − Cl_2 ions, the parent ion also fragments by loss of $FeClC_5H_5$ to yield a pair of ions of mass 214 and 216. Phenyl substitution appears to favor charge retention in the substituted cyclopentadienyl ring. The parent ion also fragments by loss of $FeCl_2C_5H_5$ in a single step to yield the base peak at mass 179 (elemental composition $C_{14}H_{11}$),[37] whose structure may be a cyclopropenium cation substituted by cyclopentadiene and phenyl groups. Loss of a hydrogen atom from the ion of mass 179 leads to an ion of mass 178 (elemental composition $C_{14}H_{10}$)[38] whose structure may be a phenyl-substituted calicene cation radical.[39] The ion of mass 178 further fragments by loss of C_2H_2 to form an ion of mass 152.

TABLE V

MASS SPECTRAL DATA AT 70 eV FOR 1,1-DICHLOROPHENYLFERROCENYLCYCLOPROPANES

Ion	1,1-Dichloro-*trans*-2-phenyl-3-ferrocenylcyclopropane (**5**)		1,1-Dichloro-2-phenyl-2-ferrocenylcyclopropane (**4**)	
	Rel intensity	m*	Rel intensity	m*
Parent	19.4		55.9	
P − Cl	3.2		8.4	
P − HCl	6.1		13.1	
P − Cl_2	44.8		9.5	
P − HCl_2	6.0		10.7	
P − CCl_2	11.9		4.8	
P − $HCl_2C_5H_5$	14.9			
P − $FeClC_5H_5$	13.5	123.9	17.9	123.9
P − $FeCl_2C_5H_5$	100.0	86.6	100.0	86.6
[P − $FeCl_2C_5H_6$] − H	80.6	177, 135.4	95.0	177, 135.4
[P − $FeCl_2C_5H_5$ − H] − C_2H_2	17.9	129.8	23.8	129.8
C_5H_5Fe	14.9		13.1	
Fe	28.4		19.0	

The relative intensities of some fragment ions in the mass spectrum of 1,1-dichloro-2-phenyl-2-ferrocenylcyclopropane (**4**) are quite different compared to those of 1,1-dichloro-*trans*-2-phenyl-3-ferrocenylcyclopropane (**5**), but no new fragment ions are observed. The base peak is at mass 179 (elemental composition $C_{14}H_{11}$)[40] while the ion of mass 178 (elemental composition $C_{14}H_{10}$)[41] is almost equally intense.

The mass spectrum of 1,1′-bis(1-phenyl-2,2-dichlorocyclopropyl)ferrocene (**6**) is quite simple (see Table VI). Three ions dominate the entire spectrum. The cluster of peaks associated with the parent ion, the ion of mass 179 (elemental composition $C_{14}H_{11}$),[42] and the ion of mass 178 (elemental composition $C_{14}H_{10}$)[43] are all of almost equal intensity.

TABLE VI

MASS SPECTRAL DATA AT 70 eV FOR 1,1′-BIS(1-PHENYL-2,2-DICHLOROCYCLOPROPYL)FERROCENE (**6**)

m/e	Rel intensity	m*
Parent[a]	75.5	
216	8.3	
215	12.3	
214	25.0	
213	15.3	
179	100.0	57.9
178	100.0	177.0
152	25.0	129.8

[a] Relative intensity is sum of peaks associated with the parent ion.

Experimental Section

Melting points were determined on a Thomas-Hoover apparatus (capillary method) and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 337 spectrometer either neat or in chloroform solution and were calibrated against polystyrene film. Nmr spectra were run on a Varian T-60 or HA-100 using 5–10% solutions. TMS was used as the internal standard. Mass spectra were determined on a AEI MS-902 instrument under the following conditions: ionizing voltage 70 eV; filament emission 480 μA; source temperature 100°. Exact mass determinations of the composition of certain important ions were carried out at a resolution of 10,000 by peak matching with peaks of known mass of perfluorokerosene. Microanalysis was done by Elek Microanalytical Laboratory.

All chemicals used were reagent grade. The hexane used for chromatography was redistilled Skellysolve B. Merck alumina was used for chromatography. The phase transfer catalyst used was benzyltriethylammonium chloride (TEBAC).

1,1-Dichloro-2-phenylcyclopropane (**7**) was synthesized by reaction of styrene with dichlorocarbene generated by the PTC method in 85% yield.[18] The product was purified by distilla-

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[36] Calculated for C_9H_9, 117.0702; observed, 117.0674.

[37] Calculated for $C_{14}H_{11}$, 179.0858; observed, 179.0780.

[38] Calculated for $C_{14}H_{10}$, 178.0780; observed, 178.0755.

[39] M. Cais and A. Eisenstadt, *J. Amer. Chem. Soc.*, **89**, 5468 (1967).

[40] Calculated for $C_{14}H_{11}$, 179.0858; observed, 179.0798.

[41] Calculated for $C_{14}H_{10}$, 178.0780; observed, 178.0737.

[42] Calculated for $C_{14}H_{11}$, 179.0858; observed, 179.0869.

[43] Calculated for $C_{14}H_{10}$, 178.0780; observed, 178.0807.

tion: bp 90° (0.5 mm) [lit. bp 78–83° (2 mm)].[44] Its spectral properties were in agreement with literature values.[45]

1,1-Dichloro-2,2-diphenylcyclopropane (9) was prepared by reaction of 1,1-diphenylethylene with dichlorocarbene under phase transfer catalysis conditions in 70% yield:[18] mp 111–112° (lit. mp 115–116°);[46] pmr (100 MHz, $CDCl_3$ δ 2.21 (s, 2 H), 7.26 (m, 10 H).

1,1-Dichloro-*trans*-2,3-diphenylcyclopropane (10) was prepared by reaction of *trans*-stilbene with dichlorocarbene under phase transfer catalysis conditions in 60% yield.[18] The crude reaction product was distilled at 130° (0.2 mm). After distillation, the product crystallized, mp 39–41° (lit. mp 39–40°).[2] Its spectral properties were in agreement with literature values.[2]

1,1-Dichloro-2-methyl-2-phenylcyclopropane (8) was prepared by reaction of α-methylstyrene with dichlorocarbene under phase transfer catalysis conditions in 71% yield.[18] The product was purified by distillation, bp 50° (0.15 mm) [lit. bp 75–77° (1 mm)].[44] Its spectral properties were in agreement with literature values.[2]

1,1-Dichloro-2-ferrocenylcyclopropane (2).—A 500-ml round-bottomed flask equipped with a magnetic stirring bar and a reflux condenser was charged with vinylferrocene[47] (4.5 g, 0.021 mol), $CHCl_3$ (25 ml), 50% aqueous NaOH solution (30 ml), CH_2Cl_2 (100 ml), and finally TEBAC (1 g). The reaction mixture was stirred and spontaneous reflux ensued. The stirring was continued for about 1 hr after reflux had ceased. The reaction mixture was then poured into 200 ml of ice–water and the layers were separated. The organic layer was washed with water, dried over $MgSO_4$, and filtered, and the solvents were removed by evaporation under reduced pressure. The crude product was chromatographed over alumina (150 g). The desired cyclopropane (5.2 g, 88% yield) was eluted with hexane. It was recrystallized from n-heptane to give lemon-yellow crystals (4.5 g, 75% yield): mp 81–82° (lit. mp 83–84°);[11] pmr (100 MHz, $CDCl_3$) δ 1.47 (d of d, 1 H, $J_{AX} = 8.4$, $J_{AB} = 7$ Hz), 1.87 (d of d, 1 H, $J_{AB} = 7$, $J_{BX} = 11.2$ Hz) and 2.59 (d of d, 1 H, $J_{AX} = 8.4$, $J_{BX} = 11.2$ Hz, cyclopropane protons), 4.16 (s, 5 H, C_5H_5), 4.00 (m, 4 H), 4.34 (C_5H_4).

2-Ferrocenylpropene.—A 250-ml three-necked round-bottomed flask was charged with phosgene (3.0 g, 0.03 mol), triethylamine (6.0 g, 0.06 mol), and ether (75 ml). The solution was cooled to 0° and 2-ferrocenyl-2-propanol[48] (7.1 g, 0.025 mol) in ether (50 ml) was added dropwise with stirring. The reaction mixture was maintained at 0° for 30 min. It was then allowed to warm to ambient temperature during *ca.* 1.5 hr, at which time no further CO_2 evolution was observed [$Ba(OH)_2$ solution]. The mixture was then poured onto ice (100 g) and water (100 g). A small amount of $Na_2S_2O_4$ was added, and the layers were separated. The ether layer was washed with 5% NaOH (200 ml), water (5 × 200 ml), and brine (200 ml) and finally dried over K_2CO_3. Evaporation of the solvent under reduced pressure left 5.7 g of a brown oil, which was chromatographed on silica gel (Baker 3405, 120 g, 3.5 × 32 cm). Elution with petroleum ether (bp 30–60°)–acetone (4:1, v/v) gave 2.5 g of 2-ferrocenylpropene in the first fraction, and continued elution gave residual starting material (3.1 g): yield (based on unrecovered starting material) 57%; mp 64–66° (lit. mp 66–69°);[49] pmr (100 MHz, CS_2) δ 1.96 (m, 3 H, CH_3), 3.88 (s, 5 H, C_6H_5), 4.00 (t, 2 H) and 4.16 (t, 2 H), (C_5H_4), 4.70 (m, 1 H) and 4.96 (m, 1 H) (=CH_2).

1,1-Dichloro-2-methyl-2-ferrocenylcyclopropane (3).—A 500-ml round-bottomed flask equipped with a magnetic stirring bar and a reflux condenser was charged with 2-ferrocenylpropene (1.8 g, 0.0082 mol), $CHCl_3$ (10 ml), CH_2Cl_2 (100 ml), 50% aqueous NaOH solution (50 ml), and finally 1 g of TEBAC catalyst. Stirring was commenced and the reaction mixture was warmed. The reaction mixture was stirred for *ca.* 2 hr after the exotherm ceased. The reaction was worked up as described previously. The product was chromatographed over alumina; elution with Skelly B, followed by recrystallization from n-heptane, gave the cyclopropane as a yellow-orange solid (1.6 g, 75% yield), mp 93.5–94.5°. *Anal.* Calcd for $C_{14}H_{14}FeCl_2$: C, 54.41; H, 4.57; Cl, 22.95. Found: C, 54.33; H, 4.45; Cl, 22.93. Pmr (100 MHz, $CDCl_3$): δ 1.47 (d, 1 H) and 1.70 (d, 1 H) (geminal protons, $J_{AB} = 7.5$ Hz), 1.78 (s, 3 H, CH_3), 3.97, 4.15, 4.27 (pseudo t, 9 H) (ferrocene protons).

Ferrocenylbenzyl Ketone.—A 500-ml erlenmeyer flask equipped with a magnetic stirring bar and a nitrogen inlet was charged with ferrocene (37.2 g, 0.2 mol), phenylacetyl chloride (31 g, 0.2 mol), and dry CH_2Cl_2 (200 ml). The flask was immersed in an ice bath and aluminum trichloride (28.4 g, 0.22 mol) was added in six equal portions. The mixture turned from brown to wine red and was stirred for 2 hr while warming to ambient temperature. The reaction mixture was poured onto cracked ice. The phases were separated and the aqueous phase was washed once with CH_2Cl_2 (200 ml). The combined organic material was washed with 200 ml each of 10% NaOH solution, water, and brine and then dried over $MgSO_4$ and the solvent was removed under reduced pressure to give a light red powder, 53.4 g (87.5% yield). A small sample was chromatographed over alumina to remove residual ferrocene from the product: mp 128–129° (lit. mp 130°);[50] pmr (100 MHz, CS_2) δ 3.74 (s, 2 H, $-CH_2-$), 3.90 (s, 5, H, C_5H_5), 4.28 (t, 2 H), 4.58 (t, 2 H), 7.14 (s, 5 H, C_6H_5).

1-Ferrocenyl-2-phenylethanol.—Ferrocenylbenzyl ketone (17 g, 0.056 mol) was stirred for 3 hr at ambient temperature with $NaBH_4$ (5.0 g, 0.132 mol) in 500 ml of 95% ethanol. The product was isolated in the normal fashion: yield 15 g (82%); mp 62–63° (lit. mp 64°);[50] pmr (100 MHz, CS_2) δ 1.89 (s, 1 H, $-OH$), 2.65 (d, 2 H, $J = 6.4$ Hz, $-CH_2-$), 3.96 (s, 9 H, $C_{10}H_9Fe$), 4.35 (t, 1 H, $J = 6.4$ Hz, $-CH-$), 7.01 (m, 5 H, C_6H_5).

***trans*-2-Ferrocenylstyrene.**—A 500-ml round-bottomed flask equipped with a magnetic stirring bar, reflux condenser, and N_2 inlet was charged with 1-ferrocenyl-2-phenylethanol (10 g, 0.0326 mol) and 100 ml of dry benzene. Powdered PCl_5 (10 g) was added in one portion, whereupon the benzene solution refluxed vigorously for 15 min. When the reflux had ceased, the reaction mixture was quenched with aqueous sodium carbonate solution. A small amount of sodium dithionite was added to reduce any ferrocinium ion present, and the product was extracted with ether. The organic material was washed several times with water, then dried over $MgSO_4$, and the solvents were removed by evaporation under reduced pressure. The residue was chromatographed over alumina; the product was eluted with Skelly B, yield 6 g (64%), red-orange solid, mp 119–120° (lit. mp 120–122°).[51,52] The olefin was presumed to be the trans isomer on the basis of the vinylic coupling constant, $J = 17$ Hz; pmr (60 MHz, CS_2) δ 3.96 (s, 5 H, C_5H_5), 4.08 (t, 2 H) and 4.26 (t, 2 H) (C_5H_4), 6.36 (d, 1 H) and 6.66 (d, 1 H) (vinyl protons, $J_{AB} = 17$ Hz), 7.11 (m, 5 H, C_6H_5).

1,1-Dichloro-*trans*-2-phenyl-3-ferrocenylcyclopropane (5).—A 500-ml round-bottomed flask equipped with a magnetic stirring bar and a reflux condenser was charged with *trans*-2-ferrocenylstyrene (2.0 g, 0.007 mol), $CHCl_3$ (10 ml), CH_2Cl_2 (100 ml), 50% aqueous KOH solution (20 ml), and finally 1 g of TEBAC catalyst. The reaction mixture was stirred and began to spontaneously reflux. Stirring was continued for *ca.* 2 hr after reflux had ceased and the solution was worked up as described previously. The crude product was chromatographed over alumina; elution with Skelly B gave 2.6 g (97%) of a red-orange solid, mp 101.5–102.5°. *Anal.* Calcd for $C_{19}H_{16}FeCl_2$: C, 61.50; H, 4.35; Cl, 19.11. Found: C, 61.60; H, 4.41; Cl, 18.94. Pmr (100 MHz, $CDCl_3$): δ 2.89 (s, 2 H, cyclopropane protons), 4.15 and 4.43 (pseudodoublet, 9 H, ferrocene protons), 7.38 (s, 5 H, C_6H_5).

1-Ferrocenylstyrene.—To a solution of triphenylmethylphosphonium iodide (40.4 g, 0.1 mol) in THF (600 ml) was added with stirring a solution of n-butyllithium (50 ml, 2.1 M in n-hexane). Ferrocenophenone[51] (29 g, 0.1 mol) was added as a solid. After the reaction was over, the solution was hydrolyzed and the product was isolated by chromatography over alumina. The olefin eluted with n-hexane to give a red-brown oil (21.4 g, 74%): pmr (60 MHz, CCl_4) δ 4.04 (s, 5 H, C_5H_5), 4.16 (t, 2 H) and 4.27 (t, 2 H) (C_5H_4), 5.12 (d, 1 H) and 5.51 (d, 1 H, $J_{AB} = 2$ Hz), 7.33 (m, 5 H, C_6H_5). The base peak in the mass spectrum of 1-ferrocenylstyrene is the parent ion at m/e 288.

1,1-Dichloro-2-phenyl-2-ferrocenylcyclopropane (4).—A 500-

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ml round-bottomed flask equipped with a magnetic stirring bar and a reflux condenser was charged with 1-ferrocenylstyrene (2.0 g, 0.007 mol), $CHCl_3$ (14 g, 0.12 mol), 50% NaOH solution (50 ml), CH_2Cl_2 (200 ml), and finally 1 g of TEBAC catalyst. The reaction mixture was stirred for *ca.* 5 hr, during which time a mild exotherm was noted. The reaction mixture was worked up as described previously and the crude product was chromatographed over alumina. Elution with Skelly B afforded 2.25 g of the cyclopropane, which was recrystallized from *n*-heptane to give 1.79 g (70%) of a red-orange solid melting at 124–125°. *Anal.* Calcd for $C_{19}H_{16}FeCl_2$: C, 61.50; H, 4.35; Cl, 19.11. Found: C, 61.53; H, 4.32; Cl, 18.97. Pmr (100 MHz, $CDCl_3$): δ 2.07 (d, 1 H) and 2.18 (d, 1 H) (*gem*-protons, $J_{AB} = 7.5$ Hz), 3.91 (s, 5 H, C_5H_5), 4.04 (m, 2 H) and 4.12 (m, 2 H) (C_5H_4), 7.44 (s, 5 H, C_6H_5).

1,1′-Bis(α-styryl)ferrocene.—A 500-ml three-necked flask equipped with a stirrer, a reflux condenser, an addition funnel, and a N_2 inlet was charged with triphenylmethylphosphonium iodide (33 g, 0.08 mol) and 200° ml of THF. A solution of *n*-butyllithium (40 ml, 2.1 *M* in hexane) was added and the mixture was stirred for *ca.* 10 min. A solution of 1,1′-dibenzoylferrocene[53] (15.6 g, 0.04 mol) in 100 ml of THF was added dropwise. Stirring was continued for 1 hr before hydrolyzing with water. The crude product was chromatographed over neutral alumina (Merck) using Skelly B as eluent: yield 4.0 g (25%) of a red-brown oil; pmr (60 MHz, CS_2) δ 3.95 (t, 4 H, $J = 4$ Hz), 4.05 (t, 4 H, $J = 4$ Hz, C_5H_4), 5.03 (d, 2 H, $J_{AB} = 2.2$ Hz), 5.32 (d, 2 H, $J_{AB} = 2.2$ Hz), 7.17 (m, 10 H). The base peak in the mass spectrum of 1,1′-bis(α-styryl)ferrocene is the parent ion at *m/e* 390.

1,1′-Bis(1-phenyl-2,2-dichlorocyclopropyl)ferrocene (6).—A 250-ml round-bottomed flask equipped with a stirring bar and a reflux condenser was charged with 1,1′-bis(α-styryl)ferrocene (1.5 g, 0.00384 mol), CH_2Cl_2 (40 ml), $CHCl_3$ (10 ml), 50% aqueous NaOH (20 ml), and finally 0.5 g of TEBAC catalyst. After stirring for *ca.* 5 hr, the reaction mixture was diluted with water and worked up as described previously. The crude product was chromatographed over Merck neutral alumina; elution with Skelly B, followed by recrystallization from *n*-heptane, afforded a yellow-orange solid (1.5 g, 71%). *Anal.* Calcd for $C_{28}H_{22}FeCl_4$: C, 60.47; H, 3.99. Found: C, 60.80; H, 4.05. The compound blackens at ~145°, but is not a mobile liquid below 260°. Pmr (100 MHz, CS_2): δ 1.56 (d, 2 H) and 1.82 (d, 2 H) (cyclopropane protons, $J_{AB} = 7.50$ Hz), 3.52 (m), 3.62 (m), and 3.75 (m) (total 8 H, C_5H_4), and 7.29 (s, 10 H, C_6H_5).

Registry No.—**2,** 12085-73-3; **3,** 12087-46-6; **4,** 38856-04-1; **5,** 38856-05-2; **6,** 38856-06-3; **7,** 2415-80-7; **8,** 3591-42-2; **9,** 3141-42-2; **10,** 33044-82-5; 2-ferrocenylpropene, 31725-14-1; 2-ferrocenyl-2-propanol, 12093-87-7; ferrocenylbenzyl ketone, 1277-72-1; ferrocene, 102-54-5; 1-ferrocenyl-2-phenylethanol, 12094-28-9; *trans*-2-ferrocenylstyrene, 1272-54-4; 1-ferrocenylstyrene, 35126-64-8; ferrocenophenone, 1272-44-2; 1,1′-bis(α-styryl)ferrocene, 38856-13-2; 1,1′-dibenzoylferrocene, 12180-80-2.

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Organometallic Derivatives of Cymantrene. The Formation of (Fulvalene)hexacarbonyldimanganese[1]

ROBERT F. KOVAR AND MARVIN D. RAUSCH*

Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01002

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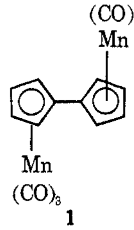
Cymantrene (**2**) has been found to undergo facile mercuration by reaction with mercuric acetate in the presence of perchloric acid. Chloromercuricymantrene (**3**) has been converted into a variety of organomanganese derivatives, including cymantrenylmagnesium iodide (**8**), cymantrenyllithium (**10**), cymantrenylferrocene (**6**), and (fulvalene)hexacarbonyldimanganese (**1**). Complex **1** undergoes Friedel–Crafts acetylation to produce (3-acetylfulvalene)hexacarbonyldimanganese (**11**).

A recent communication by us[2] reported the synthesis and properties of (fulvalene)hexacarbonyldimanganese (**1**), one of the first examples in which fulvalene serves as the sole π ligand in an organo transition metal complex.[3] We now wish to describe in detail the preparation of a number of novel organometallic derivatives of cymantrene (**2**), their utilization as intermediates in the synthesis of **1**, and the results of preliminary studies regarding the reactivity of **1** toward electrophilic substitution.[4]



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During the course of our studies in cymantrene chemistry it became necessary for us to prepare substantial quantities of the monochloromercuri derivative (**3**). We were unable in several attempts to reproduce the original direct mercuration procedure described for cymantrene (**2**),[8] but were successful in reproducing a four-step procedure described by Cais.[9] The latter method was tedious, however, and resulted in low overall yields of product (24% yield of **3** starting

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[1] Presented in part at the 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 9–13, 1968, Abstracts INOR-088.

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[3] For another example of a fulvalene–transition metal π complex, see F. L. Hedberg and H. Rosenberg, *J. Amer. Chem. Soc.*, **91**, 1258 (1969); see also ref 2.

[4] After our program in this area had been completed,[1] the isolation of **1** from (a) the halogenation of triphenylphosphinegoldcymantrene;[5] (b) the reaction of cymantreneboronic acid with copper acetate;[6] and (c) the coupling of cymantrenylmagnesium iodide (**8**) with cobalt(II) chloride[7] was independently reported.

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