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REACTIONS OF FERROCENYLCARBENE—II

REACTIONS OF FERROCENYLMETHYLCARBENE

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Abstract—The oxidation of acetylferrocene hydrazone with HgO and the thermal decomposition of acetylferrocene tosylhydrazone sodium salt in various solvents have been described. Both reactions proceed *via* ferrocenylmethylcarbene, and afford similar reaction products. In these reactions, a preferred addition reaction of the carbene to vinylferrocene is noticed. In this connection, the competitive reactivities of vinylferrocene, styrene, *p*-methoxystyrene and cyclohexene towards dichlorocarbene and diphenylcarbene have been measured.

INTRODUCTION

NUMEROUS studies[1] on the catalytic action of transition metal compounds in the decomposition of diazoalkanes, potential carbene precursors, have been carried out. It is recognized that transition metal atoms such as Cu[2], Fe[3], Ni[4], etc, influence the reactivity and the reaction course of carbene generated in the decomposition of corresponding diazo compounds. This effect has been rationalized on the basis of the formation of a intermediate complex between carbene and transition metal.

It is of interest to study the reactions of a carbene which involves a transition metal located intramolecularly close to the reacting center. From this point of view, we have investigated the reaction of a series of ferrocenylcarbenes.[5]

Previously, we have reported briefly that the reaction of some α-ferrocenylcarbenes proceeds in a radical manner and that those carbenes do not add to cyclohexene.[6]

Among those ferrocenylcarbenes investigated, ferrocenylmethylcarbene showed a somewhat complex reactivity; the carbene added selectively to vinylferrocene produced simultaneously from the carbene to afford a diferrocenylcyclopropane derivative in spite of the presence of a large amount of cyclohexene.

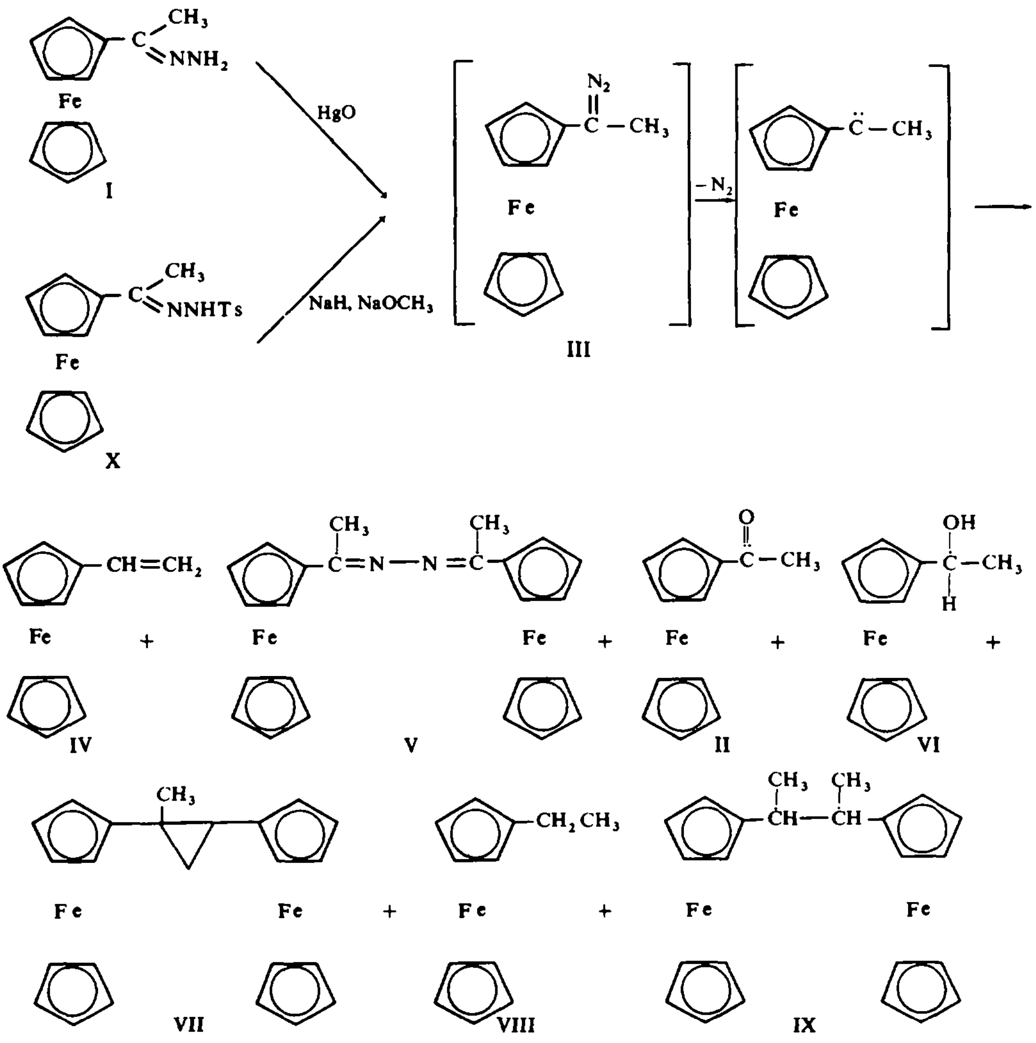
This paper is concerned with the reactions of ferrocenylcarbene as well as the relative reactivity of vinylferrocene compared with several olefins towards singlet and triplet carbenes.

RESULTS AND DISCUSSION

At first, acetylferrocene hydrazone (I) was synthesized from acetylferrocene (II) and hydrazine hydrate. The hydrazone (I) is somewhat unstable in solution. Then, the hydrazone (I) was oxidized with 3 times excess of HgO in dry benzene at various temperatures. When the oxidation was carried out at 75–80°, the formation of a diazo compound was indicated by a sharp IR absorption at 2060 cm^{-1}.[7] However the isolation of the diazo compound was not practical owing to instability at the temperature. Therefore, the decomposition of the diazo compound to carbene was carried out *in situ*.

The decomposition in benzene, yielded vinylferrocene (IV), acetylferrocene azine (V), acetylferrocene (II), ferrocenylmethylcarbinol (VI) and 1,2-diferrocenyl-1-methylcyclopropane (VII) by means of an alumina elution chromatography. Further, the similar decomposition in dry cyclohexene resulted in the formation of seven products, in which five were the same materials as above and the remaining two were ethylferrocene (VIII) and 2,3-diferrocenyl-n-butane (IX). These results are summarized in Table 1.

The alkaline thermal decomposition[8] of tosylhydrazone was then attempted. Thermal decomposition of acetylferrocene tosylhydrazone sodium salt prepared from the tosylhydrazone (X) and either sodium hydride or sodium methoxide in dry pyridine or dry cyclohexene was carried out. Although the formation of a diazo compound in the intercepted reaction mixture was also detected by IR, its isolation



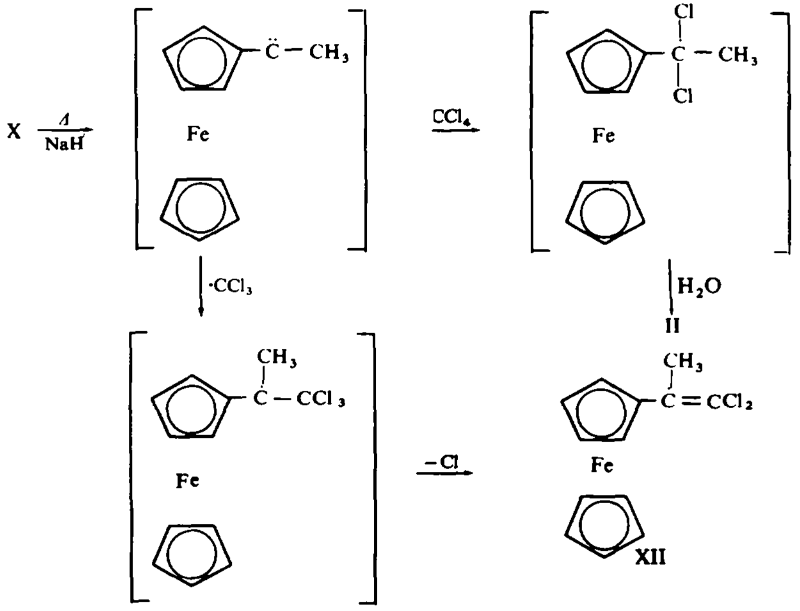
was also unsuccessful. When evolution of nitrogen was over, the reaction mixture was subjected to the alumina column chromatography and similar products were obtained. These results are shown in Table 1.

TABLE 1. REACTION PRODUCTS OF THE FERROCENYLMETHYLCARBENE

Reaction conditions	Reaction products						
	IV	V	II	VI	VII	VIII	IX
(1) I, HgO in benzene, 80°	12	17	11	2·6	6	—	—
(2) I, HgO in cyclohexene, 80°	16	12	9	2·0	2	trace	2·3
(3) X, NaH in pyridine, 90°	41	2·5	8·8	3·4	0·4	2·1	0·6
(4) X, $NaOCH_3$ in pyridine, 90°	44	3·0	4·6	—	trace	trace	trace
(5) X, NaH in cyclohexene, 100° in sealed tube	14	trace	2·4	—	0·5	0·2	1·5

It should be noted that in one run with pyridine as the solvent, a small amount of isomeric 1-ferrocenyl-1-pyridylethanes was obtained in addition to above common reaction products. Repeated recrystallizations afforded a single compound, 1-ferrocenyl-1-(γ-pyridyl)-ethane (**XI**). In these reaction products, **II**, **IV** and **VI** were identified with authentic specimen, **V**, **VII**, **VIII**, **IX** and **XI** were comfirmed by analyses, IR, UV, NMR spectra and molecular weight determinations.

The formations of **II**, **XIII** and **XI** are explicable in terms of the radical reactions of the intermediate ferrocenylmethylcarbene. The radical nature of the carbene is also shown in the reaction of the carbene with carbon tetrachloride.[9] Decomposition of the tosylhydrazone sodium salt in carbon tetrachloride under deoxygenated atmosphere afforded **II** and 2-ferrocenyl-2-methyldichloroethylene (**XII**) in 9% and 3% yields, respectively. The compound **II** is considered to be produced by the hydrolysis of 1,1-dichloro-1-ferrocenylethane,[10] and **XII** is derived from the coupling of the carbene with trichloromethyl radical followed by a loss of a Cl atom.[11]



Now the 1,2-diferrocenylcyclopropane structure* of VII was firmly characterized by the NMR spectrum. The formation of VII is explained by the addition of ferrocenylmethylcarbene to vinylferrocene. In order to confirm it, the decomposition of the sodium salt of X in pyridine containing preformed vinylferrocene was carried out. In this case, the yield of VII, the addition product, was raised up to 10%.

It is notable to point out that ferrocenylmethylcarbene does not add to cyclohexene present in a large excess, but adds to vinylferrocene to afford the addition product VII (Reaction No. 2 and 5 in Table 1). This is a strong indication that ferrocenylmethylcarbene is a triplet, since the triplet carbene adds specifically to an olefin in which the intermediate radical can be stabilized by conjugation with some unsaturated functions.[12] The ferrocenyl group may have the same ability[13] to stabilize an adjacent radical as a phenyl group. If the reacting carbene is a singlet, it should add both to cyclohexene and vinylferrocene.

In this connection, the relative reactivity of cyclohexene, vinylferrocene, styrene and *p*-methoxystyrene towards either dichlorocarbene (singlet)[14] or diphenylcarbene (triplet)[15] was examined. The relative reactivities were determined by the competitive reactions, employing two equimolar olefins in the presence of each carbene.

The results are shown in Table 2.

TABLE 2. THE RELATIVE REACTIVITIES OF SOME OLEFINS IN THE ADDITION REACTIONS OF REPRESENTATIVE CARBENE

Olefins / Carbenes	Cyclohexene	Styrene	Vinylferrocene	*p*-Methoxystyrene
Dichlorocarbene	— 1·00[a]	1·00 1·26[a]	1·27	—
Diphenylcarbene	None	1·0	6·8	83·7

[a] See ref 16.

It is clear from the Table that vinylferrocene exhibits a reactivity similar to that of styrenes towards both dichlorocarbene and diphnylcarbene. Particular attention should be drawn to the addition of diphenylcarbene to these olefins. No addition product to cyclohexene could be detected in the reaction but considerable amounts of the cyclopropane derivatives formed by the addition of the carbene to styrene, vinylferrocene and *p*-methoxystyrene were obtained. Since it is known that dichlorocarbene is a singlet and diphenylcarbene is a triplet in their addition reactions, a marked difference must exist between cyclohexene and styrene in the addition reaction of a triplet carbene.

Accordingly, it is reasonably concluded that the ferrocenylmethylcarbene is a triplet and hence reacts preferentially with vinylferrocene even in the presence of a large excess of cyclohexene in the reaction system.

EXPERIMENTAL

IR spectra were recorded on a Hitachi EPI-S2 spectrophotometer, UV spectra on a Hitachi EPS-2U spectrophotometer and NMR spectra on a Japan Electron Optics JNM-4H-100 at 100 MHz using TMS as an internal standard. VPC analyses were carried out with a Yanagimoto GCG-5DH gas chromatograph. All temperatures were uncorrected.

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* Unfortunately, the spectroscopic data obtained did not allow the determination of strict stereochemistry of the cyclopropane.

Synthesis of acetylferrocene hydrazone (I). To a soln of II[17] (11·4 g, 0·05 mole) in 500 ml hydrazine hydrate (100%) and 100 ml EtOH, 10 ml conc HCl was added. Then the soln was boiled for 3 hr. After standing overnight at room temp, I deposited as bright yellow needles, m.p. 109–110°, 9·1 g, 75%, and recrystallized from pentane as gold yellow needles, m.p. 110–111·5°. (Found: C, 59·51; H, 5·81. $C_{12}H_{14}FeN_2$ requires: C, 59·53; H, 5·93%); IR (Nujol) 3340 (N—H), 1365, 1276, 1122, 1102, 1031, 996, 893, 841, 828, and 815 cm^{-1}; UV (MeOH), λ_{max}; 220 nm (log ε 4·16), 237 (4·08), 280 (3·91), 350 sh. (3·11) and 440 (2·48).

Synthesis of acetylferrocene tosylhydrazone (X). To a mixture of II (18·3 g, 0·08 mole) and *p*-toluenesulfonylhydrazine[18] (15·0 g, 0·084 mole) in 250 ml abs EtOH, 1 ml conc H_2SO_4 was added. The soln was refluxed for 2 hr. Fine red crystals deposited even at the boiling temp. After cooling, the red crystals were collected, washed with EtOH, yielding 28·8 g of X, m.p. 186–187° dec, 90%. (Found: C, 57·59; H, 5·16; N, 7·05. $C_{19}H_{20}SO_2N_2Fe$ required C, 57·58; H, 5·09; N, 7·07%); NMR ($CDCl_3$), τ 2·05 and τ 2·63 (m; 4H, phenyl), τ 5·43 (m; 2H, substituted ring protons of ferrocene), τ 5·67 (m; 2H, substituted ring protons), τ 6·01 (s; 5H, unsubstituted), τ 7·55 (s; 3H, methyl) and τ 7·94 (s; 3H, methyl); IR (Nujol), 3260 (N—H). 3100, 1601, 1489, 1165, 1105, 1092, 1041, 1002, 830, 813 and 700 cm^{-1}.

Reaction of I *in benzene*. In a 500 ml 3-necked flask, I (8·36 g, 0·0344 mole), HgO (yellow) (23·5 g, 0·11 mole) and Na_2SO_4 (10 g) were placed. After the atmosphere was replaced with N_2, 50 ml of dry benzene and 1·5 ml of saturated KOH-ethanol soln were added. On warming to 75–80° on a water bath with mechanical stirring, colour of the soln turned to reddish brown with evolution of N_2. The gas evolution ceased after 3·5 hr. Then the cooled reaction mixture was filtered and the filtrate was evaporated under reduced press to dryness. The residual reddish brown mass (8·19 g) was dissolved in small portion of benzene and chromatographed by 140 g active alumina. Light petroleum eluted IV, m.p. 49–52°, (0·913 g, 11·8%), which was purified by sublimation, m.p. 52–53°, (lit.[19] 51–52·5°), and it was identified by IR spectrum with authentic specimen[19] and mixed m.p. Benzene–petroleum eluted VIII, m.p. 139–145°, (0·447 g, 5·8%), which was recrystallized from n-hexane as a yellow solid, m.p. 159–160°. (Found: C, 67·74; H, 5·74; M.W. 424 (VPO), $C_{24}H_{24}Fe_2$ requires: C, 67·96; H, 5·71%; M.W. 424·1); UV (MeOH), λ_{max} 270 nm (log ε 3·79), 440 (2·69); IR (H.C.B), 3090, 2995, 2950, 2925, 2880, 1478, 1451, 1393, 1141, 1103, 1051, 1024, 1000, 915 and 812 cm^{-1}; NMR (CS_2), τ 6·06 (s; 10H, ferrocenyl), τ 6·15 (m; 8H, ferrocenyl), τ 8·98 (s; 3H, methyl), τ 8·18 and τ 8·97 and τ 9·26 (q; 3H, ABX pattern of cyclopropane ring protons). Benzene-ether eluted V, m.p. 207–213°, (1·407 g, 17·1%), which was crystallized from n-hexane as a brown solid, m.p. 211–212°. (Found: C, 63·36; H, 5·59; N, 6·20; $C_{24}H_{24}Fe_2N_2$ requires: C, 63·75; H, 5·35; N, 6·20%); IR (Nujol), 1602 (C═N), 1409, 1359, 1113, 1106, 1018, 1001, 893, 825 and 818 cm^{-1}; UV (EtOH), λ_{max} 240·6 nm (log ε 3·71), and 286 (3·61). Benzene-ether eluted II, m.p. 77–84° (0·939 g, 11·4%), recrystallized from ligroin, m.p. 84·86° as a yellow solid. The m.p. was not depressed by admixture of authentic sample.[17] Ether eluted VI, m.p. 73–76° (0·220 g, 2·6%), recrystallized from hexane as yellow needles, m.p. 78–80°. This compound was identified with authentis carbinol[20] by the IR, m.p. and mixed m.p.

Reaction of I *in cyclohexene*. A mixture of I (5·642 g, 0·0233 mole), HgO (15·79 g, 0·073 mole), Na_2SO_4 (7·0 g) and dry cyclohexene 100 ml was reacted as above. Then the reaction mixture was subjected to an alumina chromatography. Besides above five products (IV; 0·781 g, 16·0%, VII; 0·099 g, 2·0%, V; 1·203 g, 11·7%, II; 0·474 g, 8·9%, and VI; 0·0926 g, 1·7%), compounds VIII and IX were isolated. VIII was eluted by light petroleum together with IV. IV and VIII were separated by a VPC (carbowax) and isolated respectively. VIII (trace) was identified with authentic specimen[20] by comparison of IR and RT of VPC. Petroleum ether–benzene eluted IX as a heavy brown oil (0·114 g, 2·3%) rechromatographed by a column of alumina. IR (liquid film), 3090, 2960, 2910, 2850, 1443, 1360, 1302, 1231, 1102, 1022, 1000, 902 and 815 cm^{-1}; NMR (CCl_4), τ 5·93 and τ 6·01 (s; 18H, ferrocenyl), τ 5·68 (m; 2H, methine) and τ 8·56, τ 8·62 (overlapped two doublet; 3H + 3H, methyl protons of erythro and threo isomers).

Reaction of X *in pyridine*. To a soln of X (7·93 g, 0·02 mole) in dry pyridine (64 ml) was added dropwise 5·74 g of sodium hydride (52% in oil) in 47 ml of pyridine under N_2. During the addition, H_2 evolution occured (total 473 ml) with the precipitation of Na salt of X. After a further addition of pyridine (120 ml), the soln was stirred at 90°. When the N_2 evolution ceased (160 min), the resulting mixture was cooled and filtered. The concentrated filtrate (under reduced press) was extracted with benzene and the benzene extract was washed to free it from pyridine with dil HCl and followed by water. The benzene soln was dried over $MgSO_4$. After the evaporation of benzene, the residue was chromatographed by a column of alumina. Repeated chromatograph over the alumina yielded following products; IV (1·750 g, 41·4%), VIII (0·087 g, 2·1%), VII (0·018 g, 0·4%), IX (0·052 g, 0·6%), II (0·401 g, 8·8%), V (0·114 g, 2·5%), and VI (0·155 g, 3·4%).

Formation of XI. A run of similar reaction of X in pyridine afforded an yellow crystalline material, m.p. 60–65°, 0·127 g, besides above reaction products. Repeated crystalizations from light petroleum yielded as a yellow solid, **XI**, m.p. 65–65·5° (0·028 g, 0·5%). (Found: C, 70·15; H, 5·97; N, 4·70, $C_{16}H_{17}NFe$ requires: C, 70·12; H, 5·89; N, 4·81%). IR (liquid film), 3120, 3040, 2985, 1597, 1411, 1106, 1000, 906 and 821 cm^{-1}; UV (EtOH), λ_{max} 255 nm (sh), (log ε 3·73) and 441 (2·15). NMR (CCl_4), τ 1·67 and 3·08 (m; 2H + 2H, α- and β-protons of pyridyl), τ 5·94 (m; 9H, ferrocenyl), τ 6·10 (m; 1H, methine) and τ 8·39 (d; 3H, methyl).

Reaction of **X** *using sodium methoxide in pyridine.* To a mixture of NaOMe (0·022 mole) and **X** (7·93 g, 0·020 mole) was added 135 ml of dry pyridine under N_2. Then the mixture was heated to 90° with stirring for 3·5 hr. The resulting reaction mixture was treated as usual, and chromatographed. Six products were obtained as following; **IV** (1·861 g, 44·0%), **VIII** (trace), **VII** (trace), **II** (0·207 g, 4·6%), **V** (0·271 g, 3·0%) and **IX** (trace).

Reaction of **X** *using sodium hydride in cyclohexene.* The sodium salt of **X** was prepared from **X** (4·045 g, 0·01 mole) and NaH (0·53 g) in dry pyridine. Then the solvent was evaporated to dryness under reduced press. To the residual salt placed in a thick glass tube was added 25 ml of dry cyclohexene under nitrogen, then the tube was sealed. After the sealed tube was immersed in a boiling water bath for 5·5 hr, the reaction mixture was taken out of the tube and treated as usual. Five products were obtained as following; **IV** (0·309 g, 14%), **VIII** (0·0034 g, 0·2%), **VII** (0·011 g, 0·5%), **IX** (0·032 g, 1·5%) and **II** (0·058 g, 2·4%).

Reaction of **X** *using sodium hydride in carbon tetrachloride.* Into a glass tube were charged a Na salt of **X** (4·00 g of **X** and 0·51 g of NaH) and thoroughly deoxygenated CCl_4 (30 ml)· The tube was flashed with N_2 and closed. Then the mixture was heated at 100° for 2·5 hr. The resulting reaction mixture was taken out of the tube and chromatographed by a column of alumina. Besides the trace amounts of **IV** and **VII**, there obtained **II** (0·210 g, 9·0%), and 2-ferrocenyl-2-methyl-dichloroethylene (**XII**), (0·08 g, 3%). The compound **XII** was crystallized from pentane as orange needles, m.p. 52–53°. (Found: C, 53·10; H, 4·11, $C_{13}H_{12}Cl_2Fe$ requires: C, 52·90; H, 4·10%); halogen test positive (Beilstein); IR (Nujol), 3100, 1600, 1273, 1104, 1025, 1000, 901, 830, 812 and 704 cm^{-1}; UV (cyclohexane), λ_{max} 232 nm (log ε 4·26), 280 (3·99) and 454 (2·47); NMR (CCl_4), τ 5·57 and τ 5·87 (m; 2H + 2H, substituted ferrocenyl ring), τ 5·98 (s; 5H, ferrocenyl) and τ 7·83 (s; 3H, methyl).

Competitive reaction of vinylferrocene and styrene towards dichlorocarbene. To a soln of **IV** (4·24 g, 0·02 mole) and styrene (2·08 g, 0·02 mole) in dry monoglyme (150 ml) was added sodium trichloroacetate (3·71 g, 0·02 mole). Then the soln was heated with mechanical stirring to 80°. After the gas evolution ceased (1 hr), the mixture was concentrated under reduced press (100 mmHg). The residual oil was chromatographed on an alumina column (200 g). The adducts of dichlorocarbene, 1,1-dichloro-2-ferrocenylcyclopropane,[21] m.p. 80·5–81·5°, and 1,1-dichloro-2-phenylcyclopropane,[22] 78–83°/2 mmHg, were isolated in yields of 13·2% (0·778 g) and 10·4% (0·524 g), respectively, besides recovery of **IV** (43%) and styrene (62%).

Competitive reaction of vinylferrocene and styrene towards diphenylcarbene. A soln of **IV** (12·7 g, 0·06 mole), styrene (6·2 g, 0·06 mole) and diphenyldiazomethane[23] (0·06 mole) derived from HgO oxidation of benzophenone hydrazone, in dry pyridine (150 ml) was heated (80°) with stirring until the gas evolution was complete (3 hr). The resulting mixture was concentrated under reduced press and then chromatographed over alumina (350 g). The adducts, 1,1-diphenyl-2-ferrocenylcyclopropane, m.p. 119–120·5°, and 1,1,2-triphenylcyclopropane, b.p. 150–155/1·5 mmHg, were isolated in yields of 14·0% (3·2 g) and 2·0% (0·36 g), respectively.

Competitive reaction of vinylferrocene and p-*methoxystyrene towards diphenylcarbene.* A soln of **IV** (8·5 g, 0·04 mole), *p*-methoxystyrene (5·4 g, 0·04 mole) and diphenyldiazomethane (0·04 mole) in 100 ml dry pyridine was allowed to react as above. The adducts, ferrocenyldiphenylcyclopropane (0·188 g, 1·2%) and 1,1-diphenyl-2-(*p*-methoxyphenyl)-cyclopropane (1·774 g, 14·8%) with m.p. 111–112° were isolated by an alumina column chromatography.

Competitive reaction of styrene and cyclohexene towards diphenyl carbene. Styrene (10·5 g, 0·1 mole) and cyclohexene (48·6 g, 0·6 mole) and diphenyldiazomethane (0·1 mole) reacted in 150 ml pyridine at 80°. Triphenylcyclopropane was obtained in 22·7% yield (6·125 g), but no adduct to cyclohexene was detected. When 4-methylcyclohexene was used instead of cyclohexene, no adduct of cyclohexene was detected.

Identifications of products formed in the competitive reactions. 1,1-diphenyl-2-ferrocenylcyclopropane; m.p. 120–120·5° from *n*-hexene. (Found: C, 79·13; H, 5·85; M.W. 389 (VPO), $C_{25}H_{22}Fe$ requires: C, 79·39; H, 5·86%; M.W. 378·3); IR (Nujol), 1603, 1499, 1101, 1073, 1050, 1031, 996, 825, 810, 755 and 699 cm^{-1}; NMR (CS_2), τ 3·05 (d; 10H, phenyl), τ 5·97 (m; 1H, ferrocenyl substituted), τ 6·09 (s; 5H, ferrocenyl), τ 6·41 (m; 1H, ferrocenyl), τ 6·88 (m; 1H, ferrocenyl), τ 7·65, 8·42 and 8·53 (q; 3H, ABX pattern of cyclopropyl ring protons).

1,1,2-triphenylcyclopropane; b.p. 150–155/1·5 mmHg. (Found: C, 93·19; H, 6·81, $C_{21}H_{18}$ requires: C, 93·29; H, 6·71%); IR (liquid film), 3130, 3080, 2960, 1600, 1500, 1450, 1072, 1026, 965, 900, 770, 760, 730 and 695 cm^{-1}; NMR (CS_2), τ 2·75–3·30 (m; 15H, phenyl), τ 7·24, 8·12 and 8·33 (q; 3H, ABX pattern of cyclopropyl ring protons).

1,1-diphenyl-2-(*p*-methoxyphenyl)-cyclopropane; m.p. 111·5–112·5° from benzene–hexane. (Found: C, 88·06; H, 6·63; M.W. 280 (VPO), $C_{22}H_{20}O$ requires: C, 87·96; H, 6·71%; M.W. 300·4); IR (Nujol), 1610, 1600, 1515, 1495, 1380, 1300, 1248, 1182, 1030, 968, 835, 812, 765, 756, 735 and 700 cm^{-1}; NMR (CS_2), τ 2·95 and 3·08 (s; 5H + 5H, phenyl), τ 3·52 (q; 4H, *p*-anisyl ring protons), τ 6·46 (s; 3H, methoxy), τ 7·38, 8·26 and 8·43 (q; 3H, ABX pattern of cyclopropyl ring protons).

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[*] On the basis of other interests, a few ferrocenylcarbenes were hitherto studied.[5]

[†] Ferrocenylcarbinyl derivatives are known to be very reactive towards nucleophiles.[10]