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Reactions of Ferrocenylcarbene. III. The Addition Reactions of Some α-Ferrocenylcarbenes to 1,1-Diphenylethylene*[1]

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The addition reactions of α-ferrocenylcarbenes (ferrocenyl, ferrocenylmethyl, and ferrocenylphenyl carbene) to 1,1-diphenylethylene have been examined by means of the thermal decomposition of the corresponding acylferrocene tosylhydrazone sodium salts. Then, the reactivities of the ferrocenylcarbenes have been compared with those of the corresponding phenyl and *p*-anisylcarbenes. It has been found that, of the carbenes investigated, the ferrocenylcarbenes show the lowest reactivity in addition reactions to the olefin. It has been established by a study of the NMR spectra that, in the ferrocenylcyclopropanes only, there is a restricted rotation about the bond between ferrocenyl and cyclopropyl groups. On this basis, the reactivity of the ferrocenylcarbenes has been discussed in terms of the steric hindrance of the bulky ferrocenyl group.

In previous papers[1] on the reactions of ferrocenylcarbenes, we have reported that the α-ferrocenylcarbenes (Ia, Ib, and Ic) are all triplets. Thus, it has been revealed that these ferrocenylcarbenes abstract hydrogen atoms or halogen atoms from solvents and easily react with oxygen to form the corresponding carbonyl compounds. Further, they add to particular olefins bearing effective radical-stabilizing group(s), such as phenyl or ferrocenyl, to form ferrocenylcyclopropane derivatives.

It is known that a triplet carbene adds to 1,1-diphenylethylene, yielding a cyclopropane derivatives.[2] This carbene trapping ability of the olefin is probably due to the intermediary formation of a stable diphenylmethylradical. In order to elucidate the reactivity of ferrocenylcarbenes, the addition reactions of these carbenes to 1,1-diphenylethylene has been investigated and compared with those of phenyl and *p*-anisylcarbenes.[3]

Results and Discussion

When the thermal decompositions of acylferrocene tosylhydrazone sodium salts[4] were carried out in a mixed solution of dry pyridine and about a tenfold excess of 1,1-diphenylethylene, as addition products 1,1-diphenyl-2-ferrocenylcyclopropane derivatives were obtained, plus a small amount of azine derivatives.

The yields of ferrocenylcyclopropane derivatives might directly reflect the addition reactivity of ferrocenylcarbenes formed in the thermal decomposition of the tosylhydrazone salts. Therefore, the reactions of the corresponding phenyl and *p*-anisylcarbenes with 1,1-diphenylethylene were investigated under similar conditions in order to estimate the effect of the ferrocenyl group on the reaction of an adjacent divalent carbon by comparing it with phenyl and *p*-anisyl groups. The yields of the cyclopropane derivatives are listed in Table 1.

TABLE 1. THE YIELDS OF CYCLOPROPANE DERIVATIVES FORMED BY THE THERMAL DECOMPOSITION OF SODIUM SALTS OF I IN 1,1-DIPHENYLETHYLENE

R′	R-		
	Ferrocenyl	Phenyl	*p*-Anisyl
H	13%	6%	35%
CH_3	41	59	75
C_6H_5	14	23	27

It appears from Table 1 that the reactivity of carbenes increases in the following sequence; ferrocenyl<phenyl<*p*-anisyl. Thus, when R′ is methyl or phenyl, the yield of ferrocenylcyclopropane was found to be the lowest. It should be

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*1 Presented at the 21st Annual Meeting of the Chemical Society of Japan, Osaka, April, 1968.

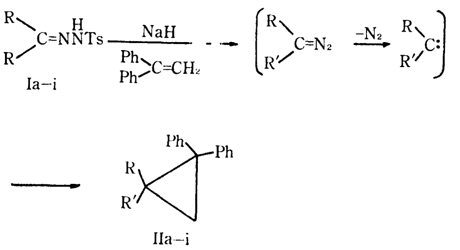
[1] A. Sonoda, I. Moritani, T. Saraie and T. Wada, *Tetrahedron Lett.*, **1969**, 2943; b) A. Sonoda, I. Moritani, S. Yasuda and T. Wada, *Tetrahedron*, **26**, 3075 (1970).

[2] a) R. M. Etter, H. S. Skovronek and P. S. Skell, *J. Amer. Chem. Soc.*, **81**, 1008 (1959); b) J. E. Hodgikins and M. P. Hughes, *J. Org. Chem.*, **27**, 4187 (1962).

[3] It is well known that arylcarbenes are triplet: W. Kirmse "Carbene Chemistry," Academic Press, New York, N. Y. (1964), Chapter 5.

[4] W. R. Bamford and T. S. Stevens, *J. Chem. Soc.*, **1952**, 4735.

Reaction scheme



	R	R′
a:	$C_{10}H_9Fe$	H
b:	$C_{10}H_9Fe$	CH_3
c:	$C_{10}H_9Fe$	C_6H_5
d:	C_6H_5	H
e:	C_6H_5	CH_3
f:	C_6H_5	C_6H_5
g:	$CH_3OC_6H_4$	H
h:	$CH_3OC_6H_4$	CH_3
i:	$CH_3OC_6H_4$	C_6H_5

noted that the reactivity of the ferrocenylcarbenes is the lowest. This fact is of interest, since the radical stabilizing effect of the ferrocenyl group may be considered to be not less than that of the *p*-anisyl group, as deduced from their resonance stabilizing effect on the α-carbonium ions.[5] Table 1 also shows that the effecs of R′ on the reactivity increases in the order of: $H \ll Ph < CH_3$. This result indicates that a steric factor palys an important role, since the expected order of the radical-stabilizing effect between phenyl and methyl groups appears to be reversed.

The structural elucidation of the addition products suggests that there is a significant steric crowding in the 1,1-diphenyl-2-ferrocenyl cyclopropane derivatives. Thus, in the NMR spectra of IIa—c, it was found that the signal of one *ortho* (adjacent to the cyclopropyl group) proton of the ferrocenyl ring shifted unusually to a higher field.[6] This phenomenon can reasonably be explained in terms of an anisotropic effect of a spacially-fixed phenyl ring attached to the cyclopropane ring in *cis* configuration to the ferrocenyl group.[7]

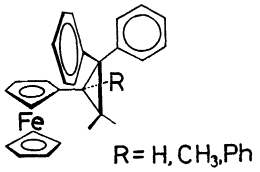


Fig. 1.

For example, in the NMR spectrum of 1,1-diphenyl-2-ferrocenylcyclopropane (IIa), ferrocenyl ring proton signals were observed at τ 5.97, 6.19,

IIb in diphenylether. (HMDS internal standard)

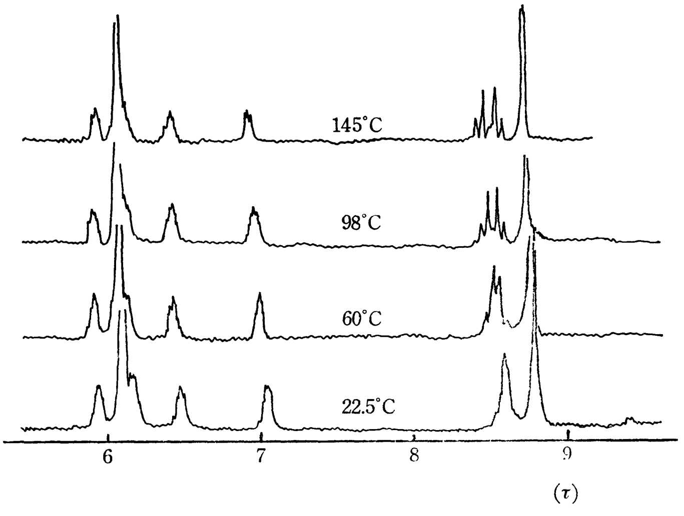


Fig. 2. Temperature dependence of NMR spectra of IIb (100 MHz).

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[5] T. G. Traylor and J. C. Ware, *J. Amer. Chem. Soc.*, **89**, 2304 (1967).

[6] It is known that in ferrocene system, electron donating groups such as alkyl substituents exert an effect of some higher field shifts on the ferrocenyl ring protons: M. Rosenblum, "Chemistry of the Iron Group Metallocenes," Interscience Publishers, New York, N. Y. (1965), p44. But, such an extraordinary high field signal of ferrocenyl ring proton as appeared in this ferrocenylcyclopropane system has not been reported.

[7] In *o*-ferrocenyl-biphenyl derivatives, the ferrocenyl ring protons of 2 and 5 position are known to be considerably shielded by a phenyl ring current: Ref. 6, p. 217. This situation resemble to our case. On the other hand, the shilding by cyclopropane ring might be estimated to be less extensive in five membered ring system than that in phenylcyclopropane.

6.41 (each one proton), τ 6.09 (five protons), and τ 6.88 (one proton). The methylene and methine protons of the cyclopropane ring gave signals of an ABX pattern at a high field. This great upfield shift of a proton signal of the ferrocenyl ring can also be observed in two other ferrocenylcyclopropanes; in both IIb and IIc the signal appears at τ 7.05. These NMR data are listed in Table 3.

By the examination of molecular models, it is found that the rotation of the bond between the ferrocenyl group and the cyclopropane ring is greatly restricted by the conflict of the *cis* phenyl group with the unsubstituted cyclopentadienyl ring.

When the temperature dependence of the NMR spectrum of 1,1-diphenyl-2-ferrocenyl-2-methylcyclopropane (IIb) was investigated in a diphenyl ether solution, using HMDS as the internal standard and at 22.5, 60, 98, and 145°C, it was observed that the higher-field one-proton signal tended to move slightly down field with an increase in the temperature, while the other signals, with the exception of the methylene signal, remained almost unchanged. The results are shown in Fig. 2.

It should be noticed here that the methylene protons of the cyclopropane in IIb, which unexpectedly give a singlet peak at τ 8.51 in CS_2 at room temperature (Table 3), split into an AB pattern with an increase in the temperature in diphenyl ether. This interesting NMR behavior the methylene signal might be reasonably interpreted as follows; at room temperature the chemical shifts of the two proton signals under the most favorable conformation of IIb become, by chance, coincident, resulting in a singlet peak, while at an elevated temperature they are split by thermal perturbation.

These observations obviously indicate that the rotation of the bond between ferrocenyl and cyclopropyl groups is highly hindered and that even at elevated temperatures, the rotation is completely restricted.

On the other hand, in the NMR spectra of 1,1-diphenyl-2-(*p*-anisyl)cyclopropanes (IIg—i), and 1,1,2-triphenylcyclopropanes (IId—e), no such anisotropy was observed. In these NMR spectra of IIg—i, the ring protons of the *p*-anisyl group showed the usual AB splitting pattern. It may safely be said that the anisyl and phenyl groups are freely rotating.

After these discussions, it can be concluded that, among these reaction products (IIa—i), there exists strongly restricted rotation only in 1,1-diphenyl-2-ferrocenylcyclopropanes, and that the addition of ferrocenylcarbenes to 1,1-diphenylethylene, producing these ferrocenylcyclopropanes, must overcome a much greater steric hindrance than those of phenyl and *p*-anisylcarbenes. Accordingly, the low reactivity of the ferrocenylcarbenes can be attributed to the steric hindrance of a bulky ferrocenyl group.

Experimental

The infrared spectra were recorded on a Hitachi EPI-S2 spectrophotometer, the visible and ultra violet spectra, on a Hitachi EPS-2U, and the NMR spectra, on a JEOLCO JNM-4H-100 at 100 MHz. All the reactions were carried out under an atmosphere of high-purity nitrogen gas or argon gas. All the temperatures are uncorrected.

Materials. The 1,1-diphenylethylene was prepared by the usual Grignard reaction of phenylmag-

Table 2. The physical constants and analytical data of tosylhydrazones I

Tosylhydrazone (Recrystallization solvent)	Mp °C (lit.)	Analysis (calcd) C%	H%	N%
Ia (benzene)	154—156*	56.62 (56.56)	5.07 (4.77)	7.29 (7.33)
Ib (benzene)	186—187*	57.59 (57.58)	5.16 (5.09)	7.05 (7.07)
Ic (EtOH)	167—169*	63.14 (62.88)	4.87 (4.80)	6.34 (6.11)
Id (benzene)	125—126 (128)[a]	61.40 (61.29)	5.15 (5.14)	10.26 (10.21)
Ie (benzene)	146—147 (148)[a]	62.29 (62.47)	5.68 (5.60)	9.88 (9.71)
If (benzene)	181—182 (184)[a]	68.33 (68.51)	5.19 (5.18)	7.89 (7.99)
Ig (MeOH)	121—122 (112—114)[b]	59.29 (59.19)	5.37 (5.30)	9.24 (9.24)
Ih (AcOEt)	175—176	60.44 (60.36)	5.85 (5.70)	8.83 (8.80)
Ii (MeOH)	156—158	66.24 (66.30)	5.21 (5.30)	7.33 (7.36)

* With decomp. a) Ref. 4. b) Ref. 18.

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8) D. G. Farnum, *J. Org. Chem.*, **28**, 870 (1963).

TABLE 3. THE NMR SPECTRAL OF II (τ-Value in CS$_2$, (Intensity, signal pattern)[a])

Compounds	Benzene ring protons		Cyclopentadienyl ring protons (unsubst.)	(subst.)		Cyclopropyl		Other
IIa	3.02(5H,s)	3.07(5H,s)	6.09(5H,s)	5.97(1H,m) 6.41(1H,m)	6.19(1H,m) 6.88(1H,m)	7.64(1H,q)	8.48(2H,m)	
IIb	2.42(5H,m)	3.12(5H,s)	6.08(5H,s)	5.90(1H,m) 6.43(1H,m)	6.09(1H,m) 7.05(1H,m)		8.51(2H,s)	8.75(3H,s)[b]
IIc	2.91(5H,m) 3.29(5H,s)	3.02(5H,s)	6.26(5H,s)	6.28(1H,m) 7.05(1H,m)	6.40(2H,m)	7.50(1H,d)[d]	8.18(1H,d)[d]	
IId	2.8—3.3(15H,c)					7.22(1H,q)	8.21(2H,m)	
IIe	2.4—3.2(15H,c)					7.85(1H,d)[e]	8.51(1H,d)[e]	8.65(3H,s)[b]
IIf	3.14(20H,s)					7.64(2H,s)		
			Anisyl ring protons					
IIg	2.96(5H,s)	3.09(5H,s)	3.41(2H,d)[f]	3.61(2H,d)		7.38(1H,q)	8.36(1H,m)	6.46(3H,s)[c]
IIh	2.6—3.3(10H,c)		3.12(2H,d)[g]	3.53(2H,d)[g]		8.03(1H,d)[i]	8.63(1H,d)[i]	8.79(3H,s)[b] 6.46(3H,s)[c]
IIi	3.11(5H,s)	3.13(5H,s)	3.21(2H,d)[h]	3.61(2H,d)[h]		7.68(2H,s)		6.46(3H,s)[c]

a) s: singlet, d: doublet, q: quartet, m: multiplet, c: complex. b) methyl protons. c) methoxy protons. d) J=6Hz. e) J=5Hz. f) J=8Hz. g) J=8Hz. h) J=8Hz. i) J=5Hz.

Table 4. The ultraviolet spectral data and analytical data of II

	Mp (Bp) °C	UV. λ_{max} in nm ($\log \varepsilon$) in n-hexane	Analysis and M.W* (calcd)		
			C%	H%	M.W.
IIa	120—120.5	250 (3.94 sh) 442 (2.21)	79.13 (79.37)	5.85 (5.86)	389 (378.3)
IIb	127—128	253 (3.85 sh) 444 (2.15)	79.51 (79.60)	6.24 (6.12)	396 (392.3)
IIc	175—176	250 (4.03 sh) 447 (2.27)	81.80 (81.79)	5.72 (5.98)	456 (455.4)
IId	(150—155/1.5 mmHg)	227 (4.23) 269 (3.27) 277 (2.99)	93.19 (93.29)	6.81 (6.71)	266 (270.4)
IIe	67—68 (161—162/2 mmHg)	214 (4.64) 254 (3.22) 261 (3.11)	92.97 (92.91)	7.06 (7.09)	278 (284.9)
IIf	165—166	212 (4.53) 241 (4.29) 270 (3.42) 278 (3.12)	93.78 (93.60)	6.51 (6.40)	357 (346.5)
IIg	111—112	225 (4.43) 236 (4.40) 272 (3.78) 278 (3.56) 292 (3.32)	88.06 (87.96)	6.63 (6.71)	280 (300.4)
IIh	82—83	227 (4.60) 279 (3.13) 285 (3.06)	88.12 (87.86)	7.17 (7.05)	308 (314.4)
IIi	142.5—143.5	240 (4.34) 277 (3.60) 286 (3.48) 291 (3.30 sh)	89.18 (89.32)	6.42 (6.43)	374 (376.5)

* VPO in benzene.

nesium bromide with acetophenone in ether, followed by dehydration with dil. sulfuric acid. The resulting crude substance was distilled twice through a short column under reduced pressure. Bp 114—115°C/3 mmHg, (lit,[9] 113°C/2 mmHg).

All the tosylhydrazones used in this study were prepared by the reactions of the corresponding ketones or aldehydes with a slight excess of tosylhydrazine in boiling ethanol. Among the starting materials, formylferrocene,[10] acetylferrocene,[10] benzoylferrocene,[11] p-methoxyacetophenone,[12] and p-methoxybenzophenone,[12] were prepared by known synthetic routes. The others were obtained from a commercial source.

The melting points and analytical data of these tosylhydrazones are summarized in Table 2.

Thermal Decomposition of Ia-i in a Pyridine-1,1-diphenlethyleyne Mixture. The physical properties, analytical data, and spectral data of the reaction products, IIa-i, are summarized in Tables 3 and 4.

Reaction of Ia. To a solution of Ia (7.65 g, 0.02 mol) in 50 ml of dry pyridine (over BaO), sodium hydride (1.38 g, 50% in oil) was added in one portion. Then the solution was mixed with mechanical stirring. After the rapid hydrogen gas evolution had been completed, 35 g (0.2 mol) of 1,1-diphenylethylene was added to the mixture. After the reaction system had then been flushed with Ar gas, the mixture was stirred vigorously at 90—98°C until the nitrogen gas evolution ceased (2 hr). The resulting mixture was cooled to room temperature, and then decomposed by adding 30 ml of water. The resulting solution was extracted with 300 ml of ether. The organic phase was separated and combined with extracts of the aqueous phase. The ether solution was washed with 100-ml portions of water seven times and dried over sodium sulfate. After the ether had then been evaporated, the residual oil was distilled under reduced pressure. The unreacted 1,1-diphenylethylene was recovered at 105—110°C/3 mmHg (31 g). The dark brown residual oil (8.5 g) was subjected to alumina-column elution chromatography (100 g of Al_2O_3). IIa was eluted with pentane as yellow needles; 0.93 g (12.5%); mp 114—118°C. Recrystallization from hexane afforded yellow needles; mp 120—120.5°C. IR spectrum (Nujol): 1603, 1496, 1102, 1073, 1050, 1030, 1015, 998, 961, 825, 810, 755, and 698 cm^{-1}.

Benzene-hexane (1 : 1) eluted orange-red crystals of formylferrocene azine; mp 267—268°C (lit,[10] 245°C). Found: C, 62.11; H, 4.92; N, 6.40%. Calcd for $C_{22}H_{20}N_2Fe$: C, 62.31; H, 4.75; N, 6.61%. IR spectrum (Nujol): 1635 (C=N), 1410, 1105, 1000, and 830 cm^{-1}. This azine was identified by means of comparing its mp with that of an authetic sample synthesized from the reaction of formylferrocene with hydrazine hydrate in boiling ethanol. The elution with methanol afforded a black polymeric material which was unidentified (ca. 3 g).

Reaction of Ib. The reaction of Ib was performed with 15.2 g (0.038 mol) of the tosylhydrazone in 95 ml of dry pyridine and 65 g (0.36 mol) of diphenylethylene under conditions similar to those above. An alumina chromatography of reaction mixture afforded 6.03 g (40.5%) of IIb, (mp 127—128°C), from hexane. IR spectrum (Nujol): 1598, 1492, 1178, 1135, 1102, 1042, 1030, 1015, 1000, 981, 943, 913, 860, 822, 808, 766, 751, and 702 cm^{-1}.

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9) C. F. H. Allen and S. Converse, "Organic Syntheties," Coll. Vol. I, p. 226 (1956).

10) P. J. Graham, R. V. Rindsey, G. W. Parshall, M. L. Peterson and G. M. Whiteman, *J. Amer. Chem. Soc.*, **79**, 3416 (1957).

11) N. Weliky and E. S. Gould, *ibid.*, **79**, 2742 (1957).

12) R. Adams and C. R. Noller, "Organic Syntheses," Coll. Vol. I, p. 111 (1956).

From the benzene-hexane eluate, small amounts of two crystalline materials (mp 149—150°C, M.W. 880, and mp 147—148°C, M.W. 392) were isolated, besides a trace amount of azine. These structures have not yet been elucidated.

Reaction of Ic. Ic, 9.15 g (0.02 mol) were reacted in 50 m*l* of pyridine and 36 g of diphenylethylene under similar conditions. This reaction afforded IIc: 1.22 g; mp 175—176°C, (13.5%). IR spectrum (Nujol): 1601, 1495, 1103, 1072, 1035, 1026, 1000, 975, 900, 813, 800, 771, 750, 712, 700, and 690 cm^{-1}. Benzene-hexane eluted benzoylferrocene azine, 1.9 g, mp 155—157°C, which was identified by comparison with an authentic specimen (mixed mp and IR).

Reactions of Id-f. Each of the tosylhydrazones, Id, Ie, and If, (0.038 mol) was reacted in the usual manner. IId was obtained as a colorless liquid; 0.580 g (5.7%); 150—155°C/1.5 mmHg. IR spectrum (liquid film): 3120, 3080, 1605, 1500, 1450, 1072, 1030, 963, 772, 760, 733, and 695 cm^{-1}. IIe was obtained as colorless crystals; 6.35 g (58.7%); mp 161—162°C. IR spectrum (liquid film): 1598, 1490, 1440, 1075, 1064, 1011, 770, 746, and 700 cm^{-1}. IIf was obtained as colorless crystals; 3.08 g (23.4%); mp 165—166°C, (lit[2b] 165—165.5°C). IR spectrum (Nujol): 1600, 1495, 1072, 1031, 1006, 907, 795, 755, 717, and 695 cm^{-1}.

Reactions of Ig-i. Ig, Ih, and Ii (0.040 mol) were all reacted as usual. However in the reactions of Ih and Ii the temperature was raised to 120°C in order to smooth the decomposition of the salts. IIg was obtained as colorless crystals; 4.20 g (35.0%); mp 111—112°C. IR spectrum (Nujol): 1610, 1600, 1514, 1495, 1300, 1245, 1185, 1030, 967, 835, 812, 766, 757, 733, and 700 cm^{-1}. IIh (9.43 g, 75%) was obtained. Mp 82—83°C. IR spectrum (liquid film): 3100, 3070, 2960, 1612, 1603, 1512, 1495, 1450, 1380, 1245, 1180, 1030, 829, 770, 750, 706, and 695 cm^{-1}. IIi (4.10 g 27%) was obtained. Mp 142.5—143.5°C. IR spectrum (Nujol): 1612, 1602, 1510, 1495, 1245, 1173, 1106, 1029, 782, 750, 730, and 699 cm^{-1}.

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