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THE ADDITION OF 2,4-DINITROBENZENESULFENYL CHLORIDE TO SOME ALKYL-SUBSTITUTED VINYLFERROCENES

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Summary

The addition of 2,4-dinitrobenzenesulfenyl chloride to alkyl-substituted vinylferrocenes has been investigated in CH_2Cl_2, 1,1,2,2-tetrachloroethane and acetic acid solutions. Product analyses were carried out by VPC and PMR techniques and reaction rates measured by a spectrophotometric method.

The orientation appears to be determined by the structural features of the intermediate episulfonium ion rather than by the site of the primary attack of the electrophile on the starting substrate. A comparison with the results previously obtained with the methoxymercuration reaction has a bearing on the mechanism of the latter reaction.

Introduction

Special attention has been drawn to the reactions of ferrocenes with electrophilic reagents because of their great ease of reaction whether ring substitution or addition to a vinyl side-chain are considered. Experimental limitations due to oxidation of the ferrocene moiety have restricted the spectrum of reactions suitable for quantitative studies in the field. In recent years we have investigated the methoxymercuration reaction of alkyl-substituted vinylferrocenes and the accompanying ring mercuration [1]. In continuation of these studies we have now considered 2,4-dinitrobenzenesulfenyl chloride (ArSCl) as the electrophile, which appeared to be a smooth reagent for addition on the vinyl side-chain. Besides the experimental accessibility of the reaction of ArSCl, a major interest in this and related reagents is its tendency to add to alkenes by a mechanism involving a bridged cation (episulfonium ion) [2—4].

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* In honor of Professor Henry Gilman who initiated one of the authors of this paper (G.I.) into organic chemistry and infused him with self-confidence.

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The aim of our work is to obtain information on the mechanism of addition when the powerful electron-releasing ferrocenyl group is linked to an unsaturated carbon of the alkene and to lay the foundation for a better understanding of the methoxymercuration reaction, for which the formation of intermediate bridged cations was shown to be likely to occur. A first account of these studies is reported in the following. The investigated ferrocenes include the following side-chains: vinyl, α-methylvinyl, *trans*-β-methylvinyl, and β,β-dimethylvinyl.

Results and discussion

Vinylferrocene and its methyl-substituted derivatives react smoothly with ArSCl at 25° C in diverse solvents and exclusively undergo addition to the double bond in the side-chain. The expected addition products are $\mathrm{Fc\overset{|}{C}(SAr)}$-$\mathrm{\underset{|}{C}Cl}$ and $\mathrm{Fc\overset{|}{C}(Cl)\underset{|}{C}SAr}$, depending on the orientation of addition. Actually, we deal with the corresponding products of hydrolysis whereby Cl is replaced by OH. Unlike methoxymercuration, the reaction is not accompanied by ring substitution. This was confirmed by the fact that ferrocene itself does not react with ArSCl even under the conditions of the slowest-reacting member of the vinyl-substituted series, i.e., β,β-dimethylvinylferrocene.

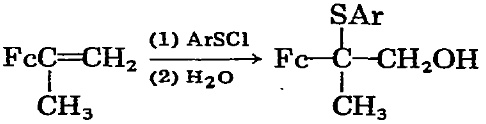
Product analysis was performed for the reaction carried out in CH_2Cl_2 solution using VPC and PMR techniques, and produced consistent results, since both techniques showed that α-methylvinyl- and β,β-dimethylvinyl-ferrocenes yield only one addition product whereas vinyl- and *trans*-β-methylvinyl-ferrocenes lead to the two possible addition products of roughly comparable composition in each case (eq. 1). The reaction of vinylferrocene in acetic acid solution also yielded two addition products.

$$\mathrm{FcCH{=}CH_2 \xrightarrow[(2)\ H_2O]{(1)\ ArSCl} FcCH(SAr)CH_2OH + FcCH(OH)CH_2SAr} \qquad (1)$$

On running the reaction of vinylferrocene in CD_3CO_2D or $CDCl_3$, the vinyl proton signals in the δ range of 3.9—4.8 ppm gradually disappear together with those of the ring protons of the starting substrate whilst new signals for the reaction products are observed.

Unlike the PMR spectrum for the addition reaction of styrene [3b], the signals for the side-chain of the ferrocene products cannot be reliably identified since they fall in the Cp protons region (δ 4—5 ppm).

When two addition products are formed they are clearly indicated by two sets of signals corresponding to the ArS moiety as bound to the α or β carbon atoms (δ 7.5—9.1 ppm).



$$\mathrm{Fc\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH_2 \xrightarrow[(2)\ H_2O]{(1)\ ArSCl} Fc{-}\overset{\displaystyle SAr}{\underset{\displaystyle \underset{CH_3}{|}}{\overset{|}{C}}}{-}CH_2OH} \qquad (2)$$

A firm structural assignment was possible for the reaction of the α-methylvinyl derivative leading to a single product whose spectrum shows a clean-cut triplet at δ 6.25 ppm (*J* 1.5 Hz) due to the OH proton in the grouping CH_2OH. Therefore, the reaction in such a case occurs according to eq. 2.

The rate of the reaction was followed by a spectrophotometric method in the visible taking advantage of the increase in absorbance as the reaction proceeds to yield strongly colored products. The reaction was found to be first order in each reactant for all tested substrates and both in acetic acid and some nonhydroxylic solvents (1,1,2,2-tetrachloroethane and dichloromethane). The rate constants are collected in Table 1.

The reactivity in the nonprotic solvents tetrachloroethane (TCE) and CH_2Cl_2 is comparable to that observed in acetic acid and this can be related to the mediocre polarity of such solvents (solvent, ϵ at 20°C, μ): TCE, 8.20, 1.71; CH_2Cl_2, 8.93, 1.14; AcOH, 6.15, 1.68 [5]. The hydroxylic character of acetic acid does not seem to be particularly effective although we would expect some assistance in the removal of the chloride ion as noted for electrophilic aromatic chlorination by Cl_2 [6].

As expected, the ferrocene compounds are markedly more reactive than the corresponding benzene compounds. The reactivity of styrene was studied by Kharasch [2] with the same reagent in acetic acid solution. We now find that vinylferrocene is 640 times as reactive as styrene. With the methoxymercuration the related ratio was found to be ca. 22 in methanol solution. Although the comparison is subject to some reservation because of the different solvent, it would appear that ArSCl is a more selective reagent than mercuric acetate towards addition to the ethylene linkage.

If vinylferrocene is taken as the reference compound, substitution of hydrogen by one methyl group at the position α is rate-enhancing, in line with the electrophilic nature of the reaction. It is noteworthy that no large difference in selectivity between chlorosulfenylation and methoxymercuration is observed within the vinylferrocene series. In fact, the α-methylvinyl/vinyl reactivity ratio is closely similar in the two reactions, i.e., 3.2 (Table 1) and 4.0 (see ref. [1]), respectively.

At the β position one and two methyl groups have increasing rate-depressing effects. The reactivity sequence α-CH_3 > H > β-CH_3 > β,β-$(CH_3)_2$ is analogous to that found with the methoxymercuration reaction and can be similarly interpreted in terms of predominant steric hindrance effect of the methyl group at the position β.

When compared to the mercurating reagent, ArSCl appears to possess lower steric requirements, however. A β-methyl group produces depressing factors of

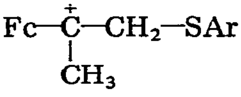
TABLE 1

SECOND-ORDER RATE CONSTANTS AND RELATIVE RATES FOR THE REACTION BETWEEN SOME ALKYLVINYLFERROCENES AND ArSCl IN VARIOUS SOLVENTS, AT 25°C.

Substrate	in AcOH		in TCE		in CH_2Cl_2	
	$k_2(M^{-1}s^{-1})$	k_{rel}	$k_2(M^{-1}s^{-1})$	k_{rel}	$k_2(M^{-1}s^{-1})$	k_{rel}
$FcCH=CH_2$	0.47 ± 0.02	1	0.85 ± 0.04	1	0.31 ± 0.09	1
$FcC(CH_3)=CH_2$	1.53 ± 0.04	3.2	6.0 ± 0.9	7.1	4.2 ± 0.7	13.5
$FcCH=CHCH_3$	1.15 ± 0.01	0.3	0.44 ± 0.02	0.5	0.45	1.4
$FcCH=C(CH_3)_2$	(5.7 ± 0.2)	1.2	2.65	3.1	1.86	6.0
	$\times 10^{-3}$	$\times 10^{-2}$	$\times 10^{-2}$	$\times 10^{-2}$	$\times 10^{-2}$	$\times 10^{-2}$

3.3 and 2 for the ArSCl reaction in acetic acid and TCE solution, respectively, and a factor of 3.4×10^3 for the mercuric acetate reaction in methanol solution. It is of interest that the effect of the β-methyl group for the ArSCl reaction is moderately solvent dependent and becomes slightly rate-enhancing with methylene chloride as a solvent. Changes in solvation in going from the initial state to the transition state in diverse solvents may be held responsible for the dependence of the apparent steric requirements of the reaction on solvent within the modest rate factors observed.

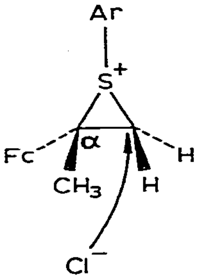
The formation of the anti-Markownikoff product from the α-methylvinyl derivative (eq. 2) and the occurrence of both orientations as observed in the reaction of the vinyl- and β-methylvinyl-ferrocenes show that the reaction does not involve a carbocation as an intermediate. Such an ion in the case of the α-methylvinyl derivative would exclusively consist of I in view of the strong stabilizing effect of the Fc and CH_3 groups on the adjacent positive charge and



$$\mathrm{Fc{-}\overset{+}{\underset{\displaystyle CH_3}{\underset{|}{C}}}{-}CH_2{-}SAr}$$

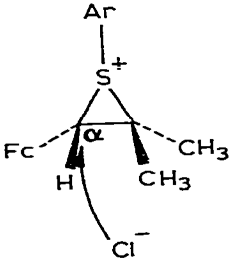
(I)

of the minimum steric hindrance met by the reagent on the attack to the CH_2 side of the double bond. Failure in the formation of ion I is in accord with the known tendency of the sulfenyl chloride reagent to form episulfonium ions. The product-determining reaction then results from attack of the least hindered position by the chloride ion (II). The effect of the Fc group to promote the



(II)

attack of Cl^- to the position α should emerge when hindrance is decreased at the position α. This explains why in the unsubstituted vinylferrocene and in the β-methyl-substituted derivative both positions compete for attack by Cl^-. Furthermore, when there are two β-methyl groups and, again, only one product is obtained, there is some evidence that such product is of the Markownikoff type and will result from attack of Cl^- to the less hindered position α (III).



(III)

The role of the ArSCl reagent to provide a diagnostic criterion of mechanism is thus confirmed in the ferrocene series and permits us to conclude with a comment concerning a comparison of the behavior of the ArSCl reagent with that of the methoxymercurating reagent [1]. The comparison is allowed by the analogy in the course of addition and kinetic form. The two reactions, however, display several differences in reactivity features and orientation. Despite the larger steric requirements of the methoxymercurating reagent, the exclusive Markownikoff orientation observed [1] with the tested substrates (vinyl-, α-methylvinyl-, β-methylvinyl-ferrocenes) suggests that any reaction intermediate of the bridged cation type should still retain appreciable carbocation character at the carbon. Such a circumstance would permit the orientation of attack of the nucleophile in the second step of the reaction, whereby the product is determined, to be analogous to that expected from a free carbocation having the charge located at the α carbon. As the present work has shown, the product-determining stage of the chlorosulfenylation reaction seems to be independent of the site of attack of the electrophilic atom due to the symmetrical nature of the intermediate episulfonium ion. In contrast, the intermediate mercurinium ion, for which evidence was provided for the methoxymercuration of the ferrocene derivatives [1], appears to have an unsymmetrical structure involving a relatively weak α-carbon—Hg bond as already suggested [7].

Further work is planned for a more detailed and extensive investigation of the chlorosulfenylation reaction in the ferrocene series.

Experimental

Materials

2,4-Dinitrobenzenesulfenyl chloride (ArSCl) was prepared by chlorinolysis of bis(2,4-dinitrophenyl) disulfide with SO_2Cl_2 [8]. The disulfide was obtained in a 75% yield from 2,4-dinitrochlorobenzene and a freshly prepared solution of sodium disulfide in 95% ethanol [9]. The disulfide was crystallized from ethanol and the sulfenyl chloride from carbon tetrachloride.

Vinylferrocene and the alkyl-substituted derivatives were prepared by the dehydration of the corresponding alcohols [1].

Commercially available dichloromethane and anhydrous acetic acid (Erba RS) have been used without further purification. 1,1,2,2-Tetrachloroethane (TCE) was purified according to standard methods [3a] and distilled before use.

Spectral characterization

The electronic spectra were recorded with Beckman DB-GT and Varian DMS 90 spectrophotometers, using silica cells.

PMR spectra were recorded on a Jeol C60-HL spectrometer with CCl_4 or $CDCl_3$ as solvents and TMS as an internal standard.

Product analyses

On mixing the vinylferrocenes and ArSCl in various solvents ($CHCl_3$, CH_2Cl_2, TCE, AcOH), the solution turns from orange-yellow to deep red.

Known amounts of vinylferrocene, α-methylvinylferrocene, β-methylvinylferrocene, and β,β-dimethylvinylferrocene were each mixed with equimolar amounts of ArSCl in CH_2Cl_2 solution. The reaction mixtures were kept 24 h at room temperature, then each was eluted over an alumina (neutral, Brockman II—III) column with diethyl ether. The resulting purified products were analyzed by VPC, by using a Hewlett-Packard Mod. 5830 A gas chromatograph, equipped with a 183 cm × 5.5 mm 2% OV 17 on 80—100 mesh Chromosorb GAW DMCS column. The results of VPC analysis are reported in Table 2.

The same analysis was performed in AcOH with vinylferrocene (Table 2).

PMR spectra of the above purified products in CCl_4 as a solvent are in agreement with the results from VPC analysis, as illustrated in the following.

From vinylferrocene. Two products, as indicated by two series of signals for the aromatic protons: δ (ppm) 8.93 d (J 2.2 Hz), 7.97 dd (J 8.3 Hz, J 2.2 Hz), 7.66 d (J 8.3 Hz); and 9.03 d (J 2.2 Hz), 8.25 dd (J 9.0 Hz, J 2.2 Hz), 7.58 d (J 9.0 Hz). The other signals include δ 4.3—4.5 ppm, complex signal due to substituted Cp ring protons, δ 4.15 ppm, s emerging from a more complex signal (unsubstituted Cp ring protons and $-CH-CH_2-$ system), δ 6.10 and 6.86 ppm, broad singlets, OH.

From α-methylvinylferrocene. One product, δ (ppm) 9.05 d (J 2.2 Hz (1 H)), 8.28 dd (J 9.0 Hz, J 2.2 Hz (1 H)), 7.58 d (J 9.0 Hz (1 H)), aromatic protons; δ 4.53 and 4.30 ppm, two multiplets, 4 H, substituted Cp ring protons; δ 4.13 ppm, s over a more complex signal (7 H, unsubstituted Cp ring and $-CH_2-$); δ 6.25 ppm, t, J 1.5 Hz (1 H), OH; and δ 2.31 ppm, s (3 H), $-CH_3$.

From β-methylvinylferrocene. Two products, as indicated by two sets of signals for the aromatic protons, δ (ppm) 9.09 d (J 2.2 Hz), 8.28 dd (J 9.0 Hz, J 2.2 Hz), 7.50 d (J 9.0 Hz); and 9.02 d (J 2.2 Hz), 8.22 dd (J 8.4 Hz, J 2.2 Hz), 7.48 d (J 8.4 Hz). The remaining signals include δ 4.0—4.6 ppm, complex signal, substituted Cp ring protons; δ 4.18 and 4.07 ppm, two singlets, due to the two unsubstituted Cp ring protons emerging from a more complex signal ($-CH-CH-$ system); δ 6.95 ppm, broad signal, OH; δ 2.08 and 2.12 ppm, two doublets, J 3.0 and 3.8 Hz, respectively, due to the $-CH_3$ protons.

From β,β-dimethylvinylferrocene. One product, δ (ppm) 8.38 d (J 2.2 Hz), 8.11 dd (J 8.4 Hz, J 2.2 Hz), 7.80 d (J 8.4 Hz), aromatic protons; complex signal centered at δ 4.15 ppm, substitued Cp protons; δ 4.03 ppm, s, unsubstituted Cp protons; δ 4.6 ppm, broad signal, OH; and δ 1.16 ppm, d (J 1.5 Hz) $-CH_3$ protons.

TABLE 2

VPC ANALYSIS OF THE PRODUCT COMPOSITION FROM THE REACTION BETWEEN SOME ALKYLVINYLFERROCENES AND ArSCl [a]

Substrate	Products
$FcCH=CH_2$	two products (47/53) [b] two products (73/27) [c]
$FcC(CH_3)=CH_2$	one product [b]
$t\text{-}FcCH=CH-CH_3$	two products (63/37) [b]
$FcCH=C(CH_3)_2$	one product [b]

[a] Relative percentages given in parentheses, in order of increasing RTs. [b] In CH_2Cl_2 solution. [c] In AcOH solution.

The PMR spectrum of CD_3CO_2D and $CDCl_3$ solutions containing equimolar amounts of vinylferrocene and ArSCl were recorded. As the vinylferrocene signals disappear with time (the system of the double bond protons and the δ 4.10 ppm singlet, due to the unsubstituted Cp ring protons), the formation of two addition products is indicated by the appearance of two singlets for the unsubstituted Cp protons, at δ 4.17 and 4.20 ppm. The spectra in CD_3CO_2D collapse with time, probably due to the formation of paramagnetic species.

In a preparative experiment, ArSCl (160 mg, 1.97×10^{-3} mol) and vinylferrocene (430 mg, 2.03×10^{-3} mol) were made to react in 50 mg of CH_2Cl_2 under nitrogen atmosphere at room temperature. The mixture was stirred overnight and then the solvent was removed by a nitrogen stream. A deep red compound was obtained, which was purified by column chromatography over alumina (neutral, Brockman II—III), with diethyl ether as an eluent (m.p. 96—98°C), after removal of the unreacted vinylferrocene with hexane.

Treatment of a portion of the reaction product with methanol under reflux gave no change in the PMR spectrum, thus indicating the absence of solvolysis.

A second portion of the reaction product was treated with $LiAlH_4$ in anhydrous diethyl ether, according to a procedure reported for the reductive dechlorination of the adducts from the arenesulfenylation of alkenes [2a]. After usual work-up of the reaction mixture (hydrolysis, washing, drying of the ethereal layer, and evaporation of the solvent), the residue was chromatographed over an alumina column (neutral, Brockman II—III). The first band, eluted with hexane, yielded a compound, the PMR of which shows signals in the olefinic protons region (δ 5—6 ppm). The compound eluted as a second band with diethyl ether shows the same PMR as the starting material. No product from reductive dehalogenation was recovered.

Reaction of ferrocene with ArSCl

Equimolar amounts of ferrocene and ArSCl were mixed together in CH_2Cl_2 and kept under stirring for 48 h, in order to attempt ring substitution. Only the starting materials were recovered.

Another attempt was performed in the presence of $AlCl_3$ according to conditions described in the literature [10]. A solution of ferrocene (1.0 g, 5.4×10^{-3} mol) in 15 ml CH_2Cl_2 was added dropwise to an ice-cooled solution of ArSCl (1.0 g, 4.3×10^{-3} mol) and 1.0 g of anhydrous $AlCl_3$ in 15 ml CH_2Cl_2. The resulting green mixture was kept under stirring 1 h at 0°C and then allowed to reach room temperature. After cautious addition of ethanol, filtration from inorganic materials, and concentration by partial removal of the solvent, a yellow solid was obtained. By chromatography on alumina column (neutral, Brockman II—III), a band was eluted with hexane, the VPC analysis of which revealed the presence of 40% ferrocene and 55% of a compound with a retention time different from that of both the starting reagents. Ferrocene was removed by crystallization from CH_2Cl_2, hexane and the PMR spectrum of the crystallized product is in agreement with the structure $ArSCH_2CH_3$ (m.p. 124—125°C): δ (ppm) 9.04 d (J 2.2 Hz (1 H)), 8.48 dd (J 9.0 Hz, J 2.2 Hz (1 H)), 7.93 d (J 9.0 Hz (1 H)), aromatic protons; 4.01 q (J 7.5 Hz (2 H)), and 1.48 t (J 7.5 Hz (3 H)), $-CH_2CH_3$ protons.

Kinetic measurements

The reactions were followed by a spectrophotometric method using thermostatted Beckman DB-GT and Varian DMS 90 apparatus and silica cells. The kinetics were performed under pseudo first-order conditions either by keeping the substrate concentration at least 10 times as high as that of the sulfenyl chloride or vice versa.

The solutions for the kinetic experiments were prepared immediately before use.

The data are reported in Table 1 as overall second-order constants. They are mean values of several runs carried out under conditions specified in the following (wavelengths in nm given in parentheses).

In AcOH solution. $\mathrm{FcCH{=}CH_2}$: 4.29×10^{-3} *M*, ArSCl: 1.79×10^{-4} *M* (370); $\mathrm{FcC(CH_3){=}CH_2}$: 3.46×10^{-3}—3.79×10^{-3} *M*, ArSCl: 1.70×10^{-4} *M* (370); $\mathrm{FcCH{=}CHCH_3}$: 3.39×10^{-3}—5.71×10^{-3} *M*, ArSCl: 1.43×10^{-4}—2.27×10^{-4} *M* (370); $\mathrm{FcCH{=}C(CH_3)_2}$: 5.00×10^{-3}—6.25×10^{-3} *M*, ArSCl: 2.04×10^{-4}—2.56×10^{-4} *M* (370).

In TCE solution. $\mathrm{FcCH{=}CH_2}$: 5.47×10^{-4}—5.52×10^{-3} *M*, ArSCl: 2.05×10^{-4}—4.99×10^{-3} *M* (370, 380, 500, 520, 550); $\mathrm{FcC(CH_3){=}CH_2}$: 6.19×10^{-4}—8.97×10^{-3} *M*, ArSCl: 1.28×10^{-4}—9.12×10^{-3} *M* (380, 480, 500); $\mathrm{FcCH{=}CHCH_3}$: 8.18×10^{-4}—4.64×10^{-3} *M*, ArSCl: 6.60×10^{-5}—4.56×10^{-3} *M* (370, 500); $\mathrm{FcCH{=}C(CH_3)_2}$: 7.91×10^{-4} *M*, ArSCl: 9.12×10^{-5} *M* (370).

In CH_2Cl_2 solution. $\mathrm{FcCH{=}CH_2}$: 1.06×10^{-3}—5.29×10^{-3} *M*, ArSCl: 2.05×10^{-4}—4.99×10^{-3} *M* (355, 370, 500, 510, 520, 530, 540, 550); $\mathrm{FcC(CH_3){=}CH_2}$: 3.98×10^{-4}—6.86×10^{-4} *M*, ArSCl: 3.62×10^{-5}—8.16×10^{-3} *M* (380, 500); $\mathrm{FcCH{=}CHCH_3}$: 7.97×10^{-4} *M*, ArSCl: 5.75×10^{-5} *M* (370, 500); $\mathrm{FcCH{=}C(CH_3)_2}$: 7.29×10^{-4} *M*, ArSCl: 5.75×10^{-5} *M* (370).

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