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The Reaction of Vinylferrocenes with Tetracyanoethylene

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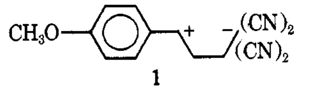
Tetracyanoethylene has been found to react readily with several substituted vinylferrocenes to produce cyclobutane derivatives. This facile reaction appears to be a two-step reaction involving the development of a charged center which can be effectively stabilized by the ferrocene system. Reaction of the cis and trans isomers of 1-ferrocenylpropene with tetracyanoethylene yields a single product. This indicates that the dipolar intermediate is sufficiently stable to allow rotation to occur prior to the product-forming step.

Tetracyanoethylene (TCNE) is one of the most reactive dienophiles known in Diels-Alder reactions.[1] However, Stewart[2] noticed that 4-methyl-1,3-pentadiene reacted with TCNE to produce not only a cyclohexene product but also a cyclobutane product. McKusick[3] and coworkers observed that a diene system was not essential for these reactions because the cyclobutane products were also readily formed by cycloaddition of TCNE to electron-rich alkenes such as methyl vinyl ether and *p*-methoxystyrene. These reactions are remarkable in that the products, obtained in high yields, are rapidly formed in tetrahydrofuran solution at 0-30°.

Woodward-Hofmann rules suggest that a concerted [$2_s + 2_s$] addition is symmetry forbidden; however, the ease with which these reactions proceed is reminiscent of the concerted [2 + 4] symmetry allowed Diels-Alder additions. McKusick[3] found the reaction rates of these [$2_s + 2_s$] reactions to be very sensitive to changes in solvent polarity, and this led him to postulate that a charged intermediate such as 1 was present. Since the ferrocene system is known to be strongly electron releasing[4] and its ability to stabilize adjacent carbonium ions has been established,[5] it appeared that vinylferrocenes should be electron-rich alkenes which would react readily with TCNE.



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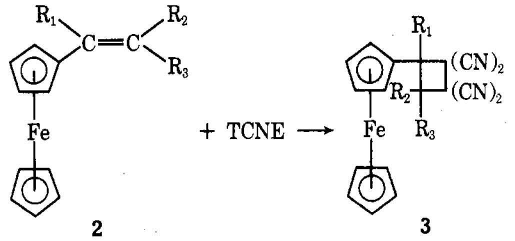
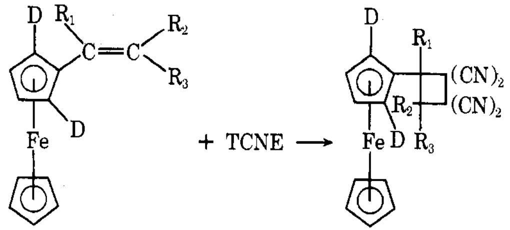
Results and Discussion

A series of substituted vinylferrocenes was prepared and allowed to react with TCNE in tetrahydrofuran solution. The parent system (**2a**) reacted quite readily (room temperature, 2 hr) to produce a yellow crystalline 1:1 adduct in 71% yield. The other alkenes reacted similarly (Table I). The nmr spectra (Table II) were consistent with a formulation such as **3**. The nmr spectra of **3b** and **3c** exhibited a one-proton multiplet absorption downfield from the singlet absorption of the unsubstituted cyclopentadienyl ring of the ferrocene system. In order to assign this absorption, the ring-deuterated alkenes **4a** and **4b** were prepared and treated with TCNE. The adducts and their nondeuterated counterparts had identical decomposition points. In each case, deuteration caused disappearance of the one-proton absorption as well as a decrease in the τ 5.59 multiplet. This indicated that the structure of the adducts was such that the α ring protons of the ferrocene system were in different magnetic environments. A molecular model of the compounds confirmed this postulate. These findings suggested that the absorption of R_1 was obscured by the ferrocene system when R_1 = H and therefore only approximate values for this proton could be assigned.



2 3

a, $R_1 = R_2 = R_3 = H$
b, $R_1 = CH_3$; $R_2 = R_3 = H$
c, $R_1 = H$; $R_2 = R_3 = CH_3$
d, $R_1 = R_3 = H$; $R_2 = CH_3$
e, $R_1 = R_2 = H$; $R_3 = CH_3$

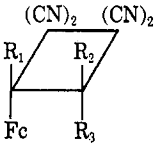


4 5

a, $R_1 = CH_3$; $R_2 = R_3 = H$
b, $R_1 = H$; $R_2 = R_3 = CH_3$

In order to examine the mechanism by which these reactions occurred, the reactions of the cis and trans isomers of 1-ferrocenylpropene (**2d** and **2e**) with TCNE were studied; however, the pure isomers had not been described previously. Their syntheses were accomplished by modifications of the Wittig reaction. Reaction of ethyltriphenylphosphonium bromide, methyllithium, and formylferrocene according to the Schlosser-Christmann procedure[6] produced the trans isomer (J = 15 Hz). The "salt-free" Wittig reaction[7] of ethyltriphenylphosphorane and formylferrocene yielded the cis isomer (J = 11.5 Hz). Nmr

Table I
Properties of Tetracyanocyclobutanes[d]



Fc = ferrocene

Alkene used	Registry no.	Yield, %[a]	Registry no.	Cyclobutane R_1	 R_2	 R_3	Mp, °C[b]
2a	1271-51-8	71	49716-63-4	H	H	H	137–139
2b	31725-14-1	69	49716-64-5	CH_3	H	H	101–103
2c	33040-03-8	80	49716-65-6	H	CH_3	CH_3	165–166
2d[c]	39534-32-2	67	49846-30-2	H	CH_3	H	176–178
2e[c]	49716-61-2	60					
8	49716-62-3	50	49716-66-7	H	H		157–160

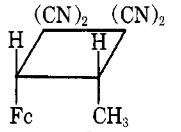
[a] Recrystallized product. [b] The compounds appear to decompose without melting at these temperatures. [c] Both **2d** and **2e** yielded the same product; nmr and ir spectra are identical. [d] Satisfactory analytical data (±0.4% for C and H) were reported for all compounds listed in the table.

Table II
Nmr Spectra of Tetracyanocyclobutanes

Product	R_1	R_2	R_3	Chemical shifts, τ Ferrocene protons			R_1	R_2	R_3	Coupling constants, Hz
3a	H	H	H	5.28 (2 H, m)	5.62 (2 H, t)	5.70 (5 H, s)	5.45 m	6.24 8-line pattern	6.48	ABX spectrum $J_{R_1R_3} = 13$ $J_{R_2R_3} = 14$ $J_{R_1R_2} = 10$
3b	CH_3	H	H	5.36 (1 H, m)	5.63 (3 H, m)	5.75 (5 H, s)	7.86 s	6.28 d	6.48 d	$J_{R_2R_3} = 14$
3c	H	CH_3	CH_3	5.30 (1 H, m)	5.59 (3 H, m)	5.63 (5 H, s)	~5.6	8.40 s	8.54 s	
3d	H	CH_3	H	5.41 (1 H, m)	5.59 (3 H, m)	5.72 (5 H, s)	~5.6	8.25 d	6.26 m	$J_{R_2R_3} = 7$ $J_{R_1R_3} = 12$
9	H	H		5.50 (1 H, m)	5.65 (2 H, m)	5.80 (5 H, s)	5.10 d	~7.4 m		$J_{R_1R_2} = 9.5$

analyses indicated a minimum of 95% stereochemical purity.

Reaction of **2d** or **2e** with TCNE in tetrahydrofuran produced the same compound as evidenced by identical decomposition points and nmr and ir spectra (**3d** = **3e**). An nmr of the crude reaction materials did not reveal the presence of a second product from either set of reactants. Since this product was similar to the other cyclobutane products, it was postulated to be either the cis (**6**) or trans (**7**) product.



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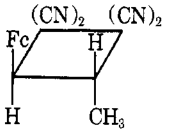

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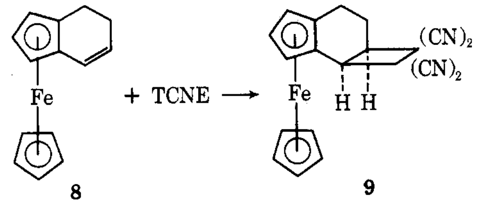
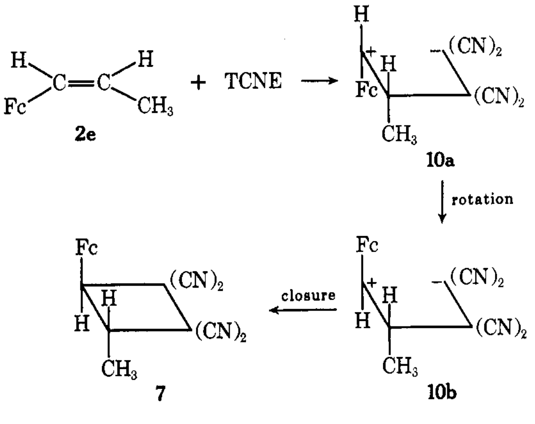
In order to establish the structure of the product, the proton coupling constants were determined. The coupling constant for the cyclobutane hydrogens of the adduct was found to be 12 Hz. It was then necessary to obtain coupling constants of a similar system for which the stereochemistry could be established. The cyclic alkene **8**[8] was treated with TCNE to form **9**. Since it is highly unlikely that this four-membered ring could have a trans ring fusion, the bridgehead hydrogens were assigned a cis configuration. Analysis of the nmr spectrum of **9** revealed a coupling constant of 9.5 Hz for these hydrogens. On the basis of these coupling constants and those of compound **3a**, the trans structure **7** is indicated as the sole detectable product of the reaction of *cis*- or *trans*-1-ferrocenylpropene with TCNE.



Since the cis and trans isomers produced the same compound, common intermediates in which rotation was possible must have existed. Reaction of the cis isomer should proceed as illustrated below. For rotation to occur **10a** must have a finite lifetime. The ability of ferrocene to stabilize an adjacent carbonium ion has been thoroughly investigated. By solvolysis studies Richards and Hill[5] found the ferrocenyl carbinyl cation to be of the same order of stability as the triphenylmethyl cation. Thus the stability of the ionic centers allowed the very bulky ferrocene system to attain the considerably less sterically strained form



10b before final collapse to product occurred. Even when these reactions were carried out in solvents whose ability to stabilize charged intermediates varied considerably, no change in the product formed could be detected. These observations once again point to the tremendous ability of the ferrocene system to direct the course of chemical reactions.

Experimental Section

Melting and decomposition points were obtained in sealed tubes under a nitrogen atmosphere. The microanalyses were performed by Chemalytics, Inc., Tempe, Ariz. Infrared spectra were recorded on a Perkin-Elmer Model 457 spectrophotometer, and nmr spectra were determined with a Perkin-Elmer R12B spectrometer using tetramethylsilane as an internal standard. Spectra of the adducts were obtained using acetone-d_6 as solvent.

Syntheses of Substituted Vinylferrocenes. A. 1-Ferrocenyl-2-methylpropene (2c). A Grignard reagent was prepared from 2-bromopropane (19.6 g, 0.16 mol), magnesium turnings (2.4 g, 0.10 mol), and 50 ml of anhydrous ethyl ether. The reagent cooled in an ice-water bath, and formylferrocene (6.7 g, 0.03 mol) dissolved in 50 ml of ether was added. After the reaction mixture had stirred for 1 hr, it was poured into a mixture of 11 ml of concentrated sulfuric acid, 100 ml of water, and 100 g of ice. The ether layer was separated and the aqueous phase extracted with three 50-ml portions of ether. The combined ether solutions were washed with 5% sodium bicarbonate solution, dried ($MgSO_4$), and concentrated. The residue, 10 g of acidic alumina, and 200 ml of benzene were transferred to a flask equipped with a Dean-Stark trap and condenser. The mixture was refluxed for 4 hr with water being collected in the trap. The suspension was filtered and the filtrate concentrated. Chromatography of the residue over alumina and elution with pentane removed a bright yellow band. Solvent removal produced 5.4 g (72% yield) of **2c**. Spectral properties of this and the following compounds (**2a, 2b**) were identical with those reported in the literature.[9]

B. Ferrocenylethene (2a). Dehydration of 1-ferrocenyl-1-ethanol[10] as above produced **2a** in 75% yield.

C. 2-Ferrocenylpropene (2b). Reaction of acetylferrocene with methylmagnesium iodide followed by dehydration of the alcohol with acidic alumina yielded **2b**.

D. Deuterated Vinylferrocenes 4a and 4b. The reactions were performed as above except that 2,5-dideuterioformylferrocene[11] or 2,5-dideuterioacetylferrocene[11] was used.

E. Fused-Ring Alkene 8. The cyclic alkene 8 was prepared by dehydration of α-hydroxy-1,2-tetramethyleneferrocene according to the method of Schlögl.[8]

F. *cis*-1-Ferrocenylpropene (2e). Into a 500-ml three-necked round bottom flask equipped with a Dry Ice-acetone condenser, mechanical stirrer, gas inlet, and bubbler outlet was condensed approximately 200 ml of ammonia. Sodium amide (2.0 g, 0.05 mol) was added followed by ethyltriphenylphosphonium bromide (18.6 g, 0.05 mol). The reaction mixture was stirred for 1 hr after which the ammonia was evaporated. Dry benzene (100 ml) was added and the mixture refluxed under nitrogen for 10 min. The suspension was filtered (nitrogen atmosphere) and the red filtrate added directly to a cooled (5°) solution of formylferrocene (4.3 g, 0.02 mol) in benzene. Stirring was continued for 1 hr followed by solvent evaporation. The residue was vigorously shaken with two 100-ml portions of pentane. The combined pentane fractions were condensed and the residue chromatographed over alumina. Elution with pentane removed the desired product (3.4 g, 75% yield): mp 26-30°; nmr (CS_2), ABX_3 spectrum, τ 3.95 (1 H, dd), 4.52 (1 H, dq), 5.90 (4 H, m), 6.08 (5 H, s), 8.22 (3 H, dd); J_{AB} = 11.5 Hz, J_{AX} = 1.5 Hz, J_{BX} = 6.6 Hz.

Anal. Calcd for $C_{13}H_{14}Fe$: C, 69.05; H, 6.25. Found: C, 69.22, H, 6.11.

G. *trans*-1-Ferrocenylpropene (2d). Ethyltriphenylphosphonium bromide (11.2 g, 0.03 mol) was suspended in a mixture of 50 ml of dry tetrahydrofuran and 30 ml of anhydrous ether. To this suspension was added 0.03 mol of methyllithium. After stirring for 10 min, the solution was cooled to −70° and formylferrocene (6.4 g, 0.03 mol) was added. The reaction mixture was stirred vigorously for 5 min at −70 to −40° followed by addition of another 0.03 mol of methyllithium. The temperature was maintained at −30° for 5 min and then 0.033 mol of ethereal HCl and 0.045 mol of potassium *tert*-butoxide (1:1 complex with *tert*-butyl alcohol) were added. The mixture was stirred overnight at room temperature. The suspension was filtered; the filtrate was washed with salt water and finally dried over $MgSO_4$. After solvent removal, the residue was chromatographed over alumina (pentane eluent) to yield 3.6 g (56%) of the desired product: mp 39-40°; bp 83° (0.3 mm); nmr (CS_2), ABX_3 spectrum, τ 3.97 (1 H, d), 4.26 (1 H, dq), 5.98 (4 H, m), 6.09 (5 H, s), 8.30 (3 H, d); J_{AB} = 15 Hz, J_{AX} = 0, J_{BX} = 5.7 Hz.

Anal. Calcd for $C_{13}H_{14}Fe$: C, 69.05; H, 6.25. Found: C, 69.05; H, 6.12.

Addition of Tetracyanoethylene to Vinylferrocenes. A. General Procedure. A solution of tetrahydrofuran (20 ml) and TCNE (5 mmol) was added to the vinylferrocene (5 mmol) with stirring under a nitrogen atmosphere. A slight color change and warming were characteristic of the initial stages of the reaction. After 2 hr, solvent was removed. An nmr spectrum of the crude material was then obtained. The adducts were purified by recrystallization from benzene-pentane mixtures.

B. Solvent Variation. The isomers **2d** and **2e** were treated with TCNE in different solvents. The residue from the reaction of **2d** with TCNE in nitromethane contained cyclobutane with no starting material remaining after 2 hr. The residue from the reaction of **2d** with TCNE in benzene (4 hr) contained a 1:3 ratio of starting material to cyclobutane. The cis isomer (**2e**) gave similar results in the same solvents. Nmr and ir spectra of the crude cyclobutane adducts from **2d** and **2e** were identical.

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Registry No. 2-Bromopropane, 75-26-3; formylferrocene, 12093-10-6; 1-ferroceneyl-1-ethanol, 1277-49-2; acetylferrocene, 1271-55-2; methyl iodide, 74-88-4; tetracyanoethylene, 670-54-2.

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