A similar procedure was used in the Tishchenko reactions of bromal and *n*-butyraldehyde.

Registry No.—Chloral, 75-87-6; bromal, 115-17-3; *n*-butylaldehyde, 123-72-8.

Aluminum Chloride Induced Cleavage and Alkylation of Ferrocene in Dichloromethane[1]

EBERHARD W. NEUSE

Missile & Space Systems Division,
McDonnell Douglas Corporation, Santa Monica, California

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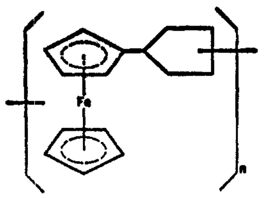
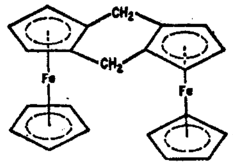
Nesmeyanov and coworkers[2] were the first to study the action of anhydrous aluminum chloride on ferrocene in boiling dichloromethane. The authors, using Lewis acid and metallocene in approximately equimolar quantities, obtained polynuclear alkylation products whose structures were assumed to comprise ferrocenylene units interlinked by a multiplicity of methylene bridges, these bridges being generated by action of the solvent as the alkylating species. However, no structural proof for any of the reaction products was established at that time. Later investigations[3] cast some doubt on these reports as one of the "alkylated" products from a related system involving 1,2-dichloroethane solvent[4] was found to arise in benzene solution as well and was identified[3b,c] as a diferrocenyldicyclopentyl. The proposed mechanism of formation involved Lewis acid induced cleavage of the metal–ring bond in the metallocene and intermediacy of cyclopentenyl and ferrocenyl cyclopentyl cations. Consistent with this concept of metal–ring bond fission, a reinvestigation[3c] of Nesmeyanov's earlier work[2] on the ferrocene–aluminum chloride–dichloromethane system revealed the presence of cyclopentylene groups in the polymeric products of this reaction, analytical results suggesting structure I.



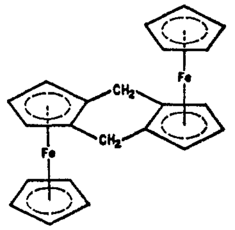
I

In a related investigation, Valot,[5] using a considerable Lewis acid excess, obtained polymers with an appreciably larger content of ferrocene cleavage products; the average repeat unit corresponded in composition to a ferrocenylenecyclopentylene skeleton plus three additional cyclopentenyl groups and one hydroxycyclopentyl moiety. No evidence of concurrent alkylation by the solvent as originally proposed[2] was found in these two later studies.[3c,5] In hopes of achieving the synthesis of [1.1]ferrocenophanes II,[6] of interest as prototype structures of double-bridged segments postulated in earlier polymer studies,[7] we have independently investigated the reaction of ferrocene with aluminum chloride in dichloromethane, using somewhat milder experimental conditions (12–24 hr, 0–25°) than previously employed. The results of this study have shown that, while the sequence of reactions based on metal–ring bond fission predominates, the alkylation of ferrocene by dichloromethane is, indeed, a competitive process. Consequently, the arising polymeric products possess structures appreciably more complex than originally[3b,c,5] assumed.

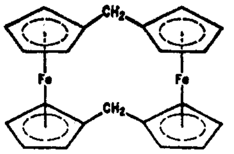
Typical experiments, employing equimolar quantities of ferrocene and aluminum chloride, resulted in the recovery of 50–60% ferrocene. Additionally, the following ferrocene derivatives were isolated: a dinuclear [1.1]ferrocenophane likely to possess structure IId (in addition to other unidentified isomers II);[8] 1,1′-(1,3-cyclopentylene)ferrocene (III);[9] 1,1′-(1-methyl-1,3-cyclopentylene)ferrocene (IV); diferrocenylmethane (V);[10] a 1,3-diferrocenylcyclopentane VI assumed previously[11] to possess the *cis* configuration; and a mixture, not further separated, essentially consisting of diferrocenylmethylcyclopentane isomers VII. In addition to these mono- and dinuclear com-



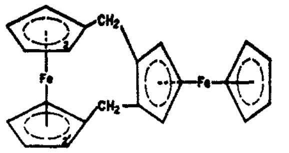
IIa



IIb



IIc



IId

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(1) Metallocene Polymers. XXIII. Part XXII: E. W. Neuse, *J. Macromol. Sci.*, in press. The denotation of the open bond on the left-hand side in structures I and VIII is the same as in previous parts of this series and implies attachment to the preceding recurring unit *via* any one position 2, 3, or 1′.

(2) A. N. Nesmeyanov, V. V. Korshak, V. V. Voevodskii, N. S. Kochetkova, S. L. Sosin, R. B. Materikova, T. N. Bolotnikova, V. M. Chibrikin, and N. M. Bazhin, *Dokl. Akad. Nauk SSSR*, **137**, 1370 (1961).

(3) (a) S. J. Goldberg, *J. Amer. Chem. Soc.*, **84**, 3022 (1962); (b) A. N. Nesmeyanov, N. S. Kochetkova, P. V. Petrovsky, and E. I. Fedin, *Dokl. Akad. Nauk SSSR*, **152**, 875 (1963); (c) S. G. Cottis and H. Rosenberg, *J. Polym. Sci., Part B-2*, 295 (1964); H. Rosenberg and S. G. Cottis, U. S. Patent 3,350,369 (1967).

(4) (a) A. N. Nesmeyanov and N. S. Kochetkova, *Dokl. Akad. Nauk SSSR*, **126**, 307 (1959); (b) A. N. Nesmeyanov, N. S. Kochetkova, and R. B. Materikova, *ibid.*, **136**, 1096 (1960); **147**, 113 (1962).

(5) H. Valot, *Double Liaison*, **130**, 775 (1966).

(6) The nomenclature and chemistry of ferrocenophanes has been reviewed most knowledgeably by W. E. Watts, *Organometal. Chem. Rev.*, **2**, 231 (1967).

(7) (a) E. W. Neuse and D. S. Trifan, *J. Amer. Chem. Soc.*, **85**, 1952 (1963); (b) E. W. Neuse and E. Quo, *J. Polym. Sci., Part A-3*, 1499 (1965).

(8) The all-heteroannular IIc was recently synthesized by W. E. Watts, *J. Organometal. Chem.*, **10**, 191 (1967). Also known is the 1,12-dimethyl derivative: W. E. Watts, *J. Amer. Chem. Soc.*, **88**, 855 (1966). We are most grateful to Dr. Watts for submitting copies of the ir, pmr, and mass spectra of both compounds for comparative purposes.

(9) (a) V. Weinmayr, *J. Amer. Chem. Soc.*, **77**, 3009 (1955); (b) S. G. Cottis and H. Rosenberg, *Chem. Ind.* (London), 860 (1963).

(10) (a) K. Schlögl and A. Mohar, *Monatsh. Chem.*, **92**, 219 (1961); (b) P. L. Pauson and W. E. Watts, *J. Chem. Soc.*, 3880 (1962); (c) E. W. Neuse and K. Koda, *Bull. Chem. Soc. Jap.*, **39**, 1502 (1966); (d) E. W. Neuse and E. Quo, *ibid.*, **39**, 1508 (1966).

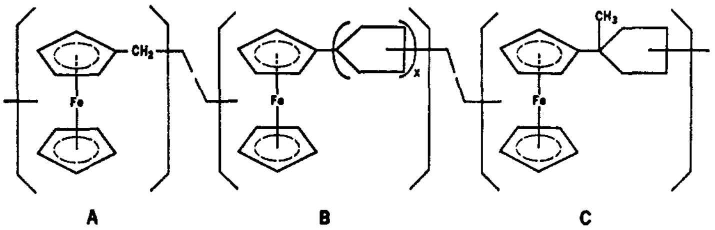
(11) E. W. Neuse, R. K. Crossland, and K. Koda, *J. Org. Chem.*, **31**, 2409 (1966).

TABLE I

Compound	Mp, °C	Mol wt[a]	Calcd, %				Found,[b] %			
			C	H	Fe	CH_3	C	H	Fe	CH_3
IId	265–268	402	66.71	5.09	28.20		66.92	5.19	28.01	
IV	109–110	284	72.20	6.82	20.98	5.6	72.45	6.85	21.24	4.3
VII[c]	Liquid	465	69.06	6.24	24.70	3.3	69.29	6.32	24.25	2.7
VIIIa[d]	60–65	680	70.42	6.19	23.39	2.1	70.57	6.31	22.97	2.4
VIIIb[e]	90–115	1050	71.96	6.68	21.36		71.68	6.80	21.55	
VIIIc	90–110	2400	73.25	7.09	19.65		72.99	6.89	19.30	

[a] Average of two runs, by vapor pressure osmometry in CH_2Br_2. Calcd for II, 396; for IV, 266; for VII, 452. [b] Combustion analyses by G. I. Robertson, Florham Park, N. J. C-Methyl determinations by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. [c] Unseparated isomer mixture. [d] Essentially the same composition found for fraction VIIIa, M_n 810, mp 75–90°. [e] Essentially the same composition found for fraction VIIIb, M_n 1720, mp 90–120°.

pounds,[12] the reactions furnished several polymeric fractions with number-average molecular weight (M_n) 600–2400. The lower molecular fractions, with $M_n < 900$, essentially corresponded in elemental composition to the idealized structure VIIIa consisting of ferrocenylenecyclopentylene, ferrocenylenemethylene, and ferrocenylene(methyl)cyclopentylene segments randomly distributed in roughly equal proportions. Higher molecular fractions were found to contain additional cyclopentylene groups; in a simplified form, their structures may be depicted by VIIIb and c.



VIIIa, $x = 1$
b, $x = 2$
c, $x = 3$

The structural assignments of the new compounds IId, IV, VIII, the isomer mixture VII rest on microanalytical results (Table I) and spectroscopic data.

Compound IId gives an ir spectrum (KBr disks) closely resembling that[10] of V except that enhanced methylene stretch and deformation bands are shown. Furthermore, the 9,10-μ bands[13] and the peak at 7.1 μ all appear in decreased intensities relative to V (insufficient solubility prevented a quantitative determination). This suggests IId as the most probable structure, whereas IIa and IIb, possessing the same high (*i.e.*, 100%) homoannularity[7a] as V, are rendered highly unlikely as alternate candidates, and IIc,[8] identified by an entirely heteroannular bonding scheme, is altogether eliminated. The nmr spectrum (60 MHz, in $CDCl_3$; chemical shifts in τ values) is characterized by a complex multiplet, of fourteen ferrocene protons at 5.8–6.1 ppm, an apparent singlet of two ferrocene protons at 6.41 ppm, and an AB-type quartet ($J_{AB} = 15$ Hz; verified at 100 MHz), due to two pairs of methylene protons, centered at 6.73 ppm. This pattern, while inconsistent with both IIa and IIb,[14] is readily accommodated by IId,[15] in which protons 2 and 2′ are well within the shielding cone of the horizontal ferrocene unit, thus producing the signal at 6.41 ppm.[16] The mass spectrum (70 eV) exhibits an intense parent ion peak at m/e 396 and its prominent doubly charged counterpart at $m/2e$ 198, and also both the $[M + 1]^+$ peak and the corresponding doubly charged species are of comparatively high intensity. Fragment ions of high abundances, deriving from the homoannularly linked ferrocene unit as the most vulnerable portion of the molecule, include $[M - 65]^+$ (loss of cyclopentadienyl), $[M - 66]^+$ (loss of cyclopentadiene following hydrogen transfer from the alkyl bridges[17]), $[M - 122]^+$ (elimination of ^{56}Fe from the preceding ion), and $[M - 78]^+$. The last-named species is probably a rearrangement product following loss of C_6H_6 as contended[17] for a similarly fragmentation-resistant ferrocene; the high-intensity peak at m/e 78 most likely due to the stable benzene cation[17] would seem to support this transition. In accord with IId (and inconsistent with IIa and IIb), no prominent peaks at m/e 266 or 264 corresponding to ions $[M - 130]^+$ (loss of 2 cyclopentadienyl rings) or $[M - 132]^+$ (loss of two cyclopentadiene units) are apparent. Of interest is the facile elimination of H_2 leading to the prominent $[M - 2]^+$ ion (m/e 394) and the doubly charged species (m/e 197); the fragments $[M - 2 - 65]^+$ with m/e 329 and $[M - 2 - 121]^+$ with m/e 273 are cor-

[12] In reactions conducted at −15°, diferrocenylcarbinol [ref 10a and R. L. Schaaf, *J. Org. Chem.*, **27**, 107 (1962)] was additionally separated. We are indebted to Dr. Schaaf for furnishing a sample of this carbinol for comparison.

[13] M. Rosenblum, Ph.D. Thesis, Harvard University, 1953; ref 10d.

[14] The methylene protons in IIa and b, located in the mutual deshielding zone of two essentially coplanar cyclopentadienyl rings, should give signals at approximately the same downfield position as shown by IIc (6.45 ppm). In addition, a singlet would be expected for the equivalent methylene protons in IIb. Similar considerations of the relative positions of the ring protons and resultant deshielding effects (in IIa) and combined deshielding and shielding effects (in IIb) would predict all ring-proton signals to arise to the low-field side of ~6 ppm in IIa and of ~6.2 ppm in IIb.

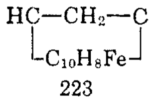
[15] Scale models show this "*trans*" form to be the less strained of the two possible configurations.

[16] (a) Furthermore, the remaining ring protons are neither especially shielded nor deshielded and, as part of a strain-free system, occupy positions essentially equally spaced from the respective Fe centers, giving a multiplet in the range typical of such methylene-bridged compounds as V or the isomeric diferrocylferrocenes.[16b] In contrast, the ferrocene proton signals shown by crude samples still containing other isomers[14] of II include broad envelopes, which extend downfield to 5.6 ppm and upfield to 6.2 ppm, and the methylene proton signals show satellites at 6.4–6.5 ppm. (b) E. W. Neuse, E. Quo, and W. G. Howells, *J. Org. Chem.*, **30**, 4071 (1965).

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

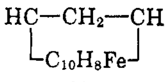
respondingly abundant. A species with *m/e* 394 and *m/2e* 197, aside from appearing in the spectrum IIc, was also found[8] to arise from 1,12-dimethyl[1.1]-ferrocenophane as one of the principal fragmentation products and precursor of *m/e* 329, which attests to the stability and importance of the methylidene-bridged ions (*m/e* 394) in the fragmentation pattern of [1.1]ferrocenophanes.

Compound IV gives an ir spectrum similar to that of III, showing the typical splitting of the 12.2-μ ferrocene CH out-of-plane deformation band into two band groups near 11.8 μ (multiplet) and 12.5 μ (sharp singlet) observed previously[11] with related hetero-bridged mononuclear ferrocenes;[18] in addition, a methyl band appears at 7.32 μ. The pmr spectrum shows ferrocenyl, methylidene, methylene, and methyl proton resonances in the calculated area ratio; the methyl signal emerges as a sharp singlet at 8.59 ppm, that is, in the region and multiplicity expected for a methyl group attached to tertiary carbon in α position to the cyclopentadienyl ring. The compactness of the bridged molecule, while causing highly intense *m/e* (266) and *m/2e* (133) molecular ion peaks, prevents high abundances of such fragments as $[M - 65]^+$ or $[M - 66]^+$, which appear to arise amply whenever cyclopentadienyl rings are available for ready primary cleavage at the iron–ring bond[17,19] or when, as in the case of $[M - 66]^+$, hydrocarbon side chains can provide a hydrogen atom for transfer to the ring.[17] Instead β cleavage is favored, as manifested by the prominent peaks at mass numbers corresponding to $[M - 14]^+$, $[M - 15]^+$, and $[M - 28]^+$. The most abundant ion in the *m/e* 100–252 range is $[C_5H_5Fe]^+$, *m/e* 121. The prominence of this peak, also apparent in III but unexpected in view of other reports[20] associating the $[C_5H_5Fe]^+$ ion with the presence of unsubstituted rings, obviously derives from the tendency of the odd-electron radical ion $[C_5H_4Fe]^{+\cdot}$ to pick up a side-chain hydrogen atom, thus converting into the more stable even-electron $[C_5H_5Fe]^+$ species. Consistent with the alicyclic position of the methyl group, the *m/e* 223 to *m/e* 224 abundance ratio is considerably higher (1.27) than found in the spectrum of III (0.75). Furthermore, the spectrum of IV fails to show prominent peaks due to $[CH_3{-}C_5H_3Fe]^{+\cdot}$ (*m/e* 134) or $[CH_3{-}C_5H_4Fe]^+$ (*m/e* 135) in higher relative intensities than shown by III. A nuclear position of CH_3 would predict abundances at least as high as that of $[C_5H_5Fe]^+$, notably for *m/e* 135 whose proven stability[21] would seem to rule out rapid depletion by further fragmentation or rearrangement.



$$\underbrace{HC{-}CH_2{-}C}_{C_{10}H_8Fe}$$

223



$$\underbrace{HC{-}CH_2{-}CH}_{C_{10}H_8Fe}$$

224

The isomer mixture VII gives an ir spectrum showing a methyl peak at 7.31 μ in addition to the typical features of diferrocenylcyclopentanes.[11] The pmr spectrum, closely related to that of VI and isomers,[11] exhibits ferrocene (5.8–6.1 ppm) and alicyclic methylidene (7.0–7.4 ppm) and methylene (7.6–8.5 ppm) proton signals; furthermore, a methyl proton singlet appears at 8.64 ppm, indicating attachment to alicyclic carbon.[22] Relative intensities are substantially in the calculated ratio. Additional weak absorption at 6.7–6.8 ppm suggests a minute percentage of methylene-bridged ingredients.

The polynuclear compounds VIII are characterized by ir spectra that can essentially be considered as composites of the spectra of I[3b,c,11] and the polymers $+C_{10}H_8Fe{-}CH_2+_n$[7] of earlier studies. In addition, weak methyl absorption appears at 7.33 μ. The pmr spectra exhibit ferrocene and alicyclic (methylidene and methylene) proton multiplets in the same ranges (5.8–6.1 and 6.9–8.5 ppm) as shown by I and, additionally, display α-methylene and side-chain methyl proton signals near 6.7 and 8.6 ppm, respectively, all signal intensities being in the required ratio.

The occurrence of compounds II–VIII suggests a mechanism involving a multiplicity of cleavage and alkylation steps. Possible routes are depicted in Scheme I. The alkylation of ferrocene by dichloromethane to give V and, hence, the ferrocenophanes II *via* ferrocenylcarbinyl and ferrocylferrocenylcarbinyl cations is straightforward. Both V and IId (and other isomers II) undoubtedly undergo substantial dealkylation under the experimental conditions of this study.[23] The comparatively high yields in which IId was isolated relative to V reflect the appreciable probability of regeneration expected for a double-bridged [1.1]ferrocenophane in contrast to the single-bridged diferrocenylmethane. Formation of III and VI (and isomeric diferrocenylcyclopentanes undoubtedly present but not isolated in this study) clearly results from metal–ring bond cleavage and secondary reactions involving ensuing cyclopentenyl and ferrocenylcyclopentyl cations.[9,11] Less obvious is the formation of IV and isomers VII. From our failure to collect these compounds in reactions conducted in carbon tetrachloride solvent[24] we must conclude that the methyl substituent originates from dichloromethane. The mechanism shown in Scheme I,[25] which represents one of several possible routes, involves the intermediacy of methylcyclopentenyl and 3-ferrocenyl-3-methylcyclopentyl cations, the former arising by cleavage of methylferrocene. This chart also depicts the reaction paths likely to lead to the segment structures A, B, and C of VIII. Termination of the growing poly-

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[18] Certain di- and polynuclear ferrocenes lacking hetero-bridged segments may also show this pattern, provided that free rotation of the rings in one of the ferrocene units is restricted sterically. The pattern, in such case, is superimposed by the regular, broad absorption near 12.2 μ associated with the unencumbered ferrocene groups. 1,1′-Diferrocylferrocene[16b] offers a case in point.

[19] C. Cordes and K. L. Rinehart, Jr., 150th National Meeting of the American Chemical Society, Atlantic City, N. J., 1965, Division of Organic Chemistry, Abstracts, p 37S.

[20] N. Maoz, A. Mandelbaum, and M. Cais, *Tetrahedron Lett.*, 2087 (1965).

[21] R. I. Reed and F. M. Tabrizi, *Appl. Spectros.*, **17**, 124 (1963).

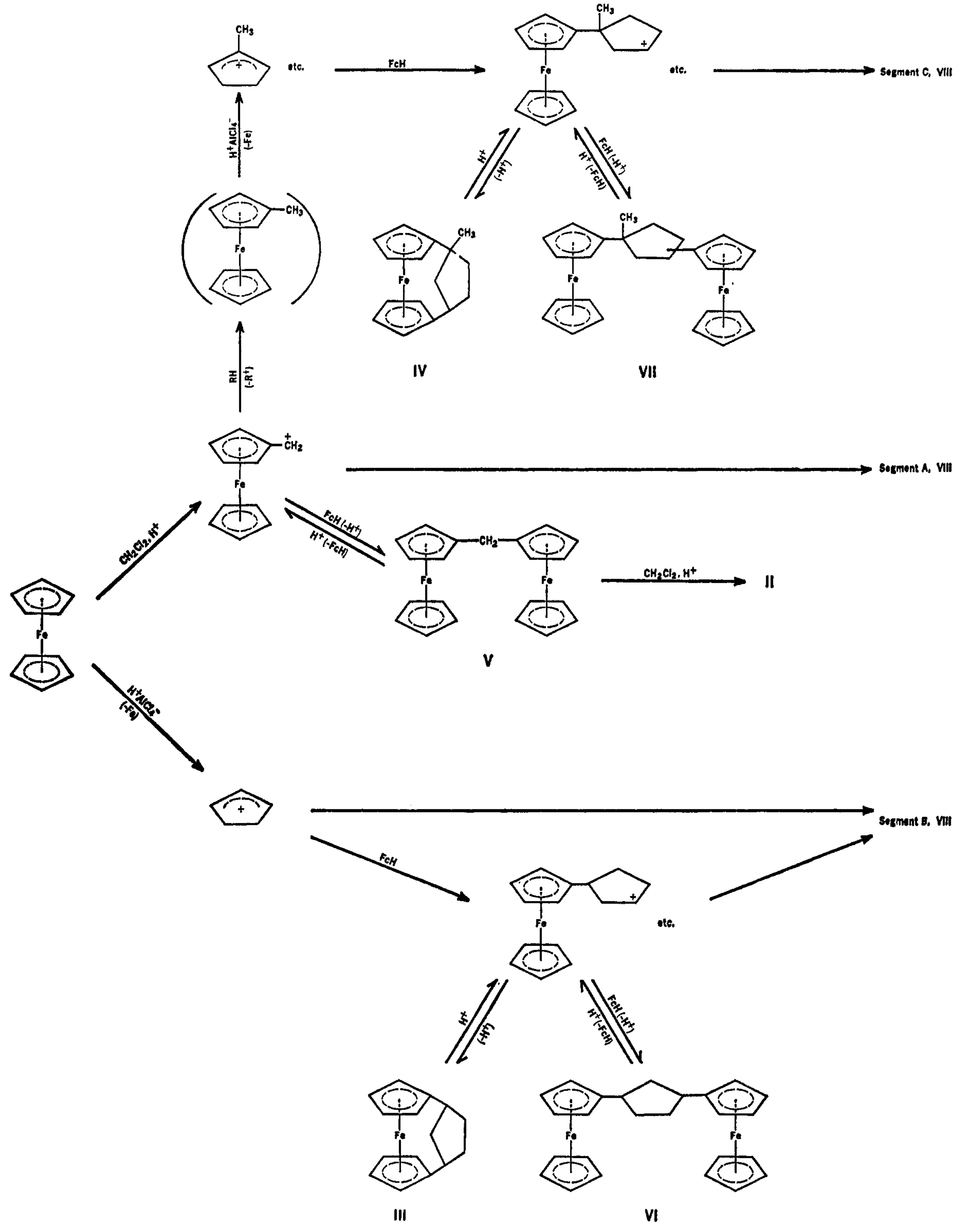
[22] Admixture of nuclearly methylated isomers, however, cannot be ruled out, as the respective signal might well be masked by methylene resonances near the expected 8-ppm position.

[23] Such dealkylation is suggested, for example, by the considerable quantities of ferrocene arising when V is substituted for ferrocene as the starting material.

[24] In addition to diferrocenyl ketone and polymeric compounds containing carbonyl and cyclopentylene bridges, reactions in CCl_4 furnished tetraferrocenylmethane, mp 202–204° (*Anal.* Found: C, 65.76; H, 5.01; Fe, 29.48. Pmr singlet at 5.87 ppm), and the stable diferrocenyldichloromethane, mp 209–211° [*Anal.* Found: Cl, 15.95; Fe, 24.50; mol wt, 440. Pmr signals at 5.10 ppm (four α protons) and 5.73 ppm (four β plus ten unsubstituted ring protons)].

[25] RH = solvent or ferrocenylalkane. The formation of diferrocenylcarbinol[12] from V may thus be explained.

SCHEME I
CLEAVAGE AND ALKYLATION OF FERROCENE (FcH = FERROCENE)



mer chains may proceed through electrophilic attack on ferrocene or a ferrocenyl unit of any of the products II–VII; self-substitution (cyclialkylation) with formation of end groups comprising, for example, the 1,1′-(1,3-cyclopentylene)ferrocene skeleton or its methyl-substituted counterpart is equally probable, although not readily detectable analytically.

Experimental Section

In an exemplifying experiment, ferrocene (0.1 mol), dissolved in dry dichloromethane (2.0 mol), was stirred under N_2 with anhydrous aluminum chloride (0.1 mol) for 3 hr at 0° and 20 hr at 25°. Following hydrolysis (0.05 mol of $SnCl_2$ added as reducing agent), the organic phase, worked up and dried in the usual manner, was evaporated *in vacuo*, and the residue was extracted with cyclohexane. Reprecipitation of the cyclohexane insolubles from benzene solution by 2-propanol gave orange-tan VIIIc, M_n 2400 (2.7%). The cyclohexane solubles were chromatographed on alumina, activity II; fast elution with hexane furnished four major zones. Rechromatography of the first zone (activity I) gave ferrocene (56% recovery), followed by III, mp 139–140° (0.8%), and IV, mp 108–109.5° (3.1%). The second zone, on rechromatography as before and laborious fractional crystallization from hexane, produced a ferrocenophane tentatively identified as IId, mp 265–268° (DTA endotherm 268°), as the least soluble species (1.7%; in addition to impure fractions, mp 240–260°, containing other isomers), followed by V, mp 145–146° (0.3%), and a fraction that, when rechromatographed, was separated into VI, mp 102–105° (0.2%; wide melting point range indicates presence of other isomers), and the oily mixture VII (3.0%). The third zone, mechanically removed from the column, extracted with ether, and rechromatographed in cyclohexane, produced two bands. The lower one, reprecipitated from hexane by partial vacuum evaporation, gave VIIIa, M_n 680 (10.1%); similarly, the upper one gave VIIIa, M_n 810 (3.2%). From the fourth zone, worked up as in the preceding case, two fractions VIIIb were isolated; the lower molecular fraction (1.6%), reprecipitated from cyclohexane solution by methanol, had M_n 1050; the higher molecular fraction (6.6%), reprecipitated from benzene solution by methanol, had M_n 1720. Analytical data for all new compounds are collected in Table I. The identities of III, V, and VI were established by elemental analysis and comparison of melting point, X-ray diffraction pattern, and ir spectra with those of authentic samples.[9–11]

Registry No.—IId, 12271-18-0; III, 12088-07-2; IV, 12271-17-9; V, 1317-11-9; VI, 12271-19-1; VII, 12271-20-4; aluminum chloride, 7446-70-0; dichloromethane, 75-09-2; ferrocene, 102-54-5.

Acknowledgment.—The author is greatly indebted to Miss K. Koda and Mr. E. Quo for their excellent contribution to the experimental work. Mr. R. K. Crossland, University of Southern California, obligingly recorded the pmr spectra.

The Novel Reaction of 2-(2′,3′,4′-Trimethoxyphenyl)cycloheptyl Methanesulfonate with Dipotassium Mercaptoacetate

F. J. LOTSPEICH

Department of Biochemistry, West Virginia University, School of Medicine, Morgantown, West Virginia 26506

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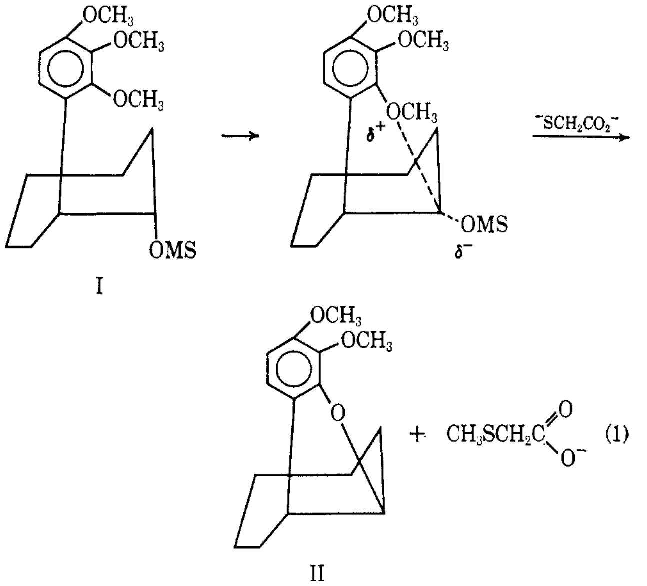
While studying the stereochemistry of 2-(2′,3′,4′-trimethoxyphenyl)cycloheptanemercaptoacetic acid obtained by the addition of mercaptoacetic acid to 1-(2′,3′,4′-trimethoxyphenyl)cycloheptene, it was necessary for the author to prepare *trans*-2-(2′,3′,4′-trimethoxyphenyl)cycloheptanemercaptoacetic acid. Because axial tosylates substituted in the axial 2 position by a phenyl group containing an electron-donating group in the *ortho* or *para* position retain their configuration when treated with nucleophilic reagents,[1] it was felt that in the present situation the desired compound could be obtained by treating *trans*-2-(2′,3′,4′-trimethoxyphenyl)cycloheptyl methanesulfonate with the dipotassium salt of mercaptoacetic acid.

Treatment of *trans*-2-(2′,3′,4′-trimethoxyphenyl)cycloheptyl methanesulfonate with the dipotassium salt of mercaptoacetic acid yielded only a small amount of the desired product. The major fraction was sulfur free and insoluble in base. The nmr spectrum of the base insoluble material showed single-proton absorptions at τ 5.0 and 6.5. These single proton absorptions were not in the region of the olefinic protons of a conjugated or unconjugated cyclic system[2] and were not in the region of the ethylenic proton of 1-(2′,3′,4′-trimethoxyphenyl)cycloheptene which absorbed at τ 4.18. Absorptions at τ 6.08 and 6.17 integrated correctly for only six protons representing two methoxyl groups rather than the expected three methoxyl groups. Thus, a methyl group of one methoxyl group was evidently lost during the reaction. Since the infrared spectrum showed no absorption in the hydroxyl region for this compound, reaction 1 is believed to occur. The structure of compound II is consistent with the nmr spectrum since the substitution pattern on the benzene ring remains unchanged, the seven-membered ring is intact, and the protons of one methoxy group are no longer present. The proton absorption at τ 5.0 is assigned to the hydrogen atom α to the oxygen of the cyclic ether. Although this value is approximately 0.57 ppm downfield from the absorption of the proton α to the ether oxygen in 2,3-dihydro-5-methoxybenzofuran (τ 5.57),[3] Fulmor, *et al.*, have assigned a proton absorption at τ 5.02 to a proton α to the cylic ether oxygen in the 6,14-*endo*-ethenotetrahydrothebaine system.[4] The proton absorption at τ 6.5 is assigned to the benzyl proton. Structure II is also consistent with the elemental analysis and the infrared spectrum. The isolation of S-methylmercaptoacetic acid also supports the postulated reaction.



Attempts to cleave the cyclic ether with gaseous hydrogen chloride at 80 and 100° were unsuccessful. Hydrogen bromide (48%) in refluxing glacial acetic acid (8 hr) cleaved the methoxyl groups but apparently failed to open the cyclic ether ring since the resulting phenolic ether could be successfully converted back into the starting compound by treatment with dimethyl sulfate and base.

Although it is generally postulated that the phenyl ring itself participates in anchimeric assistance, it has been suggested that the methoxyl group can participate directly in anchimeric assistance. Noyce[5] has postulated that the methoxyl group in 1,4-methoxycyclo-

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[3] S. D. Darling and K. D. Wills, *J. Org. Chem.*, **32**, 2794 (1967).

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