α-CARBONIUM ION STABILIZATION IN DERIVATIVES OF CYCLOPENTADIENYLMANGANESE TRICARBONYL

Thesis by
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ABSTRACT

A study has been made of the solvolyses of some acetoxy and trifluoroacetoxy compounds of cyclopentadienylmanganese tricarbonyl and of benzene. Also, a study of some addition reactions to the double bond of vinyl cyclopentadienylmanganese tricarbonyl has been made. Both studies show that an α-cyclopentadienylmanganese tricarbonyl carbonium ion is less stable than an α-ferrocenylcarbonium ion, but more stable than an α-phenyl - carbonium ion.

INTRODUCTION

Ferrocene was shown to be an aromatic substance by virtue of its ability to undergo many electrophilic substitution reactions. The infrared spectrum of ferrocene suggests that the C_5H_5 rings in ferrocene are quite similar to the benzene ring (1, 2). By now there is much evidence supporting the view that ferrocene, ruthenocene and osmocene are aromatic in nature. It appears that all π- bonded C_5H_5 rings possess aromaticity to some extent, as suggested by the general similarity of the infrared spectra of all compounds containing such rings. In some cases this can be confirmed chemically by successful Friedel-Crafts acetylation. F. A. Cotton (3) reports the successful acetylation of cyclopentadienylmanganese tricarbonyl. Cyclopentadienylmanganese tricarbonyl has been reported to be stable in air, in hydrochloric acid in ethanol, toward iodine in carbon tetrachloride and also to treatment with maleic anhydride in boiling benzene (4). Moreover, its infrared spectrum (5) suggests that the π-bonded C_5H_5 ring is aromatic in nature.

The infrared carbonyl stretching frequency of acetylcyclopentadienylmanganese tricarbonyl provides further evidence for the aromaticity of the metallocene. It has been shown for a series of substituted acetophenones that a plot of the carbonyl frequency against Hammett's sigma is linear. This indicates that changes in the carbonyl frequency parallel the ability of the substituted phenyl moiety to release electrons (6, 7). A correlation has also been observed between the carbonyl frequency and the bond order calculated by an independent method (7). Since either inductive or conjugative electron release by the aryl residue would tend to stabilize a dipolar resonance structure for the carbonyl group, greater electron release should result in a bond with less double bond character and lower stretching frequency (7, 8). Since the degree of aromatic reactivity of the a residue parallels it's ability to release electrons, the comparison of the infrared carbonyl stretching frequencies of the aryl ketones would give a qualitative estimate of the comparative reactivities of these compounds; for example, the infrared carbonyl stretching frequency of acetylferrocene is 1676 cm^{-1} while that of acetophenene is 1692 cm^{-1} indicating that ferrocene is likely to be more reactive than benzene toward electrophilic attack.

Some values of carbonyl stretching frequencies (in CCl_4) of aryl ketones are given for comparison (Table I).

Table I

Infrared Carbonyl Stretching Frequencies of Aryl Ketones in Dilute Carbon Tetrachloride Solution

Ketone	(cm^{-1})	Reference
Acetophenone	1692	(8)
Acetylcyclopentadienyl-manganese tricarbonyl	1687	(3)
p-methoxyacetophenone	1684	(8)
p-aminoacetophenone	1677	(8)
Acetylferrocene	1676	(9)

The values in Table I and the results of the competitive acetylation by Kozikowsky <u>et al</u> (10) show that the series, in decreasing reactivity toweard electrophiles becomes

$$\text{ferrocene} > \text{anisole} > C_5H_5Mn(CO)_3 > \text{benzene}.$$

This qualitative observation has been verified by the present study of the solvolytic reactions of the derivatives of cyclopentadienylmanganese tricarbonyl and of benzene.

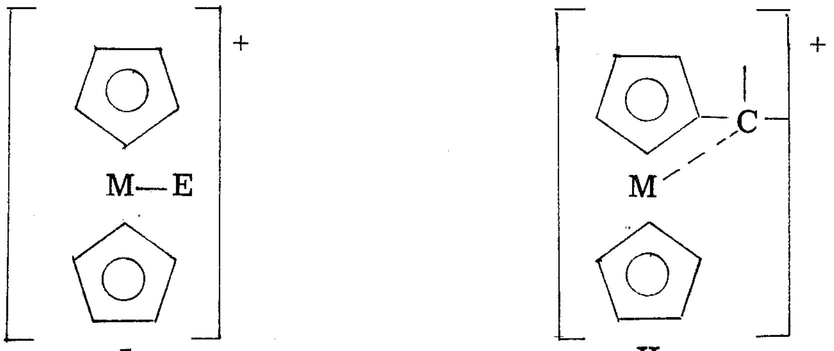
A qualitative determination of the reactivities of the iron group metallocene in Friedel-Crafts acetylation was made by Rausch, Fischer and Grubert (11). The order found,

ferrocene > ruthenocene > osmocene

parallels the relative basicities of these substances, but is in contrast with that observed for the rates of solvolyses of methylmetallocenylcarbinyl acetates (12) and for the rates of additions of acetic acid and hydrazoic acid to vinylmetallocenes (13, 14). For these processes the order is,

osmocene > ruthenocene > ferrocene.

Since all of these reactions require strong electron release by metallocene nuclei, the difference between the reactivity sequences indicates that the modes of electron release differ in these two sets of reactions. In the electrophilic substitution reaction, a direct attack on the metal by the electrophile is involved; this is confirmed by recent quantitative acetylation experiments performed by Rosenblum and co-workers (15). The reactivity of a metallocene in these reactions depends mainly on the ability of the metal to participate in additional bonding with the attacking electrophile. The reactivity of a metallocene in solvolytic reactions, however, depends on the ability of the metal to release electrons to a reaction site, (the carbinyl carbon) which is in a different geometric relation to the metal atom than that invisioned for electrophilic substitution. The ability of a metal to participate in these two types of reactions need not be parallel, since different



I

II

electrophilic substitutions.

SN_1 solvolytic reaction

Postulated Transisitons states.

Fig. I

orbitals are used and the spacing of the orbital may differ between metals. (9).

All of these experiments show that the unusual reactivity of these metallocenes in aromatic reactions is mainly due to the presence of the metal. The remarkable metal participation in the reactions of bis (π-cyclopentadienyl)-metal compounds has created an interest in the study of the similar reactions of mono (π-cyclopentadienyl) metal compounds. The case of cyclopentadienylmanganese tricarbonyl is of special interest because the metal in this compound is directly attached to three strongly electronegative carbonyl groups (16) and also because manganese is less electronegative than iron, ruthenium or osmium.

RESULTS AND DISCUSSION

Solvolysis of methylcyclopentadienylmanganese tricarbonylcarbinyl acetate: -

It was observed by Hill (9) that methylferrocenylcarbinyl acetate solvolyzes at a rate somewhat greater than that of triphenylmethyl acetate. The rates of solvolyses of methylruthenocenylcarbinyl acetate and methylosmocenycarbinyl acetate are still greater than that of methylferrocenylcarbinyl acetate. (For the exact values of rate constants of these compounds, see Table V). In order to compare the rates of solvolyses of these acetates with the solvolysis rate or methylcyclopentadienylmanganese tricarbonylcarbinyl acetate, an attempt was made to solvolyze the latter in 80% acetone, but it was found that solvolysis did not proceed at a measurable rate. The length of the reaction time and the composition of the solvent were changed in order to solvolyze the acetate but no set of conditions under which the solvolysis proceeded at a measurable rate was discovered.

Vinylcyclopentadienylmanganese tricarbonyl (17, 18) was prepared by dehydration of methylcyclopentadienylmanganese tricarbonyl carbinol. Several dehydrating agents were used under different experimental conditions in the present study. It was found that pyrolysis of the carbinol with potassium hydrogen sulfate was the most satisfactory of all the methods. (For details, see Sec. II.).

Addition Reactions to the double bond of vinylcyclopentadienylmanganese tricarbonyl: -

Several additions to the double bond of vinylcyclopentadienylmanganese tricarbonyl were attempted in order to study the stability of the α-carbonium ion in the case of the metallocene.

a) It is known that vinylferrocene is extraordinarily reactive toward addition of weak acids such as acetic acid and hydrazoic acid. (13). It is reported by Buell (14) that vinylruthenocene and vinylosmocene also undergo such addition reactions. Such electrophilic additions are generally considered to proceed through an intermediate carbonium ion, so the facility of these addition reactions in the cases of ferrocene, ruthenocene and osmocene suggests that a very stable carbonium ion is formed as an intermediate. Thus, in order to obtain some information concerning the stability of the carbonium ion in the present study, these additions were attempted to the double bond of vinylcyclopentadienylmanganese tricarbonyl; the reactions were carried out under conditions identical to those used in the case of vinylferrocene. Vinylcyclopentadienylmanganese tricarbonyl was recovered unreacted at the end of the reaction time, indicating the failure of acetic acid and hydrazoic acid to add to the double bond of the vinyl compound. Further attempts to add acetic acid to the double bond of the vinyl compound using greater reaction times and higher temperature (110°C) were made but no addition occurred.

b) Since the additions of the dilute acids to the vinyl compound did not take place, an attempt was made to add hydrobromic acid to the double bond of vinylcyclopentadienylmanganese tricarbonyl. Hydrogen bromide gas was bubbled through a solution of the vinyl compound in absolute acetic acid at 0°C, and the reaction mixture was then allowed to stand overnight at room temperature. None of the expected methylcyclopentadienylmanganese tricarbonyl bromide formed, and it was observed that the starting material had decomposed. The presence of a gray gummy solid in the reaction mixture indicated that slight polymerization of the starting material had occurred. This polymerization may have proceeded through an intermediate carbonium ion.

c) An attempt was made to effect a Diels-Alder addition to the double bond of vinylcyclopentadienylmanganese tricarbonyl with cyclopentadiene by refluxing equimolar quantities of both reagents for twenty four hours. Unreacted vinylcyclopentadienylmanganese tricarbonyl was recovered at the end of this period, indicating the inability of the vinyl compound to undergo Diels-Alder addition with cyclopentadiene.

d) Several attempts at 1,3 dipolar additions to the double bond of vinylcyclopentadienylmanganese tricarbonyl with phenyl azide were made. Equimolar mixtures of these compounds were allowed to stand at room temperature for different lengths of time. Each time the vinyl compound was recovered unreacted after the removal of the phenyl azide, indicating the failure of the reaction. Similarly, the addition of nitrone (prepared from phenylhydroxylamine) to the double bond of vinylcyclopentadienylmanganese tricarbonyl could not be effected even after refluxing the reaction mixture for several days.

Thus, all attempts at effecting addition reactions to the double bond of vinylcyclopentadienylmanganese tricarbonyl failed, indicating the inability of the vinyl compound to undergo such electrophilic additions. It should be noted here that the double bond of the vinyl compound was successfully hydrogenated by the recent method of Brown and Brown (19) for the hydrogenation of olefins. Sodium borohydride was used as the reducing agent for this reaction with platinum (chloroplatinic acid) as the catalyst.

Infrared hydroxyl stretching frequencies of carbinols of cyclopentadienylmanganese tricarbonyl: -

Trifan and co-workers (20) have reported the pressence of two peaks of the hydroxyl region of the infrared spectrum of methylferrocenylcarbinol. A detailed study of the hydroxyl stretching frequencies of the carbinols of ferrocene, ruthenocene and osmocene was carried out by Hill (9), who reported that two peaks are generally present in the hydroxyl region of the infrared spectra of these carbinols. The peak at higher frequency is assigned to a free (or ring bonded) hydroxyl stretching frequency and lower frequency peak is due to bonding between the hydroxyl hydrogen atom and the metal. (21,22).

It was observed (9) that in the series of compounds, methylferrocenylcarbinol, methylruthenocenylcarbinyl and methylosmocenylcarbinol the position of the lower frequency band shifts strongly toward lower frequencies, the band in the spectrum of methylosmocenylcarbinol being 75 cm^{-1} lower in frequency than that of methylferrocenylcarbinol. This observation is explained on the basis of the relative electronegativities of the corresponding metals; more electronegative atoms generally being considered to form stronger hydrogen bonds. Hill reports that the strengths of the intramolecular hydrogen bonds of the methylmetallocenylcarbinols follow the same sequence as the solvolyses rates of the corresponding acetoxy compounds. (See Table II).

Table II

Relative solvolysis rates of the methylmetallocenylcarbinyl acetates and infrared hydroxyl stretching frequencies of the corresponding carbinols

Compound	Rel. $K_{30°C.}$	Compound	$(cm^{-1})^a$
Methylferrocenyl-carbinyl acetate	1.00	Methylferrocenyl-carbinol	3605 3581
Methylruthenocenyl-carbinyl acetate	1.35	Methylruthenocenyl-carbinol	3608 3526
Methylosmocenyl-carbinyl acetate	5.36	Methylosmocenyl-carbinol	3609 3506

[a] spectra were taken in CS_2 (Hill, 9).

This observation was kept in mind while studying the infrared spectrum of methylcyclopentadienylmanganese tricarbonylcarbinol. The spectrum of this compound was taken in both carbon tetrachloride and carbon disulfide to avoid ambiguity. The infrared spectrum of this compound exhibits only one peak in the hydroxyl stretching region, at 3640 cm^{-1} in carbon tetrachloride and at 3600 cm^{-1} in carbon disulfide. From the results shown in Table II, it is apparent that this peak should be due to a free(or ring bonded) (21) hydroxyl stretching frequency. The absence of the peak at lower frequency indicates the absence of singnificant intramolecular hydrogen bonding to the central metal atom in this compound. This may be due to the small electronegativity of manganese, the magnitude of which is further reduced by the presence of the metal carbonyl groups in this compound.

Proof of the absence of significant intramolecular hydrogen bonding to the metal is more clearly obtained from the study of the infrared spectra of the two isomeric α-hydroxy-1,2-tetramethylene-cyclopentadienylmanganese tricarbonyls. Of these alcohols, one

Table III

Infrared Hydroxyl Stretching Frequencies of Metallocene-substituted alcohols in CS_2 and in CCl_4

Alcohol	$(\text{cm}^{-1})^a$ in CS_2		(cm^{-1}) in CCl_4
Methylcyclopentadienylmanganese tricarbonylcarbinol	3600		3640
Methylferrocenylcarbinol	3605	3581	
Methylruthenocenylcarbinol	3608	3526	
Methylosmocenylcarbinol	3609	3506	
Endo-α-hydroxy-1,2-tetramethylene-cyclopentadienylmanganese tricarbonyl	3605		3615
Exo-α-hydroxy-1,2-tetramethylene-cyclopentadienylmanganese tricarbonyl	3615		3625
Endo-α-hydroxy-1,2-tetramethylene-ferrocene	(3608)	3561	
Exo-α-hydroxy-1,2-tetramethylene-ferrocene	3610		
Endo-α-hydroxy-1,2-tetramethylene-ruthenocene		3510	
Exo-α-hydroxy-1,2-tetramethylene-ruthenocene	3648		

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[a] stronger peaks are underlined.

passes through a chromatographic column rapidly and absorbs at 3615 cm^{-1} (in carbon tetrachloride); this should be the endo-isomer. The second alcohol passes through the column less rapidly and absorbs at 3625 cm^{-1}; this should be the exo-isomer. The separation of the two isomers on the chromatographic column was possible because the hydroxyl group in the endo-isomer is sterically shielded, and thus unable to form a complex with the alumina in the column, while the hydroxyl group in the exo-isomer is sterically more available to the alumina for the formation of intermolecular hydrogen bonds. Hence, the endo-alcohol is eluted more rapidly than the exo-alcohol.

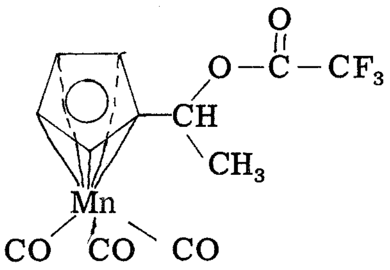
In the case of α-hydroxy-1,2-tetramethyleneferrocenes, the endo-alcohol absorbs at 3561 cm^{-1} (in carbon disulfide) and the exo-alcohol absorbs at 3610 cm^{-1} (in carbon disulfide). It is believed that the larger the difference in the frequency, the stronger the metal hydrogen bonding in the endo-isomer. The small difference between the frequencies of the absorption peaks of the endo- and exo- alcohols in the case of cyclopentadienylmanganese tricarbonyls gives evidence of the absence of strong metal-hydrogen bonding in the case of endo-α-hydroxy-1,2-tetramethylenecyclopentadienylmanganese tricarbonyl.. Moreover, the hydroxyl stretching frequency of the endo-alcohol is in the region assigned to the free hydroxyl stretching frequency rather than in the region of metal-bonded hydroxyl stretching frequency.

Solvolyses of Trifluoroacetates

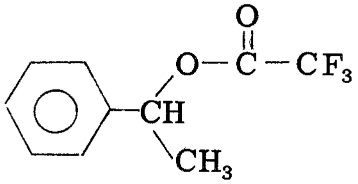
Methylcyclopentadienylmanganese tricarbonylcarbinyl trifluoroacetate

The failure to solvolyze the acetoxy compounds of cyclopentadienylmanganese tricarbonyl made necessary the study of the solvolytic reactions of the derivatives of cyclopentadienylmanganese tricarbonyl possessing more reactive leaving groups than the acetoxy group. Several attempts were made to prepare methylcyclopentadienylmanganese tricarbonyl tosylate: Methylcyclopentadienylmanganese tricarbonylcarbinol was allowed to react with tosyl chloride in pyridine or collidine at room temperature for different lengths of time. Decomposition of the starting materials was the usual result of these attempts.

Moffat et al (23, 24) reported that solvolytic reactions of trifluoroacetates of alkyl- and aryl-carbinols generally follow a clear SN_1 mechanism. Since the trifluoroacetate ion is a better leaving group than the acetate ion, the trifluoroacetate of methylcyclopentadienylmanganese tricarbonylcarbionol (I) could provide a means for the study of solvolysis of the cyclopentadienylmanganese tricarbonyl system. This compound was prepared by allowing the corresponding alcohol to react with trifluoroacetic anhydride in lutidine (24) at room temperature for twelve hours. Following Hammond's method (25) for the preparation of benzyl tosylate, α-methylbenzylcarbinyl trifluoroacetate (II) was prepared by reacting the sodium salt of α-methylbenzylcarbinol with trifluoroacetic anhydride. A solvolytic study of this compound was made, in order to compare its solvolysis rate with that of methylcyclopentadienylmanganese tricarbonylcarbinyl trifluoroacetate.



I



II

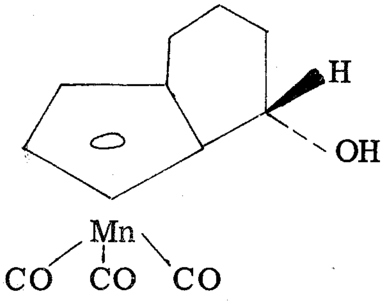
An early kinetic run in 80% acetone established that methylcyclopentadienylmanganese tricarbonylcarbinyl trifluoroacetate (I) solvolyzes to give the corresponding alcohol and trifluoroacetic acid. The products of ethanolysis of the trifluoroacetate were studied in order to determine the position of the cleavage during the solvolysis. The trifluoroacetate was refluxed with absolute ethanol for six hours. This ethanolysis produced the ethyl ether of methylcyclopentadienylmangese tricarbonylcarbinol, which was identified from its elemental analysis. A control experiment was performed by refluxing the carbinol with one half equivalent of trifluoroacetic acid in absolute ethanol. The recovery of unreacted carbinol from the reaction mixture provided a rigorous proof that the ester solvolyzes by an alkyl-oxygen fission. Therefore, by analogy, the hydrolysis of the trifluoroacetate should also proceed through an intermediate carbonium ion. A similar study of α-methylbenzylcarbinyl trifluoroacetate (II) confirmed that this ester also solvolyzes by alkyl-oxygen fission.

The trifluoroacetates were solvolyzed in 90% acetone at various temperatures to elucidate the solvolytic reaction mechanism. The magnitude of the neutral hydrolysis rate of methylcyclopentadienylmanganese tricarbonylcarbinyl trifluoroacetate is a very good indication that the reaction follows a $B_{AL}1$ mechanism. It was observed that methylcyclopentadienylmanganese tricarbonylcarbinyl trifluoroacetate solvolyzes more rapidly than α-methylbenzylcarbinyl trifluoroacetate in 90% acetone. The solvolysis rate of methylcyclopentadienylmanganese tricarbonylcarbinyl trifluoroacetate at 42.8 °C is 1.995×10^{-3} sec^{-1}, While the solvolysis rate for α-methylbenzylcarbinyl trifluoroacetate at the same temperature is 1.030×10^{-6} sec^{-1}, so methylcyclopentadienylmanganese tricarbonylcarbinyl trifluoroacetate solvolyzes at a rate greater than that of α-methylbenzylcarbinyl trifluoroacetate by a factor of 1937. The results of solvolysis of the trifluoroacetates are summarized in Table XIII.

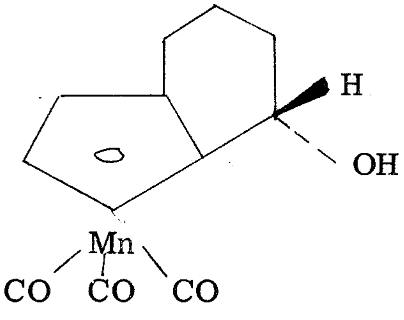
Endo- and *Exo*-α-trifluoroacetoxy-1,2-tetramethylenecyclopentadienylmanganese tricarbonyls: -

Hill (9) reports that the solvolysis rates of *exo*-α-acetoxy-1,2-tetramethyleneferrocene and *endo*-α-acetoxy-1,2-tetramethyleneferrocene differ by a factor of 2557, while Plesske (26) reports a factor of 19950 in case of the ruthenocene analogues. These large differences are considered to be the least ambiguous evidence for direct contribution of electrons to the reaction site by the metal from 'below' the plane of the ring. These results were kept in mind while studying the rates of solvolyses of *endo*- and *exo*-α-trifluoroacetoxy-1,2-tetramethylenecyclopentadienylmanganese tricarbonyls.

Reduction of α-keto-1,2-tetramethylenecyclopentadienylmanganese tricarbonyl with sodium borohydride led to the two expected isomeric alcohols. The isomer which passed through the chromatographic column more rapidly and absorbed at 3615 cm^{-1} in the infrared region was assigned the structure III (*endo*-isomer); the isomer which was eluted more slowly and absorbed at 3625 cm^{-1} was assigned the structure IV(*exo*-isomer) (21).



III



IV

The ratio of exo- and endo-isomers produced was 1:4.

The trifluoroacetates were prepared from the alcohols by treatment with trifluoroacetic anhydride and lutidine (24). Since the carbon-oxygen bond is not broken in this reaction, the configurations about the carbinyl carbon are not altered.

Stereochemistry of solvolyses: -

Pertinent data for the solvolyses of these trifluoroacetates is summarized in Table XIII

The rate constant observed for the exo-isomer is twenty (20) times greater than that of the endo-isomer. It may be mentioned here that the numbers given in the case of α-trifluoroacetoxy-1,2-tetramethylenecyclopentadienylmanganese tricarbonyls are not very accurate. Owing to the difficulty of purifying these compounds (see sectionII) kinetic measurements were taken using partially impure material. Moreover, the limited amount of the starting material available restricted the number of runs taken in the case of these isomers. In spite of these hindrances, good agreement was generally observed between the values of the rate constants for each temperature and it is believed that the ratio of the rates of exo- and endo-isomers calculated in the present study is very close to the exact figure. Since the exact numerical value of this ratio would not provide any more information on the role of the metal in the stabilization of the carbonium ion than this approximate value, conclusions drawn from the approximate value concerning metal participation in the stabilization of the carbonium ion in the present study should be of a similar nature to those drawn from the exact value, were this available.

Table IV

Solvolyses Rates

Compound	T°C.	$K \times 10^5$	K_{exo-} / K_{endo-}
Exo-α-Trifluoroacetoxy-1,2-tetramethylene-cyclopentadienylmanganese tricarbonyl	20	115.4	19.55
Endo-α-Trifluoroacetoxy-1,2-tetramethylene-cyclopentadienylmanganese tricarbonyl	20	5.900	
Exo-α-Acetoxy-1,2-tetramethyleneferrocene	30	72.1	2557.0
Endo-α-Acetoxy-1,2-tetramethyleneferrocene	30	0.0282	
Exo-α-Acetoxy-1,2-tetramethyleneruthenocene	30	141.2	19950.0
Endo-α-Acetoxy-1,2-tetramethyleneruthenocene	30	0.007	

Solvolysis of *endo*-α-trifluoroacetoxy-1,2-tetramethylenecyclopentadienylmanganese tricabonyl yielded 60% of the *exo*-alcohol, 20% of the *endo*-alcohol 11% of α, β dehydro-1,2-tetramethylenecyclopentadienylmanganese tricarbonyl and 9% of α-keto-1,2-tetramethylenecyclopentadienylmanganese tricarbonyl, while solvolysis of the *exo*-isomer gave 90% of what is presumed to be the olefin and 10% of the ketone. The presence of the ketone and olefin in the solvolysis products makes it difficult to draw any conclusion about stereospecificity of the reaction. Since the starting material used in these solvolyses was only partially pure the ratio of the alcohols obtained on solvolysis of *endo*-α-trifluoroacetoxy-1,2-tetramethylenecyclopentadienylmanganese tricarbonyl could not throw any

Table V
Relative Solvolyses Rates

Compound	T °C.	$k \times 10^5$	Rel. $k_{T\,°C.}$
Methylcyclopentadienylmanganese tricarbonylcarbinyl trifluoroacetate	20	29.85^a	1.000
Exo-α-trifluoroacetoxy-1,2-tetramethylenecyclopentadienylmanganese tricarbonyl		115.4	3.866
Endo-α-trifluoroacetoxy-1,2-tetramethylene cyclopentadienylmanganese tricarbonyl (in 90% acetone)		5.9^a	0.198
Methylcyclopentadienylmanganese tricarbonylcarbinyl trifluoroacetate	42.8	199.5^a	1.000
α-Methylbenzylcarbinyl trifluoroacetate (in 90% acetone)		0.1030	0.00052
Methylferrocenylcarbinyl acetate	30	17.02	1.000
Exo-α-acetoxy-1,2-tetramethyleneferrocene		72.1	4.24
Endo-α-acetoxy-1,2-tetramethyleneferrocene (in 80% acetone)		0.0282^a	0.00165
Methylruthenocenylcarbinyl acetate	30	23.22	1.00
Exo-α-acetoxy-1,2-tetramethyleneruthenocene		141.2^a	6.08
Endo-α-acetoxy-1,2-tetramethyleneruthenocene (in 80% acetone)		0.007^a	0.00030

[a] Extrapolated from other temperatures.

light on the reaction mechanism.

The rate constant observed for exo-α-trifluoroacetoxy-1,2-tetramethylenecyclopentadienylmanganese tricarbonyl is 3.86 times greater than that of methylcyclopentadienylmanganese tricarbonylcarbinyl trifluoroacetate, while exo-α-acetoxy-1,2- tetramethyleneferrocene solvolyzes 4.24 times faster than methylferrocenylcarbinyl acetate and exo-α-acetoxy 1,2-tetramethyleneruthenocene solvolyzes 6.08 times faster than methylruthenocenylcarbinyl acetate. The difference between solvolyses rates of exo-α-trifluoroacetoxy-1,2-tetramethylenecyclopentadienylmanganese tricarbonyl and methylcyclopentadienylmanganese tricarbonyl is due to the inductive effects of the alkyl substitutents in stabilizing the α-carbonium ions in these compounds. The greater solvolysis rate of exo-α-trifluoroacetoxy-1,2-tetramethylenecyclopentadienylmanganese tricarbonyl indicates that the 2-alkyl substituent is effective at inductive and mesomeric electron release to the carbinyl carbon, thus stabilizing the α-carbonium ion.

α-Carbonium ion stabilization in the derivatives of cyclopentadienylmanganese tricarbonyl: -

The inability of the acetoxy compounds of cyclopentadienylmanganese tricarbonyl to solvolyze gave an indication that the α-carbonium ion in the metallocene is not as stable as that in the case of ferrocene, ruthenocene or osmocene. Moreover, the failure of the electrophilic additions to the double bond of vinylcyclopentadienylmanganese tricarbonyl provide further evidence for the relative instability of the α-carbonium ion of this metallocene.

The presence of a reactive leaving group like trifluoroacetate ion in the methylcyclopentadienylmanganese tricarbonylcarbinyl trifluoroacetate enables the latter to solvolyze in 90% acetone at a measurable rate. However, the large magnitude of the rate of solvolysis of methylcyclopentadienylmanganese tricarbonylcarbinyl trifluoroacetate as compared to that of α-methylbenzylcarbinyl trifluoroacetate is evidence of the presence of a more stable α-carbonium ion in the case of the present metallocene than in the phenyl system. Thus, the present kinetic measurments show that the α-carbonium ion in the case of cyclopentadienylmanganese tricarbonyl is less stable than that in benzene. This reactivity sequence is in agreement with that for electrophilic aromatic substitution (see ‘introduction’), namely

ferrocene $> C_5H_5M_{n}(CO)_3 >$ benzene.

The study of the solvolytic reactions of α-trifluoroacetoxy-1,2-tetramethylenecyclopentadienylmanganese tricarbonyls may throw some light on the role of the metal in the stabilization of α-carbonium ions in the metallocene by direct electron release to the reaction center. A comparison of the ratio (approximately 20) of the solvolysis rates of *exo*- and *endo*-α-trifluoroacetoxy-1,2-tetramethylenecyclopentadienylmanganese tricarbonyls with those of the solvolyses rates of *exo*- and *endo*-α-acetoxy-1,2-tetramethyleneferrocene (approximately, 2500) and *exo*- and *endo*-α-acetoxy-1,2-tetramethyleneruthenocene (approximately, 19,000) show that solvolysis of *exo*-α-trifluoroacetoxy-1,2-tetramethylenecyclopentadienylmanganese tricarbonyl is not as strongly assisted by the metal as it is in the case of the *exo*-isomers of ferrocene and ruthenocene. The large difference in the solvolyses rates of the *exo*- and *endo*- isomers of ferrocene and ruthenocene is explained on the basis of the ability of the central metal atom in these metallocenes, to assist the solvolysis of the *exo*-isomer by forming a bond between carbinyl carbon and the metal and thus, stabilizing this carbonium ion to a great extent. This assistance is not available to the endo-isomers. Other factors which may contribute to the decreased rates of solvolysis of the endo-isomers are, for example; steric effects and mutual repulsion of the negative charges on the metal-carbonyl groups and the leaving group.

The small difference between the solvolyses rates of exo- and endo-α-trifluoroacetoxy-1,2-tetramethylencyclopentadienylmanganese tricarbonyls gives clear evidence for the absence of significant direct metal participation in these solvolyses. The decreased solvolysis rate of the endo-isomer could be explained largely on the basis of steric effects. If the trifluoroacetate ion departs 'downward', as it does in the case of the endo-isomer, it will be repelled by the carbonyl groups. directly attached to the metal. Moreover, the negatively charged leaving group might be repelled by the electronegative oxygen atom of the carbonyl group.

The inability of the acetoxy compounds of cyclopentadienylmanganese to solvolyze at a measurable rate, the inability of vinylcyclopentadienylmanganese tricarbonyl to undergo electrophilic addition reactions, the small difference in the solvolyses rates of exo- and endo-α-trifluoroacetoxy-1,2-tetramethylenecyclopentadienylmanganese tricarbonyls and the absence of significant intramolecular hydrogen metal bonding in the case of the carbinols of the metallocene indicate very clearly that direct metal participation in the stabilization of the α-metallocenyl carbonium ion is negligible (or even absent !) in the case of cyclopentadienylmanganese tricarbonyl compared to that in the case of ferrocene, ruthenocene or osmocene. The large difference in solvolyses rates of methylcyclopentadienylmanganese tricarbonylcarbinyl trifluoroacetate and α-methylbenzylcarbinyl trifluoroacetate can be explained on the basis of the relative aromaticity of the metallocene and the benzene ring. In the case of the metallocene the π-electron system of the five membered carbocyclic ring is more concentrated and thus more effective in the stabilization of the α-carbonium ion, while the π-electron system of the six membered benzene ring, being comparatively less concentrated, is less effective in the stabilization of the α-carbonium ion. This seems to be the most plausible explanation for the observed difference in the solvolyses rates of the above mentioned trifluoroacetates.

The absence of significant direct metal participation in the case of cyclopentadienylmanganese tricarbonyl may be due to the following reasons: the less electronegative character of manganese relative to that of iron, ruthenium and osmium is the simplest explanation for its relative inability to donate electrons to the reaction center, but the presence of three electronegative carbonyl groups directly attached to the metal may play a significant role in restricting its ability to release the electrons, directly or indirectly, to the reaction site. R. D. Fischer (27) reported that the frequencies of the completely symmetrical CO vibrations in di- or oligo-olefin-metal carbonyls, are about 40 to 60 wave numbers smaller than those in pure carbonyls. This is due to the decrease in the degree of bonding of the CO, accompanied by a partial double bond formation between the metal and carbonyl carbon, leading to a corresponding displacement in the direction of the resonance structure B.

$$\underset{\text{A}}{\underline{\mathrm{Mn}}-\mathrm{C}\equiv\mathrm{O}|} \longleftrightarrow \underset{\text{B}}{\mathrm{Mn}=\mathrm{C}=\underline{\overline{\mathrm{O}}}}$$

The charge displacement

olefin → metal → CO

is confirmed by dipole measurments, infrared spectroscopic investigations and by X-ray structure analyses (28). Owing to this charge displacement in the direction of the CO groups, the metal is not effective in the stabilization of the α-carbonium ions in the case of the derivatives of cyclopentadienylmanganese tricarbonyl.

SECTION II

EXPERIMENTAL

Reactions were invariably run under a nitrogen atmosphere. The reaction vessels were wrapped with alumina foil to protect the contents from light.

Infrared spectra were determined on a Beckman IR-7 recording spectrophotometer and a Perkin-Elmer model 237 spectrophotometer.

Elementary analyses were performed by Schwartzkopf Microanalytical Laboratories, Woodside, New York and by Spang Microanalytical Laboratories, Ann Arbor, Michigan.

Cyclopentadienylmanganese tricarbonyl was obtained commercially.

Acetylcyclopentadienylmanganese tricarbonyl was prepared by acetylating cyclopentadienylmanganese tricarbonyl with acetyl chloride and aluminum chloride according to the procedure of Kozikowski (10).

Methylcyclopentadienylmanganese tricarbonylcarbinol was prepared by reducing acetylcyclopentadienylmanganese tricarbonyl with sodium borohydride.

A solution of the acetyl compound (1 gm., 4.1mmole) in methanol (75ml.) was stirred in a flask. To this solution sodium borohydride (1 gm., 26.5mmole.) was added over a period about ten minuets at 0°C. The reaction mixture was then stirred for two hours at room temperature. Acetone (7 ml.) was added to the reaction flask. The solution was then poured into cold water and the product was extracted from the aqueous methanol phase with several portions of methylene chloride. The organic phase was separated and dried over anhydrous sodium sulfate. The solvent was removed to yield a brown oil.

This oil was chromatographed on thirty grams of neutral alumina (activity grade II) with benzene-ether (30-50% of ether) as the eluent. The eluate yielded a pale yellow oil on removal of the solvent.

The infrared spectrum of this oil exhibited a band at 3640 cm^{-1} (in carbon tetrachloride) and no band at 1700 cm^{-1}.

Methylcyclopentadienylmanganese tricarbonylcarbinyl acetate was prepared from the corresponding alcohol. About one gm. of the alcohol was mixed with pyridine (5 ml.) and acetic anhydride (2 ml.). The reaction vessel was closed to the atmosphere and was allowed to stand overnight at room temperature.

Pyridine, acetic acid, and acetic anhydride were evaporated at room temperature and at about one mm. pressure. The acetate was transferred to a molecular distillation apparatus. The acetate was distilled at a temperature of about 110°C. and a pressure of 3-4 microns.

The molecular still used in the present study for the purification of all the liquids has a heating chamber 25 mm in diameter with a path length of 20 mm between the base and the cold finger. The chamber is fitted with removable oil bath heating assembly. Since the heating chamber is in contact with a glass sleeve rather than with the oil bath itself, the temperature of the material in the heating chamber is somewhat less than the temperature of the oil bath: For this reason, the temperature reported here should be regarded as the maximum temperatures to be employed if a conventional molecular still is used to purify these compounds.

The purified acetate was collected in a micro volumetric flask stoppered under a nitrogen atmosphere.

Analysis: Calculated for $C_{12}H_{11}O_5Mn$, - C, 49.67; H, 4.09; Mn, 19.15

Found (Shwarzkopf): C, 49.88; H, 4.03; Mn, 19.29.

Vinylcyclopentadienylmanganese tricarbonyl (17, 18) was prepared by dehydration on methylcyclopentadienylmanganese tricarbonylcarbinol by several methods:

Method 1 - Methylcyclopentadienylmanganese tricarbonylcarbinol was mixed with potassium hydrogen sulfate (1.5 g.) in a flask. The reaction mixture was heated slowly to 140°C. and the temperature was kept approximately constant at this value for two hours. The flask was completely covered with glass wool to maintain uniform heating. The reaction mixture was then cooled to room temperature taking care not to let any air into the flask. This was achieved by employing mercury valve in the system. The product was extracted by washing the contents of the flask with anhydrous ether, and the insoluble materials were filtered. The removal of the solvent yielded a brown oil. Yield - 62%.

This oil was chromatographed on a column packed with alumina (activity grade II). Benzene was used as the eluent. Two bands appeared on the column. The faster moving band was eluted with benzene and yielded a pale yellow oil on removal of the solvent. This oil was identified as vinylcyclopentadienylmanganese tricarbonyl from its infared spectrum. The spectrum possesses a moderate band at 1815 ^{1} and group of bands in the 3000-3200 cm^{-1} region (CH stretching, 29). $n^{23}D$ - 1.6192. The slow moving band on the column was eluted with a benzene-ether solution (5% ether). A pale yellow solid was obtained from this eluate. This solid was identified as acetylcyclopentadienylmanganese tricarbonyl on the basis of its infrared spectrum and melting point.

Method II - Methylcyclopentadienylmanganese tricarbonylcarbinol (0.1 g) was mixed with 10 ml. of dimethyl sulfoxide. The reaction flask was heated to 160°C. and the temperature was kept constant at this for three hours. Subsequently the flask was cooled to room temperature. Cold water was added to the reaction mixture to dissolve the dimethyl sulfoxide. On removal of the solvent, vinylcyclopentadienylmanganese tricarbonyl was obtained.

Method III - The solution of the carbinol (0.5 g.) in benzene was stirred with basic alumina (5 g.) for eight days. The solution was then filtered to remove alumina. Removal of the solvent gave vinylcyclopentadienylmanganese tricarbonyl in low yield, 40%.

Ethylcyclopentnadienylmanganese tricarbonyl: The apparatus consisted of a round bottom flask fitted with a magnetic stirrer and a short manometer which allowed the escape of hydrogen at a pressure of 25 mm. above atmospheric pressure. A dropping funnel with equalising pressure was fitted on one of the inlets of the flask.

A standard 1 M stabilising solution of sodium borohydride in ethanol was prepared by dissolving sodium borohydride (3.8 g.) in 100 ml. of a solvent prepared by adding anhydrous ethanol to 5 ml. of 2 M aqueous sodium hydroxide.

One ml. of 0.2 M chloroplatinic acid (commercially available) was placed in this flask along with 40 ml. of anhydrous ethanol. The apparatus was flushed with nitrogen gas. The solution of chloroplatinic acid was vigorously stirred and to this solution was added 5 ml. of standard sodium borohydride solution. There was an immediate formation of a jet black catalyst suspension. After approximately one minute, 9 ml. of glacial acetic acid was added to neutralise the excess sodium borohydride and also to provide a hydrogen atmosphere. The reaction was initiated by adding vinylcyclopentadienylmanganese tricarbonyl (33.8 mmole.) to the reaction flask. The standard solution of sodium borohydride was then added from the dropping funnel at such a rate as to maintain atmospheric pressure in the flask.

The reaction mixture was stirred for three days at room temperature. Ice cold water was then added to the flask and resulting mixture was filtered to remove platinum. The reaction product was extracted from aqueous ethanol with n. hexane. The organic phase was then separated and dried over anhydrous magnesium sulfate. The removal of the solvent yielded a viscous yellow oil. $n^{23}D$ - 1.57930.

The infrared spectrum of this oil exhibited no absorption either at 1815 cm^{-1} or near the 3100 cm^{-1} region, that is characteristic of the vinyl group, moreover it shows a fairly strong absorption in the 2800-3000 cm^{-1} region.

The analytical sample was molecularly distilled at 115 °C. and at a pressure of 5 microns.

Analysis: Calculated for $C_{10}H_9O_3Mn$: C, 51.72; H, 3.87; Mn, 23.70

Found (Spang): C, 51.54; H, 3.78;

Found (Schwarzkopf): C, 51.52; Mn, 23.29.

Attempted additions to the double bond of vinylcyclopentadienylmanganese tricarbonyl:

(a) Acetic acid - Vinylcyclopentadienylmanganese tricarbonyl was dissolved in anhydrous benzene (5 ml.) and glacial acetic acid (5 ml.). The mixture was refluxed for three days. The acetic acid was removed at room temperature and at one mm. pressure. The brown oil that obtained, was identified as vinylcyclopentadienylmanganese tricarbonyl on the basis of its infrared spectrum.

(b) Hydrogen bromide - Vinylcyclopentadienylmanganese tricarbonyl (0. 1 g.) was dissolved in 25 ml. of glacial acetic acid. Hydrogen bromide gas was bubbled through the solution for about thirty minutes at 0°C. The reaction mixture was then allowed to stand overnight at room temperature. The subsequent addition of cold water (50 ml.) to this mixture resulted in the separation of a gray gummy solid. This solid was then separated by filtration and dried over a porous plate. However, it would not be dissolved in variety of organic solvents. Thus, it was assumed to be a polymer of vinylcyclopentadienylmanganese tricarbonyl.

(c) Cyclopentadienyl - (Diels-Alder reaction): Freshly prepared cyclopentadiene (10 ml.) was refluxed with vinylcyclopentadienylmanganese tricarbonyl (0. 1 g.) for twelve hours. Then the cyclopentadiene was removed under reduced pressure. A thick yellow oil was obtained. This oil was identified as the vinyl compound from its infrared spectrum.

(d) 1,3 dipolar additions:

1) Equimolar quantities of the vinyl compound and phenyl azide were mixed and kept at room temperature for eight days. On removal of the remaining phenyl azide, vinylcyclopentadienylmanganese

tricarbonyl was found unreacted.

2) The vinyl compound was refluxed with nitron for three days but on removal of the nitron, vinylcyclopentadienylmanganese tricarbonyl was recovered unchanged.

Exo- and endo-α-hydroxy-1,2-tetramethylenecyclopentadienylmanganese tricarbonyls were obtained by the reduction of α-keto-1,2-tetramethylenecyclopentadienylmanganese tricarbonyl *. A solution of the ketone (500 mg.) in methanol was stirred at 0°C. and sodium borohydride (1 g.) was added to the reaction flask over a period of five minutes. The reaction mixture was then stirred for an hour at room temperature. Acetone (7 ml.) was added to the solution at the end of the reaction time, to destroy the excess of the sodium borohydride. The solution was then poured into cold water and the product was extracted from the aqueous methanol phase with ethyl ether. The organic phase was separated and dried over anhydrous sodium sulfate. The solution yielded a brown oil on removal of the solvent.

This oil was chromatographed on a column packed with alumina (activity grade II). Two bands appeared on the column. The faster moving band was eluted with benzene-ether (30% of benzene and 70% of ether) solution. The column was washed with the eluent for about an hour after the first band was eluted. This was done so as to achieve a complete separation of the isomeric alcohols. The second band was eluted from the column by adding a trace of methanol to the eluent.

The first band gave a pale yellow oil on the removal of the solvent. The infrared spectrum of this alcohol (endo-isomer) exhibited

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* This compound was prepared by Dr. Klaus Plesske, (37).

a fairly strong band at 3615 cm^{-1} (in carbon tetrachloride), while the spectrum of the second alcohol (exo-isomer) exhibited a weak peak at 3625 cm^{-1}.

Preparations of metallocenylcarbinyl trifluoroacetates:

A standard procedure was used for the preparation of all the trifluoroacetates (except α-methylbenzylcarbinyl trifluoroacetate) in the present study.

In the general procedure, the alcohol (about 500 mg.) was mixed with 2:6 dimethylpyridine (lutidine) (5 ml.) and trifluoroacetic anhydride (2 ml.) at 0°C. in a round bottom flask. The reaction flask was then closed to the atmosphere and allowed to stand at room temperature for twelve hours. The reaction mixture was next washed with a solution of sodium bicarbonate several times to remove trifluoroacetic acid. The product was then extracted in ether by washing the aqueous phase several times with small portions of ether. The organic phase was washed three times with dilute hydrochloric acid to remove the lutidine from the solution. The organic phase was then dried over anhydrous magnesium sulfate. The product that was obtained after removal of the solvent was then molecularly distilled.

The purified trifluoroacetates were then stored in microvolumetric flasks, stoppered in a nitrogen atmosphere and kept in a cool, dry place. These compounds were usually used within a day of their preparation for kinetic measurements. The elementary analyses of the metallocenylcarbinyl trifluoroacetates were not satisfactory due to the simultaneous presence of the metal and fluorine in the compounds. However, the analyses of the ethers obtained from ethanolysis of these trifluoroacetates were satisfactory and such analyses of derivatives of the trifluoroacetates were accepted as proof that no unexpected change in molecular composition had occurred during ethanolysis.

α-Methylbenzylcarbinyl trifluoroacetate was prepared from the corresponding alcohol (25). Finely powdered sodium hydride (1.2 mole) was added to a solution of α-methylbenzylcarbinol (1 mole) in ether. The reaction mixture was refluxed and stirred vigorously for twelve hours. The reaction flask was then cooled to - 20°C. in a dry ice-acetone bath. Trifluoroacetic anhydride (1 mole) was added to the reaction mixture dropewise, the latter was then filtered to remove insoluble materials. The last filtration was performed by using a medium grade sintered glass funnel, in order to remove fine particles of sodium hydride. A clear pale yellow solution was obtained, which gave a yellow liquid, on removal of the solvent. The infrared spectrum of this compound exhibited a strong peak at 1778 cm^{-1} and no peak at 3630 cm^{-1}, indicating a complete esterification of the carbinol.

Analysis; Calculated for $C_{10}H_9O_2F_3$: C, 55.04; H, 4.12 F, 26.14,
Found (Schwarzkopf) C, 55.20; H, 3.89 F, 26.40.

Products of hydrolysis:

A general procedure was used for the qualitative hydrolysis of the acetates and trifluoroacetates in the present study. The technique was to dissolve about 50 mg. of the compound in 75 ml. of 80% acetone mixture (9) and to reflux the solution for a suitable length of time. The reaction mixture was then poured into cold water and the product extracted with ethyl ether. The organic phase was dried over anhydrous sodium sulfate and the solvent removed. The products of hydrolysis were identified by their infrared spectra in each case.

Methylcyclopentadienylmanganese tricarbonylcarbinyl trifluoroacetate gave the corresponding alcohol.

Endo-α-trifluoroacetoxy-1,2-tetramethylenecyclopentadienylmanganese tricarbonyl yielded a yellow oil which was a mixture of four compounds, namely, 60% of *exo*-α-hydroxy-1,2-tetramethylenecyclopentadienylmanganese tricarbonyl, 20% of *endo*-α-hydroxy-1,2-tetramethylenecyclopentadienylmanganese tricarbonyl, 11% of α,β-dihydro-1,2-tetramethylenecyclopentadienylmanganese tricarbonyl and 9% of α-keto-1,2-tetramethylenecyclopentadienylmanganese tricarbonyl. These four compounds were separated chromatographically.

Exo-α-trifluoroacetoxy-1,2-tetramethylenecyclopentadienylmanganese tricarbonyl gave a yellow solid. The infrared spectrum of this solid exhibited strong absorption at 1700 cm^{-1} (carbonyl absorption), at 1645 cm^{-1} (olefinic absorption) and a weak band at 3100 cm^{-1}. Hence, this solid was assumed to be a mixture of α-keto-1,2-tetramethylenecyclopentadienylmanganese tricarbonyl and the corresponding olefin.

α-Methylbenzylcarbinyl trifluoroacetate yielded α-methylbenzylalcohol.

Products of ethanolysis:

The general procedure was to reflux a solution of a trifluoroacetate in absolute ethanol for a suitable length of time. At the end of the reaction time, cold water was added to the solution and the product extracted with ether. The organic phase was dried and the solvent removed. The products of ethanolysis were identified either from their infrared spectra or from elemental analyses.

Methylcyclopentadienylmanganese tricarbonylcarbinyl trifluoroacetate yielded the ethylether of methylcyclopentadienylmanganese tricarbonylcarbinol. This ether was identified from its elemental analysis. It was observed that the trifluoroacetate (71.3 mg. 2.07 mmole) on refluxing in absolute ethanol (100 ml.) for four hours, yielded an equimolar quantity of trifluoroacetic acid. This was ascertained by titration of a 10 ml. aliquot which required 0.617 ml. of 0.03154 N. base, 94% of the theoretical quantity.

Analysis (Schwarzkopf): Calculated for $C_{12}H_{13}O_4Mn$;
C, 52.2 , H, 4.71; Mn, 19.91,
Found (Schwarzkopf); C, 52.03; H, 4.80; Mn, 19.77.

Endo-α-trifluoroacetoxy-1,2-tetramethylenecyclopentadienylmanganese tricarbonyl gave the ethylether of α-hydroxy-1,2-tetramethylenecyclopentadienylmanganese tricarbonyl. The ether was identified from its elemental analysis.

Analysis: Calculated for $C_{14}H_{15}O_4Mn$; C, 55.62; H, 4.96; Mn, 18.21,
Found (Schwarzkopf) C, 55.40; H, 4.68; Mn, 18.00.

α-Methylbenzylcarbinyl trifluoroacetate yielded α-methylbenzyl ether. It was identified on the basis of its infrared spectrum.

Kinetic Procedure;

The procedure is the same as that given by Hill (9). Most of the solvolyses were performed in 90% acetone, but some of the runs were done in 60% acetone. The acetone used was reagent grade solvent further purified by the procedure of Hammond and Kochi (30). The 90% acetone mixture was prepared by diluting 50 ml. of boiled distilled water to 495 ml. with acetone. (at 30°C.).

The solvolyses were carried out by bringing 99 ml. of the stock solution to the reaction temperature in a 100 ml. volumetric flask. This was achieved by keeping the reaction flask in an oil bath maintained at the temperature of the run, for thirty minutes before the reaction was started. The sample of trifluoroacetate (carefully weighed on an analytical balance) was dissolved in one ml. of purified acetone and added to the reaction flask. The flask was stoppered and the contents were mixed by swirling the flask a few times, while it was still immersed in the oil bath.

At suitable intervals after the sample was added, 5 ml. aliquots were removed and titrated with 0.03154 N. sodium hydroxide solution (standardised against potassium acid phthalate). The aliquotes were delivered into a two phase quenching solution composed of 10 ml. of carbon tetrachloride and 10 ml. of distilled water maintained at 0° (31). The quenching solution was saturated with nitrogen for at least five minutes (the minium time necessary for sharp, reproducible end points) before the aliquot was added.

The titration vessels were designed by Carter (32); they consist of flat-bottomed cylindrical flasks of about 50 ml. capacity fitted with two 19/38 standard taper necks diametrically opposed. Nitrogen was bubbled through the quenching solution by means of a glass tube passing through a rubber sleeve on a 19/38 standard taper male joint, into the quenching solution. The nitrogen delivery tube was raised to a level just above the surface of the liquid during titration. The solution was stirred with a magnetic bar stirrer. The standard base was delivered with a one ml. micro-buret equipped with a reservoir of about 30 ml. capacity. The capillary tip of the buret was placed just under the surface of the solution during the titration. Hill (9) has reported that duplicate titrations could be reproduced within 0.003 ml. or better out of a total volume of 0.700 ml.

by this method. This observation has been confirmed by Carter (32), Hall (33) and also by the present study.

Calculation of rate constants:

The reaction rate constant was determined by using the standard integrated first-order rate equation: --

$$\log_{10} (a - x) = \frac{kt}{2.303} - \log_{10} a \tag{34}$$

where a is the infinity titer, x is the titer at time t, and k is the first-order constant. The rate constants were determined graphically by plotting $\log_{10}$ (a - x) vs. t and drawing the "best straight line". The half-life was calculated from this plot and the rate constant was determined from the equation: --

$$k = \frac{\ln 2}{t^{\frac{1}{2}}} = \frac{0.693}{t^{\frac{1}{2}}} \tag{35}$$

Types of Errors:

Hill (9) has discussed the sources of error in the kinetic procedure in detail. In addition to the errors discussed by Hill, there exists another complicating factor in the present study.

A two phase quenching solution was used in the present titrations. The use of this quenching solution was recommended by R. A. Sneen (36) for the solvolyses of trifluoroacetates. Sneen reported that if a homogeneous quenching solution is used in these titrations, the base attacks the carbonyl carbon atom of the unreacted trifluoroacetate and thus, obscures the measurement of the solvolysis rate. By using a two phase quenching solution composed of 10 ml. of water and 10 ml. of carbon tetrachloride, this difficulty can be overcome.

The use of this quenching solution, however, introduces the possibility of an additional error in the kinetic procedure. Since the solvolysis rates of most of the compounds in the present study were very great and the rates did not change to a large extent with temperature, the solvolytic reaction was not completely inhibited at 0°C. at which temperature the titrations were performed. Although the unreacted trifluoroacetate was in the carbon tetrachloride phase, the presence of 10 ml. of water in contact with the organic phase could solvolyze the trifluoroacetate at an enhanced rate at 0°C. Thus, at the beginning of the solvolysis, when the quantity of unreacted trifluoroacetate is large, fading end points were observed. This problem could not be solved by freezing the aliquots at temperature lower than 0°C., owing to the presence of water as a component of the two phase quenching solution. The effect of this error was minimized by giving more weight to the measurements obtained during the later part of the reaction, when sharp end points could be observed. The straight line in the plot $\log_{10}$ (a - x) vs. t was usually drawn through the points obtained after 35% of the reaction was over and extrapolated to the point t = 0. The utmost care was taken to observe the first fading end point, in the beginning of the reaction, in order to avoid over titration, but this was difficult in those cases where the half-life of the trifluoroacetate was of the order of ten minutes.

Table VI

Run 2. Solvolysis of Methylcyclopentadienylmanganese tricarbonylcarbinyl trifluoroacetate.

90% Acetone. 15.5 °C.

Sample: 0.0928 g. Initial concentration: 2.698×10^{-3} ml.

Titration	Titer (x ml. of 0.03154 N. NaOH)	Titer of unchanged trifluoroacetate (0.427 - x) ml.	t (min).
1	0.110	0.337	4.5
2	0.129	0.298	15
3	0.152	0.275	25
4	0.187	0.240	37.5
5	0.197	0.230	44
6	0.249	0.178	62.5
7	0.278	0.149	86.5
8	0.330	0.097	115
9	0.417	0.010	129
10	0.423	0.004	162
11	0.427		
12			

Infinity titers: 0.425; 0.427; 0.427.

Theoreitical infinity titer: 0.4275 ml.

% Followed to completion: 100%

Rate constant: 0.1991×10^{-3} sec^{-1}.

Table VII

Run 6 : Solvolysis of Methylcyclopentadienylmanganese tricarbonylcarbinyl trifluoroacetate.

90% Acetone 25°

Sample : 68.1 mg. Initial concentration: 1.979 x 10^{-3} m./l.

Titration	Titer (x ml. of 0.03154 N. NaOH).	Titer of unchanged trifluoroacetate (0.290 - x) ml.	t (min).
1	0.140	0.150	3.2
2	0.234	0.056	20.6
3	0.247	0.043	29.0
4	0.258	0.032	38.5
5	0.267	0.023	49.5
6	0.273	0.017	60.0
7	0.280	0.010	77.0
8	0.290		122.0

Infinity titers: 0.290 (after 6 hrs.).
0.290 (after 12 hrs.).

Theoretical infinity titer: 0.3138 ml.

% Followed to completion: 100%

Rate constant: 0.5269 x 10^{-3} (graphically)

Table VIII

Run 8. Solvolysis of Methylcyclopentadienylmanganese tricarbonylcarbinyl trifluoroacetate.

90% Acetone. 28.3°.

Sample: 71.3 mg. Initial concentration: 2.072 x 10^{-3} m./l.

Titration	Titer (x ml. of 0.03154 N. NaOH).	Titer of unchanged trifluoroacetate (0.332 - x) ml.	t (min).
1	0.110	0.222	3.25
2	0.132	0.200	12.0
3	0.200	0.132	19.3
4	0.223	0.109	27.2
5	0.255	0.077	38.0
6	0.287	0.045	54.0
7	0.302	0.030	66.0

Infinity titers: 0.328 ml.; 0.331; 0.332 ml.

Theoritical infinity titer: 0.3285 ml.

% Followed to completion: 90.9

Rate constant: 0.6078 x 10^{-3} sec^{-1}. (graphically).

Table IX

Run 11. Solvolysis of Methylcyclopentadienylmanganese tricarbonylcarbinyl trifluoroacetate.

90% Acetone. 32.1°.

Sample: 70.6 mg.   Initial concentration: 2.036 x 10^{-3} m./l.

Titration	Titer (x ml. of 0.03154 N. NaOH).	Titer of unchanged trifluoroacetate. (0.333 - x) ml.	t (min).
1	0.132	0.201	2.4
2	0.243	0.090	14.0
3	0.257	0.076	17.2
4	0.298	0.035	25.0
5	0.313	0.020	34.0
6	0.320	0.013	46.0

Infinity titer: 0.333 ml.; 0.333 ml.; 0.333 ml.

Theoritical infinity titer: 0.325 ml.

% Followed to completion: 96.

Rate constant: 0.8884 x 10^{-3} sec^{-1}.

Table X

Run 15. Solvolysis of endo-α-trifluoroacetoxy-1, 2-tetramethylene-cyclopentadienylmanganese tricarbonyl.

90% Actone 45.3°.

Sample: 68 mg. Initial concentration: 1.798 x 10^{-3} m./l.

Titration	Titer (x ml. of 0.03154 N. NaOH).	Titer of unchanged trifluoroacetate. (0.297 - x) ml.	t (min).
1	0.136	0.171	2.5
2	0.140	0.157	17.0
3	0.206	0.091	27.0
4	0.229	0.068	37.5
5	0.266	0.031	65.5
6	0.283	0.014	122.0

Infinity titers: 0.297 ml.; 0.297 ml.

Theoretical infinity titer: 0.292 ml.

% Followed to competition: 95.2.

Rate constant: 0.4619 x 10^{-3} sec^{-1}. (graphically).

Table XI

Run 24. Solvolysis of α-methylbenzylcarbinyl trifluoroacetate.

60% Acetone. 45.2°

Sample: 71 mg. Initial concentration: 3.3×10^{-3} m./l.

Titration	Titer (x ml. of 0.03154 N. NaOH).	Titer of unchanged trifluoroacetate. (0.507 - x) ml.	t (min).
1	0.154	0.353	2
2	0.166	0.341	7
3	0.240	0.267	15
4	0.247	0.260	66
5	0.252	0.255	97
6	0.320	0.187	205
7	0.362	0.145	265
8	0.384	0.123	325
9	0.450	0.057	640

Infinity titers: 0.507 (30 hrs.);
0.507 (45 hrs.);
0.507 (60 hrs.).

Theroetical infinity titer: 0.5164

% Followed to completion: 88.7.

Rate constant: 0.6416×10^{-4} sec^{-1}. (graphically).

Table XII

Run 28. Solvolysis of α-methylbenzylcarbinyl trifluoroacetate.

60% Acetone 32.4°

Sample: 46 mg. Initial concentration: 2.1×10^{-3} m./l.

Titration	Titer (x ml. of 0.03154 N. NaOH).	Titer of unchanged trifluoroacetate. (0.352 - x) ml.	t (min).
1	0.131	0.221	2
2	0.151	0.200	35
3	0.161	0.191	68
4	0.175	0.177	109
5	0.222	0.132	300
6	0.261	0.091	376
7	0.288	0.064	527

Infinity titers: 0.348; 0.350; 0.352 ml.

Theoretical infinity titer: 0.3346 ml.

% Followed to completion: 81.8.

Rate constant: 0.3942×10^{-4} sec^{-1}. (graphically).

Table XIII

Rate constants for solvolyses^a

Compound	T °C	Run	mole/liter	% Followed	k x 10^4	k x 10^4 (ave)
Methylcyclopentadienylmanganese tricarbonylcarbinyl trifluoracetate.	15.5	1	2.139	89	2.063	1.962 ± .079
		2	2.698	100	1.991	
		3	2.124	88	1.991	
		4	1.918	100	1.805	
	25	5	2.206	92	5.029	5.139 ± .073
		6	1.979	100	5.249	
		9	2.150	98	5.139	
	28.3	7	1.659	88.4	6.416	6.247 ± .11
		8	2.072	90.9	6.078	
		10	2.78	56	6.300	
		12	1.85	75	6.196	
Exo-trifluoroacetoxy-1,2-tetramethylenecyclopentadienylmanganese tricarbonyl	32.1	11	2.036	96	8.884	8.460 ± .42
		21	1.846	100	8.249	
		13	2.604	100	8.249	
Endo-α-trifluoracetoxy-1,2-tetramethylenecyclopentadienylmangnese tricarbonyl.	20	19	1.900	60	11.54	11.54 ± .07
		20	1.678	70	11.43	
		21	2.030	100	11.65	
	20				0.5900^b	

Table XIII (cont)

Compound	T °C	Run	conc. x 10^3 mole / liter	% Followed	k x 10^4	k x 10^4 (ave).
Endo-α-trifluoroacetoxy-1,2-tetramethylenecyclopentadienylmanganese tricarbonyl.	45.3 °	15	1.79	95.2	4.619	4.530 ± .0089
		16	1.919	96.6	4.442	
	25	17	2.4	93.5	0.9166	0.8958 ± .02
		18		84.7	0.8750	
α-Methylbenzyl carbinyl trifluoroacetate. (in 60% acetone)..	45.2 °	22	2.88	86	0.5994	0.6071 ± .016
		23	3.48	87.4	0.6015	
		24	3.3	88.7	0.6416	
	38.8	26	2.98	90	0.4477	0.4545 ± .0068
		27	3.3	86.3	0.4614	
	32.4	28	2.1	81.8	0.3942	0.3862 ± .0019
		29	2.6	56.7	0.3787	
		30	2.8	100	0.3858	

Notes to Table

[a] Results in '90%' acetone unless otherwise noted.

[b] Extrapolated from other temperatures.

Table XIII (cont.)

Compound	T °C	Run	conc. x 10^3 mole / liter	% Followed	k x 10^4	k x 10^4 (ave).
α-Methylbenzylcarbinyl trifluoroacetate	42.8	31	3.012	50	0.009850	
		32	2.524	58	0.01018	0.01030[c] ±.0025
		33	3.566	60	0.01058	
Methylcyclopentadienylmanganese tricarbonylcarbinyl. trifluoroacetate	42.8				19.95[b]	

[b] Extrapolated from other temperatures

[c] Theoretical infinity titer is used in calculation of the rate constant.

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