hydroxide solution, then evaporated. Since separation of the residual organoborane from the cis-stilbene by distillation proved difficult, 50 ml. of tetrahydrofuran and 38 ml. of 3 N sodium hydroxide were added, followed by the dropwise addition of 38 ml. of 30% hydrogen peroxide to oxidize the organoborane.

The organic material was extracted with ether. The ether extract was washed with a saturated sodium chloride solution, and then dried over anhydrous magnesium sulfate. Distillation yielded 18.6 g. of cis-stilbene, b.p. 138–139° at 10 mm., n^{20}D 1.6212, a yield of 69% (Table III). Infrared examination revealed the essential absence of the trans isomer.

Preparation of cis-3-Hexene.—In a 0.5-l. flask, equipped as above, was placed 24.6 g. (0.300 mole) of 3-hexyne (b.p. 80–80.5° at 756 mm., n^{20}D 1.4114) and 83 ml. of a 1.00 M solution of sodium borohydride in diglyme (10% excess). Boron trifluoride etherate (0.11 mole) was added to the reaction mixture maintained at 0° over a period of 1 hour. After an additional 0.5 hour at 0°, the residual hydride was destroyed with ethylene glycol. After addition of 60 ml. of glacial acetic acid, the flask was permitted to remain overnight at room temperature. The product was worked up as described for the preparation of 1-hexene above.

After distillation through the Todd micro column, there was obtained 17 g. of cis-3-hexene, b.p. 67° at 754 mm., n^{20}D 1.3957, a yield of 68% (Table III).

Preparation of n-Octaldehyde.—In a three-neck flask was placed 33.6 g. of 2-methyl-2-butene (0.48 mole) and 180 ml. of a 1.00 M solution of sodium borohydride in diglyme. The flask was immersed in an ice-bath. Boron trifluoride etherate (0.24 mole) was added dropwise to the reaction mixture. The flask was permitted to remain for 2 hours at 0°, then placed in an ice-salt-bath. To the disiamylborane there was added as rapidly as possible 22.0 g. of 1-octyne (0.200 mole) in 20 ml. of diglyme, maintaining the temperature below 10°. The reaction mixture was permitted to warm up to room temperature to complete the hydroboration, and the product oxidized at 0° by the addition of 150 ml. of a 15% solution of hydrogen peroxide, maintaining the pH of the reaction mixture at 7–8 by the controlled addition of 3 N sodium hydroxide.

After oxidation, the reaction mixture was brought to the neutral point and steam distilled. The distillate was extracted with ether and the ether extract was dried over anhydrous magnesium sulfate. Distillation yielded 18 g. of n-octaldehyde, b.p. 83–85° at 33 mm., n^{20}D 1.4217 (literature[19] b.p. 171–173°, n^{20}D 1.4216) a yield of 70%.

Preparation of 3-Hexanone.—In a 0.5-l. flask was placed 28.7 g. (0.35 mole) of 3-hexyne and 100 ml. of a 1.00 M solution of sodium borohydride in diglyme. Hydroboration was achieved by adding 0.135 mole of boron trifluoride etherate to the well-stirred reaction mixture. The unsaturated organoborane was oxidized at 0° by the addition of 36 ml. of 30% hydrogen peroxide, maintaining the pH of the reaction mixture at approximately 8. The product was extracted with ether and dried over magnesium sulfate. Distillation gave 23.8 g. of 3-hexanone, b.p. 118° at 745 mm., n^{20}D 1.4004 (literature[20] b.p. 120.9–121°, n^{20}D 1.4007), a yield of 62%.

Dihydroboration of 1-Hexyne and 3-Hexyne.—In a three-neck flask was placed the acetylene (25 mmole) in 10 ml. of tetrahydrofuran. The flask was immersed in an ice-bath and a standard solution of diborane in tetrahydrofuran, 1.17 M, was added dropwise by means of a syringe to the acetylene. The reaction mixture was permitted to remain for 2 hours at 0–5°. The excess of hydride was decomposed by adding water. The oxidation was carried out with alkaline hydrogen peroxide at 30–50°. The reaction mixture was saturated with potassium carbonate, a procedure which has been shown to bring about a quantitative transfer of glycol to the tetrahydrofuran phase.[21] The upper phase was separated, dried over anhydrous magnesium sulfate, and the products estimated by gas chromatography, using 1-heptanol as internal standard and a column containing a Silicone 200 substrate on Haloport F solid support.

In individual experiments the time required for the hydrolysis step was varied, and the procedure utilized for the oxidation was altered using both normal oxidation with alkaline hydrogen peroxide and oxidation at pH 7–8.

The results are summarized in Table V.

In the experiment where dicyclohexylborane was utilized, the intermediate was synthesized by adding 2 moles of cyclohexene to 1 mole of borane in tetrahydrofuran at 0°. The 1-hexyne was added to the reaction mixture, and the reaction permitted to proceed for 24 hours at room temperature. The product was then oxidized by the normal procedure and the oxidation products determined by gas chromatography.

(19) C. D. Harries and K. Oppenheim, Chem. Zentr., **87**, II, 993 (1916).

(20) K. Owen, O. R. Quayle and W. J. Clegg, J. Am. Chem. Soc., **64**, 1295 (1942).

(21) Unpublished research with K. Nagase.

Carbonium Ion Stabilization by Metallocene Nuclei. II. α-Metallocenylcarbonium Ions

By E. Alexander Hill and John H. Richards

Acetates of methylferrocenylcarbinol, methylruthenocenylcarbinol and methylosmocenylcarbinol have been found to solvolyze with rates somewhat greater than trityl acetate, indicating a high stability for the corresponding carbonium ions. The solvolysis mechanism for methylferrocenylcarbinyl acetate has been carefully investigated to show that a carbonium ion mechanism is involved. Several possibilities for a molecular orbital description of direct metal participation are discussed. The order for carbonium ion stabilization (osmocenyl > ruthenocenyl > ferrocenyl) is found to parallel that of the strength of intramolecular hydrogen bonds to the carbinols, but is the reverse of that observed for reactivity of the parent metallocene toward acetylation.

Since its discovery in 1951,[1] ferrocene has been shown to be a reactive substance in many electrophilic, substitution-type reactions.[2] An important

(1) T. J. Kealy and P. L. Pauson, Nature, **168**, 1039 (1951); S. A. Miller, J. A. Tebboth and J. F. Tremaine, J. Chem. Soc., 632 (1952).

(2) G. D. Broadhead, J. M. Osgerby and P. L. Pauson, ibid., 650 (1958). For reviews of ferrocene chemistry, see P. L. Pauson, Quart. Revs., **9**, 391 (1955); E. O. Fischer, Angew. Chem., **67**, 475 (1955); M. D. Rausch, M. Vogel and H. Rosenberg, J. Chem. Ed., **34**, 268 (1957).

difference between the metallocenes and other aromatic systems is the presence of the metal atom. The role of this metal atom in reactions of the metallocenes presents an interesting area for mechanistic studies.

We have investigated electron-release from metallocene systems by a kinetic study of the solvolyses of esters of alcohols substituted with metallocene residues. The initial results of this

research[3] demonstrated that the metallocenes of the iron group are very effective in stabilizing a carbonium ion in the position adjacent to the ring. Thus, the acetates of α-metallocenylcarbinols were found to solvolyze at easily measurable rates, and the solvolysis rates were shown to be of magnitude comparable with trityl acetate. These results are presented fully in this paper, together with a description of the experiments by which the mechanism was shown to involve ionization of the alkyl–oxygen bond of the ester.

Other reports have been published that agree with the idea that a carbonium ion adjacent to a metallocene nucleus possesses an unusual stability. Thus, the high reactivity of vinylferrocene toward additions of weak acids[4a] and the isolation of the diferrocenylcarbonium ion as its perchlorate salt[4b] both imply a high degree of stability for such a carbonium ion. Alkylation of ferrocene with 1,2-dichlorethane produces the rearranged product 1,1-diferrocenylethane.[5] During the course of this reaction, a hydride migration presumably takes place, yielding the more stable α-ferrocenyl carbonium ion. This migration occurs before the less stable primary carbonium ion can alkylate another molecule of ferrocene. No rearrangement occurs in the analogous alkylation of benzene. Recently, Trifan and Bacskai[6] have confirmed our early results with methylferrocenylcarbinyl acetate and have found that this solvolysis has a rate exceeding that of α-tetralyl acetate by a factor of about 4.8×10^5.

In these solvolyses, the effect of the metal may be of two types: First, electron release may occur inductively by polarization of the ring–metal bonds, placing a part of the positive charge on the metal and on the far ring. A second type of stabilization may occur in which the filled orbitals of the metal participate directly by overlap with the carbonium ion orbital. Some possibilities for a molecular orbital description of this second type of stabilization will be considered later in this paper. The rather small rate decrease for α-acetoxy-1,1'-trimethylene-ferrocene relative to methylferrocenylcarbinyl acetate originally was presented[3] as evidence for a direct participation by the metal.[7] More recently, solvolyses of the exo and endo isomers of α-acetoxy-1,2-tetramethyleneferrocene,[6,8] along with other rate data obtained in these laboratories,[8] have provided more convincing evidence for direct, backside metal participation. This evidence will be considered in detail in a later paper in this series.

In addition, evidence for metal participation in cationic complexes has been reported. For example, metallocenes in strongly acidic media do not exist as simple σ-complexes.[9] Instead, the proton

is located in a position that is magnetically equivalent with respect to all of the ring hydrogens. This fact has been interpreted as signifying direct bonding between the proton and the metal atom.

Trifan and co-workers[10] have studied intramolecular hydrogen-bonding in alcohols with ferrocene substituents. Originally they suggested that a strong band at about 3575 cm.$^{-1}$ was due to hydrogen bonding to the ring bearing the carbinol substituent[10] but more recently have concluded that this band is due to hydrogen bonding directly to the metal.[11]

Solvolysis Mechanism and Carbonium Ion Stability.—Trityl acetate[12] and benzoate[13] have been shown to solvolyze by an uncatalyzed ionization of the neutral ester with cleavage of the alkyl–oxygen bond. Solvolysis results for methylferrocenylcarbinyl acetate, methylruthenocenylcarbinyl acetate, methylosmocenylcarbinyl acetate and trityl acetate are presented in Table I; and some relative rates at 0° and 30° are summarized in Table II. The activation parameters of the metallocenylcarbinyl acetates are seen to be very similar to the parameters of trityl acetate.

An ethanolysis of methylferrocenylcarbinyl acetate was carried out to determine the position of bond cleavage. The ethanolysis product proved to be identical with the ethyl ether of the carbinol prepared with ethanol and hydrogen chloride. The ethanolysis produced one mole of acetic acid. A control reaction in which methylferrocenylcarbinol and ethyl acetate were refluxed in ethanol eliminated the possibility of some unanticipated ester hydrolysis catalyzed by the metallocene nucleus. These results indicate that the solvolysis of methylferrocenylcarbinyl acetate proceeds with alkyl–oxygen fission. It will be assumed that the other metallocene derivatives studied that react at similar rates follow the same hydrolysis mechanism.

In the hydrolysis reaction, the carbinol was isolated in at least a 75% yield from a small-scale solvolysis. No other product was detected by chromatography when care was taken to prevent spontaneous ether formation. It is noteworthy that neither vinylferrocene nor 1,2-dimethyl-1,2-diferrocenylethane was detected.

The solvolysis rate of methylferrocenylcarbinyl acetate is quite dependent upon the ionizing power of the solvent, and rough calculations using interpolated data[14] yield m-values of about 0.8 at either 0° or 30° for this substance. Similarly an m-value of 0.9 for methylruthenocenylcarbinyl acetate at 0° is obtained. An m-value for trityl acetate in acetone–water mixtures of 0.9 at 0° results from the present work, while Swain, et al.,[15] have reported a value of 0.83 at 25°. This similarity in effect of the ionizing power of the solvent in all of these solvolyses provides an additional argument that they all proceed by the same mechanism.

(3) J. H. Richards and E. A. Hill, *J. Am. Chem. Soc.*, 81, 3484 (1959).

(4) (a) G. R. Buell, E. McEwen and J. Kleinberg, *Tetrahedron Letters*, No. 5, 16 (1959); (b) C. Jutz, *ibid.*, No. 1. 1 (1959).

(5) K. L. Rinehart, Jr., P. A. Kittle and A. F. Ellis, *J. Am. Chem. Soc.*, 82, 2082 (1960).

(6) D. S. Trifan and R. Bacskai, *Tetrahedron Letters*, No. 13, 1 (1960).

(7) A fuller discussion of such constrained systems will be presented in a future paper.

(8) J. H. Richards and E. A. Hill, unpublished results.

(9) T. J. Curphey, J. O. Santer, M. Rosenblum and J. H. Richards, *J. Am. Chem. Soc.*, 82, 5249 (1960).

(10) D. S. Trifan, J. L. Weissmann and L. P. Kuhn, *ibid.*, 79, 6566 (1957).

(11) D. S. Trifan and R. Bacskai, *ibid.*, 82, 5010 (1960).

(12) C. A. Bunton and A. Konasiewicz, *J. Chem. Soc.*, 1354 (1955).

(13) G. S. Hammond and J. T. Rudesill, *J. Am. Chem. Soc.*, 72, 2769 (1950).

(14) E. Grunwald and S. Winstein, *ibid.*, 70, 846 (1948).

(15) C. G. Swain, R. B. Mosely and D. E. Brown, *ibid.*, 77, 3731 (1955).

TABLE I
SOLVOLYSIS RATES OF ACETATES IN "80% ACETONE"[a]

Run	T, °C.	Concn. 10^3, m./l.	% to completion	$k \times 10^5$ sec.$^{-1}$	Av. $k \times 10^5$ sec.$^{-1}$	ΔH^*, kcal.	ΔS^*, e.u.
				Methylferrocenylcarbinyl acetate			
13	0	3.98	61	0.487 ± 0.003			
14	0	2.83	73	0.494 ± .002	0.490 ± 0.006		
15	0	3.41	73	0.484 ± .004			
16	0	3.16	59	0.494 ± .002			
34	15	3.65	94	3.07 ± .020			
35	15	4.60	71	2.966 ± .018	3.027 ± .075		
36	15	6.10	92	3.007 ± .020			
17	30	2.84	91	17.03 ± .11			
18	30	3.26	75	17.10 ± .11	17.02 ± .15		
19	30	4.36	95.5	17.10 ± .08			
58	30	4.30	86	16.85 ± .08			
7	35	4.05	94	28.17 ± .26			
8	35	4.90	96.5	30.18 ± .21	29.79 ± 1.49		
9	35	2.49	92	31.01 ± .40			
						19.0	−13.2
				Methylruthenocenylcarbinyl acetate			
50	0	3.00	53	0.622 ± 0.004	0.617 ± 0.009		
51	0	3.62	52	0.612 ± .004			
40	15	2.74	67	4.13 ± .019	4.14 ± .03		
64	21.3	2.77	76	8.68 ± .05	8.70 ± .06		
65	21.3	3.31	76	8.73 ± .05			
23	30	2.28	83	23.99 ± .18	23.22 ± 1.10		
24	30	2.56	83	22.45 ± .20			
						19.34	−11.4
				Methylosmocenylcarbinyl acetate			
49	0	2.54	91.5	2.91 ± 0.02	2.91 ± 0.02		
42	15	2.30	73	18.56 ± 0.14	18.56 ± .14		
52	30	1.42	94	91.5 ± 1.6	91.5 ± 1.6		
						18.54	−11.2
				Trityl acetate			
37	15	3.56	61	0.345 ± 0.002			
38	15	4.55	61	.341 ± .002	0.342 ± 0.003		
39	15	5.89	60	.340 ± .002			
25	30	4.32	93	2.555 ± .032			
26	30	2.96	91.5	2.588 ± .014	2.58 ± .033		
27	30	5.39	92	2.605 ± .011			
5	35	6.92	78	4.40 ± .07			
6	35	7.42	97	4.25 ± .06	4.32 ± 0.12		
31	45	6.19	95	15.11 ± .09			
32	45	5.00	95	14.95 ± .10	14.90 ± 0.26		
33	45	3.98	94.5	14.64 ± .12			
						22.1	− 6.7

[a] Solvent composition is 80.7% acetone by volume.

Addition of acetate ion to the solvolysis solution strongly depresses the solvolysis rate of methylferrocenylcarbinyl acetate. A calculation similar to that used by Swain[16] for the common-ion effect of chloride ion on trityl chloride solvolyses shows that the methylferrocenylcarbonium ion reacts with acetate ion 5500 times more rapidly than it does with water. This result can be compared with competition factors of 90 for the trityl cation in 80:20 dioxane–water and 76 for the same ion in methanol (both values being calculated from the solvolysis data of Bunton and Konasiewicz[12]). Our results thus imply that the α-ferrocenylcarbonium ion is sufficiently stable so that it reacts

very selectively with the strongest nucleophile present in the solution. This is strong evidence for the intermediacy of a carbonium ion in these solvolyses.

Results with added sodium hydroxide were complicated by a fall-off in rate due to the common-ion effect of acetate ion formed in the solvolysis. However, the maximum initial rate definitely showed no more than a 20% rate increase over the rate with no added solute. Such an increase is of about the magnitude to be expected for a second-order saponification by hydroxide ion; but kinetic results, alone, cannot rule out an S$_N$2 displacement of acetate ion.

Subtraction of the solvolysis rate for methylferrocenylcarbinyl acetate in neutral media from an analogous reaction observed in the presence of

(16) C. G. Swain, C. B. Scott and K. H. Lohmann, J. Am. Chem. Soc., 75, 136 (1953).

TABLE II

RELATIVE SOLVOLYSIS RATES

Acetate	Added solute	Solvent,[a] % acetone	$k_{50}{}^0$	$k_0{}^0$
Methylferro-	....	80	1.000	1.00
cenylcarbinyl	0.00716 M NaAc	80	0.213	...
	.00724 M Na			
	perchlorate	80	0.979	...
	.00718 M NaOH	80	1.2[b]	...
	.00160 M HCl	80	...	2.97
	....	82	0.681	...
	....	60	...	17.2
Methylrutheno-	....	80	1.36	1.3
cenylcarbinyl	....	60	...	27.1
Methylosmo-				
cenylcarbinyl	....	80	5.37	5.94
Trityl	....	80	0.152	...
		60	...	1.97

[a] "80% acetone" solvent is 80.7% acetone by volume; 60% acetone solvent is about 60% acetone by volume, but was less carefully standardized.   [b] Maximum initial rate.

hydrochloric acid allows calculation of a second-order, acid-catalyzed hydrolysis rate constant of 6.0 × 10⁻³ liter mole⁻¹ sec.⁻¹ at 0° in 80% acetone–water. This can be roughly compared to a similar rate of 2.1 × 10⁻² liter mole⁻¹ sec.⁻¹ for trityl acetate at 25° in 80% dioxane–water.[12] However, no meaningful extrapolation to equivalent conditions is possible. Another rough comparison can be obtained by extrapolation of the results obtained by Stimson[17] for benzhydrol acetate at 85°, which gives a rate constant of 1.5 × 10⁻⁷ liter mole⁻¹ sec.⁻¹ at 0°. The high rate of the acid-catalyzed reaction suggests that it too proceeds by alkyl–oxygen fission. It may be noted that despite the rapidity of the acid-catalyzed reaction, no autocatalysis by acetic acid was noted during solvolyses in neutral media.

A Molecular Orbital Description of the Interaction of Metallocenes with Electron Deficient Centers.—Results discussed and alluded to so far suggest that there exists a direct electronic interaction between the metal atom and the electron deficient carbon of the α-metallocenyl carbonium ions. To this end the theoretical feasibility of such interaction has been investigated. A rough calculation was made using an assumption such as that of Dunitz and Orgel[18] concerning the radial component of the wave function for the 3d-orbitals.[19]

Thus, the overlap integrals for the 3d ± iron[21] orbital with ring carbons and the α-carbinyl carbon indicates that the bonding to the α-carbinyl carbon is about 10% as strong as that to a ring carbon in a carbonium with a structure similar to that of the

(17) V. R. Stimson, J. Chem. Soc., 2673 (1955).

(18) J. D. Dunitz and L. E. Orgel, J. Chem. Phys., 23, 954 (1955).

(19) Calculations were performed in a manner similar to that of Dunitz and Orgel[18] using overlap integrals from standard tables.[20]

(20) R. S. Mulliken, C. A. Rieke, D. Orloff and H. Orloff, J. Chem. Phys., 17, 1248 (1949); H. H. Jaffé and G. O. Doak, ibid., 21, 196 (1953); H. H. Jaffé, ibid., 21, 258 (1953).

(21) In this discussion, the d- and p-orbitals of the metal will be identified by their angular momentum about the fivefold symmetry axis of the cyclopentadienyl ring. This is equal to the number of nodal planes that fall along the axis, and thus determines the symmetry of the part of the orbitals with which the orbitals of the ring may overlap. Thus d_z2 will be referred to as d₀; d_xz and d_yz will be referred to as d ± 1; and d_xy and d_x²-y² will be referred to as d ± 2 (cf. Fig. 2).
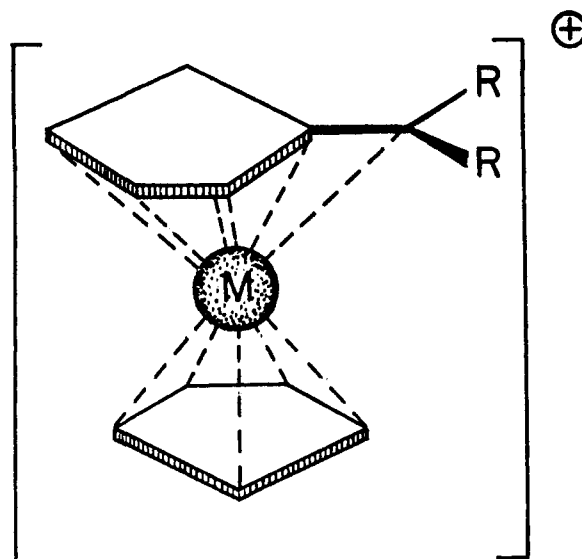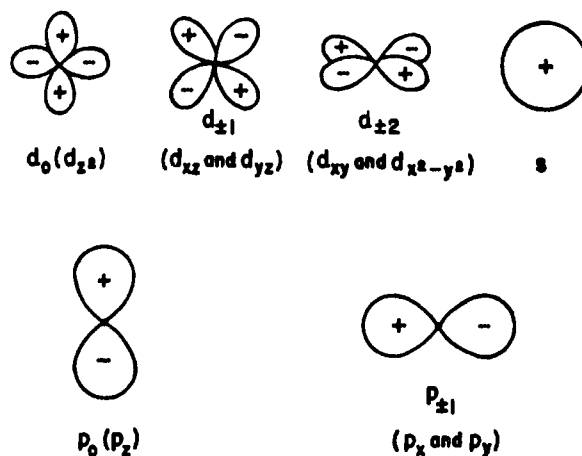
Fig. 1.

Fig. 2.—Metal orbitals for metallocene bonding.

un-ionized ester. By shifting the ring bearing the carbinyl carbon relative to the rest of the molecule, as shown in Fig. 1, a somewhat more stable state may result. Such a shift results in an increase in the total calculated overlap integral; however, the magnitude of the increase is essentially within the errors of these crude calculations and allows only the statement that a structure for an α-metallocenyl carbonium, such as that in Fig. 1, is reasonable on the basis of these calculations but is not demanded by them.

A simple molecular-orbital treatment[22a,b] will be most useful for discussion of the electronic structure of the α-metallocenyl carbonium ions. As the high symmetry of the ferrocene system is lost in the metallocenyl carbonium ions, it will be more convenient to use the treatment of Craig, et al.,[22a] than the more sophisticated one of Moffitt.[22b]

A metallocenyl carbonium ion is formally derived from the parent metallocene by replacing one of the cyclopentadienyl radicals by the fulvene skeleton containing five π-electrons. If the ring bearing the

(22) (a) D. P. Craig, A. Maccoll, R. S. Nyholm, L. E. Orgel and L. E. Sutton, J. Chem. Soc., 332 (1954); (b) W. Moffitt, J. Am. Chem. Soc., 76, 3386 (1954).
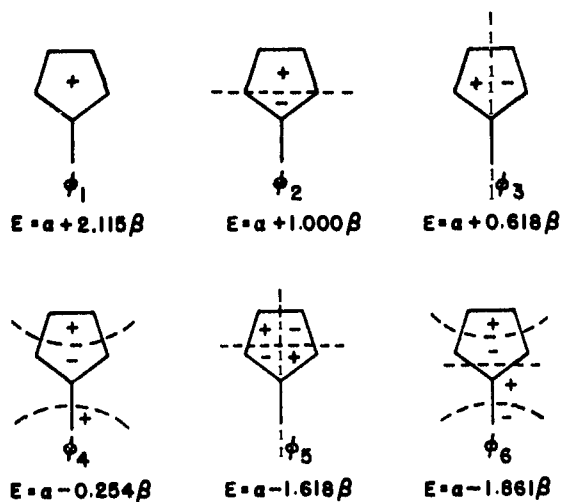
Fig. 3.—LCAO molecular orbitals for fulvene system.

carbinyl carbon is considered as an isolated system with five π-electrons, it is possible to calculate the increase in delocalization energy that results on ionization to the carbonium ion. This treatment is complicated by the fact that the ϕ_2 and ϕ_3 orbitals of the fulvene system (those orbitals of proper symmetry type for bonding with the metal 3d $\pm$ 1 orbitals; cf. Fig. 3) are of different energy. One of the five π-electrons must be placed in one of these two orbitals for formation of the ring–metal bond. If this single electron is placed in ϕ_2, the increase in delocalization energy on ionization to the carbonium ion is 0.994β. If the single electron is placed in ϕ_2, the corresponding value is 0.612β. This is a very crude estimate of the stability of the α-metallocenyl carbonium ions due solely to delocalization of the charge into the ring. These values may be compared with gains in delocalization energies of 0.72β[23] and 1.80β[24] on ionization of benzyl derivatives and trityl derivatives to their respective cations.

It is now appropriate to consider the bonding of the fulvene system to the metal in the same terms as those used for a description of the bonding of the parent metallocene.[22a] Two electrons will reside in orbital ϕ_1 since it is very strongly bonding within the fulvene carbon framework. Two canonical forms must be considered for bonding between the fulvene and metal. In one of these ϕ_2 participates in ring–metal bonding, while in the other ϕ_3 is used. In either case, the orbital not used in ring–metal bonding contains an electron pair that contributes primarily to bonding within the carbon framework. The carbonium ion has an important difference when compared to the parent metallocene: Orbital ϕ_2 has considerable density on the carbinyl carbon, and it is reasonable to suppose that overlap of ϕ_2 with a metal 3d $\pm$ 1 orbital will include a contribution from that part of ϕ_2 in the presence of the carbinyl carbon. This is an MO description of direct participation of the metal in bonding to the carbinyl carbon of α-metallocenyl carbonium ions.

A further change in bonding in the carbonium ion might also be considered. Whereas a dative bond

(23) J. D. Roberts and A. Streitwieser, Jr., J. Am. Chem. Soc., 74, 4723 (1952).
(24) A. Streitwieser, Jr., ibid., 74, 5288 (1952).

from the metal 3d $\pm$ 2 orbitals to the cyclopentadienyl ring ϕ_4 and ϕ_5 orbitals[22a] makes a relatively small contribution to bonding in the parent metallocene, the situation is probably considerably different in the carbonium ion. In this case, the fulvene ϕ_4 orbital is only slightly antibonding; while its symmetry is not precisely that of the metal 3d $\pm$ 2 orbital, overlap might still be appreciable. Moreover, perturbation by the field of the metal may well bring about mixing of the simple one-electron LCAO orbitals to produce an orbital of more favorable symmetry. Therefore, a much stronger dative bond between ring orbital ϕ_4 and metal orbital 3d $\pm$ 2 may be formed in the carbonium ion than is present in the neutral ester. This would provide an acceleration of the rate of ionization; and since ϕ_4 has considerable density on the carbinyl carbon, it would represent an appreciable direct bonding between the metal and the carbinyl carbon.

The recent report of Winstein and Battiste[25] on the rate enhancement observed in the solvolysis of the tosylate of pentamethylcyclopentadienyl-methanol requires comment since it could possibly be argued that similar participation by the electrons of the cyclopentadienyl ring was responsible for the high reactivity of the metallocenyl carbinyl acetates. We do not feel this is the dominant stabilizing participation for these metallocenyl ions for three reasons: First, the metallocenyl carbonium ions are very much more stable than would be anticipated if this effect were the cause of their stability. Second, the geometry about the cyclopentadienyl-α-carbonium ion bond requires that the α-carbon be coplanar with the five-membered ring, making the type of participation discovered by Winstein improbable in the metallocenyl cations. Third, the stereochemical consequences of participation[6,8] are different than would be anticipated if participation in the metallocenyl ions were similar to that in the cyclopentadienyl carbonium ions.

Effect of Changing the Metal.—The relative solvolysis rates for ferrocenyl, ruthenocenyl and osmocenyl derivatives are 1.00:1.36:5.37, respectively. This reactivity sequence may be compared to that for acetylation, in which case the opposite order is observed. Competitive acetylation results[26] indicate that ferrocene is more reactive by a factor of 10.5 than ruthenocene toward acetylation by boron trifluoride–acetic anhydride.[27] The results of Rausch, Fischer and Grubert[28] show quite clearly that osmocene requires more vigorous acetylation conditions than ferrocene or ruthenocene. On the other hand, the order of reactivity of methyl α-metallocenylcarbinyl acetate solvolyses parallels the strength of the metal–hydrogen bond (cf. ref. 11 and Table III) where it is seen that the osmium–hydrogen bond (3505 cm.$^{-1}$, $\Delta\nu = 104$ cm.$^{-1}$) is stronger than the ruthenium–hydrogen bond (3525 cm.$^{-1}$, $\Delta\nu = 83$ cm.$^{-1}$) which in turn is stronger than the iron–hydrogen bond (3582 cm.$^{-1}$, $\Delta\nu = 24$ cm.$^{-1}$). However, the differing geometrical factors

(25) S. Winstein and M. Battiste, ibid., 82, 5244 (1960).
(26) J. H. Richards and D. C. Garwood, unpublished results.
(27) C. R. Hauser and J. K. Lindsay, J. Org. Chem., 22, 482 (1957).
(28) M. D. Rausch, E. O. Fischer and H. Grubert, J. Am. Chem. Soc., 82, 76 (1960).

in the alcohols of the different metallocenes make it somewhat difficult to ascribe unambiguously the order of hydrogen bond stabilities to the basicities of the three metals, which from n.m.r. experiments[9] actually seem to be in the reverse order.

TABLE III

INFRARED HYDROXYL STRETCHING FREQUENCIES OF α-METALLOCENYLCARBINOLS[a]

Carbinol	Hydroxyl stretching frequencies, cm.$^{-1}$[b]
Methylferrocenyl-	3606, 3582
Methylruthenocenyl-	3608, 3525
Methylosmocenyl-	3609, 3505

[a] All spectra observed in carbon disulfide solution with a Beckman IR-7 infrared spectrometer equipped with sodium chloride prism and diffraction grating. [b] Lower frequency band is more intense and increases in relative intensity with the shift to lower frequencies.

Since there are a number of reasonable possibilities for the reversal in the reactivity sequences, and especially because the differences in reactivities are so small, it is not possible to use these observed differences as strong arguments in favor of any specific type of metal effect. However, the results to date are most economically interpreted as implying that metal participation is important in the solvolysis and in electrophilic substitution reactions, as well as in hydrogen-bond interactions.

Experimental[29,30]

Materials.—Trityl acetate (m.p. 84–84.5°) was prepared from trityl chloride and silver acetate by the method of Bunton and Konasiewicz.[12]

Methylferrocenylcarbinol (m.p. 78.2–78.7°), from reduction of acetylferrocene with lithium aluminum hydride, was treated with acetic anhydride in pyridine as described by Arimoto and Haven.[31] The solvent was removed under vacuum at room temperature, and the product was directly sublimed to a cold finger condenser, m.p. 70.2–71° (lit.[31] m.p. 67–68°). Recrystallization from isopropyl ether did not change the melting point. This same procedure was used to prepare the other metallocenylcarbinyl acetates.

Acetylruthenocene was prepared by acetylation of ruthenocene.[32,33] The product was purified by chromatography on alumina (80 g.) with benzene–ether mixtures (1 to 5% ether). The light yellow crystalline product, m.p. 112.5–113°, weighed 2.55 g. (85%). Sublimation (60–70°) and two recrystallizations from hexane yielded product melting 113.5–114° (lit.[28] m.p. 111–112°).

Methylruthenocenylcarbinol from reduction of acetylruthenocene with lithium aluminum hydride melted at 60–63°. Recrystallization from heptane raised the melting point to 64–64.2°.

Anal. Calcd. for C$_{12}$H$_{10}$ORu: C, 52.23; H, 5.11. Found (E): C, 52.16; H, 5.16.

Methylruthenocenylcarbinyl acetate prepared as above melted at 64–64.5° after recrystallization from isopropyl ether.

Anal. Calcd. for C$_{14}$H$_{16}$O$_2$Ru: C, 52.88; H, 5.07. Found (E): C, 53.01; H, 5.03.

Osmocene.—Osmium tetrachloride was prepared in a number of small batches by passing chlorine gas over finely powdered osmium metal in a quartz tube heated to 700–750°.[34] The crude, somewhat moist, product which con-

densed beyond the heated portion of the tube was used for the reaction without further purification.

Sodium sand (3.8 g., 165 mmoles) was stirred in 75 ml. of tetrahydrofuran (purified by refluxing the commercial solvent over potassium hydroxide and distilling from lithium aluminum hydride) in a 500-ml. three-necked flask provided with a condenser, a Hershberg stirrer, a dropping funnel and a nitrogen atmosphere. Freshly cracked cyclopentadiene (16.1 ml., 12.1 g., 194 mmoles) was added dropwise over 15 min., and the mixture was stirred until the sodium had completely reacted (4.5 hr.). Osmium tetrachloride (12.7 g., 38 mmoles) was added as a solid, and the reaction mixture was stirred for 5 days at room temperature. The solvent was removed under reduced pressure, and the flask was swept with nitrogen for 8 hr. A cold-finger condenser was inserted in the flask, and the product was sublimed at 95–105° and about 1 mm. pressure. In this manner, 1.25 g. (10%) of pale yellow crystalline product was obtained, m.p. 227–229° (lit.[35] m.p. 229–230°).

Acetylosmocene.—Osmocene (0.41 g., 1.28 mmoles), acetic anhydride (40 ml.) and 85% phosphoric acid (5 ml.) were mixed in a flask under a nitrogen atmosphere. Nitrogen previously had been passed through the acetic anhydride and phosphoric acid for at least 20 min. The osmocene dissolved with considerable evolution of heat, and the flask was then maintained at 80° for 4 hr. The reaction mixture was cooled to room temperature and decomposed with aqueous sodium carbonate solution for 1.5 hr. The product was extracted into methylene chloride, the solution was dried over magnesium sulfate, and the solvent was distilled to yield a yellow solid. The product was chromatographed on alumina with benzene. Elution of the major yellow-product band and removal of the solvent yielded 0.385 g. (85%) of yellow crystals, m.p. 129–129.5°. Sublimation at 70–80° followed by two recrystallizations from n-heptane raised the melting point to 129.5–130° (lit.[27] m.p. 126°).

Methylosmocenylcarbinol from reduction of acetylosmocene with lithium aluminum hydride melted at 72.5–74°, and after two recrystallizations from heptane melted at 74–74.5°.

Methylosmocenylcarbinyl acetate prepared in the usual fashion melted at 67.2–67.7° after recrystallization from isopropyl ether–heptane.

Anal. Calcd. for C$_{14}$H$_{16}$O$_2$Os: C, 41.37; H, 3.97; Os, 46.79. Found (S): C, 41.22; H, 4.17; Os, 47.16, 46.38.

Kinetic Procedure.—Acetone used was reagent grade solvent further purified by the procedure of Kochi and Hammond.[36] Most of the solvolyses were performed in an "80% acetone" mixture. This solvent was prepared by diluting 200 ml. of boiled distilled water to 990 ml. at 25° with purified acetone. A 99-ml. aliquot of this solvent (measured at 30°) was equilibrated at the reaction temperature in a 100-ml. volumetric flask. A small tube containing the sample in 1 ml. of acetone was added to start the reaction. By measurement of the density, the exact composition of the resulting solvent was found to be 76.65% acetone by weight, or 80.7% acetone by volume. At suitable intervals after the start of the reaction, aliquots were removed, quenched and titrated with standard sodium hydroxide to the phenol red end-point. The quenching solution consisted of approximately 10 ml. of 85% acetone which had been cooled on an ice- or ice–salt-bath and through which nitrogen had been bubbled for at least 5 minutes. A flow of nitrogen was maintained over the surface of the solution during the titration. The time when the pipet was half empty was recorded as the time for that point. Kinetic runs were performed in a constant temperature bath which maintained the temperature within better than ±0.03°, and temperatures were checked against an NBS calibrated thermometer. Infinity titers were taken after a time estimated as greater than ten half-lives.

Rate constants were calculated from the standard integrated first-order rate equation[37] by a weighted least squares technique similar to that proposed by Roseveare.[38,39] The

(29) All melting points are uncorrected.

(30) Microanalyses by A. Elek, Los Angeles, Calif. (E), and by Schwartzkopf Microanalytical Laboratory, Woodside, N. Y. (S).

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weighting function was used, where z is the titer for unreacted acetate and z_1 is this value for the first point. This weighting

$$w = \frac{1}{(2/z_1) + (1/z)}$$

function was chosen arbitrarily so that the contribution from errors linear in time and errors linear in the titer would become equal at 1 half-life. Calculations of the rate constant and its standard deviation were performed on a Burroughs 220 computer, and are recorded in Table I.

Product Recovery from Hydrolysis.—A sample of methylferrocenylcarbinyl acetate (0.153 g., 0.56 mmole) was solvolyzed in 100 ml. of 80% acetone at 45° for 10 half-lives. The solution was diluted with water and the product was extracted into methylene chloride. The organic solution was washed several times with water, an equal volume of benzene was added to the extract, and the solvent was removed at reduced pressure and temperatures not exceeding 50° to yield a yellow solid, m.p. 75.5–77.5°. Recrystallization produced 0.67 g. (52%) of alcohol melting at 77.5–78.5°. The crude product accounted for at least 75% of the starting acetate, and no other product was detected by chromatography. A sample of solvolysis solution had an extinction coefficient at 440 mμ which was nearly identical with that of a solution made up with an equivalent amount of the carbinol, and gave no evidence of a shift in the maximum.

Ethanolysis of Methylferrocenylcarbinyl Acetate.—The ethyl ether of the carbinol was prepared by slowly bubbling dry hydrogen chloride for 20 sec. into a solution of 1.65 g. of methylferrocenylcarbinol in 35 ml. of absolute ethanol. After standing 1 hour the mixture was poured into an excess

of dilute aqueous sodium acetate, the product extracted into methylene chloride and washed with water. The solution was evaporated to an oil, and the product was chromatographed on neutral alumina with 50:50 benzene–ether. After the solvent had been removed, the product was distilled in a molecular still at 50° and 10 mμ pressure to yield a red-orange oil, n^{25}D 1.5739.

Anal. Calcd. for $C_{14}H_{18}OFe$: C, 65.14; H, 6.98. Found (E): C, 65.12; H, 7.06.

Refluxing a solution of 1.5 g. of methylferrocenylcarbinyl acetate in 300 ml. of absolute ethanol for 3.5 hr. and isolating the product as before produced an oil with n^{25}D 1.5741 and an infrared spectrum identical with that of the ether, which lacked carbonyl or hydroxyl absorption.

Methylferrocenylcarbinol (10.5 g., 2 mmoles) in 150 ml. of absolute ethanol with 0.06 ml. (1 mmole) of acetic acid added was refluxed for 3.5 hr. When the product was chromatographed, it was found that most of the carbinol had been converted to the ether.

A sample of methylferrocenylcarbinyl acetate (0.101 g., 0.37 mmole) was refluxed in absolute ethanol. Samples were removed after 1.5 and 6 hr., and titrated with standard sodium hydroxide. Both aliquots required about 5% in excess of the predicted volume of base. A control containing 0.1 g. (0.39 mmole) of the carbinol and 0.04 g. (0.45 mmole) of ethyl acetate required an amount of base equal to the indicator blank after 6 hr. reflux.

A sample of methylferrocenylcarbinol was refluxed in the presence of ethyl acetate with a trace of added acetic acid in ethanol solution. No further acetic acid was produced.

The ortho-Claisen Rearrangement. IV. The Rearrangement of X-Cinnamyl p-Tolyl Ethers[1]

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The rates of rearrangement of ten X-cinnamyl p-tolyl ethers were determined with the object of obtaining information to define the electronic character of the transition state of the Claisen rearrangement. The rates were best correlated by σ^+-constants and a ρ-value of −0.40. Since the rates of rearrangement of allyl p-X-phenyl ethers are similarly correlated by negative ρ- and σ^+-constants, the transition state must involve a depletion of electrons in both the aryl and allyl portions of the molecule. This might result from simultaneous homolysis of the allyl–oxygen bond and homogenesis of the allyl-ortho-carbon bond to give a highly electronegative, electron-deficient oxygen capable of withdrawing electrons from both the allyl and aryl groups.

Introduction

Although the over-all course of the Claisen rearrangement, in terms of the structural restrictions on reactants, intermediates and products, is well understood[4,5] the conformation and electrical character of the transition state have until recently escaped elucidation. The conformation of the transition state is now known,[6] but available experimental results[7,8] do not permit an unambiguous description of its electrical character.

An understanding of the electronic nature of the transition state is required to complete the description of the mechanism of the Claisen rearrangement. This can be studied by determining the effect of solvent and of substituents of varying electrical character on the rate of reaction. Some information concerning the electrical nature of the transition state is available from studies of the rates of rearrangement of allyl p-X-phenyl ethers.[7,8] The substituent effects on the rates of rearrangement of the allyl p-X-phenyl ethers are best correlated by σ^+-substituent constants[9] and a negative value of ρ in Hammett's equation.[10]

If the transition state involves a charge separation, then there should be polar effects of substituents in the allyl group also. Very little information is available which concerns the polar effects of substituents in the allyl group. It is known that α- and γ-allyl substituents affect the rate of rearrangement while β-substituents have no significance influence.[7,11] However, these results

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(3) From the thesis submitted by Wilmer K. Fife in partial fulfillment of the requirements for the Doctor of Philosophy Degree at The Ohio State University.

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