methyl Sulfoxide and Potassium *t*-Butoxide.—A mixture of 1.5 g. (5.4 mmoles) of the sulfone and 0.60 g. of potassium *t*-butoxide in 25 ml. of dimethyl sulfoxide was stirred for 30 min. under nitrogen. The reaction mixture was then added to approximately 200 ml. of ice–water and after 30 min. the precipitate that formed was filtered and dried over phosphorus pentoxide to give a white solid, m.p. 42–110°. The filtrate was continuously extracted with ether for 45 hr. The ether extract was dried over magnesium sulfate and evaporated to give a white solid; this solid after drying over phosphorus pentoxide had m.p. 125–135°. Both solids had infrared spectra almost superimposable upon that of the sulfoxide I but with an additional carbonyl absorption. Absorption due to the sulfone group was not apparent. Recrystallization of the solid (m.p. 125–135°) from ethanol gave 472 mg. (34%) of I, m.p. 138–142°, no depression of mixture melting point with an authentic sample, large depression with the corresponding sulfone. When, the solids were combined and washed with about 50 ml. of ether a yellow oil was obtained upon evaporation of the solvent which when treated with 2,4-dinitrophenylhydrazine gave 21 mg. (1%) of the 2,4-dinitrophenylhydrazone of benzophenone, m.p., 242–243°, no depression of the melting point of an authentic sample.

β-(Methylsulfonyl)-*p*-methoxystyrene (III).—To a stirred solution of 1.884 g. (20 mmoles) of dimethyl sulfone and 1.12 g. of sublimed potassium *t*-butoxide in 20 ml. of 80% dimethyl sulfoxide–20% *t*-butyl alcohol was added over a period of 5 min. 1.4 g. (10 mmoles) of *p*-anisaldehyde dissolved in 5 ml. of the solvent mixture. The solutions were purged with nitrogen before and during the reaction. The reaction mixture was allowed to stir for an additional 30 min. after which a few pieces of ice were then added until the solution turned cloudy. The cloudy solution was then added to 200 ml. of ice–water to give 0.512 g. (24%) of III, m.p. 138–141°, after recrystallization from a mixture of ethanol and chloroform.

Anal. Calcd. for $C_{10}H_{12}O_3S$: C, 56.58; H, 5.70; S, 15.11. Found: C, 56.39; H, 5.70; S, 14.98.

Upon standing the aqueous solution deposited 0.143 g. (8.7%) of V, m.p. 161–164°. Extraction of the filtrate, after the removal of V, by ether yielded an additional 74 mg. (3.5%) of III.

Bis(*p*-methoxy-β-styryl) Sulfone (V).—Dimethyl sulfone (941 mg., 10 mmoles) and 1.12 g. of potassium *t*-butoxide were dissolved in 17 ml. of DMF at 60–63°, 0.68 g. of *p*-anisaldehyde (5 mmoles) added, and the reaction mixture kept at 60–63° for 5 min. After 30 min. at room temperature an additional 2.1 g. of *p*-anisaldehyde (15.4 mmoles) and 1.12 g. of potassium *t*-butoxide were added. The reaction mixture was kept between 30–50° for 70 min. Addition of 100 ml. of ice–water and 50 ml. of ether caused the precipitation of crystalline material which was filtered and washed with ether. The crystals were washed with ethanol, to yield 1.04 g. of V (32%), m.p. 158–160°. Recrystallization from an ethanol–chloroform mixture raised the melting point to 161–163°.

Anal. Calcd. for $C_{18}H_{18}O_4S$: C, 65.44; H, 5.49; S, 9.69. Found: C, 65.48; H, 5.75; S, 9.78.

The aqueous filtrate was extracted with 200 ml. of ether. The yellow ether solution was dried over sodium sulfate, filtered, and evaporated to yield a yellow oil. Treatment with ethanol gave 410 mg. of VI (12%).

2,6-Di-*p*-anisyl-1,4-oxathian-4,4-Dioxide (VI).—Dimethyl sulfone (941 mg., 10 mmoles) and 560 mg. of sublimed potassium *t*-butoxide were dissolved in 10 ml. of DMF at 50°. *p*-Anisaldehyde (2.8 g., 20.6 mmoles) was added dropwise and the reaction mixture was kept at 50° for 2 min. and at room temperature for 60 min. Addition of 100 g. of ice caused an oily precipitation to appear which upon treatment with a little ethanol gave 185 mg. of V. The aqueous filtrate was kept in an open beaker for 4 days, during which time an oil separated. The solution was decanted from the oil and the oil was boiled in ethanol. Upon cooling at room temperature 1.33 g. (38%) of VI crystallized in prismatic needles. Two recrystallization from ethanol gave material melting at 117–119°.

Anal. Calcd. for $C_{18}H_{20}O_5S$: C, 62.06; H, 5.79; S, 9.20. Found: C, 62.05; H, 5.85; S, 8.93.

Bis(*p*-methoxyphenyl-β-hydroxyethyl) Sulfone (VII).—The reaction of *p*-anisaldehyde and dimethyl sulfone in DMSO solution in the presence of potassium *t*-butoxide produces mainly resinous material. Low yields of VII can be isolated during the early stage of the reaction. Dropwise addition of 0.7 g. of *p*-anisaldehyde (5 mmoles) to 47 g. of dimethyl sulfone (5 mmoles) in 8 ml. of DMSO containing 0.88 g. of sublimed potassium *t*-butoxide immediately produced a brown coloration. After 1 min. at room temperature the solution was added to 200 ml. of ice water and acidified with dilute hydrochloric acid to give a crystalline precipitate contaminated with a brown oil. Addition of 25 ml. of ether dissolved most of the oil. Recrystallization of the precipitate from a mixture of ethanol and chloroform gave 54 mg. (6%) of VII, m.p. 132–133°. The integrated n.m.r. was completely consistent with VII including the presence of two protons exchangeable with deuterium oxide.

Anal. Calcd. for $C_{18}H_{22}O_6S$: C, 59.00; H, 6.05; S, 8.75. Found: C, 59.53; H, 6.41; S, 9.98.

Kinetics of the Ethanolysis of α-Ferrocenylethyl Chloride

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The extremely rapid solvolysis of α-ferrocenylethyl chloride is reported in this paper. Results obtained are in accord with the high stability of the α-metallocenylcarbonium ion previously shown in solvolyses of α-metallocenylcarbinyl acetates[1] and in the addition of weak acids to vinylmetallocenes.[2]

α-Ferrocenylethyl chloride[3] was solvolyzed at temperatures from −42° to −82° in a mixture of 60% ether–40% ethanol. Kinetics were followed by the "rapid intermittent titration" technique,[4] using an ether–ethanolic solution of tri-*n*-butylamine. There was a marked decrease in the instantaneous first-order rate constant as the reaction progressed. Such kinetic behavior is characteristic of a solvolysis in which the intermediate carbonium ion may either react with solvent to form product, or with the chloride ion liberated in the reaction to form starting material.[5] This is illustrated in eq. 1, where the abbreviation Fc represents the ferrocenyl group, $C_{10}H_9Fe$.

$$\mathrm{FcCHClCH_3} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{Fc\overset{+}{C}HCH_3} + \mathrm{Cl^-} \tag{1}$$

$$\mathrm{Fc\overset{+}{C}HCH_3} + \mathrm{C_2H_5OH} \xrightarrow{k_3} \mathrm{FcCH(OC_2H_5)CH_3} + \mathrm{H^+}$$

The same carbonium ion previously has been shown to be trapped very efficiently by acetate ion in solvolyses of α-ferrocenylethyl acetate in aqueous acetone. As predicted in eq. 1, added trimethylammonium chloride decreased the solvolysis rate, while trimethylammonium bromide and phenyltrimethylammonium bromide produced the slight rate increases expected as normal kinetic salt effects. Treatment of the rate data on the basis of eq. 1 allows the extraction of values for k_1 and

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the ratio of second-order rate constants k_2/k_3. Details are included in the Experimental, and results are tabulated in Table I. In some runs, the data had too much scatter to allow a simultaneous determination of k_1 and k_2/k_3; so k_1 was calculated assuming the average value of k_2/k_3 obtained in other runs in the same temperature range. Also listed in Table I are experimental values of k_{inst}, as determined at $[\text{Cl}^-] = 1.5 \times 10^{-5}$ M, wherever possible.

TABLE I

RATE CONSTANTS AND RATE CONSTANT RATIOS FOR α-FERROCENYLETHYL CHLORIDE SOLVOLYSIS

Temp., °C.[a]	Initial concn. $\times 10^4$ M[b]	$10^5 k_1$, sec.$^{-1}$	$10^{-4}\frac{k_2}{k_3}$	Method	$10^5 k_{\text{inst.}}$ $[\text{Cl}^-] = 1.5 \times 10^{-4}$ M
−42.8	4.9	890 ± 60	1.02	A, B	712
−45.3	3.9	620 ± 100	0.82	A	550
−45.1	4.3	684 (650)[c]	0.76[d]	C	603
−45.5	21.5	580 ± 160	0.45	A, B	292[e]
−66.0	3.9	48 ± 5	1.36	A, B	35.3
−66.2	4.2	54 ± 5	1.60	B	38.5
−69.6	4.3	40 ± 5[f]	1.3	B	29.7
−67.2	2.0	62 ± 10[g]	3.2	B	
−68.8	3.9	39 (51)[c,h]	1.4[d]	C	17[i]
−67.3	3.3	50 (53)[c,j]	1.4[d]	C	19[k]
−81.3	10.2	7.0 ± 2.0	4.8	A, B	3.26
−82.0	4.7	5.8 (6.3)[c]	4.8[d]	C	

[a] All temperatures ±0.7°. [b] Without correction for volume changes on solvent mixing or cooling to reaction temperature. [c] First value based on assumed k_2/k_3; value in parenthesis calculated from activation parameters. [d] Assumed value used to calculate k_1. [e] $[\text{Cl}^-] = 12 \times 10^{-4}$ M. [f] Saturated with $[\text{CH}_3]_3\text{NHBr}$. [g] Saturated with $\text{C}_6\text{H}_5(\text{CH}_3)_3\text{NBr}$. [h] Added initially 5.6×10^{-4} M $(\text{C}_4\text{H}_9)_3\text{NHCl}$. [i] $[\text{Cl}^-] = 6 \times 10^{-4}$ M. [j] Added initially 7.2×10^{-4} M $(\text{CH}_3)_3\text{NHCl}$. [k] $[\text{Cl}^-] = 7.5 \times 10^{-4}$ M.

Activation parameters for the ionization rate constant were determined from the temperature dependence of k_1 in the runs for which the simultaneous evaluation of rate constants was performed. Values of k_1 from the other runs fell close to this line. Activation parameters are listed in Table II, along with similar values for trityl chloride in the same solvent[6] and for trityl and α-ferrocenylethyl acetates solvolyzing in "80% acetone."[1c] k_2/k_3 ratios were not sufficiently precise to allow the evaluation of reliable activation parameters, but the observed temperature dependence of this ratio is well outside of experimental error.

TABLE II

ACTIVATION PARAMETERS FOR α-FERROCENYLETHYL CHLORIDE AND RELATED SOLVOLYSES

Solvolysis	Temp. range, °C.	ΔH, kcal.	Δ5, e.u
α-Ferrocenylethyl chloride 60% ether–40% ethanol	−42 to −82	10.9 ± 0.7	−22
Triphenylmethyl chloride[a] 60% ether–40% ethanol	0 to 25	13.2	−23
α-Ferrocenylethyl acetate[b] "80% acetone"	0 to 35	19.0	−13
Triphenylmethyl acetate[b] "80% acetone"	15 to 45	22.1	− 7

[a] Recalculated from data at 4.8×10^{-4} M in ref. 4. [b] See ref. 1b.

A product study was carried out on one solvolysis. The main isolated product, as characterized by its n.m.r. spectrum and analyzed quantitatively by its visible spectrum, was the ethyl ether of α-ferrocenyl ethanol[1c] in about 90% yield. None of the alcohol was found, and the amine hydrochloride formed did not contain a detectable amount of ferrocene chromophore. Thus, the amine titrant did not divert a significant fraction of the carbonium ions from their normal reaction.

The most striking feature of the results is the rapidity of the solvolysis of α-ferrocenylethyl chloride. Extrapolation of the trityl chloride solvolysis rate[6,7] to −45° gives a rate constant smaller than that of α-ferrocenylethyl chloride by a factor of over 500. The difference is due primarily to the smaller activation enthalpy of α-ferrocenylethyl chloride, and is similar to that found with the corresponding acetates.[1c]

Values of the second-order rate constant ratio k_2/k_3 for competition between chloride ion and ethanol vary from about 8000 at −45° to 48,000 at −82°. A value of 3100 was found by Swain, Scott, and Lohmann[5c] for competition between chloride ion and water for the trityl cation in 85% acetone at −34.5°, and comparable results have been observed for acetate ion.[1c,5c] While the exact significance of carbonium ion selectivity expressed as a ratio of second-order rate constants may be uncertain, it is generally agreed that high selectivity implies high carbonium ion stability.

The very high solvolytic reactivity of α-ferrocenylethyl chloride, the strong common ion inhibition, and the close parallel between acetate and chloride solvolyses in the trityl and α-ferrocenylethyl systems provide strong confirmation of the high stability of carbonium ions adjacent to a metallocene nucleus.

Experimental

α-Ferrocenylethyl Chloride.—Vinylferrocene (0.5 g.) in 40 ml. of pentane was purged with dry nitrogen and cooled to −78°. Hydrogen chloride was bubbled through the solution for a few minutes. Almost immediately the solution turned cloudy and a precipitate formed. Most of the solvent was removed by siphon under pressure of dry nitrogen, and the remainder, along with excess hydrogen chloride, was evaporated at reduced pressure as the flask warmed to room temperature. The resultant yellow solid could be kept under vacuum at −15° for several days, but turned black after standing at room temperature or in contact with air for a few hours. Purification could be effected by vacuum sublimation (50 μ, 40°). The product melted at 66–68°, lit.[3] m.p. 66–68°. The n.m.r. spectrum[8] exhibited a doublet at 8.21 (methyl group), a quartet at 5.09 (α-hydrogen), and a narrow multiplet at 5.94 τ (ring protons). Splittings in the doublet and quartet were 7.5 c.p.s. Crude chloride was used for several of the kinetic runs, and gave results indistinguishable from sublimed product.

Kinetics.—Reactions were followed by a rapid intermittent titration technique.[4] The reaction flask was cooled in a stirred dewar containing chlorobenzene, chloroform, or acetone, to which solid carbon dioxide had been added. During the course of a run, the temperature in the flask remained constant within

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(7) As a rough check on the rapid intermittent titration procedure used in this study, several solvolyses of trityl chloride were carried out at 0° The rates obtained were about 20% greater than those reported by Nixon and Branch.[6] The reported dependence of rate constant on initial concentration was found, but added triphenylmethanol did not depress the rate. Since a slight curvature in rate plots was observed by us, it is possible that the apparent dependence upon initial concentration might be explained as a common ion effect, if (as in this work) an appreciable fraction of the very rapid reaction had occurred before kinetic measurements were begun.

(8) All n.m.r. spectra were in carbon tetrachloride with tetramethylsilane as internal standard.

about 0.5° or less. Solvents were measured by volume at room temperature. A small portion of the ether was withheld for addition of the substrate.

A kinetic run was started by injection of the substrate solution. Temperature equilibrium was attained again within about 1 min. Acid was titrated as formed with a solution of tri-*n*-butylamine (b.p. 208–209°) in 60% ether–40% ethanol. The acid end point of thymol blue (pH 1.2–2.8 in water) was shown to be satisfactory by potentiometric titration. Between 12 and 45 points were taken during an individual run. Runs at −45° were followed through the range from about 45 to 90% completion; the beginning of the reaction was inaccessible due to the time needed for temperature equilibration. Reactions at −65° were followed to about 80% completion; those at −82° were followed only to 20% completion because of their slowness.

The rate constant k_1 and the ratio k_2/k_3 were evaluated in three ways.

Method A.—The customarily obtained steady state rate expression[5], eq. 2, may be rearranged to yield eq. 3 as follows.

$$\frac{d[\mathrm{RCl}]}{dt} = \frac{k_1[\mathrm{RCl}]}{\dfrac{k_2[\mathrm{Cl}^-]}{k_3[\mathrm{C_2H_5OH}]} + 1} = \frac{k_1[\mathrm{RCl}]}{\dfrac{k_2[\mathrm{Cl}^-]}{k'_3} + 1} = k_{\mathrm{inst}}[\mathrm{RCl}] \quad (2)$$

$$k_{\mathrm{inst}} = k_1 - \frac{k_2}{k'_3}\, k_{\mathrm{inst}}\, [\mathrm{Cl}^-] \quad (3)$$

Then a plot of k_{inst} *vs.* k_{inst} $[\mathrm{Cl}^-]$ should yield a straight line of slope k_2/k_3 and *y*-intercept k_1. Instantaneous rate constants obtained from the slope of the curved "first-order" plots at several points were treated in this manner.

Method B.—The substitution $[\mathrm{Cl}^-] = c + r - [\mathrm{RCl}]$ is made in eq. 2, where c is chloride concentration at a time taken as $t = 0$ and r is the concentration of substrate at $t = 0$. This equation may now be integrated to yield, after rearrangement

$$\frac{2.303 \log \dfrac{[\mathrm{RCl}]}{r}}{t} = \frac{k_1}{\dfrac{k_2}{k'_3}(c + r) + 1} + \frac{k_2/k'_3}{\dfrac{k_2}{k'_3}(c + r) + 1}\; \frac{([\mathrm{RCl}] - r)}{t} \quad (4)$$

A linear plot is again obtained, from which k_1 and k_2/k_3 may be evaluated as functions of the slope and intercept.

Method C was used in runs with too much scatter for application of methods A or B. The average value of k_2/k_3 for runs in that temperature range was assumed, and k_1 was calculated from eq. 2. (It should be noted that these were in general still quite acceptable kinetic plots for most purposes, with no point deviating from a reasonable curve by more than 1% of the total final titer. However, both of the simultaneous rate constant evaluations are in principle a measurement of the deviation from linearity, and as such are very sensitive to experimental errors.) Error limits were assigned to values of k_1 by inspection of plots obtained from methods A and B. In general, k_2/k_3 was more sensitive to scatter in the data, and so values quoted are less reliable.

Product Study.—A sample of the chloride (0.054 g., 0.22 mmole) was solvolyzed as in a kinetic run. The solvent was evaporated under reduced pressure. The residue was extracted with pentane and diluted with heptane to obtain the visible spectrum. The spectrum was qualitatively the same as that of α-ferrocenylethanol [$\lambda_{\max}$ 437 mμ (ε 105) in 12.5:1 heptane–ether], and, if the extinction coefficient is assumed to be the same for the two spectra, the product solution is calculated to contain 0.198 mmole of ferrocene chromophore, or 90% of the starting chloride. The pentane-insoluble residue of ammonium salts contained the indicator, but nothing with the ferrocene chromophore.

The reaction product was chromatographed on alumina with benzene as eluent. Two yellow bands which passed through the column close together were isolated. The first was present in a trace amount too small to characterize. The second was an orange oil whose n.m.r. spectrum[8] was consistent for the ethyl ether of α-ferrocenylethanol.[1c] It had a triplet centered at 8.89 and a quartet at 6.63 τ with splittings of 6.5 c.p.s., corresponding to the ethyl group. The ring proton resonance came at 5.95 τ. The $-\mathrm{CH-CH_3}$ group should appear as a doublet and a quartet. The doublet appeared at 8.56 τ, but the quartet was partially obscured by the ring protons. Two peaks of the quartet, with splitting of 5.5 c.p.s. (the same as the doublet) were readily visible, and shoulders on the ring proton resonance fell at the proper places to complete a quartet centered at 5.83 τ.

The Ritter Reaction of Tertiary Trihalomethylcarbinols and Related Substances

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It has been shown[1-3] that the transformation of diaryltrifluoromethylcarbinols (I) into substituted fluorenes by successive treatment with concentrated sulfuric acid and a compound containing reactive hydrogen proceeds through a carbonium ion. Likewise, the rearrangement of diaryltrichloromethylcarbinols (II) into benzils under similar conditions[4] can be rationalized as involving carbonium ion intermediates. As it has been proved, on the other hand, especially by the experiments of Mousseron and co-workers,[5] that the so-called Ritter reactions of carbinols with nitriles in concencentrated sulfuric acid proceed *via* carbonium ion intermediates, it seemed of interest to study this reaction on compounds of type I and II.

When a solution of di(*p*-chlorophenyl)trifluoromethylcarbinol (I, X = Cl) in concentrated sulfuric acid was added to acetonitrile, the intense color of the carbonium ion faded immediately, and a white crystalline compound was formed, which according to the analysis was the expected N-[1,1-di(*p*-chlorophenyl)-2,2,2-trifluoroethyl]acetamide (III). Analogously, with benzonitrile the benzamide derivative was obtained. These compounds are extremely resistant to hydrolysis with either acidic or alkaline reagents, which was not altogether unexpected[6]; N-triphenylmethylacetamide could not be deacetylated.[7] Di(*p*-chlorophenyl)- and di(*p*-fluorophenyl)trichloromethylcarbinol (II, X = Cl, F) behave similarly towards acetonitrile, giving IV (X = Cl, F). The products of positive Ritter reactions of other diarylperfluoroalkylcarbinols are summarized in Table I. This table also includes the reaction of benzilic acid with acetonitrile and concentrated sulfuric acid, which expectedly gave acetamidodiphenylacetic acid (V); treatment of V with alkali did not cause deacetylation, but decarboxylation, giving N-benzhydrylacetamide (VI).[8]

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