or water. Hydrolysis was carried out either by placing the sample directly in water or dilute hydrochloric acid, or by adding it to a mixture of 40 ml. of ether and 10 ml. of 95% ethanol in a nitrogen atmosphere, stirring for 25 min., and adding 5 ml. of water.

Calcium–Pyridine, 1:1.—Compositions of products of five reactions, C_5H_5N per Ca, were 1.00, 1.00, 0.96, 0.98, 1.00; NH_3 1.01, 1.07, 0.91, 0.79, 0.98; av. $Ca(C_5H_5N)_{0.99}(NH_3)_{0.95}$. Only traces of hydrogen were formed. Combustion analysis of four yellow insoluble hydrolysis products were C, 57.79, 59.02, 67.88, 60.76; H, 7.74, 8.43, 8.05, 7.40; N, 9.72, 11.22, 13.27, 11.28; O (by difference), 24.75, 21.33, 10.80, 20.56; av. empirical formula, $C_5H_{7.7}N_{0.8}O_{1.2}$. Evacuation of two original products at 90° for 20 hr. left empirical compositions, $Ca(C_5H_5N)_{0.81}(NH_3)_{0.63}$ and $Ca(C_5H_5N)_{0.80}(NH_3)_{0.49}$.

Calcium–Pyridine, 1:2 (or More).—Compositions of products of ten reactions, when evacuated at 30°, were $Ca(C_5H_5N)_{1-2}$. Only traces of hydrogen were produced. Evacuation at 0° left $Ca(C_5H_5N)_{2.08}$ and $Ca(C_5H_5N)_{2.21}$ in two preparations. Evacuation at 110° for 20–30 hr. produced, in three preparations- $Ca(C_5H_5N)_{0.84}$, $Ca(C_5H_5N)_{1.12}$, and $Ca(C_5H_5N)_{1.06}$ These ma, terials smoked in air and changed from black to tan. Hydrolysis by ether–alcohol–water gave a semisolid yellow product; combustion analyses: C, 68.61; H, 6.28; N, 10.29; O, 14.82. Decomposition of $Ca(C_5H_5N)$ at 110–360° produced a very small amount of sublimate, 4,4′-dipyridyl, identified by infrared spectrum, m.p. 108° (lit. m.p. 112°), and combustion analysis: C, 77.9; H, 5.7 (theory: C, 76.90; H, 5.16).

Calcium–2-Picoline, 1:1.—Two reactions were run. Each went rapidly, evolving only traces of hydrogen. One product was evacuated for 24 hr. at 0° and then for 6 hr. at 28°, then having the composition $Ca(pic)_{0.98}(NH_3)_{1.09}$. Its reactivity with air and water appeared very similar to that of $Ca(C_5H_5N)(NH_3)$. Hydrolysis with dilute hydrochloric acid liberated 35.4% of the original picoline. The other initial product was evacuated for 9 hr. at 30° and then for 24 hr. at 110°, then having the composition $Ca(pic)_{0.82}(NH_3)_{0.77}$.

Calcium–2-Picoline, 1:Excess.—One reaction with an 8:1 excess of picoline, and another with a 12:1 excess, both formed green precipitates which turned red at −80° and back to green again near −33°. Evaporation of the bulk of ammonia left a dark blue solid, which after a 27-hr. evacuation at 25° had the composition $Ca(pic)_{1.46}$. This lost additional picoline at 120°, leaving a greenish black solid, $Ca(pic)_{0.80}$. This resembled the pyridine compounds in its vigorous reaction with air and water, and formed a viscous yellow oil by ether–alcohol–water hydrolysis. Evacuation of the product of the second reaction left a dark blue $Ca(pic)_{1.87}$ after 18 hr. at 0°, which lost picoline during 22 hr. at 110° becoming black $Ca(pic)_{0.88}$, similar to the first product.

Calcium–3-Picoline, 1:1.—Addition of this picoline to the ammonia solution of calcium produced promptly a bright yellow-green precipitate which changed to brown as most of the excess ammonia was removed, and evacuation for 27 hr. at 28° left a red-brown solid of empirical composition, $Ca(pic)_{0.99}(NH_3)_{1.10}$. This was very reactive in air. Hydrolysis with dilute hydrochloric acid gave a clear yellow solution which was shown to contain 38.2% of the original picoline.

Calcium–3-Picoline, 1:8.—Addition of the picoline to the $Ca-NH_3$ solution produced promptly a bright yellow-green precipitate which turned to a viscous, red-brown sludge when most of the liquid ammonia had evaporated. Evacuation for 21 hr. at 28° left a glassy, olive green solid of composition, $Ca(pic)_{1.91}$. This was heated to 110° *in vacuo* for 11 hr., which reduced the picoline content to $Ca(pic)_{0.86}$, a green-black solid. In air, this turned tan at once, with evolution of considerable heat and smoke. Hydrolysis by the ether–alcohol–water method gave an orange yellow oil which solidified partially on addition of water, but became an oil again when subjected to evacuation.

Calcium–4-Picoline, 1:1.—Addition of the picoline turned the ammonia solution light green with production of a precipitate and evolution of no more than a trace of hydrogen. Evaporation of the ammonia left a yellow solid which turned tan after 45 hr. evacuation at 28°, and had the composition, $Ca(pic)_{0.99}(NH_3)_{1.13}$. This material became quite hot in air and smoked. It reacted vigorously with water with no evolution of hydrogen. The insoluble solid hydrolysis product dissolved in dilute hydrochloric acid giving a deep orange, almost red solution. Spectrophotometric examination of this solution showed it to contain 54.4% of the original 4-picoline.

Calcium–4-Picoline, 1:8.—Addition of the picoline turned the mixture dark brown, and after evaporation of the ammonia and 17 hr. evacuation at 29°, a dark brown solid having the composition $Ca(pic)_{2.02}$ remained. Heating this material for 19 hr. *in vacuo* at 120° produced black $Ca(pic)_{1.04}$, a water-reactive substance that in air became somewhat warm and turned brown in 2 min. Hydrolysis by the ether–alcohol–water method led to isolation of a tacky, orange polymeric material which was not further examined.

Calcium–2,6-Lutidine, 1:1.—Addition of the lutidine caused appearance of a yellow precipitate. The ammonia was allowed to evaporate and collected in dilute hydrochloric acid. This solution was found by spectrophotometric analysis to contain a small amount of lutidine. Additional lutidine was collected in traps at −196° while the reaction flask was being evacuated at 29° for 22 hr. From these quantities and the original amounts of reagents, the composition of the light green residual solid was found to be $Ca(lut)_{0.80}(NH_3)_{0.69}$. In air this quickly evolved smoke, became incandescent, and turned orange. It reacted vigorously with dilute hydrochloric acid, giving a yellow solution containing 28.1% of the lutidine in the compound.

Calcium–2,6-Lutidine, 1:8.—A greenish yellow precipitate appeared when the lutidine was added. Evaporation of the ammonia left a blue-green solid initially containing 2.7 moles of lutidine per mole of calcium. Evacuation at 31° for 24 hr. reduced the lutidine content to the more stable Ca(lut), a sky blue solid of high reactivity. In air it smoked, became incandescent while throwing off sparks, and turned tan. Hydrolysis by the ether–alcohol–water method left a white precipitate [presumably chiefly $Ca(OH)_2$] and a yellow solution, from which a yellow oil was separated by evaporation of the ether. Addition of water to this oil changed it to a semisolid, but subsequent evacuation changed it back to a yellow-orange oil.

Calcium–2,4,6-Collidine.—Collidine was found to react with calcium in a similar manner but more detailed studies were not completed.

Calcium and Liquid Ammonia Alone.—Several experiments were run to determine the maximum rate of amide formation likely under the experimental conditions used for the pyridine reactions, by dissolving the usual size sample of calcium in liquid ammonia and, without adding pyridine, measuring the hydrogen evolution as the ammonia was allowed to evaporate. For reasons not known, inconsistent results were obtained, the amount of amide after 90 min. in four similar experiments being 37, 36, 56, and 18%. Nevertheless, these experiments showed consistently less than 10% reaction in the first 15 min. at −34°, whereas the pyridine reactions were all conducted at temperatures close to −70° and occurred almost instantaneously, reacting with all the calcium present before the solution could become warmer. It was, therefore, concluded that only traces of calcium amide could have been present when the pyridine reactions took place.

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Condensation of Aromatic Aldehydes with Dimethyl Sulfone[1,2]

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Direct condensations of methyl *p*-tolyl sulfone with benzaldehyde in the presence of alkoxide or hydroxide

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[1] Reaction of Resonance Stabilized Anions, part XI. For part X, see H.-D. Becker, G. J. Mikol, and G. A. Russell, *J. Am. Chem. Soc.*, **85**, 3410 (1963).

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[3] Alfred P. Sloan Foundation Fellow, 1959–1963.

ions has been reported to give only a low yield of the benzal derivative contaminated with impurities difficult to separate.[4] Dimethyl sulfone has been condensed with benzophenone and benzaldehyde to give the β-hydroxy sulfones in good yield in benzene solution using butyllithium[5] or the Grignard reagent derived from dimethyl sulfone.[5,6] The condensation of alkylsulfonyl acetates with aldehydes in benzene solution containing alkylammonium acetates is also well known.[7]

In our hands attempts to bring about a direct condensation between dimethyl sulfone and benzophenone have been unsuccessful in both dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) solutions containing potassium *t*-butoxide. No reaction is observed in DMF at 60° while in DMSO at room temperature only the dimethyl sulfoxide adduct of benzophenone, $(C_6H_5)_2C(OH)CH_2SOCH_3$ (I), is formed.[8] When the expected addition product of dimethyl sulfone and benzophenone, $(C_6H_5)_2C(OH)CH_2SO_2CH_3$ (II), was added to DMSO containing an excess of potassium *t*-butoxide, I and benzophenone were formed indicating the versibility of the addition reaction.

$$\mathrm{II} \overset{\mathrm{OR}^-}{\rightleftharpoons} (C_6H_5)_2CO + CH_3SO_2CH_3$$

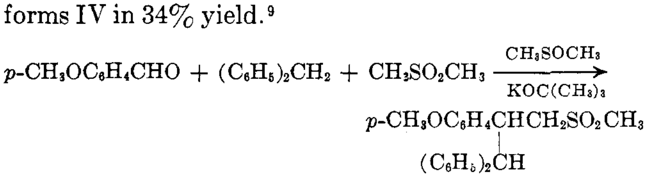
$$(C_6H_5)_2CO + CH_3SOCH_3 \xrightarrow{\mathrm{OR}^-} \mathrm{I}$$

We, therefore, turned our attention to the condensation of aromatic aldehydes with dimethyl sulfone. The reaction of *p*-anisaldehyde in DMSO solution containing an excess of potassium *t*-butoxide is difficult to control and yields mainly resinous products. However, at room temperature and in the presence of an excess of dimethyl sulfone moderate yields of the α,β-unsaturated sulfone (III) have been obtained in DMSO (80%)-t-butyl alcohol (20%) mixed solvents.

$$CH_3SO_2CH_3 + p\text{-}CH_3OC_6H_4CHO \xrightarrow[\mathrm{KOC(CH_3)_3}]{\mathrm{DMSO}\text{-}t\text{-}\mathrm{BuOH}} p\text{-}CH_3OC_6H_4CH{=}CHSO_2CH_3$$

III

When diphenylmethane, *p*-anisaldehyde, dimethyl sulfone, and potassium *t*-butoxide are allowed to react in equal molar quantities in DMSO solution at room temperature, an asymmetric tricarbon condensation forms IV in 34% yield.[9]



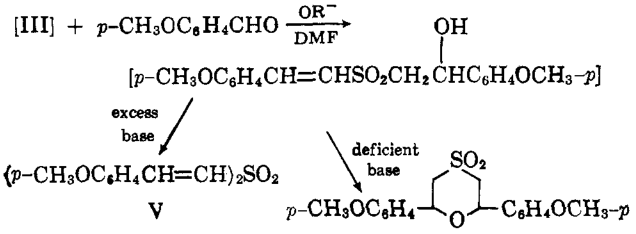
$$p\text{-}CH_3OC_6H_4CHO + (C_6H_5)_2CH_2 + CH_3SO_2CH_3 \xrightarrow[\mathrm{KOC(CH_3)_3}]{\mathrm{CH_3SOCH_3}} p\text{-}CH_3OC_6H_4\underset{\substack{|\\(C_6H_5)_2CH}}{CH}CH_2SO_2CH_3$$

IV

When this tricarbon condensation was attempted as a two-step operation in which *p*-anisaldehyde and dimethyl sulfone were first allowed to react in DMSO containing potassium *t*-butoxide to give the intermediate unsaturated sulfone (III), and diphenylmethane added in a second step, the yield of IV decreased from 34 to 6%[9]. It thus appears that a reasonable yield of IV results only when there is diphenylmethide ion present to trap III as it is formed, presumably because of the reactivity of III in further condensation reactions.

Attempts to form III or IV in dimethylformamide solution at 60° were unsuccessful. Instead, two other condensation products of dimethyl sulfone and *p*-anisaldehyde were formed in the presence or absence of diphenylmethane. At 60-65° in the presence of an excess of potassium *t*-butoxide the bis-α,β-unsaturated sulfone, V, is formed whereas at 50° in the presence of a deficiency of potassium *t*-butoxide the major product is the heterocyclic compound, 2,6-di-*p*-methoxyphenyl-1,4-oxathian 4,4-dioxide, VI.

$$CH_3SO_2CH_3 + p\text{-}CH_3OC_6H_5CHO \xrightarrow[\mathrm{DMF}]{\mathrm{OR}^-} [\mathrm{III}]$$



V

VI

These condensation products involving two moles of aldehyde and one mole of dimethyl sulfone are the major insolable products even when the aldehyde and sulfone are used in a 1:1 mole ratio. A 2:1 mole ratio is obviously preferred for the synthesis of V and/or VI. These results suggest that the intermediate α,β-unsaturated sulfone (III) contains a methyl group which is extremely reactive in further condensation reactions.

The formation of the substituted 1,4-oxathian from dimethyl sulfone and *p*-anisaldehyde adds support to the suggestion of Fromm[10a] that the compound formed from dibenzyl sulfone and aqueous formaldehyde in the presence of potassium hydroxide is the 3,5-diphenyl-1,4-oxthian 4,4-dioxide.[10b]

Experimental[11]

Preparation of 2-(Methylsulfinyl)-1,1-diphenylethanol (I).—A mixture of 1.82 g. of benzophenone and 1.12 of sublimed potassium *t*-butoxide in 5 ml. of dimethyl sulfoxide was stirred for 30 min. under a nitrogen atmosphere. The reaction mixture was then added to 200 ml. of water and cooled in an ice bath. The precipitate was separated by filtration, washed with 50 ml. of ether, and dried to give 2.18 g. (83%) of the addition product, m.p. 145-146°, lit.[12] m.p. 148-148.5°. Slow evaporation of the ether washings gave 0.3 g. (16.5%) of unchanged benzophenone.

Preparation of 2-(Methylsulfonyl)-1,1-diphenylethanol (II).—To a solution of 1 g. (3.85 mmoles) of I in 3 ml. of glacial acetic acid was added 4 ml. of 30% hydrogen peroxide and the solution maintained at 50-60° for 12 hr. Large colorless crystals formed which were filtered, washed with water and ethanol to yield 890 mg. (84%) of II, m.p. 135-136°, lit.[5] m.p. 139-139.5°.

Anal. Calcd. for $C_{15}H_{16}O_3S$: C, 65.21; H, 5.84; S, 11.58. Found: C, 65.24; H, 6.05; S, 11.82.

Reaction of 2-(Methylsulfonyl)-1,1-diphenylethanol with Di-

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[5] W. E. Truce and K. R. Buser, *ibid.*, **76**, 3577 (1954).

[6] L. Field, *ibid.*, **74**, 3919 (1952); L. Field and J. W. McFarland, *ibid.*, **75**, 5582 (1953).

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[8] A variety of products from the pyrolysis of the anion derived from I in DMSO solution have been recently reported: M. Chaykovsky and E. J. Corey, *J. Org. Chem.*, **28**, 254 (1963); C. Walling and L. Bollyky, *ibid.*, **28**, 256 (1963).

[9] G. A. Russell and H.-D. Becker, *J. Am. Chem. Soc.*, **85**, 3406 (1963).

[10] (a) E. Fromm, *Ber.*, **41**, 3397 (1908); E. Fromm and F. Erfurt, *ibid.*, **42**, 3823 (1909); (b) see also, C. M. Suter, "Organic Chemistry of Sulfur," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 688.

[11] All melting points were determined using a Fisher-Johns apparatus and are uncorrected. Integrated n.m.r. and infrared spectra consistent with the proposed structures were obtained for all new compounds.

[12] E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **84**, 866 (1962).

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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