6.70 (s, 2 H); mass spectrum, *m/e* 212 (M^+, 80).

Anal. Calcd for $C_{16}H_{20}$: C, 90.51; H, 9.49. Found: C, 90.00; H, 9.50.

Acknowledgment. We acknowledge financial support from the Deutsche Forschungsgemeinschaft as well as the Fonds der Chemischen Industrie. Work at Princeton was supported by the National Science Foundation through Grants CHE-77-10025 and CHE-77-24625.

Registry No. 6, 70080-30-7; **7**, 72610-89-0; **15**, 72610-67-4; **17**, 70080-31-8; **18**, 70087-70-6; **19**, 70080-39-6; **20**, 70244-22-3; **21**, 70080-37-4; **22a**, 72610-68-5; **22b**, 70080-33-0; **22c**, isomer 1, 72610-69-6; **22c**, isomer 2, 72657-60-4; **22d**, isomer 1, 72657-61-5; **22d**, isomer 2, 72657-62-6; *cis*-**22e**, 72610-70-9; *trans*-**22e**, 72610-71-0; *cis*-**22f**, 72610-72-1; *trans*-**22f**, 72610-73-2; *cis*-**22g**, 72610-74-3; *trans*-**22g**, 72610-75-4; *cis*-**22h**, 72610-76-5; *trans*-**22h**, 72610-77-6; *cis*-**22i**, 72610-78-7; *trans*-**22i**, 72610-79-8; **23**, 70080-38-5; **25a**, 72610-80-1; **25a′**, 72610-81-2; **25b**, 72610-82-3; **25b′**, 72610-83-4; **25c**, 72610-84-5; benzenediazoniumcarboxylate hydrochloride, 4661-46-5; anthranilic acid, 118-92-3; 1,1-dichlorobenzocyclobutene, 68913-13-3; 1,1-dichloroethylene, 75-35-4; benzocyclobutenone, 3469-06-5; benzocyclobutenone tosylhydrazone, 72610-85-6; benzocyclobutenone azine, 19164-69-3; benzocyclobutenone tosylhydrazone sodium salt, 72610-86-7; (*E*)-benzocyclobutenone dimer, 72610-87-8; (*Z*)-benzocyclobutenone dimer, 72610-88-9; 4,6-dimethylbenzocyclobutenone tosylhydrazone, 20643-23-6; dicyclopropylethylene, 822-93-5; 4,6-dimethylbenzocyclobutenone azine, 20643-22-5; 1,1-dichloro-4,6-dimethylbenzocyclobutene, 6590-38-1; cyclohexene, 110-83-8; 2-methyl-2-butene, 513-35-9; *cis*-4-methyl-2-pentene, 691-38-3; *trans*-4-methyl-2-pentene, 674-76-0; *m*-bromostyrene, 2039-86-3; *p*-chlorostyrene, 1073-67-2; styrene, 100-42-5; *p*-methylstyrene, 622-97-9; *p*-methoxystyrene, 637-69-4.

Preparation and Acetolysis of β-[7-[π-(Norbornadienyl)iron tricarbonyl]]ethyl Methanesulfonate. Inhibition of Delocalization by Complexation[1]

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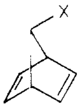
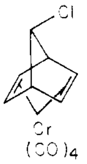
Received July 24, 1979

In the absence of oxygen the acetolysis of β-[7-[π-(norbornadienyl)iron tricarbonyl]]ethyl methanesulfonate at 98 °C is about 5×10^{-5} times as rapid as that of β-(7-norbornadienyl)ethyl methanesulfonate and produces β-[7-[π-(norbornadienyl)iron tricarbonyl]]ethyl acetate as the only product. π complexation with tricarbonyliron completely inhibits double bond participation in both the rate- and product-determining steps of the reaction.

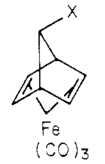
We have long been interested in π-electron delocalization during solvolysis[2] and in the possible inhibition of such delocalization by π complexation to a transition metal.[3] In this latter connection we once attempted to compare the relative solvolysis rates of 7-chloronorbornadiene (**1**-Cl) and its tetracarbonylchromium π complex **2**-Cl[4] but found that in 80% ethanol the complex dissociates about as rapidly as it solvolyzes.[5] The first clear demonstration of such inhibition was provided by Hunt, Lillya, and Rausch, who estimate that 7-[π-(norbornadienyl)iron tricarbonyl] tosylate (**3**-OTs) hydrolyzes in 80% acetone at least 10^6 times more slowly than would 7-norbornadienyl tosylate (**1**-OTs) itself.[6]



1-X, X = Cl, OTs, OMs

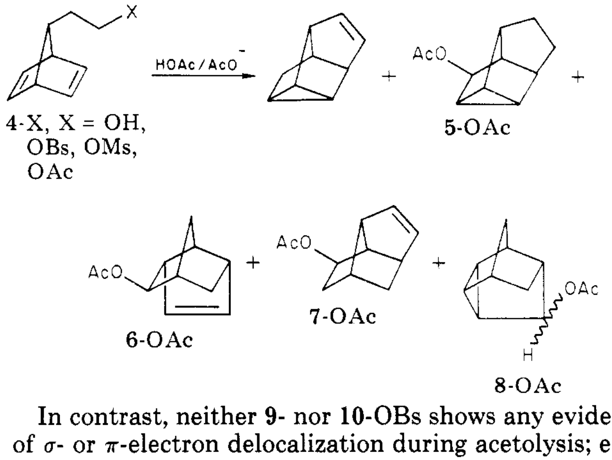


2-Cl



3-X, X = OTs, H

More recently we observed that β-(7-norbornadienyl)ethyl brosylate (**4**-OBs) acetolyzes with extensive π-electron delocalization in both the rate- and product-determining steps.[7] At 98 °C it is about $10^{4.5}$ times as reactive as either β-(*anti*-7-norbornenyl)ethyl or β-(7-norbornyl)ethyl brosylate, **9**- and **10**-OBs, respectively.[2c] It produces no products of direct solvolytic displacement, viz., **4**-OAc; only tri- and tetracyclic products, eq 1, are formed.[7]



4-X, X = OH, OBs, OMs, OAc

5-OAc

6-OAc

7-OAc

8-OAc

(1)

In contrast, neither **9**- nor **10**-OBs shows any evidence of σ- or π-electron delocalization during acetolysis; each yields only the unrearranged acetate; cf. eq 2 and 3.[2c]

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(1) Abstracted from the Ph.D. thesis of T.L.M., University of South Carolina, 1975.

(2) (a) R. S. Bly and R. T. Swindell, *J. Org. Chem.*, **30**, 10 (1965); (b) R. K. Bly and R. S. Bly, *ibid.*, **31**, 1577 (1966); (c) R. S. Bly, R. K. Bly, A. O. Bedenbaugh, and O. R. Vail, *J. Am. Chem. Soc.*, **89**, 880 (1967); (d) R. S. Bly, A. R. Ballentine, and S. U. Koock, *ibid.*, **89**, 6993 (1967); (e) R. S. Bly and S. U. Koock, *ibid.*, **91**, 3292, 3299 (1969); (f) R. S. Bly, R. K. Bly, J. B. Hamilton, and S. P. Jindal, *ibid.*, **99**, 204 (1977); (g) R. S. Bly, R. K. Bly, J. B. Hamilton, J. N. C. Hsu, and P. K. Lillis, *ibid.*, **99**, 216 (1977).

(3) (a) R. S. Bly and R. L. Veazey, *J. Am. Chem. Soc.*, **91**, 4221 (1969); (b) R. S. Bly, R. C. Strickland, R. T. Swindell, and R. L. Veazey, *ibid.*, **92**, 3722 (1970); (c) R. S. Bly, R. A. Mateer, K. K. Tse, and R. L. Veazey, *J. Org. Chem.*, **38**, 1518 (1973); (d) R. S. Bly and T. L. Maier, *ibid.*, **43**, 614 (1978).

(4) (a) R. S. Bly and M. S. Kablaoui, Abstracts, 19th Southeastern Regional Meeting of the American Chemical Society, Atlanta, GA, Nov 1–3, 1967, No. 312; (b) Abstracted from the Ph.D. thesis of M.S.K., University of South Carolina, 1967.

(5) D. F. Hunt, C. P. Lillya, and M. D. Rausch, *Inorg. Chem.*, **8**, 446 (1969); cf. footnote 16.

(6) D. F. Hunt, C. P. Lillya, and M. D. Rausch, *J. Am. Chem. Soc.*, **90**, 2561 (1968).

(7) R. S. Bly, R. K. Bly, G. B. Konizer, and S. P. Jindal, *J. Am. Chem. Soc.*, **98**, 2953 (1976).

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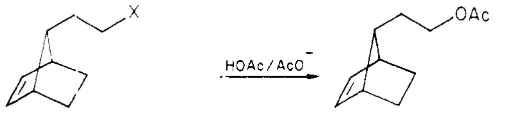
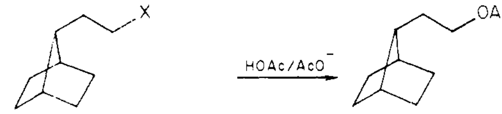


(2)

9-X, X = OBs, OMs, OAc 9-OAc



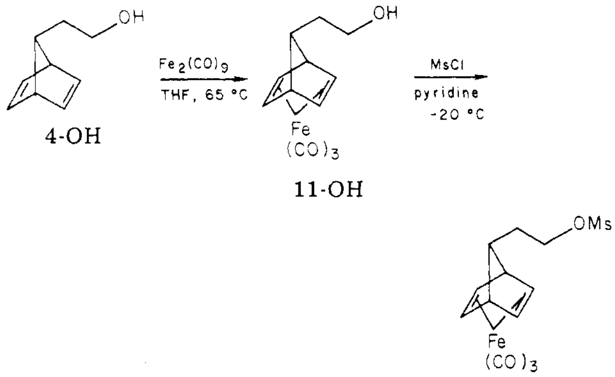
(3)

10-X, X = OBs, OMs, OAc 10-OAc

Feeling that these results could be used to assess the extent to which π complexation modifies π-electron delocalization in both rate- and product-determining steps, we have prepared and investigated the acetolysis of β-[7-[π-(norbornadienyl)iron tricarbonyl]]ethyl methanesulfonate (11-OMs).

Results

The starting material was prepared in 33% overall yield from the known[7] β-(7-norbornadienyl)ethanol (4-OH) as outlined in eq 4. Iron pentacarbonyl can also be used to



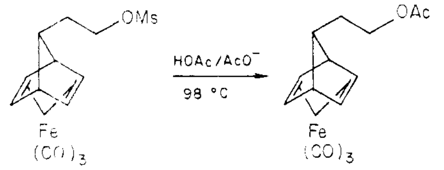
4-OH 11-OH

(4)

11-OMs

prepare the complex, but diiron noncarbonyl in THF appears to be superior.[8] An attempt to prepare 11-OH by complexing methyl α-(7-norbornadienyl)acetate and reducing the complex with lithium aluminum hydride was unsatisfactory in our hands because of a poor yield in the second step.

The solvolysis of 11-OMs in oxygen-free, buffered acetic acid at 98 °C appears to yield only the complexed acetate 11-OAc (eq 5). Thin-layer chromatography of incompletely solvolyzed 11-OMs in deoxygenated acetic acid reveals the presence of only two π complexes: unreacted starting material and unrearranged acetate, 11-OAc. After 32 h at 98 °C, 0.13 mmol (23%) of 11-OMs and 0.24 mmol (43%) of 11-OAc can be isolated from a 0.023 M solution originally containing 0.56 mmol of the complexed methanesulfonate. No noncomplexed materials were detected, though some decomplexation probably occurred during the workup as air was not rigorously excluded at this point.[6,9] Any volatile products produced by oxidative decomplexation—polycyclic hydrocarbons, acetates, or alcohols from 11-OMs (eq 1), bicyclic acetate 4-OAc from 11-OAc—would probably have been lost during the extraction and concentration steps. When the products from titrated rate samples were analyzed, some 11-OH was also detected. Apparently, it is formed by hydrolysis of 11-OAc during the workup; cf. Experimental Section.



(5)

11-OMs 11-OAc

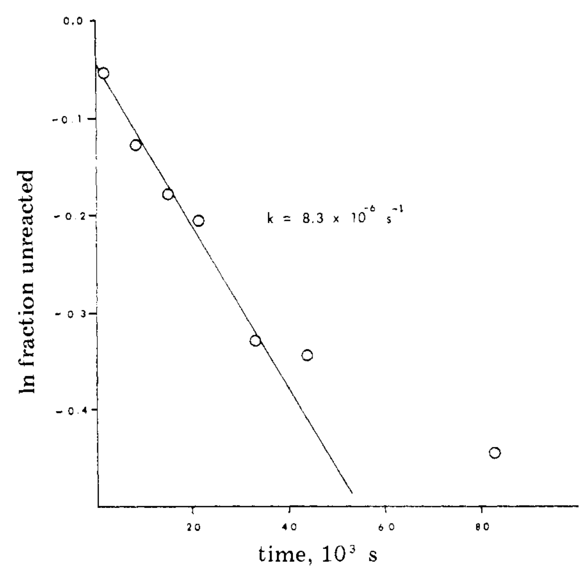


Figure 1. First-order plot for the acetolysis of 11-OMs at 97.8 °C.

Several attempts were made to measure the acetolysis rate of 11-OMs at temperatures ranging from 50 to 85 °C. In all cases individual samples retained their original color throughout the reaction and showed no evidence of decomplexation or decomposition,[6] yet the intercepts of titrimetric first-order plots at zero time do not go through the origin but vary widely from run to run. The plots themselves are nonlinear, the rate constant appearing to decrease with time.[6] The titrimetric infinity titers after 9 half-lives show considerably less than 100% reaction.[6] The rate constants of duplicate runs vary by as much as 300% whether they are calculated from the slope of the least-squares line through the first few percent of reaction, by the Guggenheim method,[10] or by correction of the experimental infinity titer to give a linear plot.[3d,11] We attribute these problems to the difficulty of obtaining and storing pure samples of 11-OMs uncontaminated with 11-OH and 4-OMs and to varying amounts of adventitious oxygen in the "degassed" individual rate runs and/or samples. The effect of oxygen is to cause oxidative decomplexation[3,6,9] which apparently increases the solvolysis rate in the early stages of the reaction[6] yet causes it to appear slower in the latter stages by producing acetate ion,[3d] the disappearance of which is monitored titrimetrically to assess the acetolysis rate.

In view of the uncertainties associated with our attempts to determine the acetolysis constant of 11-OMs titrimetrically, we decided to estimate the maximum and minimum values from our product study at 98 °C, vide supra. Assuming that the isolated complexes 11-OMs and 11-OAc are pure and solvent free, the maximum acetolysis constant under these conditions cannot be greater than $[\ln (1/0.23)]/(1.15 \times 10^5)$ or less than $[\ln [1/(1 - 0.43)]]/(1.15 \times 10^5)$, i.e., $1.3 \times 10^{-5}\ s^{-1} \geq k \geq 4.9 \times 10^{-6}\ s^{-1}$.

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[8] F. A. Cotton and J. M. Troup, *J. Am. Chem. Soc.*, **96**, 3438 (1974).

[9] Cf. ref 6, footnote 38.

[10] E. A. Guggenheim, *Philos. Mag.*, **2**, 538 (1926); cf. E. S. Swinbourne, "Analysis of Kinetic Data", Thomas Nelson, London, 1971, pp 79–83, and references cited therein.

[11] Cf. K. B. Wiberg, "Computer Programming for Chemists", W. A. Benjamin, New York, 1965, pp 170–6.

Table I. Apparent Acetolysis Constants at 97.8 °C

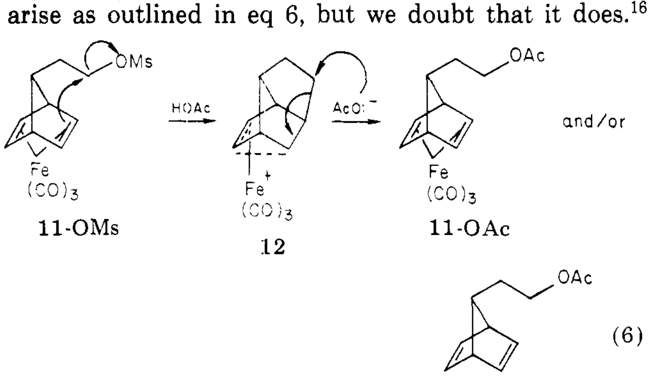
compd	k, s^{-1}	k_{rel}
4-OMs[a,7]	1.8×10^{-1}	$\sim 2 \times 10^4$
9-OMs[b,2c]	1.2×10^{-5}	~2
10-OMs[b,2c]	1.2×10^{-5}	~2
11-OMs[15]	$\sim 8 \times 10^{-6}$	1

[a] Estimated from the brosylate by assuming k(OMs) = k(OBs)/2.9.[13] [b] Estimated from the brosylate by assuming k(OMs) = k(OBs)/1.4.[14]

In an effort to confirm this estimate kinetically we carried out a single kinetic determination at 97.8 °C, taking great care to exclude oxygen and to use a freshly prepared, crystalline sample of **11**-OMs. Titrating this run potentiometrically,[3d] which permits the sample handling and analysis to be carried out under nitrogen with greater ease and avoids end-point errors due to the colored solutions, we obtained the first-order plot shown in Figure 1. The rate constant derived from the least-squares line through the first five points (28% reaction) is 8.3×10^{-6} s^{-1} with a coefficient of determination[12] equal to 0.98 and an intercept at t = 0 of ln 0.95.

Discussion

The π-electron delocalization during acetolysis is apparently completely inhibited in **11**-OMs. At 97.8 °C the π complex is $(1.4\text{–}3.7) \times 10^4$ less reactive than **4**-OMs, Table I. While **4**-OBs produces no bicyclic acetate (**4**-OAc) under these conditions (cf. eq 1), **11**-OMs apparently produces no tri- or tetracyclic products (eq 5). It is conceptually possible that unrearranged bicyclic acetate could arise as outlined in eq 6, but we doubt that it does.[16]

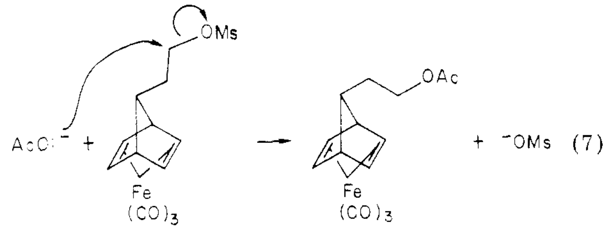


11-OMs **12** **11**-OAc

(6)

4-OAc

Comparison of the acetolysis rate of **11**-OMs with that of **9**- and of **10**-OMs (Table I), which also produce unrearranged acetate (cf. eq 2 and 3), suggests that **11**-OAc is formed by direct solvolytic displacement (eq 7). Apparently, π complexation to tricarbonyliron depletes the electron density of the syn double bond of **11**-OMs to the point that internal nucleophilic participation is no longer competitive with external displacement by the solvent.



(7)

11-OMs **11**-OAc

Experimental Section[17]

β-[7-[π-(Norbornadienyl)iron tricarbonyl]]ethanol (11-OH). A solution of 0.80 g (5.9 mmol) of β-(7-norbornadienyl)ethanol (**4**-OH)[7] and 1.5 g (4.1 mmol) of nonacarbonyldiiron (Ventron) in anhydrous tetrahydrofuran was heated at reflux for 12 h. Chromatography on alumina (Alcoa K-20) using 2:1 hexane–tetrahydrofuran followed by rotary evaporation at aspirator pressure produced 0.78 g (2.8 mmol, 48%) of **2**-OH as a dark brown oil: IR ($CHCl_3$) 3570 and 3430 (OH), 3060, 3000, 2970, 2940, and 2875 (CH), 2045 and 1975 (C≡O), 1306, 1210, and 1040 cm^{-1} (C—O); NMR ($CDCl_3$) δ 3.46 (t, J = 6.5 Hz, 2 H, $CH_2\mathbf{CH_2}OH$), 3.16 (s, 4 H, π =CH) overlapping a multiplet at 3.04 (2 H, **>CH**), ~1.88 (perturbed t, 2 H, $>CHCH_2$ and CH_2OH), 1.17 (q, $J \approx 3$ Hz, 2 H, $>CH\mathbf{CH_2}CH_2O$); mass spectrum, m/e $M^{+\cdot}$ = 276.

Anal. Calcd for $C_{12}H_{12}FeO_4$: C, 52.21; H, 4.38; Fe, 20.23; O, 23.18. Found: C, 51.90; H, 4.44.

β-[7-[π-(Norbornadienyl)iron tricarbonyl]]ethyl Methanesulfonate (11-OMs). To a cold solution of 0.55 g (2.0 mmol) of **11**-OH in 25 mL of anhydrous, distilled pyridine was added 0.60 g (5.2 mmol) of methanesulfonyl chloride. A precipitate was evident after 8 h at −20 °C. TLC on silica gel (benzene eluent) of the yellow-brown supernatant solution indicated the absence of starting material and the presence of a single product (R_f 0.37). The solvent was removed by evaporation, and the resulting yellow-brown solid was chromatographed under nitrogen on a 1.0 × 10 cm column of alumina (Woelm neutral grade, activity II) with benzene as eluent. Evaporation of the single yellow band yielded 0.48 g (1.4 mmol, 68%) of a yellow-brown oil which subsequently solidified to a microcrystalline solid: mp 37–39 °C; IR ($CHCl_3$) 3015 and 2970 (CH), 2045 and 1980 (C≡O), 1375, 1360, and 1169 cm^{-1} (SO_2); NMR ($CDCl_3$) δ 3.98 (t, $J \approx 6$ Hz, 2 H, $CH_2\mathbf{CH_2}O$), 3.12 (s, 4 H, π =CH) overlapping a multiplet at ~2.95 (2 H, >CH) overlapping a singlet at 2.90 (3 H, SO_2CH_3), 1.64 (perturbed q, $J \approx 6$ Hz, 3 H, $>CH\mathbf{CH_2}CH_2O$).

Anal. Calcd for $C_{13}H_{14}FeO_6S$: C, 44.09; H, 3.99; Fe, 15.77; O, 27.11; S, 9.05. Found: C, 44.30; H, 4.15; S, 8.94.

Acetolysis of β-[7-[π-(Norbornadienyl)iron tricarbonyl]]ethyl Methanesulfonate (11-OMs). Method A. A 25-mL sample of a 0.023 M solution of **11**-OMs (0.200 g, 0.565 mmol) in deoxygenated acetic acid containing 0.026 M sodium acetate was heated under nitrogen in a sealed tube for 32 h at 97.8 °C. The contents of the tube, still having the original yellow

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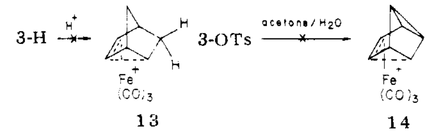
[12] H. L. Alder and E. B. Roessler, "Introduction to Probability and Statistics", W. H. Freeman, San Francisco, 1964, p 172.

[13] The titrimetric acetolysis constant of neophyl brosylate at 98 °C [R. Heck and S. Winstein, *J. Am. Chem. Soc.*, **79**, 3432 (1957)] exceeds that of the methanesulfonate[3b] by 2.9 times.

[14] The titrimetric acetolysis constant of 3-phenyl-1-propyl brosylate at 98 °C [R. Heck and S. Winstein, *J. Am. Chem. Soc.*, **79**, 3105 (1957)] exceeds that of the methanesulfonate [unpublished work of T. G. Traylor and R. L. Veazey) by 1.4 times.

[15] Complexation of a conjugated or homoconjugated diene by tricarbonyliron has been shown to decrease net electron withdrawal by the double bonds [J. M. Landesburg and L. Katz, *J. Organomet. Chem.*, **43**, 175 (1972)]; thus **11**-OMs is expected to be slightly more reactive than **9**-OMs. In this case the effect would be small,[2c] certainly well within the uncertainty of our estimated rate constant.

[16] We note that Rausch et al. could find no evidence of the formation of cations similar to **12**, viz., **13** or **14**, either during the protonation of **3**-H [J. R. Falkowski, D. F. Hunt, C. P. Lillya, and M. D. Rausch, *J. Am. Chem. Soc.*, **89**, 6387 (1967)] or the hydrolysis of **3**-OTs.[6]



13 **14**

[17] Melting and boiling points are uncorrected. Microanalyses were performed by Bernhardt Mikroanalytisches Laboratorium, West Germany. Spectra were determined on a Perkin-Elmer grating infrared spectrometer, Model 337, a Varian A-60 NMR spectrometer using tetramethylsilane as an internal standard, and a Hitachi Perkin-Elmer RMU-6 single-focusing mass spectrometer. Vapor-phase gas chromatographic analyses were done on a Varian Model 1800 gas chromatograph equipped with 6 or 10 ft × 0.25 in. copper columns packed with 5–15% Carbowax 20-M on 60–90 mesh Chromosorb W, helium being used as a carrier gas at flow rates of ~100 mL/min. For analytical thin-layer chromatography Eastman Chromagram precoated silica gel sheets were used. Potentiometric titrations were accomplished on a Radiometer-Copenhagen system composed of an Autoburette Model ABU 1b, a Titrator Model TTT 1c, and a Titragraph Model SBR2C.

color, were cooled and poured over ~50 mL of ice–water. The resulting suspension was extracted with several 20-mL portions of ether until the aqueous layer was colorless. The ethereal extract was washed successively with water, 10% sodium carbonate, and water. The dried (Na_2SO_4) ethereal solution was filtered and concentrated to ~0.5 mL by rotary evaporation at aspirator pressure. TLC on silica gel (4:1 benzene–hexane) of the resulting dark yellow oil indicated the presence of two complexes, R_f's 0.30 and 0.43. Column chromatography on alumina (3 × 10 mm, Woelm neutral grade, activity II, benzene eluent) of the dark yellow solution showed two cleanly separated yellow bands.

The first band was eluted with benzene. Evaporation of the solvent produced 0.076 g of a yellow oil with an esterlike odor having the following spectral characteristics: IR (CCl_4) 3055, 2950, 2925, and 2865 (CH), 2045 and 1975 ($C\equiv O$), 1475 and 1380 ($>CH_2$), 1235 and 1040 cm^{-1} (C—O); NMR ($CDCl_3$) δ 3.90 (t, J = 6.0 Hz, 2 H, $CH_2C\mathbf{H}_2O$), 3.14 (s, 4 H, π =CH), 3.01 (m, 2 H, $\geqslant$CH), 2.01 (s, 3 H, CH_3), 1.61 (m, ~3 H, $>\mathbf{CH}C\mathbf{H}_2CH_2$); mass spectrum, m/e 318 ($M^{+\cdot}$).

Anal. Calcd for $C_{14}H_{14}FeO_5$: C, 52.86; H, 4.44; Fe, 17.56; O, 25.15. Found: C, 53.05; H, 4.49.

This material is β-[7-[π-(norbornadienyl)iron tricarbonyl]]ethyl acetate (**11-OAc**) and corresponds to 43% (0.24 mmol) of the total starting material.

The second band, which was washed from the column with 1:1 benzene–tetrahydrofuran and concentrated as before (rotary evaporation, aspirator pressure), gave 0.047 g (0.13 mmol) of yellow-brown oil identical in all respects with the starting material, **11-OMs**.

No other products could be detected in the acetolysis mixture by thin-layer chromatography either by examination of the plates visually or after exposure to iodine vapor or to concentrated sulfuric acid.

Since ~34 mol % of the initial material is unaccounted for in the above analysis, we examined the total product balance from some of the kinetic runs.

Method B. Individual acetolysis rate samples after titration with 0.02 M perchloric acid in acetic acid to a Crystal Violet end point were frozen until completion of the run, thawed, combined, diluted with ether, and washed with cold, 10% aqueous sodium bicarbonate until most of the blue color of the indicator had been removed. The faintly colored ethereal solution was dried over anhydrous sodium sulfate and analyzed by thin-layer chromatography (benzene eluent) for starting material and product(s).

Most runs showed evidence of unreacted, complexed methanesulfonate and two other complexed materials. No noncomplexed derivatives were observed when the plates were treated with iodine vapor or with concentrated sulfuric acid.

The ethereal solution was filtered through Celite and concentrated on a Rotovac at aspirator pressure, and the resulting blue-green solution was chromatographed on activity II, Woelm alumina suspended in hexane. Development with benzene followed by 1:1 benzene–tetrahydrofuran showed three yellow bands which were eluted sequentially, concentrated as before, pumped at 10^{-2} mm for several hours, and analyzed spectroscopically.

The first band was identical with the complexed acetate **11-OAc** isolated previously, the second band consisted of the unreacted starting material, **11-OMs**, and the third band was found to be complexed alcohol **11-OH** contaminated with a small amount of Crystal Violet.

When this analysis was carried out on an 85 °C rate run originally containing 0.0398 g (0.111 mmol) of **11-OMs**, the following compounds were recovered: 0.0123 g (0.039 mmol) of **11-OAc**, 0.0192 g (0.054 mmol) of **11-OMs**, and 0.0122 g (0.044 mmol) of **11-OH** contaminated with a trace of Crystal Violet.

In an effort to determine whether the complexed alcohol **11-OH** was a contaminant of the starting methanesulfonate, **11-OMs**, or whether it resulted from hydrolysis of the complexed acetate **11-OAc** during the workup, a duplicate kinetic run (i.e., from the same batch of **11-OMs**) was analyzed under anhydrous conditions in the following manner.

Method C. The samples were removed from an 85 °C bath prior to titration, opened, and combined under a nitrogen atmosphere, and the solvent was evaporated to dryness under vacuum in a Rotovac. The resulting brown solid was pumped on a vacuum line at 10^{-3}–10^{-4} mm for several hours. TLC analysis under nitrogen showed the presence of two complexed materials: **11-OMs** and **11-OAc**. No complexed alcohol **11-OH** was observed nor could any noncomplexed products be detected.

We conclude on the basis of the three methods of analysis described above that the acetolysis of **11-OMs** produces the acetate **11-OAc** as the only complexed product. The **11-OH** detected in some of the kinetic runs after titration apparently results from the hydrolysis of **11-OAc** under the conditions of the workup. While it is possible that a small amount of noncomplexed material could have been lost during the evaporation of the solvent (method A), we have seen no indication that any is actually produced during the acetolysis of **11-OMs**. We presently attribute the relatively poor product balance in method A to losses resulting from the relatively small size of the sample which was employed.

Kinetic Studies. Several attempts were made to determine the acetolysis constant of **11-OMs** at temperatures ranging from 50 to 85 °C. The solvent was degassed, the ampules were sealed, and the individual samples were titrated to a Crystal Violet end point as described previously.[2a] Unfortunately, the first-order plots of such runs were nonlinear, the apparent rate constant appearing to decrease, sometimes by as much as 100%, throughout the course of a run. Most of these first-order plots did not intersect the ordinate at 0.0, i.e., ln 1.0, when $t = 0$. When the same sample of **11-OMs** was used to prepare replicate runs on succeeding days, the intercept at $t = 0$ became more negative with each run. The slopes of such replicate runs varied by as much as 300%. In most cases the titrimetric infinity titer after ~9 half-lives was considerably less than 100% and seemed also to vary from run to run.

Reasoning that nonlinear first-order plots could result from impure starting material and/or oxidative decomplexation of starting material and/or product, we attempted to increase the reproducibility of replicate determinations by treating our data by the Guggenheim method, which does not require a prior knowledge of either the initial or the final concentration of reactant.[10] Plots of milliliters of titrant vs. time were made from which the fractions reacted at constant time intervals could be estimated. Reproducibility was not improved by this treatment. A final attempt to treat the data was made by increasing the infinity titer at 9 half-lives until the first-order plot became linear.[3d,11] Again, no improvement in the reproducibility of replicate runs was achieved.

To obtain the data shown in Figure 1, we degassed a freshly prepared sample of **11-OMs**, mp 37–39 °C, on a vacuum line, dissolved it in degassed solvent, and transferred the solution to stoppered ampules in a nitrogen-filled glovebag. Individual samples were titrated potentiometrically[3c] under nitrogen. The rate constant calculated for this run, 8.3×10^{-6} s^{-1}, represents the negative slope of the least-squares regression line drawn through the first five points (28% reaction). When all seven points are used (36% reaction) $k = 5 \times 10^{-6}$ from the least-squares regression line, 3×10^{-5} from the Guggenheim treatment, and 3×10^{-5} from the corrected infinity titer treatment. For reasons cited in the Results section we quote $\sim 8 \times 10^{-6}$ s^{-1} as the most likely value for the rate constant (cf. Table I).

Registry No. 11-OH, 72726-69-3; 11-OMs, 72726-70-6; 11-OAc, 72726-71-7; $Fe_2(CO)_9$, 15321-51-4.