

syringe. The solids were washed with cold cyclohexane. Benzene (20 ml) was added to the reaction flask and the mixture was stirred for several minutes. An aliquot was removed and centrifuged and analysis of the supernatant showed it to be 0.61 *N* in total base, 0.21 *M* in magnesium, and 0.19 *M* in rubidium.

F. Reaction of Cesium with Di-*sec*-butylmagnesium.—A weight of 1.0 g (0.0075 g-atom) of cesium in a vial was placed in a 100-ml three-neck round-bottom flask equipped with a reflux condenser and two rubber septum caps. The cesium was dispersed under cyclohexane in the usual manner and the dispersing cyclohexane was removed. The reaction flask was immersed in an ice bath, 16 ml (0.0077 mol) of 0.48 *M* di-*sec*-butylmagnesium in cyclohexane was added, and the mixture was stirred vigorously for 3 hr. The supernatant was removed and the solids were washed with two 10-ml portions of cold cyclohexane. To the solids was added 12 ml of dry benzene and the mixture was stirred for several minutes, after which the benzene was removed by syringe and centrifuged. The supernatant separated into an upper, mobile, orange phase and a lower, wine-red, viscous phase. The upper phase was analyzed and found to be 0.30 *N* in total

base, 0.13 *M* in magnesium, and 0.09 *M* in cesium. After all of the upper layer was removed, 8 ml of benzene was added to the remaining lower layer. The tube was shaken vigorously for several minutes and centrifuged once again. Phasing was observed again; however, the volume of the lower layer was decreased. Analysis of the upper layer showed it to be 0.24 *N* in total base, 0.10 *M* in magnesium, and 0.07 *M* in cesium. To the remaining two phases in the centrifuge tube was added 8 ml of diethyl ether and the tube was shaken by hand for a few minutes and centrifuged. No phasing was observed and the solution was found to be 0.61 *N* in total base, 0.23 *M* in magnesium, and 0.15 *M* in cesium.

Acknowledgment.—The authors gratefully acknowledge the financial support of the Lithium Corporation of America in the form of a research assistantship.

Registry No.—Di-*sec*-butylmagnesium, 17589-14-9; di-*tert*-butylmagnesium, 14627-81-7; di-*n*-butylmagnesium, 1191-47-5; *n*-butyl chloride, 109-69-3; magnesium, 7439-95-4.

Acid-Catalyzed Reaction of Acetylferrocene with Triethyl Orthoformate

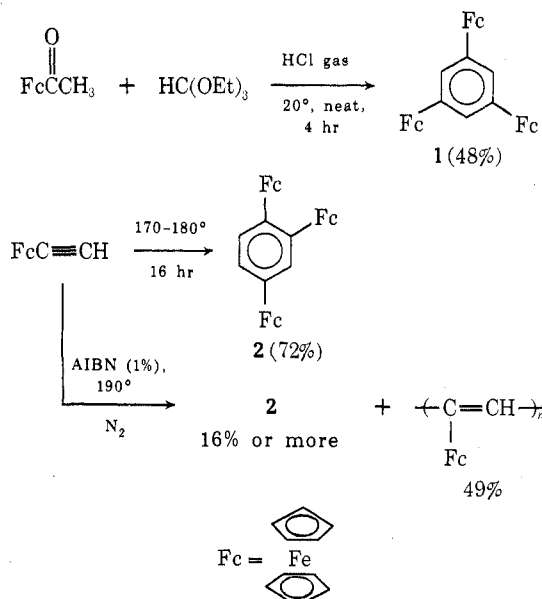
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The major product obtained when acetylferrocene was allowed to react with triethyl orthoformate and dry hydrochloric acid was 1,3-diferrocenylbut-2-en-1-one, and only a small amount of the cyclic trimer, 1,3,5-triferrocenylbenzene, was obtained. This result was found using either benzene or methylene chloride as the solvent or upon running the reaction without solvent. The reaction of acetylferrocene with triethyl orthoformate in ethanol, upon catalysis by *p*-toluenesulfonic acid, gave 2-ferrocenylpropene, ethyl ferrocenoate, polyvinylferrocene, a more complex polymer, and small amounts of 1,3,5-triferrocenylbenzene, 1,2,4-triferrocenylbenzene, and 1,3-diferrocenylbut-2-en-1-one. These results are compared with previous studies, and mechanisms are discussed.

Schlögl¹ reported that the reaction of acetylferrocene with a slight excess of triethyl orthoformate (1.2 equiv) in the presence of anhydrous hydrochloric acid at 20° for 4 hr gave a 48% isolated yield of 1,3,5-triferrocenylbenzene (1). The unsymmetrical 1,2,4 isomer, 2, was not formed and other products were



not discussed. The 1,2,4 isomer has been prepared by the thermal cyclotrimerization of ethynylferrocene,¹ and it is also a by-product in the free-radical polym-

erization of ethynylferrocene.^{2,3} Since ketones readily give ketals in the presence of triethyl orthoformate and catalytic amounts of acids,⁴ the formation of 1 reported by Schlögl was presumed to proceed *via* an elimination product of the diethyl ketal of acetylferrocene. To our surprise, attempts to generate 1 by Schlögl's method resulted in the isolation of large quantities of 1,3-diferrocenylbut-2-en-1-one (3), and only small amounts of the cyclotrimer 1. Thus, we studied this reaction under several different conditions and found that the use of *p*-toluenesulfonic acid led to a complex mixture of products, including 2-ferrocenylpropene (one carbon addition) and ethylferrocenoate (one carbon removed). Increased yields of cyclotrimer 1 can be obtained at very high gaseous HCl rates of bubbling into the reaction.

Results and Discussion

Acetylferrocene was allowed to react at 20° with triethyl orthoformate and dry HCl gas (1) in dry benzene, (2) in dry methylene chloride, and (3) without solvent (Schlögl's conditions). In each case the major product was dimer 3, and only small yields of symmetrical cyclotrimer 1 were observed. None of the unsymmetrical trimer 2 was detected. The yields of

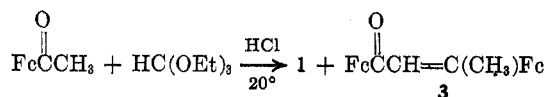
(2) C. Simionescu, T. Lixandru, J. Mazilu, and L. Tataru, *Makromol. Chem.*, **147**, 69 (1971).

(3) C. U. Pittman, Jr., and Y. Sasaki, unpublished results using AIBN as the initiator.

(4) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Wiley, New York, N. Y., 1967, p 1206.

(1) K. Schlögl and H. Soukup, *Monatsh. Chem.*, **99**, 927 (1968).

3 varied from 62 to 81%, while **1** was not obtained in excess of 12.1%. This is only one fourth that previ-



ously reported.¹ Representative results are summarized in Table I. The studies conducted during the

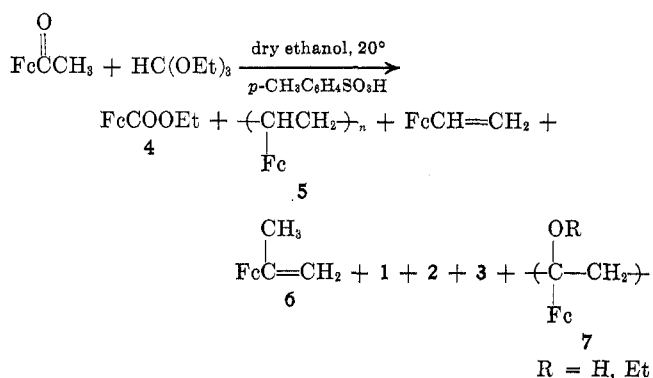
TABLE I
REACTION OF ACETYLFERROCENE AND TRIETHYL
ORTHOFORMATE WITH HCl AT 20°

Solvent	Acetylferrocene ^a reacted, mmol	Time, hr	1,3,5-Triferrocenyl- benzene ^b		1,3-Diferrocenylbut- 2-en-1-one ^b	
			Mmol	Yield, %	Mmol	Yield, %
C ₆ H ₆	17.5	4	0.477	8.2	7.06	80.5
CH ₂ Cl ₂	16.7	4	0.492	8.8	6.60	79.0
None	18.7	21	0.754	12.1	5.82	62.0
None ^c	18.7	22	1.89	29.9	4.42	47.1

^a Amount charged to reactor was 21.9 mmol of acetylferrocene and 23.6 mmol of triethyl orthoformate in every case. ^b Yields are based on the amount of acetylferrocene that reacted (some acetylferrocene was recovered in each reaction). ^c In this experiment the HCl was added by bubbling so fast that the reactants were vigorously sprayed throughout the reaction vessel.

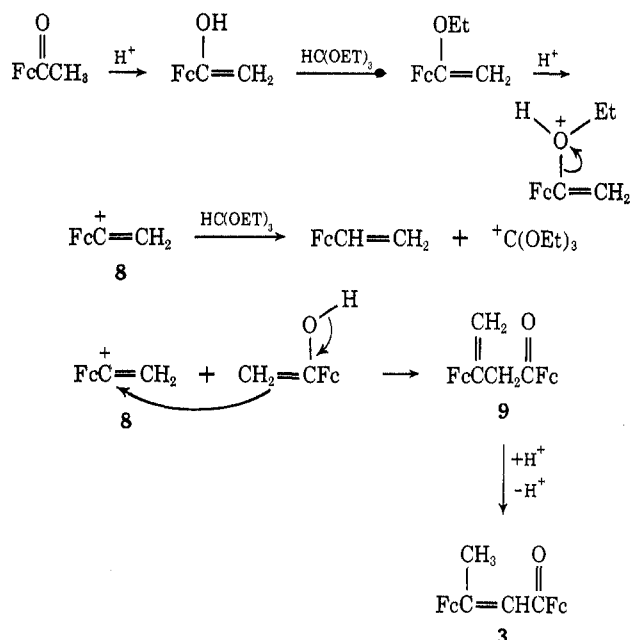
course of the reaction gave no evidence for an intermediate buildup of **1** at reactions times between 1 and 20 hr.

The reaction was far more complicated when catalytic amounts of *p*-toluenesulfonic acid in ethanol were used in place of anhydrous HCl. The major products were ethyl ferrocenoate (**4**, 45%), low molecular weight (\bar{M}_n 1800) polyvinylferrocene (**5**, 15%), and 2-ferrocenylpropene (**6**, 8%). Other products included both cyclotrimers **1** and **2** (4% total), dimeric ketone **3** (5-6%), a polymer, **7**, similar to polyvinylferrocene but

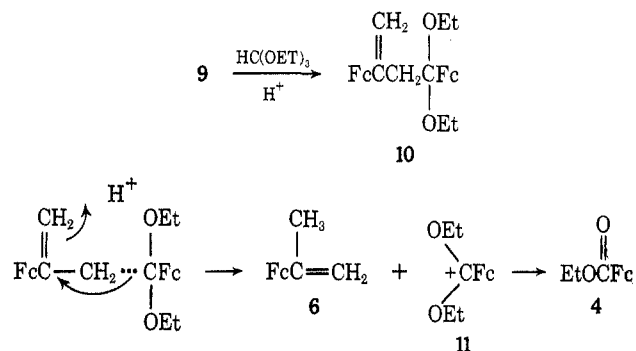


containing many polar groups such as OH moieties (6%), and unreacted acetylferrocene. Traces of vinylferrocene were recovered in some runs. Despite this complexity, the results were reproducible. It is quite likely that the unexpected products (particularly **4** and **6**) result from an intermediate cationic species rendered especially stable by an adjacent ferrocene unit, since analogous products are not found with aliphatic or phenyl ketones.

Two mechanisms are readily envisioned to account for the production of dimer **3** in all the reactions. The first involves an α -ferrocenylvinyl cation intermediate, **8**, which could readily react with the enol form of acetylferrocene to give β,γ -unsaturated ketone **9** which, in turn, would readily isomerize to **3** in the presence of



acid. The involvement of **9** is attractive because the production of both **6** and **4** from its diethyl acetal, **10**, can be explained by the fragmentation of **10** to give **6** and the stable ferrocenyldiethoxy carbonium ion, **11**,



which would hydrolyze to **4**. Fragmentation of **10** would lead, initially, to equal amounts of **6** and **4**, but some incorporation of **6** into the polymeric products could be occurring.

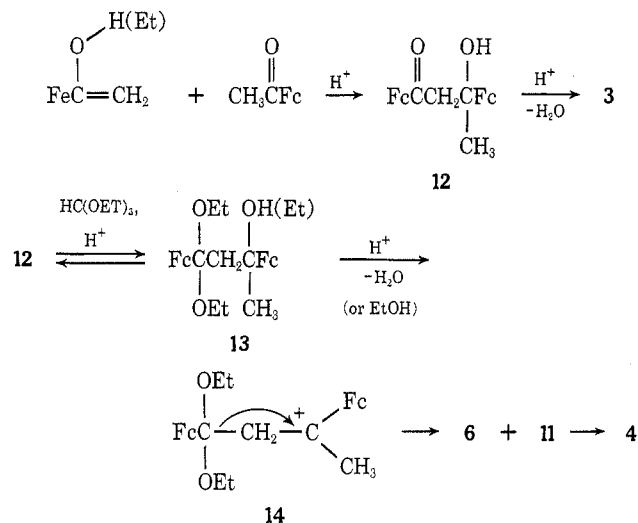
Vinyl cation **8** could also lead to vinylferrocene by hydride transfer from triethyl orthoformate. In the acidic media, polyvinylferrocene would arise by cationic polymerization where proton, $\text{C}^+(\text{OEt})_3$, etc., could initiate polymerization. All cationic polymerizations of vinylferrocene previously studied have generated only low molecular weight polymers similar to those found in this study.⁵

Control experiments demonstrated that α,β -unsaturated ketone **3** could not give rise to **4** or **6** under the conditions of the *p*-toluenesulfonic acid reaction. Thus, if **9** (via **10**) is the correct route to **4** and **6**, no kinetically important quantity of **9** can be generated in equilibrium from the more stable isomer **3**.

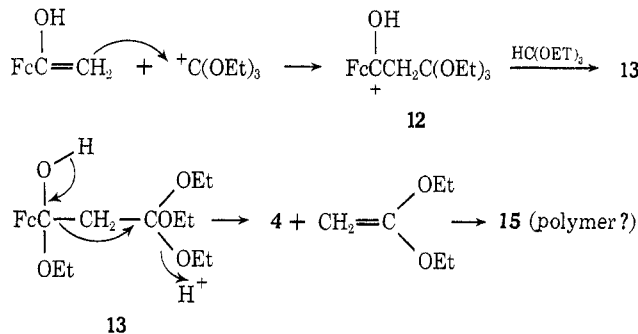
The second mechanism readily envisioned for the production of **3** is the condensation of protonated acetylferrocene with its enol form, followed by dehydration. This route also provides a potential path to **4** and **6** if 1,3-diferrocenyl-3-hydroxybutan-1-one (**12**) can be converted to its diethyl acetal, **13**, in com-

(5) C. Aso, T. Kunitake, and T. Nakashima, *Makromol. Chem.*, **124**, 232 (1969).

petition with dehydration. In acid, 13 could lose H₂O (EtOH) generating cation 14, which would give 6 and ultimately 4.



An alternate pathway to 4 involves the addition of the triethoxycarbonium ion to the enol form of acetylferrocene followed by EtO⁻ transfer to cation 12 and subsequent elimination of ethanol and 1,1-diethoxyethylene from 13.



The incorporation of 1,1'-diethoxyethylene into a polymeric species is possible and would account for a portion of polar polymer 7.

A choice between these general routes is not yet possible. However, the general bias against vinyl cations probably cannot be invoked here based on the marked ability of ferrocene to stabilize adjacent cation sites⁶⁻⁹ and on recent observations showing that many vinyl cations may be far more easily generated than had previously been recognized.¹⁰ It is clear that the cyclotrimerization of acetylferrocene using triethyl orthoformate and acid is a more complex reaction than was previously thought. The ability of ferrocene to stabilize adjacent positive charge plays a major role in this behavior. Finally, if higher yields of cyclotrimer 1 are desired in neat reactions (Schlogl's method¹), the HCl addition rate should be exceedingly rapid.

Experimental Section

Melting points were not corrected. Infrared spectra were obtained on a Beckman IR-33 spectrometer; nmr spectra were

- (6) E. A. Hill and R. Wiesner, *J. Amer. Chem. Soc.*, **91**, 509 (1969).
 (7) T. G. Traylor and T. C. Ware, *J. Amer. Chem. Soc.*, **89**, 2304 (1967).
 (8) M. Cais, *Organometal. Chem. Rev.*, **1**, 435 (1966).
 (9) C. U. Pittman, Jr., *Tetrahedron Lett.*, **No. 37**, 3619 (1967).
 (10) K. Yates, G. H. Schmid, T. W. Regulski, D. G. Garratt, H. W. Leung, and R. McDonald, *J. Amer. Chem. Soc.*, **95**, 160 (1973).

measured on a Hitachi Perkin-Elmer R-20 spectrometer; mass spectra were obtained using a Consolidated Electronics Corp. Model 31-104 mass spectrometer; gel permeation chromatograms were obtained on a Waters Associates GPC Model 301 equipped with 16 ft of styragel columns calibrated *vs.* polystyrene standards. The Universal calibration technique was employed.

Materials.—Acetylferrocene was recrystallized from octane, mp 85–86° (lit.¹¹ mp 85–86°). Alumina used for column chromatography was alumina F-20 (Alcoa). The studies employed silica gel PF-254 (E. Merck). Anhydrous hydrochloric acid (Matheson Co.) was used directly from the tank. Petroleum ether used in the chromatographic separations was a 30–60° cut.

Reaction of Acetylferrocene with Triethyl Orthoformate in Benzene Catalyzed by Hydrochloric Acid.—Acetylferrocene (5.0 g, 21.9 mmol) and triethyl orthoformate (3.5 g, 23.6 mmol) were dissolved in dry benzene (100 ml). HCl gas was bubbled from a tank into the stirred solution for 3 hr at 20°. The resulting dark green solution was stirred for an additional 1 hr and then benzene (300 ml) was added. The solution was washed with water (500 ml) and aqueous NaHCO₃ (5%, 500 ml) and then dried (anhydrous MgSO₄). After solvent was removed *in vacuo*, the resulting red oil was chromatographed on 150 g of alumina. The products are listed below in the order of their elution. Elution with 1:1 benzene-petroleum ether afforded 300 mg of 1,3,5-triferrocenylbenzene (1), which was recrystallized from cyclohexane-methylene chloride: mp 264–265° (lit.¹ mp 265–266°); nmr (CS₂) δ 3.98 (s, 5 H), 4.25 (m, 2 H), 4.56 (m, 2 H), 7.30 (s, 1 H). Further elution with 2:1 benzene-petroleum ether afforded 3.1 g of α,β-unsaturated ketone 3, which was recrystallized from hexane: mp 121–122° (lit.¹² mp 118–120°); ir (KBr) 1635 (s), 1585 cm⁻¹ (s); nmr (CS₂) δ 2.49 (d, *J* = 1 Hz, 3 H), 4.09 (s, 10 H), 4.35 (m, 4 H), 4.51 (m, 2 H), 4.67 (m, 2 H), 6.62 (d, *J* = 1 Hz, 1 H); mass spectrum (70 eV) *m/e* (assignment, rel intensity) 438 (M⁺, 7.6), 373 (M⁺ - C₂H₆, 14), 253 (M⁺ - C₁₀H₈Fe, 1.9), 219 [M⁺ - C₁₀H₈FeC(CH₃)=CH-, 4.8], 185 (C₁₀H₈⁺, 2.7), 56 (Fe⁺, 100).

Further elution with benzene afforded 1.0 g of acetylferrocene. The column contained a small quantity of brown residue at the top. This was not further studied.

Reaction of Acetylferrocene with Triethyl Orthoformate in Methylene Chloride Catalyzed by Hydrogen Chloride.—Acetylferrocene (5.0 g, 21.9 mmol) and triethyl orthoformate (3.5 g, 23.6 mmol) were dissolved in dry methylene chloride (100 ml). HCl gas was bubbled into the stirred solution for 3 hr at 20°. The reaction mixture was treated exactly as the product from the benzene reaction mentioned above.

The products obtained were 310 mg of 1, 2.9 g of 3, and 1.2 g of unreacted acetylferrocene.

Reaction of Acetylferrocene with Triethyl Orthoformate, without Solvent, Catalyzed by Hydrogen Chloride.—Hydrochloric acid (gas) was bubbled into a mixture of acetylferrocene (5.0 g, 21.9 mmol) and triethyl orthoformate (3.5 g, 23.6 mmol) at 20° for 3 hr. The reaction mixture was stirred for an additional 18 hr, and then worked up exactly as described for the reaction in benzene.

The products obtained were 481 mg of 1, 2.55 g of 3, and 700 mg of unreacted acetylferrocene.

Reaction of Acetylferrocene with Triethyl Orthoformate in Ethanol Catalyzed by *p*-Toluenesulfonic Acid.—Acetylferrocene (5.0 g, 21.9 mmol), triethyl orthoformate (4.0 g, 27.0 mmol), and *p*-toluenesulfonic acid monohydrate (200 mg, 1.05 mmol) were dissolved in 50 ml of dry ethanol (distilled from magnesium ethoxide). At room temperature, the stirred reaction mixture turned a deep green color within 15 min. The reaction mixture was refluxed for 4 hr. Then diethyl ether (100 ml) was added to the reaction mixture, and it was filtered. A brownish solid (95 mg) was collected on the filter and this material was not identified.

The remaining product was collected by stripping the solvent to give a brown solid. Tlc (benzene) indicated the presence of at least seven components (*R_f* values of 0.6, 0.3, 0.25, 0.17, 0.1, 0.08, and 0.0). This reaction mixture was chromatographed on 200 g of alumina. The products obtained are listed in the order of their elution. Elution with 2% benzene in petroleum ether gave 300 mg of 2-ferrocenylpropene (6), which was purified by recrystallization from methanol-water: mp 62–63° (lit.¹³ mp

- (11) V. Weinmayr, *J. Amer. Chem. Soc.*, **77**, 3009 (1955).
 (12) P. L. Pauson and W. E. Watts, *J. Chem. Soc.*, 3880 (1962).
 (13) A. F. Ellis, *Diss. Abstr.*, **24**, 510 (1963).

63–65°; ir (KBr) 1628 cm^{-1} (s); nmr (CCl_4) δ 2.01 (s, 3 H), 3.97–4.26 (m, 9 H), 4.53 (s, 1 H), 5.02 (s, 1 H).

Immediately after this fraction, 560 mg of polyvinylferrocene (5) was eluted: mol wt (gpc) \sim 1800; ir identical with that of an authentic sample obtained by radical polymerization of vinylferrocene.^{14,15}

Further elution with 1:3 benzene–petroleum ether afforded 150 mg of a mixture of the two isomers of triferrocenylbenzene, 1 and 2 (roughly in the same amount by nmr analysis).

Continued elution with 1:1 benzene–petroleum ether afforded 1.90 g of ethyl ferrocenoate (4), which was recrystallized from ethanol–water: mp 62–63° (lit. mp 61–62°,¹¹ 63–64°¹⁶); ir (KBr) 1700 cm^{-1} (s); mass spectrum (70 eV) *m/e* (assignment and rel intensity) 258 (M^+ , 100), 229 ($\text{M}^+ - \text{C}_2\text{H}_5$, 99), 213 ($\text{M}^+ - \text{C}_2\text{H}_5\text{O}$, 10), 185 ($\text{C}_{10}\text{H}_9\text{Fe}^+$, 11), 56 (Fe^+ , 85); nmr (CCl_4) δ 1.32 (t, 3 H), 4.1–4.35 (m, 9 H), 4.70 (m, 2 H).

Elution with pure benzene afforded 1.01 g of acetylferrocene followed by 200 mg of dimer 3.

(14) F. S. Arimoto and A. C. Haven, *J. Amer. Chem. Soc.*, **77**, 6295 (1955).

(15) Y. Sasaki, L. L. Walker, E. L. Hurst, and C. U. Pittman, Jr., *J. Polym. Sci.*, **11**, 1213 (1973).

(16) R. F. Schaaf, *J. Org. Chem.*, **27**, 107 (1962).

Further elution with 1:2 benzene–diethyl ether afforded 200 mg of hydroxyl-bearing polymeric species 7: mol wt (gpc) \sim 2900; ir (KBr) 3400 (broad), 3070 (s), 2890 (s), 1450 (s), 1370 (s), 1105 (s), 1000 (s), 820 cm^{-1} (s); nmr (CDCl_3) δ \sim 4.2 (very broad, \sim 9 H), 1.9 (very broad, \sim 3 H).

Treatment of Dimer 3 with Triethyl Orthoformate in Ethanol in the Presence of a Small Amount of *p*-Toluenesulfonic Acid.—Dimer 3 (1.00 g, 2.28 mmol), triethyl orthoformate (1.3 g, 9 mmol), and *p*-toluenesulfonic acid (50 mg, 0.26 mmol) were dissolved in 10 ml of dry ethanol and stirred well at room temperature. Tlc studies were conducted from time to time. Even after 2 weeks, no reaction occurs to give any of compounds 1–7.

Acknowledgments.—This work was supported in part by the Air Force Cambridge Laboratories under Contract No. F19628-71-C-0107. The work reported here does not necessarily reflect endorsement by the Air Force. Partial support was provided by the Office of Naval Research.

Registry No.—1, 39324-45-3; 3, 39336-59-9; 4, 1273-91-2; 6, 33362-30-0; acetylferrocene, 1271-55-2; triethyl orthoformate, 122-51-0.

Fused Organic Salts. VII.¹ The System Tetra-*n*-pentylammonium Nitrate–Silver Nitrate. Melt Stability. The Silver Nitrate–Carbon Tetrachloride Reaction

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Tetra-*n*-pentylammonium nitrate (fp 113.9°)–silver nitrate (fp 210°) is a simple eutectic system with eutectic temperature 41.7° and eutectic composition 42.2 ± 0.5 mol % AgNO_3 . While pure tetra-*n*-pentylammonium nitrate gives 1-pentyl nitrate and tripentylamine on pyrolysis at 275°, AgNO_3 – R_4NNO_3 mixtures yield in addition dipentylnitrosamine. This oxidation of tertiary amine by AgNO_3 is observable also in protic and aprotic solvents. Ag metal is formed and the tertiary iminium cation and tertiary amide are thought to be intermediates. The AgNO_3 – CCl_4 reaction, which is very slow in ethanol but very rapid with AgNO_3 adsorbed on silicic acid, proves also to be very slow in molten AgNO_3 – R_4NNO_3 . Consequently the difference in reactivity in the first two media cannot be attributed to deactivation by ion solvation, and the high reactivity of AgNO_3 /silicic acid must be a surface-chemical phenomenon.

Results and Discussion

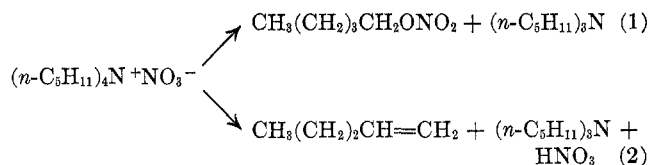
Phase Diagram.—Tetra-*n*-pentylammonium nitrate–silver nitrate displays a simple eutectic diagram (Figure 1) with a remarkably low eutectic temperature ($41.7 \pm 0.5^\circ$). The eutectic melt contains 42.4 ± 0.5 mol % (25.7 wt %) of silver nitrate. The availability of such melts containing high concentrations of unsolvated silver ion at moderate temperatures suggests a variety of chemical applications. Here we report on stability relationships in these melts and one test of the electrophilic reactivity of Ag^+ in Ag^+ , $\text{R}_4\text{N}^+/\text{NO}_3^-$.

Stability of the Melt.—While pure liquid $\text{R}_4\text{N}^+\text{NO}_3^-$ is more stable than its analogs with more nucleophilic anions, slow decomposition is known to occur at 140°.² This reaction could take either of two paths: nucleophilic displacement (eq 1) or elimination (eq 2).³ Application of the vacuum pyrolysis technique which provided clean-cut results for the halides^{1a} produced the result shown in Table I. Only reaction 1 is important.

(1) (a) Part VI: J. E. Gordon and P. Varughese, *Chem. Commun.*, 1160 (1971). (b) Part V: J. E. Gordon, J. E. Selwyn, and R. L. Thorne, *J. Org. Chem.*, **31**, 1925 (1966). (c) Part IV: J. E. Gordon, *J. Amer. Chem. Soc.*, **87**, 4347 (1965).

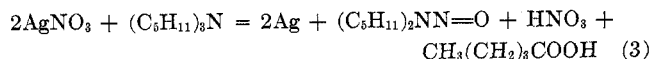
(2) J. E. Gordon, *J. Org. Chem.*, **30**, 2760 (1965).

(3) J. E. Gordon in "Techniques and Methods of Organic and Organometallic Chemistry," D. B. Denney, Ed., Marcel Dekker, New York, N. Y., 1969, p 78.



The behavior of R_4N^+ , $\text{Ag}^+/\text{NO}_3^-$ mixtures is expected to be similar, with possible secondary reactions of the products of eq 1 with Ag^+ . The observations (Table I) are indeed similar, but the yield of tripentylamine is reduced and some dipentylnitrosamine appears. The latter was shown to result from reaction of tripentylamine with AgNO_3 .

This reaction takes the course shown in Table II and eq 3. Oxidation of tertiary amines by Ag^+ has



apparently never been reported, though other oxidants (ClO_2 , MnO_2 , $\text{Hg}(\text{OAc})_2$, KMnO_4) are known to produce the enamine or its conjugate acid.⁴ We in-

(4) (a) P. A. S. Smith, "Open-Chain Nitrogen Compounds," Vol. I, W. A. Benjamin, New York, N. Y., 1965, p 49; (b) L. A. Hull, et al., *J. Amer. Chem. Soc.*, **89**, 1163 (1967).