Experimental

About 10 g. of technical grade potassium hydrogen fluoride was placed in a platinum crucible and heated over a burner until molten. Approximately 0.5 g. of praseodymium trifluoride was placed in the melt and stirred with a platinum rod. Within five minutes the praseodymium fluoride had dissolved completely, giving a pale yellow-green color to the melt. After the melt had cooled and solidified to a hard, brittle mass, it was placed in a beaker and water (containing a few drops of ammonium hydroxide solution) was added to dissolve the excess potassium fluoride and potassium hydrogen fluoride. After several leachings with water, a pale green residue mixed with dark particles of impurities from the potassium hydrogen fluoride remained. The washings, even after concentration, gave no evidence for the presence of praseodymium ions. However, light reflected from the green residue gave the characteristic absorption spectrum of praseodymium ions.

This green residue, but not the black particles, was readily soluble in 3 *N* hydrochloric acid when slightly warmed. This behavior is quite different from that of praseodymium trifluoride.

Purification of potassium hydrogen fluoride by crystallization eliminated the dark impurities. The purified material with praseodymium trifluoride gave a residue completely soluble in the 3 *N* hydrochloric acid. This marked difference in solubility of the two praseodymium-fluoride compounds indicates the formation of a complex ion containing both praseodymium and fluorine.

When Pr_6O_{11} was added to fused potassium hydrogen fluoride a vigorous reaction took place, and the final green residue showed the same characteristics as that obtained by treatment of the praseodymium trifluoride with potassium hydrogen fluoride.

Investigations to determine whether the composition of this substance is similar to the $KLaF_4$ described by W. H. Zachariasen[2] and also to determine the properties of this substance are being continued.

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[2] Zachariasen, This Journal, **70**, 2147 (1948).

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Acid Catalyzed Reaction of Diarylformamidines with Ethyl Orthoformate

By Royston M. Roberts

Ethyl N-phenylformimidate (I) was first prepared by Comstock and Clapp[1] from ethyl iodide and the silver salt of formanilide; the yield was low, and although it has been improved by Smith and Nichols[2] the procedure is expensive and tedious. Claisen[3] prepared this compound from aniline and ethyl orthoformate. He reported that the preparation was accomplished only after numerous unsuccessful attempts and that his directions must be followed exactly; even so, the yield he obtained was only 44% from a reaction mixture heated nine hours. Our attempt to repeat this work resulted in a yield of 11%. Claisen postulated a two-step mechanism for the reaction: first, the formation of N,N′-diphenylformamidine (rapid), and second, reaction of this compound with a second mole of ethyl orthoformate (much slower).

$$2C_6H_5NH_2 + (C_2H_5O)_3CH \longrightarrow C_6H_5N{=}CH{-}NH{-}C_6H_5 + 3C_2H_5OH \qquad (A)$$

$$C_6H_5{-}N{=}CH{-}NH{-}C_6H_5 + (C_2H_5O)_3CH \rightleftarrows \underset{\text{I}}{2C_6H_5N{=}CHOC_2H_5} + C_2H_5OH \qquad (B)$$

There is no doubt regarding the ease with which the first step (A) takes place, but we have found that the second step (B), is practically completely dependent on acid catalysis. This undoubtedly explains the many unsuccessful experiments mentioned by Claisen and also our first attempt in which we took some care to avoid traces of acid. When we heated pure N,N′-diphenylformamidine with ethyl orthoformate containing a little anhydrous potassium carbonate for twenty-four hours, we found practically no alcohol was produced and the N,N′-diphenylformamidine was recovered unchanged. Prompted by the observation of acid catalysis in the reaction of ethyl N-phenylformimidate with amines (to be published separately) we added a small amount of aniline hydrochloride to the ethyl orthoformate and N,N′-diphenylformamidine and found that the calculated amount of ethanol was evolved rapidly and a 96% yield of ethyl N-phenylformimidate was produced. Other acids are also effective in catalyzing the reaction; sulfuric and *p*-toluenesulfonic acids gave comparable results and even acetic acid was fairly effective. Ethyl N-*p*-tolylformimidate[4] was produced from *p*-toluidine or N,N′-di-*p*-tolylformamidine under similar conditions. The formamidines need not be isolated when the aromatic amine is the starting material. In fact, the acid catalyzed reaction of orthoformate with aromatic amine may not proceed by intermediate formamidine formation but may be more direct. The mechanism of this reaction will be discussed more completely in a subsequent paper. It is interesting to note that reaction (B) is apparently reversible and has previously been described as it occurs in the opposite direction from that reported here! Knott[5] treated ethyl N-phenylformimidate in alcoholic solution with carboxylic and sulfonic acids; he obtained N,N′-diphenylformamidine salts and was able to identify ethyl orthoformate as the other product in one case.

Recently Hamer, Rathbone and Winton have reported modifying Claisen's procedure obtaining yields of 81–85% by "including aniline hydrochloride to inhibit the formation of carbylamine."[6] Their reason for choosing aniline hydrochloride for this function is not given and there is no mention of acid catalysis.

It is perhaps pertinent to recall attention to the fact that in 1941 Smith and Nichols[2] showed that the reaction of Grignard reagents with ethyl N-phenylformimidate was the most satisfactory general method for the synthesis of aromatic

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[1] Comstock and Clapp, *Am. Chem. J.*, **13**, 527 (1891).

[2] Smith and Nichols, *J. Org. Chem.*, **6**, 489 (1941)

[3] Claisen, *Ann.*, **287**, 363 (1895).

[4] Wheeler and Johnson, *Ber.*, **32**, 35 (1899).

[5] Knott, *J. Chem. Soc.*, 686 (1945).

[6] Hamer, Rathbone and Winton, *J. Chem. Soc.*, 954 (1947).

aldehydes from the corresponding halides except for the difficulty of obtaining the ethyl N-phenylformimidate, a reagent which is now easily available.

Experimental

Materials.—Ethyl orthoformate, Eastman Kodak Co., redistilled, b. p. 142–144°; N,N′-diphenylformamidine (m. p. 138.5–139.5°, cor.), N,N′-di-*p*-tolylformamidine (m. p. 141.4–142.8°, cor.), prepared from the amines and ethyl orthoformate[7]; aniline hydrochloride, *p*-toluidine hydrochloride, prepared from the amines and concentrated hydrochloric acid, dried in a vacuum desiccator.

N,N′-Diphenylformamidine and Ethyl Orthoformate. A. Aniline Hydrochloride as Catalyst.—In a 200-ml. flask was placed 19.6 g. (0.10 mole) of N,N′-diphenylformamidine, 29.6 g. (0.20 mole) of ethyl orthoformate and 1.0 g. (0.008 mole) of dry aniline hydrochloride. An efficient 40-cm. distilling column having a total reflux partial take-off type head was attached and the reaction mixture was heated. Ethanol began to reflux immediately. After one hour of reflux the ethanol was distilled; 6.7 ml. was collected in about fifteen minutes. Anhydrous potassium carbonate (2.0 g.) was added and the mixture was shaken and allowed to stand two hours. The reaction mixture was then distilled through the same column under reduced pressure. Excess ethyl orthoformate was first recovered, 12.3 g., b. p. 83–85° (93 mm.). The pressure was then lowered to 40 mm. and colorless ethyl N-phenylformimidate distilled constantly at 117° (40 mm.); 28.7 g. or 96% of the theoretical amount was obtained.

The difference in the conditions under which the two steps of the reaction take place is illustrated by the following experiment. A mixture of 0.40 mole of aniline and 0.60 mole of ethyl orthoformate was heated in a flask to which was attached a 40-cm. distilling column. During one and one-quarter hours 36 ml. of ethanol distilled and then the distillation practically stopped. Aniline hydrochloride (1.30 g., 0.01 mole) was added to the reaction mixture and heating was resumed; distillation of ethanol now took place again at a rapid rate and 11.5 ml. was collected in thirty minutes, then the evolution practically stopped again. Anhydrous potassium carbonate (2.60 g.) was added and the mixture was distilled under reduced pressure. The excess ethyl orthoformate (27.2 g.) was removed first, b. p. 83° (90 mm.), then the product was distilled at 10-mm. pressure; 53.2 g. (89% of the amount calculated from aniline was obtained, b. p. 87–88° (10 mm.), n^{25}_{D} 1.5275 (lit., 1.52787[8]).

B. Sulfuric Acid as Catalyst.—Aniline (1 mole), ethyl orthoformate (1.5 moles) and sulfuric acid (10 drops, *ca.* 0.04 mole) were heated under reflux thirty minutes and then 117 ml. of ethanol was distilled through a short column. The catalyst was neutralized with 3.5 g. of dry sodium *t*-butoxide and the mixture was distilled under reduced pressure. After the excess ethyl orthoformate was recovered, 121.6 g. (82% of the theoretical amount) of ethyl N-phenylformimidate was obtained, b. p. 117–119° (40 mm.).

C. Acetic Acid as Catalyst.—N,N′-Diphenylformamidine (0.10 mole), ethyl orthoformate (0.20 mole) and glacial acetic acid (0.6 ml., 0.01 mole) were heated under reflux for one hour, then 4.5 g. of distillate, b. p. 76–80°, was collected during forty minutes; the distillation temperature then began to rise sharply. Ethyl orthoformate (*ca.* 17 g.) was recovered at 82–83° (90 mm.), and 14.6 g. (55% of the theoretical amount calculated from 0.09 mole of N,N′-diphenylformamidine) of ethyl N-phenylformimidate was obtained, b. p. 117–118° (40 mm.).

N,N′-Di-*p*-tolylformamidine and Ethyl Orthoformate; *p*-Toluenesulfonic Acid as Catalyst.—N,N′-Di-*p*-tolylformamidine (0.10 mole), ethyl orthoformate (0.20 mole) and *p*-toluenesulfonic acid (0.001 mole) were heated in a 100-ml. flask to which was attached a 15-cm. Vigreux column with a total reflux partial take-off head. After one hour of reflux 5.8 ml. of ethanol, b. p. 75–79°, was removed. Calcium carbonate was added and the mixture was stirred overnight. Distillation of the filtered reaction mixture gave *ca.* 12 ml. of ethyl orthoformate, b. p. 83° (93 mm.), and 24.0 g. of ethyl N-*p*-tolylformimidate,[4] b. p. 133.5–134° (40 mm.). This was 74% of the calculated amount of product.

Treatment of *p*-toluidine or N,N′-di-*p*-tolylformamidine with ethyl orthoformate in the presence of *p*-toluidine hydrochloride or sulfuric acid as described above gave similar results—yields of 74–76% of ethyl N-*p*-tolylformimidate.

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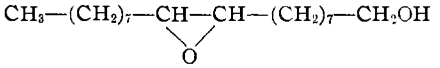
(7) Roberts, *J. Org. Chem.*, **14**, 277 (1949).

(8) Schmidt, *Z. physik. Chem.*, **58**, 523 (1907).

Chemistry of Epoxy Compounds. X.[1] Polymerization of the Isomeric 9,10-Epoxyoctadecanols

BY DANIEL SWERN AND GERALDINE N. BILLEN

The thermal polymerization of the isomeric 9,10-epoxystearic acids was recently reported.[2] The present note reports the results of the thermal polymerization of the isomeric 9,10-epoxyoctadecanols (I), m. p. 54 and 48°, respectively, in



$$\mathrm{CH_3{-}(CH_2)_7{-}\underbrace{CH{-}CH}_{O}{-}(CH_2)_7{-}CH_2OH} \qquad \text{(I)}$$

the presence of naphthalene-2-sulfonic acid as catalyst.

Starting Materials.—The isomeric 9,10-epoxyoctadecanols, m. p. 54 and 48°, were prepared from oleyl[3] and elaidyl[4] alcohols, respectively, by epoxidation with peracetic[5] or perbenzoic acid.[6] Calcd. for $C_{18}H_{36}O_2$, oxirane oxygen,[7] 5.62%; found, 5.62%.

Polymerization Procedures.—9,10-Epoxyoctadecanol (either isomer) and the required quantity of naphthalene-2-sulfonic acid were mixed and then ground until the catalyst was uniformly distributed. Approximately 5-g. portions of the mixture were then weighed into a series of test-tubes which had been flushed with nitrogen or carbon dioxide. After being filled, the tubes were again flushed with inert gas, stoppered tightly, and then immersed in a constant-temperature oil-bath which maintained the desired temperature to ±0.2°. Fifteen minutes was allowed for the establishment of temperature equilibrium before the polymerization time was counted. During the equilibration period, the tubes were shaken occasionally to ensure homogeneity. At selected time intervals, a tube was removed from the oil-bath, cooled rapidly to room temperature, and then analyzed within twenty-four hours.

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(1) For the previous paper in this series, see THIS JOURNAL, **71**, 2219 (1949).

(2) Swern, Billen and Eddy, THIS JOURNAL, **70**, 1228 (1948).

(3) Swern, Knight and Findley, *Oil and Soap*, **21**, 133 (1944).

(4) Swern, Jordan and Knight, THIS JOURNAL, **68**, 1673 (1946).

(5) Swern, Findley and Scanlan, *ibid.*, **66**, 1925 (1944).

(6) Findley, Swern and Scanlan, *ibid.*, **67**, 412 (1945).

(7) Swern, Findley, Billen and Scanlan, *Anal. Chem.*, **19**, 414 (1947); Nicolet and Poulter, THIS JOURNAL, **52**, 1186 (1930).