

uct obtained was ethyl α,β -epoxycyclohexylideneacetate. This reaction illustrates a new modification of the Darzens-Claisen reaction¹ in which the *p*-toluenesulfonic acid group replaces the chlorine in ethyl chloroacetate. We have not attempted to work out the conditions for maximum yields.

Experimental

***p*-Toluenesulfonate of Ethyl Glycolate.**—To a solution of 52 g. (0.5 mole) of distilled ethyl glycolate and 95 g. (0.5 mole) of *p*-toluenesulfonyl chloride in 200 cc. of dry ether was added with stirring 80 g. (1 mole) of dry pyridine over a period of two hours. The temperature was kept at 0–5°. After treatment with water, the reaction products were distilled to yield 78 g. (61%) of the *p*-toluenesulfonate of ethyl glycolate as a colorless somewhat impure liquid, b. p. 171–174° at 2 mm.

Anal. Calcd. for C₁₁H₁₄O₃S: C, 51.2; H, 5.5; S, 12.4. Found: C, 51.8, 51.8; H, 5.7, 5.7; S, 13.5, 13.9.

Ethyl α,β -Epoxycyclohexylideneacetate.—To a suspension of 4 g. (0.1 mole) of sodium amide in 30 cc. of dry benzene was added 9.8 g. (0.1 mole) of cyclohexanone. After refluxing for ninety minutes under a stream of pure nitrogen, the mixture was cooled and 25.8 g. (0.1 mole) of the above sulfonic ester added. After refluxing for five hours the mixture was treated with dilute hydrochloric acid. On vacuum distillation at 10 mm. there was obtained 9.2 g. (50%) of glycidic ester, *n*_D²⁰ 1.4600, b. p. 115–117°. This compound was identified by the close agreement in physical properties with those of authentic glycidic ester and also by hydrolysis to the glycidic acid which on steam distillation yielded an oil which gave the semicarbazone, m. p. 167–168°, of hexahydrobenzaldehyde.³

(1) Darzens, *Compt. rend.*, **139**, 1214 (1904); Claisen, *Ber.*, **38**, 702 (1905).

(2) Microanalyses by the Arlington Laboratories.

(3) Wallach and Issac, *Ann.*, **347**, 331 (1906), give m. p. 167–168°.

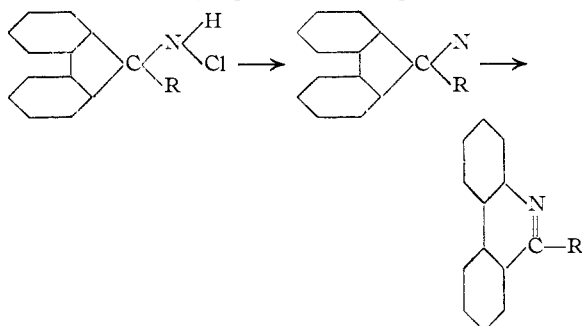
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Preparation and Decomposition of 9-Fluorylchloramines

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The rearrangement of 9-substituted 9-fluorylchloramines yields substituted phenanthridines² where R is methyl, phenyl and naphthyl. If R is



hydrogen the 9-fluorylchloramine rearranges to fluorylidene-imine hydrochloride. This change

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(2) Pinck and Hilbert, *THIS JOURNAL*, **59**, 8 (1937).

was observed during the course of its preparation and also upon heating it above the melting point. Phenanthridine was not detected.

9-Fluoryldichloramine and fluorylidene-iminochloride also were prepared and found to be considerably more stable. The photochemical decompositions of benzene solutions of the above-named compounds were studied and found to yield several decomposition products. 9-Fluoryldichloramine yielded 44.2% of 9-fluorylamine hydrochloride, 9.4% of fluorylidene-imine hydrochloride, 6.6% of fluorenone ketazine and an oily fraction which was not identified. Fluorylidene-iminochloride decomposed yielding 46.8% of fluorylidene-imine hydrochloride, 9.5% of fluorenone ketazine, 9.1% of fluorenone, 0.7% of dichlorodibiphenylene-ethane and an unidentified oil. The formation of fluorenone probably resulted from hydrolysis of fluorylidene-imine, moisture being absorbed from the atmosphere during the various operations.

We wish to express our appreciation to Mrs. M. S. Sherman for carrying out the recorded microanalyses.

Experimental

9-Fluorylchloramine.—A solution of 1 g. of 9-fluorylamine hydrochloride in 200 cc. of 50% ethyl alcohol was treated at 0° with a molal equivalent of a cold, neutral hypochlorite solution. The reaction mixture was shaken in an ice-water-bath for fifteen minutes and filtered in subdued light. The white precipitate was dried in an evacuated desiccator over phosphorus pentoxide. The dried product (0.48 g.) had partially decomposed forming the orange colored fluorylidene-imine hydrochloride (0.25 g.). The chloramine was extracted and crystallized from petroleum ether (b. p. 35–42°), yielding colorless needles, m. p. 70°, which solidified on further heating to an orange solid indicating a rearrangement to the imine hydrochloride, which melted with decomposition at 307°. The compound was so unstable that it could not be stored for the complete analyses; one preparation was therefore used for the determination of N and active Cl, and another for C and H.

Anal. Calcd. for C₁₃H₁₀NCl: C, 72.37; H, 4.68; N, 6.50; Cl, 16.45. Found: C, 72.42; H, 4.81; N, 6.65; Cl, 16.26.

9-Fluoryldichloramine was synthesized by treating a solution of 10 g. of 9-fluorylamine hydrochloride in a liter of 50% ethyl alcohol with 2 mole equivalents of potassium hypochlorite. Prior to the addition of the hypochlorite it was treated with standard acid neutralizing the excess free base and one-half of the hypochlorite, the other half being taken care of by the acid of the amine salt. A colorless cheesy precipitate was obtained, which was dried in an evacuated desiccator over phosphorus pentoxide and stored in the refrigerator overnight; yield 11.1 g., m. p. 108–109°. Upon crystallization from hexane, colorless needles were obtained, m. p. 110°.

Anal. Calcd. for C₁₃H₉NCl₂: C, 62.40; H, 3.63; N, 5.60; Cl, 28.37. Found: C, 62.72; H, 3.82; N, 5.71; Cl, 27.88.

Fluorylidene-iminochloride was obtained by treating a solution of 5 g. of 9-fluoryldichloramine in 50 cc. of benzene with 3 cc. of anhydrous pyridine. Heat was evolved and a yellow precipitate was formed immediately. The benzene and excess pyridine were removed by suction, and the residue was crystallized from hexane, yielding 3.35 g. of yellow needles, m. p. 75–76°.

Anal. Calcd. for C₁₃H₈NCl: C, 73.06; H, 3.78; N, 6.56. Found: C, 72.71; H, 3.90; N, 6.48.

The iminochloride was also obtained from 9-fluorylamine hydrochloride by the method of Peterson.³

Photochemical Decomposition of 9-Fluoryldichloramine.—Within a few hours of exposure to sunlight of a solution of 11.8 g. of 9-fluoryldichloramine in 100 cc. of dry benzene contained in a stoppered Erlenmeyer flask, a white crystalline deposit settled on the wall of the flask. This behavior necessitated daily filtration and reexposure of the filtrate. In the course of a week 4.52 g. of 9-fluorylamine hydrochloride was deposited, which when recrystallized melted at 255° and the free amine melted at 61–62°. The melting points of mixtures with authentic specimens were unaltered. Subsequent exposures of the benzene solution yielded 0.95 g. of fluorylidene-imine hydrochloride, m. p. 300–305°. The hydrochloride was converted to the free base by treatment with aqua ammonia and crystallized from hexane, yellow needles, m. p. and mixed m. p. with fluorylidene-imine 124°. Upon concentration of the benzene filtrate to a brownish red oil and dilution with alcohol it yielded 0.55 g. of fluorenone ketazine, m. p. and mixed m. p. with an authentic specimen 269°. Attempts to identify other products in the oily residue were not successful.

Photochemical Decomposition of Fluorylidene-iminochloride.—This decomposition study was carried out in a manner similar to the one described above. From 7.8 g. of fluorylidene-iminochloride were obtained the following products in designated yields: 3.68 g. of fluorylidene-imine hydrochloride, 0.62 g. of fluorenone ketazine, 0.60 g. of fluorenone and 0.05 g. of dichlorodibiphenylene-ethane,⁴ m. p. 236°.

Anal. Calcd. for C₂₈H₁₆Cl₂: C, 78.18; H, 4.04. Found: C, 78.21; H, 4.20.

Fractionation of the residual oil did not yield any other identifiable products.

(3) Peterson, *Am. Chem. J.*, **46**, 325 (1911).

(4) Schmidt and Wagner, *Ber.*, **43**, 1796 (1910).

BUREAU OF PLANT INDUSTRY
SOILS AND AGRICULTURAL ENGINEERING
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NEW COMPOUNDS

2-(*p*-Chlorophenyl)-1-(1-diethylamino-4-pentyl)-5-methoxybenzimidazole

N-(1-Diethylamino-4-pentyl)-2-nitro-4-methoxyaniline¹ (7.3 g., 0.024 mole) was dissolved in 20 cc. of dry ether and reduced at room temperature in the presence of Raney nickel under an initial pressure of 2 atmospheres of hydrogen. Complete reduction was indicated by the complete loss of the original deep red color coincident with the theoretical consumption of hydrogen. The resulting solution² was dried over potassium carbonate and filtered free of drying agent and catalyst. To this solution was added 25 cc. of dry pyridine and 4.6 g. (0.026 mole) of *p*-chlorobenzoyl chloride, and after allowing to stand for one hour, the mixture was heated overnight on a steam-bath under an air-cooled condenser. Dilute alkali was added, the product was extracted with ether, and the ethereal solution was dried over potassium carbonate and distilled through a small Claisen flask having a heated Vigreux column. The product was obtained in a yield of 5 g. (52% yield) of a red-brown oil boiling at 240° (3 mm.).

(1) Clemo and Swan, *J. Chem. Soc.*, 274 (1944).

(2) Since previous experience had indicated that the hydrogenation proceeded quantitatively and that the resulting amine was unstable, the ethereal solution was used directly for preparation of the benzimidazole.

Anal. Calcd. for C₂₃H₃₀ClN₃O: N, 10.51. Found: N, 10.34.

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(3) Wm. S. Merrell Co., Postdoctoral Fellow.

1-(3-Diethylamino-1-propyl)-6-methoxy-1,2,3,4-tetrahydroquinoline

To a boiling solution of 21.5 g. (0.132 mole) of 6-methoxy-1,2,3,4-tetrahydroquinoline¹ (thalline) in 200 cc. of 95% alcohol was added dropwise over a period of three hours 15.0 g. (0.101 mole) of 3-diethylaminopropyl chloride.² After refluxing for twelve hours, the solvent was distilled and the residue was heated to 100° for six hours (oil-bath). The dark oil was treated with dilute sodium hydroxide, extracted with ether, and the ethereal solution was dried over sodium sulfate. After removal of the solvent, the oil was distilled under diminished pressure.

A small fore-run was collected, the main portion of the product distilling from 157 to 165° (3 mm.). Redistillation yielded a product boiling at 158° (3 mm.), weighing 22 g. (79% of the theoretical). The product was water-clear but began to darken quickly on exposure to air. Consequently, dry hydrogen chloride was passed through a dry ethereal solution, the dihydrochloride separating as a gum which solidified on chilling. The ether was decanted and the solid was recrystallized from dry methyl alcohol by the addition of dry acetone.

The product appeared as a white, crystalline powder, melting at 185–186° with evolution of gas. Its analysis was rendered difficult by its extremely hygroscopic nature.

Anal. Calcd. for C₁₇H₂₅N₃O·2HCl: N, 8.02. Found: N, 7.60.

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(1) Cromwell, Caughlan and Gilbert, *THIS JOURNAL*, **66**, 401 (1944).

(2) Goldfarb, *ibid.*, **63**, 2280 (1941); Marxer, *Helv. Chim. Acta*, **24**, 209 E (1941).

(3) Wm. S. Merrell Co., Postdoctoral Fellow.

Phenoxy and Hydroxylated Aliphatic Acids¹

ω -Phenoxyundecylic Acid.—A neutral solution of 106 g. (0.40 mole) of ω -bromoundecylic acid (m. p. 49–50°) in 400 cc. of 75% aqueous alcohol was added dropwise to a boiling solution of 40 g. (0.42 mole) of phenol and 26 g. of potassium hydroxide in 200 cc. of 75% alcohol. After refluxing overnight most of the alcohol was removed under reduced pressure. The residue was diluted with water and acidified to yield the desired product. After recrystallization from acetic acid there was obtained 83.5 g. (75%) of crystals melting at 76–77°.

Anal. Calcd. for C₁₇H₂₈O₃: C, 73.4; H, 9.5; neut. equiv., 278. Found: C, 73.4; H, 9.4; neut. equiv., 276.

ω -(*p*-Chlorophenoxy)-undecylic Acid.—In a like manner from 68 g. (0.25 mole) of ω -bromoundecylic acid and 33 g. (0.26 mole) of *p*-chlorophenol there was obtained 54.5 g. (68%) of product, m. p. 72–73°.

Anal. Calcd. for C₁₇H₂₅O₃Cl: C, 65.2; H, 8.1; Cl, 11.3; neut. equiv., 312.5. Found: C, 65.5; H, 8.1; Cl, 11.7; neut. equiv., 310.

ω -(*m*-Trifluoromethylphenoxy)-undecylic Acid.—By the same procedure as above this compound was obtained in

(1) These compounds were prepared under a contract between the B. F. Goodrich Company and The Ohio State Research Foundation.