

jected to vacuum distillation. At 3 mm. pressure a few drops of liquid distilled below 200°, the main product distilling from 200–225° as a red-brown viscous liquid which soon crystallized. The residue (9.0 g.) could not be distilled or crystallized. After recrystallization from acetone and petroleum ether, the volatile portion weighed 9.3 g. (34%) and was found to be 2-*p*-methoxystyryl-3-methylquinoxaline (m. p. 124–125°).

Of the starting materials 0.041 mole of anisaldehyde and 0.038 mole of dimethylquinoxaline are unaccounted for; thus the 9.0 g. of undistillable residue probably consists of a polymeric 1:1 condensation product.

THE VENABLE CHEMICAL LABORATORY
UNIVERSITY OF NORTH CAROLINA
CHAPEL HILL, NORTH CAROLINA

RECEIVED NOVEMBER 25, 1946

The Critical Concentration of Dodecanesulfonic Acid

By H. F. WALTON

The writer recently measured the activity of 1-*n*-dodecanesulfonic acid in aqueous solution at two temperatures by an electromotive force method, and concluded from the results that the critical concentration, above which the association of negative ions to form micelles begins, is 0.0064 *M* at 25°, and 0.003 *M* at 0°. These values, especially that at 0°, are at variance with those found by other methods, as in Table I.

TABLE I

Method	Critical concn., molar		Ref.
	0°	25°	
E. m. f.	0.003	0.0064	1
Conductivity	.010	.0072	2, 3
Freezing point	.010	3
Indicator	.0095 (4°)	.0075	This work

This note describes measurements of the light absorption by a dissolved indicator dye, thymol blue. This indicator normally changes from red to yellow in the *pH* range 1.2–2.8, but in 0.01 *M* dodecanesulfonic acid it is a darker red than in 2 *M* hydrochloric acid. The position of the absorption bands of the indicator is not changed appreciably by the colloidal electrolyte, but their intensity is increased, and the red form appears to be solubilized or stabilized in some way. Solubilization is a property of micelles rather than simple molecules, as Hartley showed,⁴ and the concentration where solubilization first occurs is approximately equal to the critical concentration of the colloidal electrolyte.^{4,5,6}

Experimental

Solutions of the yellow form of thymol blue in water and in 0.02 *M* dodecanesulfonic acid were prepared, the indicator concentration being the same in both. The optical density of the sulfonic acid solution was measured at 550 μ , using a Beckman spectrophotometer with 1-

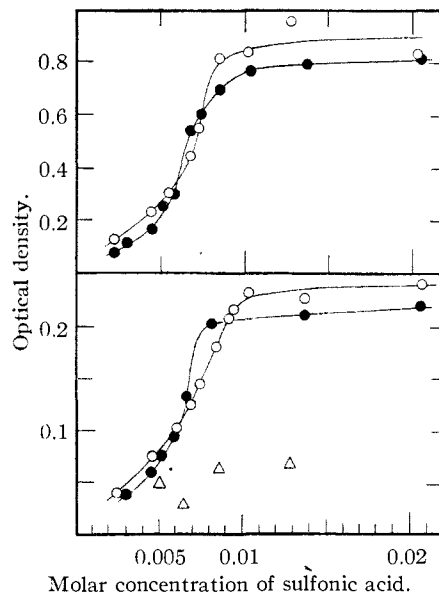


Fig. 1.—Optical density versus acid concentration: upper curves, 10 p.p.m. thymol blue; lower curves, 2.5 p.p.m. thymol blue; open circles, 4°; filled circles, 25°; triangles, hydrochloric acid plus 2.8 p.p.m. thymol blue at 25°.

cm. cell. Five hundred and fifty μ is the peak of the main absorption band of the red form; the yellow form absorbs hardly at all at this wave length. The sulfonic acid concentration was progressively reduced by diluting a measured volume of solution with the aqueous indicator solution added from a buret; the indicator concentration thus remained constant. Runs were made with two different indicator concentrations, 10 p. p. m. (2.1×10^{-6} *M*) and 2.5 p. p. m. (5.2×10^{-6} *M*), and at two temperatures, 25 and 4°; the 4° measurements were made in the cold room. The results are shown in the graph, with comparative data for the indicator in hydrochloric acid. The curves for the lower indicator concentration show the sharper inflections. Since the concentration of indicator is so much less than that of the acid, the effect of the indicator in promoting micelle formation must be very small, and these inflections, coming at 0.0095 *M* at 4° and 0.0075 *M* at 25°, probably represent the critical concentrations of sulfonic acid for micelle formation. If so, they agree well with conductivity and freezing point measurements, as is shown in Table I. Why the electromotive force method should give different results is still not apparent.

A comparison of the optical densities in hydrochloric acid and in dodecanesulfonic acid shows that the red indicator color is considerably enhanced by the sulfonic acid even below the critical concentration. At 25°, the optical density rises approximately with the square of the sulfonic acid concentration, suggesting that a binary complex, such as $(C_{12}H_{25}SO_3)_2^-$, is formed which associates with the indicator.

NORTHWESTERN UNIVERSITY
EVANSTON, ILLINOIS

RECEIVED SEPTEMBER 13, 1946

Note on the Darzens-Claisen Reaction

By MELVIN S. NEWMAN AND BARNEY J. MAGERLEIN

On attempting to alkylate cyclohexanone by treating its sodium enolate with the *p*-toluenesulfonic acid ester of ethyl glycolate, the main prod-

- (1) Walton, *THIS JOURNAL*, **68**, 1180 (1946).
- (2) Brady, Thesis, Stanford University, 1944.
- (3) McBain, Dye and Johnston, *THIS JOURNAL*, **61**, 3210 (1939).
- (4) Hartley, *J. Chem. Soc.*, 1988 (1938).
- (5) Sheppard and Geddes, *J. Chem. Phys.*, **13**, 63 (1945).
- (6) Corrin, Klevens and Harkins, *ibid.*, **14**, 216 (1946).

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°.

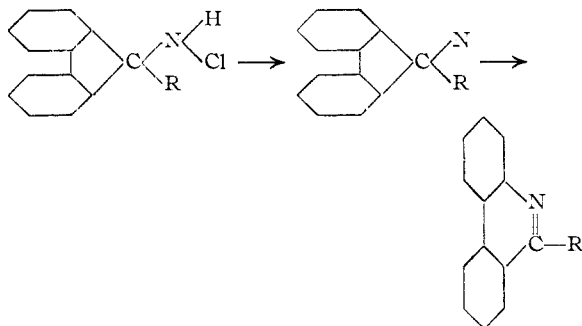
DEPARTMENT OF CHEMISTRY
THE OHIO STATE UNIVERSITY
COLUMBUS 10, OHIO

RECEIVED JULY 5, 1948

Preparation and Decomposition of 9-Fluorylchloramines

BY LOUIS A. PINCK AND GUIDO E. HILBERT¹

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

(1) Present address: Bureau of Agricultural and Industrial Chemistry, U. S. Department of Agriculture, Peoria, Illinois.

(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.