from the slope of the line obtained when log c is plotted against time.

The most striking feature of these results is the observed increase in effectiveness of the catalyst with *decrease* in concentration in certain ranges both for the chloride and bromide. This increase is well beyond the range of experimental error in the determination of k. Values in the table are averages of several independent determinations. The *maximum* variation in individual values was ± 0.002, and in most cases it was much less.

Time and circumstances have not yet permitted us to make further studies to determine the reaction mechanism. One might assume the rate-determining step to be one involving a single halide ion, and the k values above should then be divided by the concentrations of Cl^- or Br^-. This still gives a series of "constants" increasing steadily with dilution.

As a result of the oxidizing action of the cerium (IV) and of hydrolysis, both the free halogens and different oxidation states such as hypohalites must be present, and some one of these must be a better catalyst than the halide ion. The concentration range in which the effect occurs suggests the hypohalite as a first possibility since shifts in hydrolytic equilibrium would favor its formation in the lower concentration ranges. Connick[3] has observed an effect of this sort in the reaction of hydrogen peroxide with chlorine in solution.

Further experiments are being carried out to test this possibility.

This work was supported by a grant from the University of Texas Research Institute.

[3] Robt. E. Connick, This Journal, **69**, 1509 (1947).

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RECEIVED MARCH 3, 1949

The Liberation of Dialkylaminoalkyl Chlorides from Their Hydrochlorides

By ROBERT R. BURTNER

The lower molecular weight dialkylaminoalkyl chlorides, particularly $(C_2H_5)_2NCH_2CH_2Cl$, $(CH_3)_2NCH_2CH_2Cl$ and $ClCH_2CH(CH_3)N(CH_3)_2$, are becoming increasingly important as intermediates in the synthesis of spasmolytics, antihistamine agents and analgesics. The methods commonly cited for the preparation of these compounds involve the treatment of the hydrochlorides with a concentrated aqueous solution of sodium hydroxide or potassium carbonate followed by extraction. Because of their water solubility and tendency to form emulsions, the extraction of these bases is frequently troublesome and inefficient. The following typical procedure is submitted as a convenient, efficient modification.

One mole (172 g.) of β-diethylaminoethyl chloride hydrochloride is placed in a two-liter three-necked flask fitted with a suitable vacuum-tight stirrer and an efficient condenser set for distillation. Two moles (80 g.) of *flake* sodium hydroxide is added all at one time, and the mixture stirred manually for a few minutes until the mass begins to liquefy. Water pump vacuum (30–40 mm.) is applied to the receiver, and the stirrer is started. The mixture promptly assumes a slushy consistency with evolution of sufficient heat to maintain brisk distillation. Intermittent cooling may be required, depending on the efficiency of the condenser. (With the more volatile dimethylaminoethyl chloride a chilled receiver is necessary.) Distillation is continued to dryness using a steam-bath during the latter phase. After a brief drying with potassium carbonate, the product is obtained in 85–95% yield and is sufficiently pure for most purposes. It may be stored for several months in the refrigerator with only slight dimerization, such dimer being easily removed by filtration. It may also be preserved by dilution with an equal volume of dry xylene, which solution is exceptionally stable in the cold. The latter storage method is mandatory for dimethylaminoethyl chloride, which otherwise dimerizes completely at low temperatures in one or two days. In such concentrated solutions the amount of xylene introduced does not adversely affect subsequent condensation reactions.

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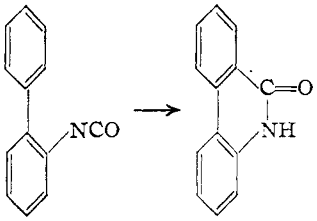
RECEIVED MARCH 5, 1949

A Convenient Synthesis of Phenanthridone

By JOHN MANN BUTLER

The literature contains a number of methods for the preparation of phenanthridone[1]; but all are troublesome or give poor yields of product. It has now been found that phenanthridone can be obtained readily in 77.5% yield by the ring closure of *o*-biphenyl isocyanate with aluminum chloride.



This new type of cyclization is an intramolecular modification of Leuckart's synthesis of N-aryl amides from aromatic hydrocarbons and aryl isocyanates.[2]

Experimental

With stirring, 48.8 g. of *o*-biphenyl isocyanate[3] was added over a period of twenty minutes to a suspension of 37.0 g. of aluminum chloride in 190 ml. of *o*-dichlorobenzene. The rate of addition was so adjusted that the heat of reaction maintained the temperature between 70 and 80°. Stirring was continued for one hour while the temperature gradually dropped to 25°. The fine gray precipitate which had formed was collected and washed on the filter with 100 ml. of *o*-dichlorobenzene. The solid was stirred well with about 250 ml. of cold 15% hydrochloric acid and collected; the process was repeated with 200 ml. of ethanol. The dried product amounted to 38.0 g.

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[1] (a) Pictet and Gonset, *Arch. Sci. phys. Genève* (IV), **3**, 37-51 (1897); *Chem. Zentr.*, **68**, 413 (1897); (b) Graebe and Wander, *Ann.*, **276**, 248 (1893); (c) Pictet and Hubert, *Ber.*, **29**, 1188 (1896).

[2] Leuckart, *Ber.*, **18**, 873 (1885).

[3] Fraenkel-Conrat and Olcott, This Journal, **66**, 845 (1944).