cholesterol; and (2) in view of the relative stability[1] of the starting materials, it was reasonable to assume that vitamin D_3 chloride and bromide would be stable (but to a lesser extent) under the conditions of the experiments. In connection with the latter argument it should be pointed out that 7-dehydrocholesteryl bromide was recovered in 77% yield when refluxed for five hours in xylene with aniline. No attempt was made to isolate the irradiated products in a pure state.

In summary, it may be stated that replacement of the hydroxyl group in vitamin D_3 by chlorine or bromine gave products devoid of vitamin activity.

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Halide Catalysis in the Reaction of Cerium(IV) with Arsenic(III)

BY ROBBIN C. ANDERSON, JAMES A. LASATER AND DAVID LIPPMANN

Lang[1] observed that halides were effective catalysts for the oxidation of arsenite with permanganate. Willard and Young and others[2] have noted similar effects on the oxidation of arsenite by ceric salts.

In these earlier experiments emphasis was usually placed on analytical uses. The concentrations of halide used were large (0.02–2 M) and most experiments were carried out in presence of hydrochloric acid. The experiments reported in the present paper were undertaken to obtain quantitative data on the rate effects of small concentrations of added salts and thus to obtain evidence on the mechanism of the catalytic action.

Experimental.—The apparatus and procedures were essentially those of Moore and Anderson.[2] Reactions were carried out in an all-glass system under nitrogen. Equivalent quantities of cerium (IV) sulfate and sodium arsenite were used and changes in concentration determined by titrating samples of the reaction mixture at various time intervals with iron(II) ammonium sulfate, using orthophenanthroline indicator.

For the present series of experiments, all reagent mixtures contained 0.02 mole/l. of cerium (IV) sulfate, 0.01 mole/l. of sodium arsenite and 0.355 mole/l. of sulfuric acid. Sufficient halide was added to the arsenite solution before mixing to provide the desired final concentration of catalyst.

Results.—The chloride, bromide and iodide had a definite catalytic effect even at very low concentrations. Colors of the free halogens could be detected in the experiments in which the largest concentrations of halide were present, and in some cases the characteristic odor was also detectable. In contrast to the cerium(IV)–arsenic(III) reaction itself, which shows a complex, third-order type dependence on concentration,[2] the halide-catalyzed reactions were pseudo first-order reactions. For a given catalyst concentration, straight lines were obtained when log c (where c is one-half the concentration of oxidant at time t) is plotted against the time t. Typical results for a run using 0.01 M sodium bromide as catalyst are shown in Fig. 1. (c is expressed in g.-ions/l.) The simple titration method used in these preliminary tests would not distinguish between the cerium(IV) present and some other oxidizing agent which might be formed by reaction of cerium(IV) with the halide, but the close correlation with first-order type dependence on concentration indicates these systems react differently from the cerium(IV) and arsenic(III) solutions.

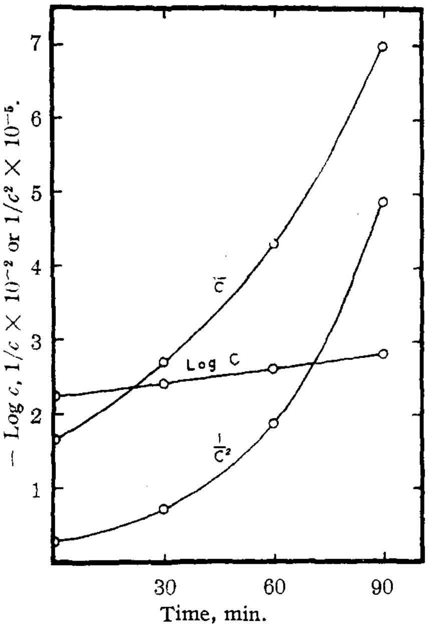

Fig. 1.—Order of reaction.

In general, the order of effectiveness as catalysts is $I^- > Br^- > Cl^-$. Reaction in the presence of iodide was too fast to be measured by the titration method. Comparison of the effects of chloride and bromide is shown in Table I. k is the pseudo first-order constant determined

TABLE I

Catalyst	Concn. of catalyst (g.-ions/l.)	k(min.$^{-1}$) (psuedo first-order constant)
Cl^-	0.02	0.016
	.01	.011
	.005	.024
	.001	.006
Br^-	.02	.018
	.01	.014
	.005	.011
	.001	.050

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[1] Lang, *Z. anorg. Chem.*, **152**, 197 (1926).

[2] H. H. Willard and Philena Young, THIS JOURNAL, **50**, 1376 (1928); E. H. Swift and C. H. Gregory, *ibid.*, **52**, 901 (1930); J. W. Moore and R. C. Anderson, *ibid.*, **66**, 1476 (1944).

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.

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[3] Robt. E. Connick, THIS JOURNAL, **69**, 1509 (1947).

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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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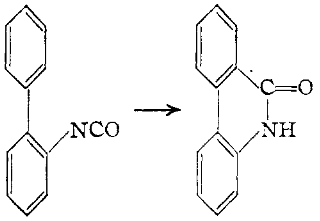
A Convenient Synthesis of Phenanthridone

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).