carbonate but a k_D/k_H ratio of 0.60 for the same reaction catalyzed by acetic acid is readily accommodated. This result is nicely consistent with the theories of solvent isotope effect[19] if the proton catalyzed reaction proceeds mostly through the protonated substrate, formed reversibly prior to the rate-determining step, while the acetic acid–catalyzed reaction involves principally a rate-determining proton transfer from acetic acid to the substrate.

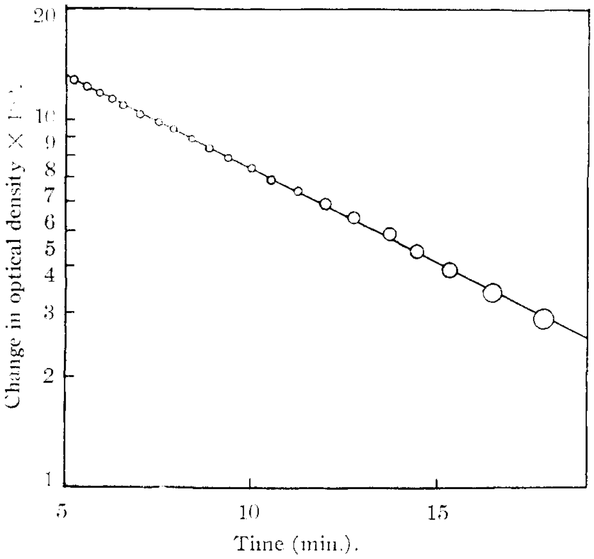

Fig. 1.—A sample rate experiment illustrating the precision of the first-order rate law for chloroacetal in strong acid: chloroacetal in 3.04 M $HClO_4$.

Experimental

Materials.—The chloroacetal was Eastman Kodak Co. "White Label," redistilled; b.p. 155.5–157.5°.[20] Acetal was prepared by the method of "Organic Syntheses"[21]; b.p., 104°. Dioxane was purified by the method of Vogel,[22] b.p. 99.5–100.5°, n^{25}_D 1.4227. All other materials were C.P. reagents.

Kinetic Procedure.—All rate measurements were made by following the appearance of the carbonyl peak in the ultraviolet with a Beckman D.U. spectrophotometer. For runs involving chloroacetal 4 cc. of a 10% (by volume) solution of chloroacetal in dioxane was diluted to 100 cc. with the required amount of distilled water and mineral acid. All the components were brought to 25° before mixing. Part of this solution was then transferred to a 10-cm. glass-stoppered quartz cell and intermittent determinations of the optical density were made until at least 75% of the reaction was complete. Except during the periods of measurement, the cell was kept in a thermostatic bath maintained at 25.00 ± 0.05°.

For each of the acetal experiments 4.00 ml. of dioxane, aqueous acid or buffer, and enough distilled water to give a total volume of 10.00 ml. were added to 1.00 ml. of 10% solution of acetal in dioxane. All the components were brought to 25° before mixing. Five ml. of dioxane made up to 10.00 ml. with water was analytically found to correspond to 49.6% dioxane and 50.4% water by weight. Part of the acetal solution was then transferred to a 1.00-cm. quartz cell and placed in a water-jacketed cell compartment for the course of the reaction. Water was pumped through the jackets from the thermostated bath and the cell temperature was found never to vary from the bath temperature by more than 0.1°. The optical density was determined at convenient intervals over a range of at least 75% of its total change.

A number of aldehydes, particularly chloroacetaldehyde, are in equilibrium with hydrates. Since the hydration reaction is relatively fast and reversible in the acidic solutions used[23] the optical density is directly proportional to the sum of the hydrolyzed material throughout the course of the reaction. Thus it is possible to obtain the hydrolysis rates directly from the time change in optical density of the system.[24] Within a given rate run the reactions follow a first-order rate law with very good precision (*ca.* 1%). Constants determined under identical conditions were averaged and the mean deviations are given.

A first-order plot typical of the rate runs is shown in Fig. 1. Under the conditions employed the reaction is essentially irreversible.[25]

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(19) R. P. Bell, "Acid-Base Catalysis," Oxford at the Clarendon Press, 1941, p. 143.

(20) All boiling points are uncorrected.

(21) H. Adkins and B. N. Nissen, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 1.

(22) A. I. Vogel; "Practical Organic Chemistry," Longmans, Green and Co., New York, N. Y., 1948, p. 175.

(23) R. P. Bell and B. B. Darwent, *Trans. Faraday Soc.*, **46**, 34 (1950).

(24) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 28.

(25) W. H. Hartung and H. Adkins, THIS JOURNAL, **49**, 2517 (1927), found that the equilibrium constant for the reaction (R = aliphatic)

$$RCHO + 2C_2H_5OH \rightleftharpoons RCH(OC_2H_5)_2 + H_2O$$

is always less than 0.15 in a medium somewhat different from the present one but nevertheless containing about 50% water. This makes it very unlikely that more than 1.5% of any acetal we have discussed remains unhydrolyzed at equilibrium.

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The Preparation and Hydrolysis of a Dineopentyl Acetal[1]

BY C. A. MACKENZIE AND J. H. STOCKER

RECEIVED FEBRUARY 7, 1955

Investigations of the hydrolysis of acetals derived from formaldehyde[2] or acetaldehyde[2-4] and optically active alcohols or glycols have led to a revision of the hydrolytic mechanism proposed earlier by Hammett.[5] The recovery of the non-racemized and non-inverted alcohol in all cases supported the conclusion that the alkyl carbonium ion corresponding to the alcohol cannot be an intermediate in the reaction.

Recent work in this Laboratory has demonstrated that hydrolysis of the dineopentyl acetal of benzaldehyde results in the recovery of neopentyl alcohol; no rearranged products were observed. While it has been pointed out that the scission of a neopentyl–oxygen bond may occur without rearrangement,[6] such reactions are considered to follow an S_N2 route; the existence of a neopentyl fragment with an incomplete octet gives rise to rearranged products.[7] Thus the present results are in agreement with the previously cited work with optically active acetals.

Experimental

Neopentyl alcohol was prepared by the lithium aluminum

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(1) Aided by a grant from the Research Corporation.

(2) H. K. Garner and H. J. Lucas, THIS JOURNAL, **72**, 5497 (1950).

(3) J. M. O'Gorman and H. J. Lucas, *ibid.*, **72**, **5489** (1950).

(4) E. R. Alexander, H. M. Busch and G. L. Webster, *ibid.*, **74**, 3172 (1952).

(5) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1950, p. 304.

(6) L. H. Sommer, H. D. Bankmann and P. C. Miller, THIS JOURNAL, **73**, 3542 (1951).

(7) I. Dostrovsky, E. D. Hughes and C. K. Ingold, *J. Chem Soc.*, 193 (1946).

hydride reduction of trimethylacetic acid.[8] Benzaldehyde was freed of benzoic acid and redistilled immediately prior to use.

Preparation.—Six and one-half grams (0.074 mole) of neopentyl alcohol, 3.9 g. (0.037 mole) of benzaldehyde, 90 ml. of dry benzene and about 75 mg. of *p*-toluenesulfonic acid monohydrate were heated together until the calculated amount of water had been collected in a standard water separator. The acid was destroyed by the addition of a few ml. of sodium ethoxide in ethanol. The mixture was washed with water then dried over potassium carbonate. The product was collected by fractionation through 15 cm. of glass helices; yield 6.6 g. (68%); b.p. 102° at 0.8 mm.; n^{22}D 1.4682; d^{22}_4 0.913; *MR* (calcd.) 80.4 (found) 80.5.

Anal. Calcd. for $C_{17}H_{28}O_2$: C, 77.2; H, 10.7. Found: C, 77.1; H, 10.6.

Hydrolysis.—Thirty milliliters of 1% sulfuric acid and 6.2 g. of dineopentyl acetal of benzaldehyde were placed in a 50-ml. round bottom flask connected to a simple head leading to a long-stemmed adapter and an 8-in. test-tube resting in an ice-water bath. Distillation was continued until the head temperature reached 100°. The organic layer was separated and to it was added ether extracts of the water layer. The mixture was dried over potassium carbonate. The material was distilled through 15 cm. of glass helices to yield 3.4 g. (80%) of neopentyl alcohol, b.p. 111–112°. The 3,5-dinitrobenzoate derivative showed no depression of the melting point when mixed with an authentic sample.

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[8] R. F. Nystrom and W. G. Brown, THIS JOURNAL, **69**, 2548 (1947).

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Synthesis of Silylmethyl Thiocyanates and Isothiocyanates

BY JOHN E. NOLL

RECEIVED NOVEMBER 24, 1954

In the course of a study of the reactions of chloromethyl- and aminomethylsilanes, a few silylmethyl thiocyanates and isothiocyanates were prepared. The isothiocyanates were prepared[1] by a series of reactions from the corresponding silylmethylamine.[2]

$$\equiv SiCH_2NH_2 + CS_2 + OH^- \rightleftarrows \equiv SiCH_2NHC(=S)S^- + H_2O$$

$$\equiv SiCH_2NHC(=S)S^- + C_2H_5OC(=O)Cl \rightleftarrows \equiv SiCH_2NHC(=S)SC(=O)COC_2H_5 + Cl^-$$

$$\downarrow$$

$$\equiv SiCH_2NCS + C_2H_5OH + COS\uparrow$$

The thiocyanates were prepared from the corresponding chloromethylsilane and potassium thiocyanate in acetone.

$$\equiv SiCH_2Cl + KCNS \rightleftarrows \equiv SiCH_2SCN + KCl$$

The isothiocyanates were found to react with amines in the usual manner to produce substituted thioureas.

Experimental

Trimethylsilylmethyl Isothiocyanate.—Trimethylsilylmethylamine–water azeotrope[2] (30 g., 0.25 mole) dissolved in 200 cc. of alcoholic sodium hydroxide (10 g., 0.25 mole) was treated with carbon disulfide (15 g., 0.2 mole) at 0°. On standing, sodium N-trimethylsilylmethyl dithiocarbamate (37 g., 90% yield) precipitated. *Anal.* Calcd. for $C_5H_{12}NS_2SiNa$: Na, 11.40; S, 31.84. Found: Na, 11.37; S, 31.60, 31.57.

Addition of ethyl chloroformate (27.5 g., 0.25 mole) to an aqueous solution of sodium N-trimethylsilylmethyl dithiocarbamate (50.4 g., 0.25 mole) produced an oil and evolved a gas. The oil was extracted and distilled in a still of about ten plates to yield trimethylsilylmethyl isothiocyanate (33 g., 91%), b.p. 199° (741 mm.), 90° (25 mm.), n^{25}D 1.4984, d^{25}_4 0.938. *Anal.* Calcd. for $C_5H_{11}NSSi$: S, 22.07; sp. ref.,[3] 0.3083. Found: S, 22.08; sp. ref., 0.3128. Trimethylsilylmethyl isothiocyanate reacted with aniline to produce N-phenyl-N′-(trimethylsilylmethyl)-thiourea which was found to be identical to the thiourea prepared from phenyl isothiocyanate and trimethylsilylmethylamine by a mixed melting point (121–122°); N-phenyl-N′-(trimethylsilylmethyl)-thiourea, m.p. 122–123°. *Anal.* Calcd. for $C_{11}H_{18}N_2SSi$: Si, 11.77. Found: Si, 11.72.

Triethoxysilylmethyl Isothiocyanate.—Trimethylammonium triethoxysilylmethyl dithiocarbamate prepared from a benzene solution of trimethylamine (18 g.), triethoxysilylmethylamine[2] (48.5 g., 0.25 mole) and carbon disulfide (20 g.) on treatment with ethyl chloroformate (32.5 g., 0.3 mole) gave a precipitate of trimethylamine hydrochloride (m.p. 270–276° dec.). The filtrate was distilled to yield triethoxysilylmethyl isothiocyanate (29 g., 50% yield), b.p. 120° (3 mm.), n^{25}D 1.4558, d^{25}_4 1.034. *Anal.* Calcd. for $C_8H_{17}O_3NSSi$: Si, 11.93; S, 13.62; sp. ref.,[3] 0.2586. Found: Si, 12.12, 12.27; S, 13.13, 13.51; sp. ref., 0.2628.

Tetramethyldisiloxane-1,3-bis-(methyl Thiocyanate).—Bis-chloromethyltetramethyldisiloxane (115 g., 0.5 mole) was refluxed in an acetone (2 l.) solution of potassium thiocyanate (116 g., 1.2 moles) for 24 hours. The acetone solution was diluted with water and the insoluble oil separated and dried over $CaCl_2$ to give pure tetramethyldisiloxane-1,3-bis-(methyl thiocyanate) (52 g., 40% yield), n^{25}D 1.4843, d^{25}_4 1.083. *Anal.* Calcd. for $C_8H_{16}ON_2S_2Si_2$: Si, 20.32; sp. ref.,[3] 0.2656. Found: Si, 20.21, 20.29; sp. ref., 0.2642.

Trimethylsilylmethylthiocyanate.[4]—Trimethylsilylmethyl thiocyanate was prepared in 90% yield by refluxing chloromethyltrimethylsilane (61 g., 0.5 mole) with potassium thiocyanate (75 g., 0.77 mole) in 600 cc. of acetone. Distillation yielded trimethylsilylmethyl thiocyanate, b.p. 199° (741 mm.), n^{25}D 1.4650, d^{25}_4 0.943. *Anal.* Calcd. for $C_5H_{11}NSSi$: Si, 22.07; sp. ref.,[3] 0.2931. Found: Si, 21.54, 21.5; sp. ref., 0.2936.

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[1] *Org. Syntheses*, **21**, 84 (1941).

[2] J. E. Noll, B. F. Daubert and J. L. Speier, THIS JOURNAL, **73**, 3867 (1951).

[3] Calcd. from bond refraction values of E. L. Warrick, *ibid.*, **68**, 2455 (1946).

[4] G. D. Cooper, *ibid.*, **76**, 2499 (1954), b.p. 196–197°; n^{20}D 1.4676; d^{20}_4 0.9426.

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Highly Halogenated Alkanes Derived from Fluorine-containing Alcohols

BY E. T. MCBEE, D. H. CAMPBELL AND C. W. ROBERTS

RECEIVED OCTOBER 22, 1954

The reaction of the *p*-toluenesulfonates of 2,2,2-trifluoroethanol, 2,2,3,3,3-pentafluoropropanol and 2,2,3,3,4,4,4-heptafluorobutanol[1] with alkali halides was utilized for the preparation of highly halogenated alkanes. The tosyl esters were prepared following standard procedures,[3,4] and the displacement of the tosyl group was effected by reaction with the suitable potassium halide in refluxing di-

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[1] 2,2,2-Trifluoroethanol and 2,2,3,3,4,4,4-heptafluorobutanol were obtained from Minnesota Mining and Manufacturing Co., St. Paul, Minnesota. 2,2,3,3,3-Pentafluoropropanol was prepared by lithium aluminum hydride reduction[2] of pentafluoropropionic acid, obtained from the same company.

[2] D. R. Husted and A. H. Ahlbrecht, THIS JOURNAL, **74**, 5422 (1952).

[3] C. S. Marvel and V. C. Sekera, *Org. Syntheses*, **20**, 50 (1940).

[4] A. T. Roos, H. Gilman and N. J. Beaber, "Organic Syntheses," Coll. Vol. I, 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1941, p. 145.