water, methanol, or ethanol.[7] Reduction of the double bond in the unsaturated esters is also noteworthy.

Thus, in some cases where it is desirable not to use a stronger reducing agent, a large excess of sodium borohydride in methanol may serve quite effectively to reduce saturated or unsaturated esters to saturated alcohols. When a ketone or an aldehyde is to be reduced in the presence of an ester function, care should be taken to avoid a large excess of borohydride and elevated temperatures if partial reduction of the ester is to be avoided.

Experimental

Sodium Borohydride.—The sodium borohydride used was obtained from Metal Hydrides, Inc., Beverly, Mass., Lot. No. 191-1, rated purity, 98 plus %. Spectrographic analysis indicated the following: Li, not detectable; K, 0.01%; Ca and Si, traces.

Esters.—The heterocyclic unsaturated esters were prepared by esterification of the appropriate acids with methanol and hydrochloric acid, the acids having been prepared[8] by condensation of the appropriate methyl heterocycle with chloral and hydrolysis of the product with alkali. Methyl 3-(4′-pyridyl)propanoate was prepared from the saturated acid obtained by hydrogenation of the unsaturated acid. The other esters were obtained from stock or prepared by esterification of the appropriate acid. All the esters [except methyl 3-(4′-pyrimidyl)propenoate, which see] are known compounds, and structures and purity were confirmed by n.m.r. spectroscopy.

Reductions.—All the reductions were done in a similar manner. A weighed amount of the ester was dissolved in methanol and added to a weighed amount of sodium borohydride. When the initial vigorous reaction had subsided, the mixture was heated under reflux for 1–2 hr. The solution was cooled, an equal volume of water was added, and some of the methanol was removed on a rotary evaporator. The aqueous solution was extracted with five 50-ml. portions of chloroform, the combined extracts were dried over sodium sulfate, and the chloroform was removed on the rotary evaporator at 30 to 40°. A portion of the product was dissolved in carbon tetrachloride or deuteriochloroform, and its n.m.r. spectrum was determined with a Varian A-60 spectrometer. Peak assignments were made by comparison with the spectra of the expected products where available or by analogy with similar compounds. The per cent of each product in the mixture was calculated from the integral of the spectrum. The reduction products from methyl cinnamate and methyl 2-nonenoate gave n.m.r. spectra which were too complex to allow calculation of the composition, but vapor phase chromatography (carried out on a 0.25-in. Ucon polar column at 210° for the methyl cinnamate reduction product and at 185° for the methyl 2-nonenoate reduction product), in conjunction with the n.m.r. data, allowed calculation of the per cents. The values given in Table I are probably accurate to within a few per cent.

3-(4′-Pyrimidyl)-1-propanol.—3-(4′-Pyrimidyl)propenoic acid[8] was esterified by treatment at room temperature with methanolic hydrochloric acid for 3 days. Concentration of the reaction mixture, addition of aqueous sodium bicarbonate, extraction into chloroform, evaporation of the chloroform, and crystallization of the residue from cyclohexane gave **methyl 3-(4′-pyrimidyl)-propenoate** in 71% yield, m.p. 86–88°.

Anal. Calcd. for $C_8H_8N_2O_2$: C, 58.5; H, 4.9; N, 17.1. Found: C, 58.8; H, 5.1; N, 16.8.

The ester was reduced and the product was isolated by the standard procedure as described. Short-path distillation at 90° (50 μ) gave **3-(4′-pyrimidyl)-1-propanol** as a clear, slightly viscous oil; ultraviolet absorption, $\lambda_{max}^{CH_3OH}$ 245 mμ (ε 2950), 270 (330); n.m.r. absorption (in deuteriochloroform), C-2′ H, δ 9.50 (s); C-6′ H, 9.00 (d); C-5′ H, 7.67 (d); C-3 H_2, 4.05 (t); C-1 H_2, 3.28 (t); C-2 H_2, 2.42 (m).

Anal. Calcd. for $C_8H_{10}N_2O$: C, 60.8; H, 7.3; N, 20.3. Found: C, 60.6; H, 7.1; N, 20.1.

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Optically Active Benzylamine-α-*d*[1]

A. STREITWIESER, JR., AND J. R. WOLFE, JR.[2]

Department of Chemistry, University of California, Berkeley, California

Received January 30, 1963

As part of a study of optically active benzyl-α-*d* compounds,[3–5] we prepared the corresponding amine. Since we contemplate no further work with this material in the near future, we report herein the preparation and properties of optically active benzylamine-α-*d*. The preparation followed our previous stereospecific preparations of 2-octylamine and 1-aminobutane-1-*d*[6]; namely, conversion of the alcohol to an arenesulfonate, displacement by sodium azide, and reduction of the product azide with lithium aluminum hydride. By this procedure, alcohol having $[\alpha]_D$ −0.215° gave a 54% over-all yield of crude amine which, on purification, had $[\alpha]_D$ +0.24°. The reactions involve a single inversion of configuration; hence, amine and alcohol of the same sign of rotation have the same configuration.

The degree of optical purity of the amine relative to the alcohol was checked by the method of Snyder and Brewster.[7] The benzylamine-α-*d* was converted to the N,N-dimethylamine with formic acid and formaldehyde and thence to the trimethylammonium acetate by treatment successively with methyl iodide, silver oxide, and acetic acid. Pyrolysis of the quaternary acetate gave benzyl-α-*d* acetate which was reduced with lithium aluminum hydride to benzyl-α-*d* alcohol having $[\alpha]_D$ −0.180°. Snyder and Brewster used a similar sequence to convert α-phenethylamine to α-phenethyl acetate with essentially complete inversion of configuration. In our over-all conversion of benzyl-α-*d* alcohol to amine and back to alcohol, there occurred 18% racemization.

We suspect that most, if not all, of this racemization occurred in the first step, the preparation of benzyl-α-*d* tosylate. During the Schotten–Bauman procedure used, any reaction of the aqueous sodium hydroxide with the benzyl-α-*d* tosylate formed would generate alcohol of inverted configuration and would result in tosylate having lower optical purity than the starting alcohol; hence, this method is not recommended for stereochemical studies. The benzyl-α-*d* tosylates used in our other studies were prepared in dry pyridine in which this problem does not occur.[4,5]

Experimental

(+)-**Benzylamine-α-*d*.**—A solution of 50 ml. of 25% sodium hydroxide was added over a period of 1.5 hr. to a stirred mixture of 21 g. of benzyl-α-*d* alcohol,[3] $\alpha^{25}D$ −0.860 ± 0.004°, $\alpha^{25}{}_{5463}$ −1.044 ± 0.007° (*l* 4), and 29 g. of *p*-toluene sulfonyl chloride,

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[1] Stereochemistry of the Primary Carbon. XII. This research was supported in part by a grant from the Petroleum Research Fund.

[2] Monsanto Chemical Company Fellow, 1956–1957.

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[4] A. Streitwieser, Jr., and J. R. Wolfe, Jr., *ibid.*, **81**, 4912 (1959).

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[6] A. Streitwieser, Jr., and W. D. Schaeffer, *J. Am. Chem. Soc.*, **78**, 5597 (1956).

[7] H. Snyder and J. Brewster, *ibid.*, **71**, 291 (1949).

maintained at 5°. An additional 29 g. of *p*-toluene sulfonyl chloride and 50 ml. of 25% sodium hydroxide were added during 1.5 hr. After additional stirring for 3 hr. at 5°, the mixture was poured into water and filtered. The solid product was dissolved in ether, dried with potassium carbonate, reprecipitated by cooling with Dry Ice, and centrifuged. Residual solvent was evaporated and the product was crystallized from benzene–hexane at low temperature. Yields by this procedure were about 70%. (Note: During one such run, the product polymerized spontaneously while being stored overnight in the refrigerator during recrystallization.)

The resulting benzyl-α-*d* tosylate was added to a solution of 20 g. of sodium azide in 58 ml. of water and 260 ml. of methanol and maintained at 60° for 1 day. The mixture was diluted with water and extracted with ether. The washed and dried ether solution was treated with 10 g. of lithium aluminum hydride in the usual manner. The reaction mixture was decomposed with water and the washed and dried ether solution was distilled giving 11.7 g. (54%) of amine, b.p. 72–95° (10–11 mm.), contaminated by some benzyl alcohol (infrared).

The combined product from two such runs was dissolved in dilute hydrochloric acid and washed with ether. The aqueous solution was made basic with sodium hydroxide and extracted with ether. The dried extract was distilled and the residue was fractionated giving two fractions: fraction 1, b.p. 79.5–81° (17 mm.), 9.6 g., α^{25}_{D} 0.940 ± 0.006°, α^{25}_{5463} 1.087 ± 0.003° (*l* 4); fraction 2, b.p. 81–83° (18–19 mm.), 9.5 g., α^{25}_{D} 0.941 ± 0.005° α^{25}_{5463} 1.105 ± 0.011° (*l* 4). The combined product had n^{25}_{D} 1.5404; freshly fractionated benzylamine had n^{25}_{D} 1.5410.

(−)-Benzyl-α-*d* Alcohol from (+)-Benzylamine-α-*d*.—A mixture of 9.8 g. of the benzylamine-α-*d*, 26.2 g. of 88% formic acid and 25.7 g. of 37% formalin was heated at 95–100° until a vigorous evolution of gas commenced. The flask was removed from the oil bath and when the reaction subsided, 25.7 g. of the formalin and 26.2 g. of 88% formic acid were added and the mixture was refluxed for 8 hr. After cooling, 75 ml. of 4 *N* hydrochloric acid was added and the mixture was evaporated *in vacuo* to a thick sirup. The mixture was diluted with water, made basic with sodium hydroxide, and extracted with ether. Evaporation of the solvent left a pale yellow liquid which was difficult to distil because of excessive foaming; hence, the crude product was stirred with 30 g. of methyl iodide and 90 ml. of ether for 2 hr. in an ice bath and 14 hr. at room temperature. The trimethylbenzyl-α-*d*-ammonium iodide was filtered, washed with ether, and dried *in vacuo*; yield, 22.7 g. (90% from amine).

A solution of this product in 250 ml. of water was treated with a suspension of silver oxide in 125 ml. of water prepared from 68 g. of silver nitrate.[8] After stirring for 8 hr., the mixture was filtered with Filter-aid and the solid was washed with water. To the combined aqueous solutions was added 69 g. of glacial acetic acid. The mixture was evaporated to a thick sirup which was distilled *in vacuo*. The distillate was dissolved in ether, washed, dried and distilled, yielding 7.5 g. (55% from amine) of benzyl-α-*d* acetate, b.p. 98–99° (10–11 mm.), identified by the infrared spectrum. Reduction in the usual way with lithium aluminum hydride gave benzyl-α-*d* alcohol, α^{27}_{D} −0.355 ± 0.004°, α^{25}_{5463} −0.431 ± 0.004° (*l* 2). The alcohol was converted to the hydrogen phthalate, recrystallized from benzene–cyclohexane and again reduced to alcohol with lithium aluminum hydride giving benzyl-α-*d* alcohol, b.p. 92–94° (7–8 mm.), α^{25}_{D} −0.352 ± 0.005°, α^{25}_{5463} −0.418 ± 0.012° (*l* 2).

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Organosilicon and Tin Alkylthiols

WALTER STAMM

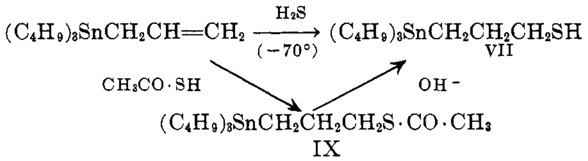
Research Center, Stauffer Chemical Company, Chauncey, New York

Received July 1, 1963

Only a few organometallic alkylthiols have been described previously. Marvel and Cripps[1] prepared bismethylbis(propyl-3-thiol)silane by saponification of the respective thiolacetate. Later[2] several additional silicon-containing thiols were synthesized by this method. Noller and Post[3] prepared methylthioltrimethylsilane by alkaline hydrolysis of its isothiouronium bromide; Cooper[4] and Schmidt and Wieber[5] described the synthesis of methylthiolsiloxanes from chloromethylsiloxanes and potassium hydrosulfide. Only one publication[6] has become known describing the direct addition of hydrogen sulfide to unsaturated organosilanes at high temperatures and under pressure. However, the principal reaction products were organosilicon sulfides. Organosilicon alkylthiols were only identified as by-products in yields below 10%.

No organotin alkylthiols are reported in the literature. Noltes and van der Kerk[7] attempted the synthesis of propyl-3-thioltriphenyltin by the addition of triphenyltin hydride to allyl mercaptan, but obtained propene, H_2S, and bis(triphenyltin)sulfide instead. And Seyferth[8] observed only cleavage of vinyltin compounds by mercaptans as well as other electrophilic reagents.

This note describes the synthesis of the first reported organotin alkylthiols by two different routes and a new method for the preparation of organosilicon alkylthiols. These methods consist of either radiation-induced free-radical ("anti-Markovnikov") addition of hydrogen sulfide to olefinic unsaturated organometallic compounds at Dry Ice bath temperatures, or free-radical addition of thiolacetic acid at or below room temperature, followed by alkaline hydrolysis. The alkylthiols obtained by both methods were identical as demonstrated with tributylallyltin in the following example.



A quartz mercury vapor lamp was the most effective source of radiation, especially if used in connection with the quartz reactor described in the Experimental reaction. Considerably lower yields were obtained in Vycor flasks and also with long wave ultraviolet light.

The primary mercaptan structure was unequivocally confirmed by 60-Mc. n.m.r. spectra.[9]

Main by-product of the hydrogen sulfide addition was sulfide, which—as shown by independent experiments—was formed by the following reaction.

$$(C_4H_9)_3Sn(CH_2)_3SH + CH_2{=}CH{\cdot}CH_2Sn(C_4H_9)_3 \xrightarrow{h\nu} [(C_4H_9)_3Sn(CH_2)_3]_2S$$

In order to suppress this side reaction a larger excess of hydrogen sulfide was employed. The use of low-boiling aliphatic hydrocarbon diluents influenced favor-

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