since a 46% yield of the coupled product was obtained by heating for six hours at 200° in the presence of 2% by weight of the catalyst.

With a related compound, 4-methylquinazoline, we failed to obtain any coupled product upon heating at 200° for four hours in the presence of 2% by weight of 5% palladium-on-carbon.

Experimental

3,3′-Dimethyl-2,2′-biquinoxaline.—2-Methylquinoxaline (50.0 g., 0.347 mole) was placed in a glass liner for a Pendaclave high pressure hydrogenation apparatus, and 1.0 g. of 5% palladium-on-carbon catalyst was added. The mixture was agitated and heated at 200° for 6 hr. The solid reaction mixture was taken up in 200 ml. of hot ethyl acetate and filtered, using suction. The filtrate was cooled in an ice bath and the product was collected by suction filtration. Yield was 16.3 g. of brown-red crystalline material having m.p. 256–258.5°. The filtrate was evaporated and the residue was distilled at reduced pressure, leaving an additional 5.8 g. of product having m.p. 245–252° as residue. Total yield was 22.1 g. (46%). Twenty-three grams of 2-methylquinoxaline was recovered from the vacuum distillation. An analytical sample as long brownish red needles having m.p. 256.5–258.5° was prepared by vacuum sublimation.

Anal. Calcd. for $C_{18}H_{14}N_4$: C, 75.5; H, 4,9; N, 19.6. Found: C, 76.0; H, 4.6; N, 19.6.

Infrared (KBr): 3.20 (w), 3.24(w), 6.20(m), 6.45 (m,sh), 6.52 (s), 6.80 (s), 7.04 (s), 7.30 (w), 7.67 (m), 7.93 (m), 11.76 (m), 12.33 (m), 13.20 (s), 15.32 (m)μ. Ultraviolet ($CHCl_3$): λ_{max} 277 mμ (ϵ38,500), 367 mμ (ϵ12,900), 383.5 mμ (ϵ15,000), 468 mμ (ϵ 5600).

Cleavage of 1,3-Butanediol Cyclic Sulfate with Hydrogen Chloride

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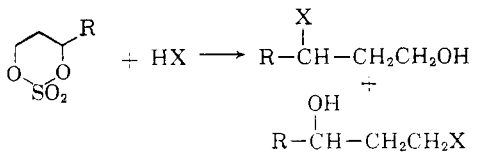
Reactions of 1,3-diol cyclic sulfates with hydrogen halides have been shown to give 1,3-halohydrins.[1,2] Symmetrical sulfates can provide only one product, but unsymmetrical materials could lead to isomers.



The reactions of 1,3-butanediol cyclic sulfate with hydrogen halides have been described to furnish only 3-halo-1-butanols,[1,2] while similar reactions of hydrogen chloride with 1,3-butanediol or 2-methyloxetane have been shown to provide mixtures of 3-chloro-1-butanol and 4-chloro-2-butanol under a variety of conditions.[3] In no case was one isomer obtained exclusively. A desire for a convenient source of pure 3-chloro-1-butanol stimulated a reinvestigation of the cyclic sulfate–hydrogen chloride reaction.

Reaction of 1,3-butanediol cyclic sulfate with hydrochloric acid was carried out as described.[1] The product, a distillable liquid, exhibited physical properties which were quite similar to those reported for 3-chloro-1-butanol[1,4]; however, vapor phase chromatography indicated that the product was a mixture of two materials in approximately a three to one ratio. Syntheses of 3-chloro-1-butanol and 4-chloro-2-butanol were performed by known methods.[3] Vapor phase chromatographic retention times of these materials demonstrated that the product from the cyclic sulfate reaction was indeed a mixture of 73% 3-chloro-1-butanol and 27% 4-chloro-2-butanol rather than pure 3-chloro-1-butanol.

The corresponding reaction with hydrobromic acid has provided a three component mixture comprised of the isomeric 1,3-bromobutanols and a lower boiling material.

Experimental[5]

Instrument.—A Beckman GC-2 Vapor Fractometer with a 6-ft. column of lac 446 polyester on Chromosorb-W was employed for gas chromatography at 130° with a helium flow of 60 ml./min.

1,3-Butanediol Cyclic Sulfate (I).—The method of Lichtenberger[1] was employed; however, 20% oleum was used in place of 47% material.

A solution of 104 g. of 1,3-butanediol in 600 ml. of chloroform was placed in a 2-l. flask equipped with a stirrer, condenser, thermometer, and dropping funnel. The solution was cooled in an ice bath and the temperature maintained at 0–10° as 1060 g. of 20% oleum was slowly added. After addition, the reaction mixture was kept at ice-bath temperature for 1 hr. and then poured onto ice. The layers were separated and the aqueous layer was extracted with chloroform. The chloroform portions were combined, washed with water, 10% aqueous sodium bicarbonate, and water again. Activated charcoal was added to the chloroform solution and then the solution was filtered, dried, and evaporated leaving 99.5 g. (56% yield) of a clear oil which solidified on cooling. Recrystallization from ether provided white crystals of I, m.p. 44–46° (reported,[1] m.p. 43–44°).

Reaction of I and Hydrochloric Acid.—A mixture of 20 g. of the cyclic sulfate of 1,3-butanediol and 50 ml. of concentrated hydrochloric acid was heated on the steam bath for 40 min. During this time the two layer mixture became homogeneous. The mixture was cooled, 200 ml. of water was added and the solution was extracted with three 100-ml. portions of ether. Washing of the combined ether extracts with 10% aqueous sodium bicarbonate and then with water was followed by drying over magnesium sulfate. Evaporation of the ether left 9 g. of an oil which was distilled *in vacuo* to give 7.5 g. (53%) of a clear liquid, b.p. 70–71°/17 mm., n^{25}D 1.4397.

Anal. Calcd. for C_4H_9ClO: C, 44.25; H, 8.34; Cl, 32.66. Found: C, 44.34; H, 8.16; Cl, 32.25.

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[1] J. Lichtenberger and R. Lichtenberger, *Bull. soc. chim. France*, 1002 (1948).

[2] J. Lichtenberger and L. Dürr, *ibid.*, 664 (1956).

[3] S. Searles, Jr., K. A. Pollart, and F. Block, *J. Am. Chem. Soc.*, **79**, 952 (1957).

[4] J. Velhulst, *Bull. soc. chim. Belges*, **40**, 85 (1931).

[5] All boiling and melting points are uncorrected.

Vapor phase chromatography showed two peaks representing 27% and 73% of the product, respectively.

3-Chloro-1-butanol.—This material was prepared by lithium aluminum hydride reduction of 3-chlorobutyric acid as described by Searles, *et al.*,[3] b.p. 70–72.5°/17 mm., $n^{25}\mathrm{D}$ 1.4399. (Reported, b.p. 67–68°/15 mm.[4] and 74°/16 mm.;[3] $n^{25}\mathrm{D}$ 1.4446[4] and 1.4398[3]). Vapor phase chromatography showed only one peak with the same retention time as that of the large peak from the above mixture.

4-Chloro-2-butanol.—Lithium aluminum hydride reduction of 4-chloro-2-butanone gave this material, b.p. 68–70°/20 mm., $n^{25}\mathrm{D}$ 1.4395 (reported, b.p. 67°/20 mm.,[6] $n^{20}\mathrm{D}$ 1.4408[6] and 1.4440[3]). Gas chromatography showed a single peak with a retention time equal to that of the small peak from the cyclic sulfate product.

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(6) F. Sondheimer and R. B. Woodward, *J. Am. Chem. Soc.*, **75**, 5438 (1953).

Vinylogy in Alkylation of *t*-Butyl Esters

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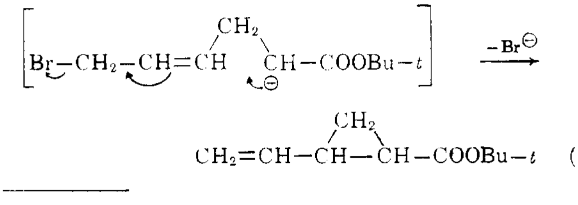
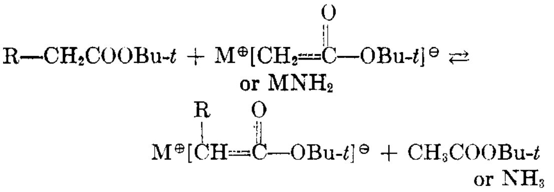
In an extention of studies on alkylation of *t*-butyl acetate with organic halides,[1] the reaction of 1,4-dibromo-*trans*-2-butene and *t*-butyl acetate has been investigated. When a mixture of *t*-butyl acetate with an equivalent amount of lithium amide suspended in liquid ammonia was treated with 1,4-dibromo-*trans*-2-butene dissolved in anhydrous tetrahydrofuran, a crystalline diester was obtained in 64–67% yields based on the bromide. The ester was found to be di-*t*-butyl *trans*-4-octene-1,8-dioate, as hydrolysis with ethanolic potassium hydroxide afforded *trans*-4-octene-1,8-dioic acid in an 88% yield and catalytic hydrogenation of the ester over Raney nickel gave crystalline di-*t*-butyl suberate, which was subsequently hydrolyzed to suberic acid.

The condensation of 1,4-dibromo-2-butene with sodiomalonate has already been described as resulting in the exclusive formation of 2-vinylcyclopropane 1,1-dicarboxylate.[2] An analogous reaction of *t*-butyl acetate according to equation 1 had been anticipated, but no cyclopropanecarboxylate could be isolated from the condensation product. A prerequisite to the cyclization should be the deprotonation of monoalkylated ester (equation 2).[3] As described previously,[1] the second alkylation of the *t*-butyl monoalkylacetates is scarcely perceptible with lithium amide, while dialkylated esters along with monoderivatives are produced in condensation by means of sodium or potassium amide. Accordingly the present reaction was repeatedly examined for possible formation of cyclized products in the presence of the latter amides, but the sole reaction product isolated in reduced yields was di-*t*-butyl *trans*-4-octenedioate, as before.



(1)



$$\mathrm{R{-}CH_2COOBu\text{-}}t + \underset{\text{or } \mathrm{MNH_2}}{\mathrm{M^{\oplus}[CH_2{=}\overset{\overset{O}{|}}{C}{-}OBu\text{-}}t]^{\ominus}} \rightleftarrows \mathrm{M^{\oplus}[\overset{\overset{R}{|}}{C}H{=}\overset{\overset{O}{|}}{C}{-}OBu\text{-}}t]^{\ominus} + \underset{\text{or } \mathrm{NH_3}}{\mathrm{CH_3COOBu\text{-}}t} \quad (2)$$

α-Dialkylation of ester by means of lithium amide was observed in the benzylation of *t*-butyl crotonate. When a mixture of *t*-butyl crotonate and lithium amide suspended in liquid ammonia was treated with an equivalent amount of benzyl chloride and the condensation products were hydrolyzed by boiling hydrochloric acid dissolved in dioxane, two crystalline acids melting at 101–102° and 98.5–99.5°, respectively, were isolated. Analyses of the higher melting acid agreed with a monobenzylated crotonic acid, while the lower melting acid with a dibenzylated product. Infrared spectrum of the dibenzylated acid indicated the presence of a vinyl group and a carbonyl group which is *not* in conjugation with the ethylene bond. The assigned structure of 2,2-dibenzyl-3-butenoic acid was confirmed by NMR spectrum as described in the Experimental.[4] Infrared spectrum of the monobenzylated crotonic acid revealed the presence of a carboxyl group in conjugation with an ethylene bond, but comparison with authentic 5-phenyl-2-pentenoic acid[5] exhibited remarkable differences and a mixed melting point showed depression. Evidence supporting the structure of 2-benzyl-2-butenoic acid was again obtained by means of NMR spectrum. These benzylated crotonic acids were always accompanied by a considerable amount of insoluble polymeric products, which were not investigated. The yields and relative ratio of mono- and dibenzylated products were variable. In most favorable conditions 2-benzyl-2-butenoic acid was obtained in a 31% yield, while 2,2-dibenzyl-3-butenoic acid in a 36% yield.

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(1) K. Sisido, Y. Kazama, H. Kodama, and H. Nozaki, *J. Am. Chem. Soc.*, **81**, 5817 (1959).

(2) (a) R. W. Kierstead, R. P. Linstead, and B. C. L. Weedon, *J. Chem. Soc.*, 3610 (1952); (b) S. F. Birch, R. A. Dean, and N. J. Hunter, *J. Org. Chem.*, **23**, 1390 (1958); (c) J. Nickl, *Chem. Ber.*, **91**, 553 (1958).

(3) For a recent publication on related problems see (a) W. R. Dunnavant and C. R. Hauser, *J. Org. Chem.*, **25**, 1693 (1960). (b) O. Mårtensson and E. Nilson, *Acta Chem. Scand.*, **15**, 1026 (1961).

(4) The signal of benzyl methylene protons of 2,2-dibenzyl-3-butenoic acid was observed as a quartet of typical AB coupling pattern. This is a token indicating that two protons of the methylene group are non-equivalent possibly because of the hindered free rotation of benzyl groups.

(5) H. Staudinger and H. Schneider, *Ber.*, **56**, 699 (1923).