Experimental

Dibenzothiophene-5-oxide was prepared by the method of Brown, Christiansen and Sandin.[1] Six grams (0.03 mole) of dibenzothiophene-5-oxide was partially dissolved in 50 ml. of carbon tetrachloride, and a pinch of aluminum trichloride added. The solution was warmed and stirred while 5.0 g. (0.04 mole) of bromine was added dropwise. Stirring and heating below reflux temperature were continued for 24 hours, with no apparent evolution of hydrogen bromide. Complete solution occurred, but a precipitate was formed on cooling. The precipitate was filtered and washed well with water. Two recrystallizations from *n*-butanol gave 3.7 g. (36%) of a white solid melting 223–224°. A mixed m.p. with 2,8-dibromodibenzothiophene[7] (m.p. 223–224°), prepared by direct bromination of dibenzothiophene, was not depressed. Infrared absorption measurements have confirmed the original presence of the sulfoxide group and its absence in the final product; also, nuclear bromo-substitution is indicated. Additional research is in progress to determine the mechanism and scope of this reaction.[8]

Acknowledgment.—The authors are grateful to Dr. Velmer A. Fassel and Mr. Marvin Margoshes for their infrared absorption measurements and to Mr. Donald Esmay for preparation of the 2,8-dibromodibenzothiophene.

(7) C. R. Neumoyer and E. D. Amstutz, THIS JOURNAL, **69**, 1921 (1947).

(8) Experimental evidence shows that the HBr from initial bromination rapidly reduces the sulfoxide, and thus releases additional bromine for nuclear substitution.

DEPARTMENT OF CHEMISTRY
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RECEIVED MARCH 5, 1951

Replacement Reactions of 1-(*trans*-2-Bromocyclohexyl)-piperidine

BY F. N. HAYES AND D. E. PETERSON

The reaction of cyclohexene, pyridine and bromine has been reported[1] to give 1-(*trans*-2-bromocyclohexyl)-pyridinium bromide which was subsequently hydrogenated to 1-(*trans*-2-bromocyclohexyl)-piperidinium bromide. This has been treated with aqueous potassium hydroxide to give 1-(*trans*-2-hydroxycyclohexyl)-piperidine.[1,2] In a similar manner, the corresponding methoxy, ethoxy, phenoxy, ethylthio and diphenylcyanomethyl derivatives have been prepared.

(1) F. N. Hayes, H. K. Suzuki and D. E. Peterson, THIS JOURNAL, **72**, 4524 (1950).

(2) T. S. Kusner, *Ukrain. Khem. Zhur.*, **7**, Wiss. Abt. 179 (1932).

Experimental

An aqueous solution of 39.2 g. of 1-(*trans*-2-bromocyclohexyl)-piperidinium bromide was treated with 6.73 g. of potassium hydroxide at 0–5°. The free amine was obtained in 71% yield by ether extraction. Further reaction with aqueous base at 100° gave 62% of 1-(*trans*-2-hydroxycyclohexyl)-piperidine.[1,2]

Reactions of 1-(*trans*-2-bromocyclohexyl)-piperidinium bromide with two equivalents of methoxide ion in methanol, ethoxide ion in ethanol, phenoxide ion in phenol and ethyl sulfide ion in ethyl mercaptan gave the corresponding methoxy, ethoxy, phenoxy and ethylthio derivatives.

Diphenylacetonitrile and sodamide were treated with 1-(*trans*-2-bromocyclohexyl)-piperidine, using the procedure of Easton, Gardner and Stevens,[3] to give 1-(*trans*-2-diphenylcyanomethylcyclohexyl)-piperidine.

(3) N. R. Easton, J. H. Gardner and J. R. Stevens, THIS JOURNAL, **69**, 2941 (1947).

DEPARTMENT OF CHEMISTRY
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Alkylation of *m*-*t*-Butylphenol

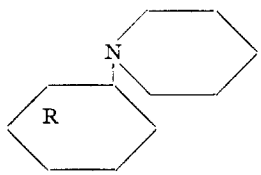
BY HAROLD HART AND WILLIAM G. VOSBURGH[1]

In connection with another investigation, it became necessary to determine the course of the non-catalyzed alkylation of *m*-*t*-butylphenol (I) with *t*-butyl chloride. I was synthesized according to a scheme analogous to that recently published by Carpenter, Easter and Wood.[2]

It was found that I reacts spontaneously with *t*-butyl chloride (no solvent) at 50–60° to furnish a nearly quantitative yield of 2,5-di-*t*-butylphenol. The alkylation product was identical with a sample synthesized from *p*-di-*t*-butylbenzene according to the procedure of Carpenter, *et al.*[2] The ultraviolet absorption spectrum of the alkylation product, determined in cyclohexane, clearly demonstrated the absence of an alkyl group para to the hydroxyl.[3,4] The peaks, located at 272 mμ (log ε equals 3.31) and at 279 mμ (log ε equals 3.29), were essentially identical with those found for *m*-*t*-butylphenol itself.

TABLE I

1-(*trans*-2-SUBSTITUTED CYCLOHEXYL)-PIPERIDINES



R	Yield, %	M.p.,[a] °C.	B.p. °C.	B.p. Mm.	Carbon, %[b] Calcd.	Carbon, %[b] Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
Br	..	...	138	6	53.66	53.92	8.19	8.14	5.69	5.81
CH_3O-	53	...	121	9	73.04	72.87	11.95	11.65	7.10	7.06
CH_3CH_2O-	54	...	128	9	73.88	73.61	11.92	11.60	6.63	6.45
C_6H_5O-	50	77	...	.	78.71	78.84	9.71	9.68	5.40	5.38
CH_3CH_2S-	65	...	153	8	68.66	68.51	11.08	10.83	6.16	6.38[c]
$(C_6H_5)_2C(CN)$-	64	155-156	...	...	83.75	83.83	8.44	8.42	7.81	7.70

[a] Melting points taken on a Fisher–Johns block. [b] Analyses by Micro-Tech Laboratories, Skokie, Illinois. [c] Calcd.. S, 14.10. Found: S, 14.42.

(1) This paper is taken in part from the M.S. Thesis of Mr. Vosburgh, June, 1950.

(2) M. S. Carpenter, W. M. Easter and T. F. Wood, *J. Org. Chem.*, **16**, 586 (1951).

(3) H. Hart, THIS JOURNAL, **71**, 1966 (1949).

(4) H. Hart and E. A. Haglund, *J. Org. Chem.*, **15**, 396 (1950).

Experimental

During the course of the synthesis of *m*-*t*-butylphenol,[2] several derivatives were prepared which have not previously been reported.

2,4,6-Tribromo-3-*t*-butylaniline.—*m*-*t*-Butylaniline (b.p. 118–118.5° at 15 mm., 127–128° at 35 mm.) was brominated at room temperature in glacial acetic acid to give 2,4,6-tribromo-3-*t*-butylaniline, colorless needles from dilute methanol, m.p. 117–118°.

Anal. Calcd. for $C_{10}H_{12}NBr_3$: Br, 61.6. Found: Br, 61.4.

Derivatives of *m*-*t*-Butylphenol.—The following derivatives were prepared in the usual manner: (a) 3-*t*-butylphenoxyacetic acid, m.p. 113.5–114°, colorless needles from dilute ethanol; calcd. for $C_{12}H_{16}O_3$, neut. equiv., 208; found, neut. equiv., 207.5. (b) 3,5-dinitrobenzoate, m.p. 103.5–104°, shiny plates from dilute ethanol.

Anal. Calcd. for $C_{17}H_{16}O_6N_2$: N, 8.14. Found: N, 8.16.

Alkylation of *m*-*t*-Butylphenol.—Five grams of *m*-*t*-butylphenol[2] and 3.1 g. of *t*-butyl chloride were heated to 50–60°. Evolution of hydrogen chloride began immediately. During the course of the heating, an additional 2 g. of *t*-butyl chloride was added to replace entrainment losses carried past the condenser by the evolved gas. After warming for 24 hours, crystals formed on cooling. The product, recrystallized from petroleum ether (35–75°), m.p. 120.5–121° (lit. value[2] for 2,5-di-*t*-butylphenol, 118–119°). The yield of crude product was essentially quantitative, of recrystallized material, 6.0 g. (87%). Mixed melting point with an authentic sample prepared by the procedure of Carpenter, *et al.*,[2] showed no depression.

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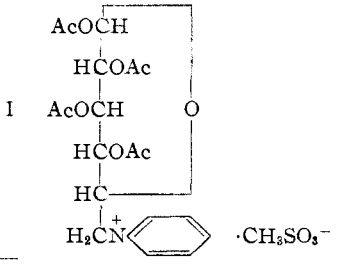
Salts of 6-Pyridinium-6-desoxy-D-glucose

BY B. M. ISELIN[1] AND JOHN C. SOWDEN[2]

Numerous investigators have reported the synthesis of sugar derivatives in which carbon-1 is linked with cyclic tertiary amines such as pyridine or nicotinamide by replacement of the hemiacetal hydroxyl.[3] The present note describes the preparation of derivatives in which the tertiary amine, pyridine, is linked to carbon-6 of the D-glucose chain by replacement of the primary alcoholic hydroxyl. When 1,2,3,4-tetraacetyl-6-methanesulfonyl-β-D-glucose[4] was heated with anhydrous pyridine, there resulted, in good yield, 1,2,3,4-tetraacetyl - 6 - pyridinium - 6 - desoxy - β - D-glucose methanesulfonate, I. Replacement of the methanesulfonyl anion by bromide ion was accomplished by means of ion exchange to give 1,2,3,4 - tetraacetyl - 6 - pyridinium - 6 - desoxy - β - D-glucose bromide. While tetraacetyl-D-glucosylpyridinium bromide is reduced readily in the aromatic nucleus to the corresponding 1,2-dihydropyridine derivative by treatment with sodium dithionite ($Na_2S_2O_4$),[3b] the attempted reduction of the 6-pyridinium-6-desoxy-D-glucose salts was unsuccessful. This is not surprising in view of the fact that N-alkylpyridinium salts, analogous to tetraacetyl-6-pyridinium-6-desoxy-D-glucose salts, undergo secondary changes upon treatment with sodium dithionite.[5] The amino-acetal linkage, present in tetraacetyl-D-glucosylpyridinium salts, seems to facilitate the partial reduction of the aromatic nucleus.[6]



I

Removal of the acetyl groups from tetraacetyl-6-pyridinium-6-desoxy-β-D-glucose methanesulfonate by catalytic saponification with sodium methoxide in chloroform solution gave crystalline 6-pyridinium-6-desoxy-D-glucose methanesulfonate.

Experimental

1,2,3,4-Tetraacetyl-6-pyridinium-6-desoxy-β-D-glucose Methanesulfonate (I).—A solution of 8 g. of 1,2,3,4-tetraacetyl-6-methanesulfonyl-β-D-glucose in 80 ml. of anhydrous pyridine was refluxed for 2.5 hours. On cooling, the dark red reaction mixture deposited a gelatinous precipitate which solidified on gradual addition of 150 ml. of ether. The crude product (7.83 g.) was dissolved in 1 l. of boiling acetone, 0.5 g. of decolorizing carbon was added, and the hot solution was filtered. After concentration to 300 ml., the clear filtrate yielded 5.65 g. (60%) of tetraacetyl-6-pyridinium-6-desoxy-β-D-glucose methanesulfonate as felted needles showing m.p. 225–226° and $[\alpha]^{24}D$ −16° in chloroform, *c* 1.27.

Anal. Calcd. for $C_{20}H_{27}O_{12}NS$: C, 47.52; H, 5.39; N, 2.77; acetyl, 34.1. Found: C, 47.16; H, 5.41; N, 2.77; acetyl, 34.3.

The substance showed an ultraviolet absorption spectrum typical for pyridinium salts with a maximum at $\lambda_{max.}^{alc.}$ 260 mμ (log ε 3.62).

1,2,3,4-Tetraacetyl-6-pyridinium-6-desoxy-β-D-glucose Bromide.—A solution of 1 g. of tetraacetyl-6-pyridinium-6-desoxy-β-D-glucose methanesulfonate in 25 ml. of water was passed through a column containing 50 g. of Amberlite IRA-400 ion-exchange resin which had been pretreated with dilute hydrogen bromide solution. The sulfur-free effluent was concentrated to dryness at 0.3 mm. pressure and room temperature. The solid residue was recrystallized from methyl ethyl ketone to give 520 mg. of the bromide, melting at 232–234°. Two additional recrystallizations from the same solvent gave the pure product showing m.p. 238–239° and $[\alpha]^{24}D$ −15° in water, *c* 0.95.

Anal. Calcd. for $C_{19}H_{24}O_9NBr$: Br, 16.3. Found: Br, 16.7.

6-Pyridinium-6-desoxy-D-glucose Methanesulfonate.—To a solution of 1.65 g. of tetraacetyl-6-pyridinium-6-desoxy-β-D-glucose methanesulfonate in 15 ml. of dry chloroform at −10° was added 1.65 ml. (0.5 eq.) of a 1 *N* solution of sodium methoxide in absolute methanol. After standing for 90 minutes at this temperature, 5 ml. of water was added and the mixture was neutralized with dilute sulfuric acid. The aqueous layer was treated with decolorizing carbon, evaporated to dryness at 0.3 mm. and room temperature and the residue extracted with hot methanol. After removal of inorganic material by centrifugation, the solution was concentrated to dryness at reduced pressure and the residual sirup (1.07 g.) was dissolved in ethanol. On prolonged standing, the solution deposited prisms of 6-pyridinium-6-desoxy-D-glucose methanesulfonate. Recrystallization from methanol–ether gave 638 mg. (58%) of the product melting at 152–155°. After several recrystallizations from methanol–acetone, the substance showed m.p. 155–157°; $[\alpha]^{24}D$

(1) Squibb Institute for Medical Research, New Brunswick, N. J.

(2) Department of Chemistry, Washington University, Saint Louis, Mo.

(3) (a) E. Fischer and K. Raske, *Ber.*, **43**, 1750 (1910); (b) P. Karrer, B. Ringier, J. Büchi, H. Fritzsche and U. Solmssen, *Helv. Chim. Acta*, **20**, 55 (1937); (c) L. J. Haynes and A. R. Todd, *J. Chem. Soc.*, 303 (1950).

(4) B. Helferich and A. Gnüchtel, *Ber.*, **71**, 712 (1938).

(5) P. Karrer, F. W. Kahnt, R. Epstein, W. Jaffé and T. Ishii, *Helv. Chim. Acta*, **21**, 223 (1938).

(6) P. Karrer and F. J. Stare, *ibid.*, **20**, 418 (1937).