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.

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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

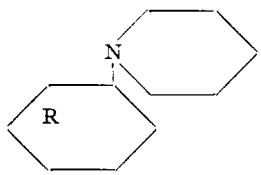
BY HAROLD HART AND WILLIAM G. VOSBURGH[1]

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).