alcohol, but are higher than in most ordinary solvents.[4a,4c] No measurable polymerization, as determined by titration, took place under our experimental conditions. Similarly, attempts at isolation of polymer by removal of monomer indicated the absence of polymeric material. The reaction of acetyl peroxide and allyl bromide is reported to yield a small quantity of polymer.[10] This is analogous to the finding that 1,1-dichloro-2,2-difluoroethylene polymerizes in the presence of acetyl peroxide but not in the presence of benzoyl peroxide.[11]

### Experimental

**Materials.**—Allyl alcohol, b.p. 96.5–97.0°, and allyl bromide, b.p. 70–70.5°, were distilled before use. Benzoyl peroxide from the Matheson Co. was purified by precipitation with methanol from chloroform solution.

**Experimental Procedure.**—Solutions of benzoyl peroxide in the allylic compound were sealed in glass tubes under vacuum. The tubes were immersed in a constant temperature oil-bath at 80 ± 0.1° for measured lengths of time and weighed samples were withdrawn and titrated for unsaturation and peroxide concentration.

Unsaturation was determined by the method of Bartlett and Altschul[12] after standardization of the bromate–bromide solution with the allylic compound under investigation. The concentration of peroxide was determined by the method of Siggia[13] involving back titration of excess arsenious oxide with standard iodine.

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[10] M. S. Kharasch and G. Buchi, *J. Org. Chem.*, **14**, 84 (1949).

[11] E. T. McBee, H. M. Hill and G. B. Bachman, *Ind. Eng. Chem.*, **41**, 70 (1949).

[12] P. D. Bartlett and R. Altschul, THIS JOURNAL, **67**, 812 (1945).

[13] S. Siggia, "Quantitative Organic Analysis via Functional Groups," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 102.

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## The Naphthyltrichlorosilanes

BY JOHN W. GILKEY AND LESLIE J. TYLER

The synthesis of the isomeric naphthyltrichlorosilanes has been completed in this Laboratory and the physical properties of these compounds are described below.

Whereas previous investigators[1] listed α-naphthyltrichlorosilane as a heavy, fuming liquid, it actually is a white solid, melting at 55–57°. However, it does exhibit a pronounced tendency to supercool and a sample has been kept liquid at room temperature for over a year. β-Naphthyltrichlorosilane is also a white solid melting at 52–53°. The two compounds liquify on mixing giving a mixed melting point range of 21–33°.

Both of these compounds were synthesized by reaction of the corresponding naphthylmagnesium bromide with silicon tetrachloride. Infrared absorption spectra of the isomers show absorption maxima for the alpha isomer at 8.18, 8.68, 10.15, 12.03, 12.56, 12.95 and 13.68 microns and for the β-isomer at 9.18, 11.72, 12.30 and 13.52 microns.

### Experimental

**α-Naphthyltrichlorosilane.**—From 262 g., 1.27 moles, of α-bromonaphthalene (redistilled Eimer and Amend, C.P.) and 36 g., 1.5 moles, of magnesium in 450 ml. of ether there was prepared α-naphthylmagnesium bromide. This reagent was added slowly to 503 g., 2.96 moles, of silicon tetrachloride. The reaction mixture was stirred at reflux temperature for 16 hours and then filtered. Fractionation of the filtrate gave 90.2 g., 0.35 mole, a 28% yield of α-naphthyltrichlorosilane as a pale yellow liquid, b.p. 181° (30 mm.), $d^{20}_4$ 1.355, $n^{20}_D$ 1.6085.

On freezing or seeding, the liquid solidified completely. This solid, after recrystallization from petroleum ether, gave fine, white crystals, melting at 55–57°.

*Anal.* Calcd. for $C_{10}H_7SiCl_3$: Si, 10.64; Cl, 40.68; specific refraction, 0.2525. Found: Si, 10.63, 10.79; Cl, 40.07, 40.02; specific refraction, 0.2554.

**β-Naphthyltrichlorosilane.**—In the usual manner a Grignard reagent was prepared from 90 g., 0.43 mole, of β-bromonaphthalene (Eastman Kodak Co.) and 18 g., 0.75 mole, of magnesium turnings. The reaction proceeded smoothly to give a dark brown, two-phased Grignard reagent. This was decanted from the excess magnesium and added slowly to 170 g., 1.0 mole, of silicon tetrachloride. The coupling reaction product was filtered and fractionation gave 53.0 g., 0.20 mole, a 47% yield of β-naphthyltrichlorosilane, b.p. 185° (30 mm.), m.p. 52–53°, a white, hard crystalline material.

*Anal.* Calcd. for $C_{10}H_7SiCl_3$: Si, 10.64; Cl, 40.68. Found: Si, 10.90, 10.95; Cl, 40.11, 40.51.

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[1] (a) W. Melzer, *Ber.*, **41**, 3390 (1908); (b) K. A. Andrianov, *J. Gen. Chem.* (*U. S. S. R.*), **16**, No. 3, 487 (1946).

DOW CORNING CORPORATION
MIDLAND, MICHIGAN
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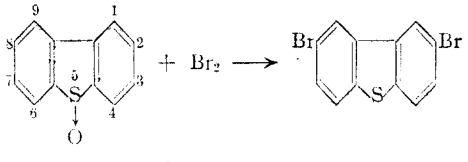
## The Reaction of Dibenzothiophene-5-oxide with Bromine

BY HENRY GILMAN AND ROBERT K. INGHAM

The nitration of dibenzothiophene-5-oxide has been shown to yield the 3-monosubstituted derivative.[1] It was thought that reaction of the -5-oxide with bromine might give 3-bromodibenzothiophene-5-oxide; however, the product of this reaction has been identified as 2,8-dibromodibenzothiophene.



With hydrogen bromide, certain sulfoxides give halogen-addition products[2]

$$R_2S \rightarrow O + 2HBr \longrightarrow R_2S \cdot Br_2 + H_2O$$

Aromatic sulfoxides when treated with dry hydrogen chloride can be reduced to the corresponding sulfides[3]; this reaction may also give nuclear chlorination and even elimination of the sulfur.

The reaction of dibenzothiophene with chlorine gives first the -5-dichloride[1] and nuclear substitution if additional chlorine is employed. With bromine and dibenzothiophene, however, nuclear substitution proceeds, apparently without the formation of a stable -5-dibromide.[4] The analogous compound, dibenzoselenophene, forms the -5-dibromide,[5,6] which on heating above its melting point is converted to 2-bromodibenzoselenophene.[6]

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[1] R. K. Brown, R. G. Christiansen and R. B. Sandin, THIS JOURNAL, **70**, 1748 (1948).

[2] R. Connor, p. 872 of H. Gilman, "Organic Chemistry," 2nd ed., Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1943.

[3] (a) M. Gazdar and S. Smiles, *J. Chem. Soc.*, **97**, 2250 (1910). (b) Also benzyl sulfoxide has been reduced to the sulfide; J. A. Smythe, *ibid.*, **95**, 349 (1909).

[4] N. M. Cullinane, C. G. Davies and G. I. Davies, *ibid.*, 1435 (1936).

[5] C. Courtot and A. Matamedi, *Compt. rend.*, **199**, 531 (1934).

[6] O. Behagel and K. Hofmann, *Ber.*, **72B**, 697 (1939).

### 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.

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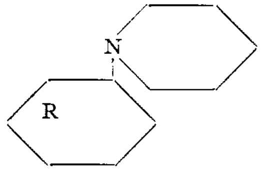
## Replacement Reactions of 1-(*trans*-2-Bromocyclohexyl)-piperidine

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.

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] |
| $(C_6H_5)_2\underset{\mathrm{CN}}{\underset{\vert}{C}}$- | 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.

### 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.

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(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).

(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 m$\mu$ (log $\epsilon$ equals 3.31) and at 279 m$\mu$ (log $\epsilon$ equals 3.29), were essentially identical with those found for *m*-*t*-butylphenol itself.

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(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).