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were immersed in a constant temperature oil-bath at 80 ± 0.1° for measured lengths of time and weighed samples were withdrawn and titrated for unsaturation and peroxide concentration.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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INSTITUTE OF POLYMER RESEARCH
POLYTECHNIC INSTITUTE OF BROOKLYN
BROOKLYN 2, NEW YORK
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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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DOW CORNING CORPORATION
MIDLAND, MICHIGAN
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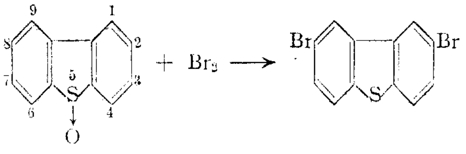
The Reaction of Dibenzothiophene-5-oxide with Bromine

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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