The infrared absorption spectrum showed bands at 1655 and 3370 cm.$^{-1}$, of the carbonyl and hydroxyl groups, respectively. Absorption bands for the terminal methylene group were found at 915 and 991 cm.$^{-1}$.

2,4-Dimethyl-5-allyloxyphenylmesitylphenylcarbinol (I, R = Mesityl).—Mesityllithium was prepared by the method described by Fuson, Speranza and Gaertner.[2b] Four grams of bromomesitylene and 0.28 g. of lithium in 100 ml. of dry ether were stirred under reflux in a nitrogen atmosphere for 3 hours. The milky solution was cooled to 10° and 1.33 g. of the ketone (III) in 20 ml. of dry ether was added. After being stirred one hour the complex was decomposed with crushed ice and the ether layer separated. Steam-distillation of the ether solution removed the ether and also the mesitylene formed by hydrolysis of the excess mesityllithium. The viscous, dark brown oil which remained was extracted from the water with ether and the extract dried. Evaporation of the ether gave a brown oil which crystallized when allowed to stand. Recrystallization from dilute methanol solution yielded 1.8 g. (93%) of crude product. Two more recrystallizations from the same solvent gave the carbinol in the form of colorless, cube-shaped crystals; m.p. 97–98°. If the methanol solution of the carbinol was subjected to prolonged heating it developed a violet color.

Anal. Calcd. for $C_{27}H_{30}O_2$: C, 83.90; H, 7.82. Found: C, 83.73; H, 7.66.

2,4-Dimethyl-5-allyloxyphenyl-*o*-tolylphenylcarbinol (I, R = *o*-Tolyl).—*o*-Tolyllithium was prepared from 3.42 g. of *o*-bromotoluene in the manner described for mesityllithium. The ketone (III) was added after the solution had been cooled and the carbinol was isolated in the manner described for the mesityl analog. The yield of crude product was 1.3 g. (73%); m.p. 78–81°. The pure carbinol melted at 81°.

Anal. Calcd. for $C_{25}H_{26}O_2$: C, 83.77; H, 7.32. Found: C, 83.94; H, 7.57.

Attempted Rearrangement of 2,4-Dimethyl-5-allyloxyphenylmesitylphenylcarbinol.—The carbinol (0.3 g.) was heated at 200–220° at a pressure of 0.05 mm. for one hour. Treatment of the resulting brown mass with alcohol gave 0.27 g. of the original carbinol. When the same procedure was employed with the exception that the heating was continued for two hours, an alcohol-insoluble, resinous mass was obtained from which no pure product was isolated.

Attempted Rearrangement of 2,4-Dimethyl-5-allyloxyphenyl-*o*-tolylphenylcarbinol.—The carbinol (0.18 g.), blanketed with nitrogen, was heated at 200–210° for 90 minutes. At 150° the colorless, molten carbinol began to darken, finally becoming a red-brown, viscous mass. Attempts to obtain a pure fraction from this resinous material by crystallization from dilute acetone solution failed.

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Decomposition of Benzoyl Peroxide in Allyl Alcohol and Allyl Bromide[1,2]

BY NORMAN G. GAYLORD[3] AND FREDERICK R. EIRICH

The decomposition of benzoyl peroxide in solvents is a first order reaction accompanied by a free radical induced chain reaction.[4] This results in a variation of the rate of decomposition with the initial concentration of peroxide.[4a,5,6]

The initial decomposition of benzoyl peroxide in allyl alcohol is a very rapid, kinetically first order, reaction but some or all of the ultimate reaction products act as inhibitors, and their accumulation slows down the decomposition, as shown in Fig. 1.

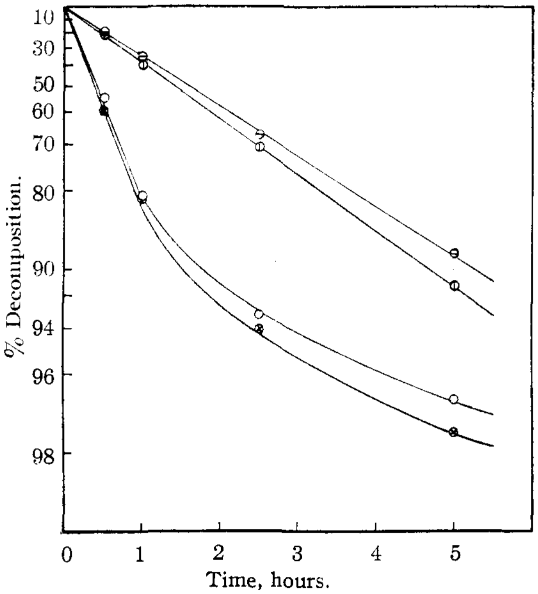

Fig. 1.—The decomposition of benzoyl peroxide in allyl compounds at 80°: allyl bromide: ⦶, P_0 = 0.172 m./kg.; ⊖, P_0 = 0.0848 m./kg.; allyl alcohol: ⊗, P_0 = 0.114 m./kg.; O, P_0 = 0.0833 m./kg. The ordinate scale is proportional to log (100 − % decomposition).

Due to this retardation effect, a circumstance observed in the decomposition of benzoyl peroxide in other alcohols,[7] the rate constant shown in Table I was calculated from the initial first order decomposition. Percentage conversion to polymer in allyl alcohol is very small, polymerization ceasing after a short period, presumably after the catalyst is essentially used up. Originally Staudinger had believed that no polymer could be obtained from allyl alcohol.[8] It has since been shown that in order to obtain a reasonable yield of polymer from allyl alcohol it is necessary to add fresh catalyst to the reaction mixture to replace that which is destroyed or consumed.[9]

TABLE I

THE DECOMPOSITION OF BENZOYL PEROXIDE AT 80 ± 0.1°

Monomer	Initial wt. % peroxide	Peroxide, m./kg.	k_1, hr.$^{-1}$	% polymer 24 hr.
Allyl alcohol	2.02	0.0833	1.66[a]	3.0
	2.77	.114	1.69[a]	4.2
Allyl bromide	2.05	.0848	0.433	0
	4.16	.172	0.480	0

[a] Falling off of rate after one hour; k_1 calculated from initial decomposition.

The decomposition of benzoyl peroxide in allyl bromide is also a first order reaction as shown in Fig. 1. The rate constants, as indicated in Table I, are not as high as for the decomposition in allyl

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[1] Allyl Polymerization. I. This work was carried out with the support of the U. S. Navy, Bureau of Aeronautics.

[2] Abstracted from a portion of the dissertation submitted by N. G. G. to the Graduate Faculty of the Polytechnic Institute of Brooklyn, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[3] E. I. du Pont de Nemours and Co., Yerkes Research Laboratory, Buffalo, N. Y.

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[6] P. D. Bartlett and R. Altschul, *ibid.*, **67**, 816 (1945).

[7] P. D. Bartlett and K. Nozaki, *ibid.*, **69**, 2299 (1947).

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[9] H. Dannenberg and D. E. Adelson, British Patent 566,344 (1944).

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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RECEIVED JUNE 8, 1951

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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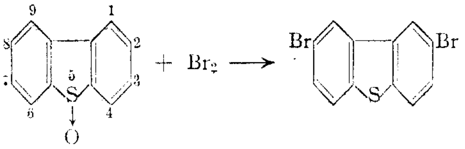
The Reaction of Dibenzothiophene-5-oxide with Bromine

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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