Exposed samples of N-pentylhexanamide were extracted with water and the extract evaporated to dryness. The low-melting residue was recrystallized from isoöctane to obtain white crystals melting at 88–90° (hexanamide melts at 97–98°). The identity of these crystals as hexanamide was established by the exact correspondence of the X-ray diffraction pattern obtained from them with that given by authentic hexanamide.

Addition of 10% sodium hydroxide solution to photo-oxidized N-pentylhexanamide caused evolution of sufficient amounts of either ammonia or an amine to be detected by litmus paper. Quantitative estimation by the ninhydrin procedure and by the method of Van Slyke and Cullen[15] established that less than 2 mg. of ammonia was formed upon exposure of 10 g. of N-pentylhexanamide for 285 hours. Qualitative tests for hydroxylamine and hydrazine[16] were negative. Infrared spectra of irradiated N-pentylhexanamide and of the residual amide after acids had been removed showed no indication of nitriles.

Gas samples were analyzed by the Orsat procedure using a Burrell build-up laboratory model analyzer. Carbon dioxide, oxygen and unsaturated hydrocarbons were determined by usual absorbing reagents. Hydrogen and carbon monoxide were determined by combustion over hot copper oxide in the normal way. Oxygen was added and paraffin hydrocarbons were burned to carbon dioxide over platinized silica at 500°. Inert residual gas was reported as nitrogen. Identity of the inert gas was verified by mass spectrometric analysis.

Acknowledgments.—We are indebted to Dr. J. H. Peterson of this Laboratory for radioactivity measurements. Many helpful discussions with Professors C. S. Marvel and Carl Niemann are gratefully acknowledged.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF BRANDEIS UNIVERSITY]

Some Light Induced Reactions with Disulfide and Mercaptan

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RECEIVED DECEMBER 16, 1958

Thiyl radicals from α-thioglycerol and from sun lamp irradiation of bis-(2,2′-carboxyphenyl) disulfide (II) failed to abstract hydrogen from acetic acid or an electron from acetate anion, and irradiated II failed to undergo intramolecular hydrogen or electron transfer. On irradiation, II was reduced to thiosalicylic acid I by ethanol and 2-propanol, and compound I was oxidized to II by acetone. Pinacol appeared to be the major product of oxidation of 2-propanol by di-*n*-butyl disulfide and of reduction of acetone by thiosalicylic acid. Disulfide II was not reduced under our conditions by *t*-butyl alcohol, diisopropyl ether, isopropyl acetate, benzene, toluene, chloroform and lactic acid, but appeared to be reduced by ethyl lactate, leading to ethyl pyruvate. The course of these reactions is discussed.

In the course of our study of the exchange of diphenylmethyl radical, produced from azo-bis-diphenylmethane, with diphenylmethane, we have observed[2] catalysis of this process by thiophenol by the reversible process 1. Conditions were

$$(C_6H_5)_2CH\cdot + C_6H_5SH \underset{b}{\overset{a}{\rightleftarrows}} (C_6H_5)_2CH_2 + C_6H_5S\cdot \qquad (1)$$

found under which approximately half of the diphenylmethyl radicals which became free reacted with mercaptan (reaction 1a) before dimerizing or reacting with thiyl radical, while approximately one-fourth of the thiyl radicals so formed abstracted α-hydrogen from solvent diphenylmethane (reaction 1b) before dimerizing or reacting with diphenylmethyl. It seemed desirable to review and investigate hydrogen transfer reactions of mercaptans and thiyl radicals.

Mercaptans are oxidized by a variety of reagents, including organic free radicals,[3] the first product normally isolated being the disulfide. The transient thiyl radicals may, before entering into radical combination processes, act as hydrogen abstracting agents. Thiyl radicals, formed by reaction of 2-cyano-2-propyl radicals with mercaptans,[3] oxidize 9,10-dihydroanthracene to a derivative of 9,9′-dianthranyl,[4] an aliphatic azo compound to an azine,[4] and a disubstituted hydrazine to an aliphatic azo compound.[5] They may also abstract hydrogen from the carbonyl carbon of aldehydes, catalyzing their decarbonylation,[6] leading in this case to chain reactions.

The disulfides are also very reactive, undergoing rupture of the S–S linkage under acidic[7a,b] and basic[7a,c] catalysis and by radical dissociation.[8a,b] The dissociation into thiyl radicals may be thermal, at elevated temperature,[9a] and this may be facilitated by radical-type initiators,[9b] or it may be induced by light. Diisoamyl disulfide, presumably acting by formation of thiyl radicals, aromatizes tetralin and ionene,[9b] and diphenyl disulfide aromatizes[10] tetralin and other hydroaromatics at 260° and is reduced by cyclohexene at 140°. The photolysis of disulfides initiates the polymerization of styrene,[11] catalyzes the addition of mercaptans to olefins[12] and converts diphenylmethane to tetraphenylethane.[2] Disulfides in

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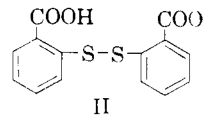
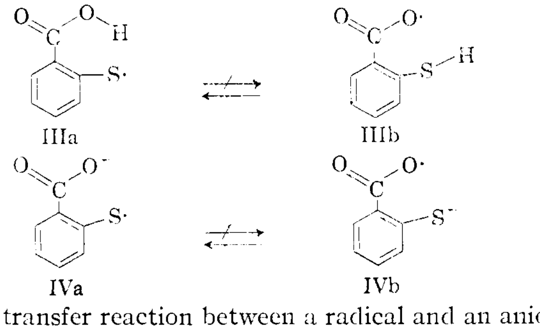
light convert benzohydrol to benzopinacol and benzyl alcohol to some extent to benzaldehyde, while mercaptans convert benzophenone to benzopinacol.[13] These aromatic systems may be particularly reactive, photochemical reduction of benzophenone to benzopinacol being very readily effected by alcohol[14] and even by ether,[14] and certain hydrocarbons[15a]; such reductions are sensitive to structural change[15a,b] in both components. It seemed to us to be of interest to examine the oxidation–reduction reactions of disulfide–mercaptan with some organic compounds in which reactivity was not highly enhanced by allylic or benzyl-type resonance. In most of the experiments solutions or suspensions of a disulfide were irradiated with a sun lamp in Pyrex for several days.

In one group of experiments the action of thiyl radical on carboxylic acids and carboxylate anion was examined. In some preliminary experiments azo-bis-isobutyronitrile was decomposed in acetic acid containing potassium acetate and α-thioglycerol, and in others the acetic acid–sodium acetate–mercaptan solution was warmed with hexaphenylethane. Thiyl radicals presumably were formed in both cases,[16] but there did not appear to be any appreciable reaction between them and the acetic acid or the acetate anion. In the experiment with the azo compound the loss in weight was less than the theoretical weight of the nitrogen to be evolved, indicating that abstraction by the thiyl radical of the carboxyl hydrogen or the carboxylate electron, which would lead to evolution of carbon dioxide, probably had not occurred. The reaction in the presence of hexaphenylethane was examined for succinic acid, but none was found, indicating that abstraction of α-hydrogen had not occurred. Irradiation of bis-(2,2′-carboxyphenyl) disulfide (II) then was examined as a source of thiyl radicals in a variety of solvents. This compound was used primarily because both the mercaptan and disulfide could be isolated fairly readily as solids without excessive inconvenience.



II

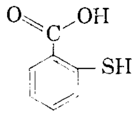
A suspension of this in acetic acid was irradiated for 92 hours, the disulfide being recovered in 73% yield as the only isolable product. Similarly, irradiation of (i) a suspension of the disulfide in water for ten days, (ii) of a solution of the disulfide in dioxan–water for one day, and (iii) of a solution of the potassium salt of the disulfide in water for six hours led to recovery of the original disulfide in greater than 90% yield. In this example the carboxyl group or carboxylate anion and the sulfur radical appear to be well located for interaction. The reactions would be reversible, and, on energetic grounds, the initial radicals IIIa and IVa would be favored over the possible product radicals IIIb and IVb. However, decarboxylation might displace the equilibria and lead to consumption of the initial disulfide. Recovery of the disulfide indicated that the forward reactions were too unfavorable under our conditions. It may be noted that the electron transfer reaction between a radical and an anion of type IVa, IVb, need not be very rapid; it has been reported recently that the thermoneutral exchange between benzoyloxy radical and benzoate anion at 70° is rather slow, considerably slower than the rate of decomposition of benzoyl peroxide at that temperature.[17]



IIIa IIIb (2a)

IVa IVb (2b)

Irradiation of disulfides in alcohols and their derivatives was next examined. Irradiation of II in ethanol led to reduction of the disulfide and isolation of thiosalicylic acid (I), in 40% yield and recovery of none of the disulfide, while a control run under similar conditions in the dark led to recovery of the disulfide in 88% yield. Irradiation of a suspension of II in 2-propanol, led to reduction: the mercaptan I was isolated in 88% yield and a small quantity of the disulfide was recovered. However, irradiation of II in *t*-butyl alcohol led to recovery of 63% of the disulfide and a gum from which a small quantity of lower melting solid was obtained. Although a reaction appeared to occur to some extent with the tertiary alcohol, only the primary and secondary alcohol led to ready reduction of the disulfide and isolation of the mercaptan.



I

The carbon–hydrogen bond has a lower dissociation energy than the oxygen–hydrogen bond and a value not much greater than that of the sulfur–hydrogen bond, *ca.* 90 kcal.[18] In alcohols and ethers the hydrogen on the carbon of the functional group may be the more readily abstracted, the resulting radical being stabilized by resonance with the *p*-electrons of the oxygen, the pertinent carbon–hydrogen bond being in effect weakened. Hydrogen is removed by methyl radical from the carbinol carbon of primary and secondary alcohols in preference to hydrogen on oxygen or on more distant carbon atoms, as shown by deuterium labeling[19a,b]; it probably is removed preferentially

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by *t*-butoxy radical also, as shown by alkylation of such alcohols at the carbinol carbon[20] by olefins in the presence of di-*t*-butyl peroxide. On the other hand, the 1-isobutenyl radical attacks the hydroxyl[19a] hydrogen of ethanol preferentially, while the hydroxyl radical is comparatively indiscriminate, attacking hydrogen on the carbinol carbon and on more distant carbons[21] and on the hydroxyl of tertiary alcohols.[22] The thiyl radical would appear to be a selective one which preferentially attacks hydrogen on the carbinol carbon; abstraction of hydrogen from hydroxyl would presumably be even less favored than abstraction from carboxyl.

However, irradiation of the disulfide II in diisopropyl ether led to recovery of II in 94% yield and detection of no acetone, while irradiation of II in isopropyl acetate led to its recovery in 82% yield and formation of a viscous residue. The carbon–hydrogen bond at the carbinol carbon in the alcohol and the ether, and perhaps in the ester, have similar dissociation energies, and this bond in ether is sensitive to attack by radicals in autoxidation, in reaction with acyloxy radicals[23] and in light-induced reactions with ketones. Observable reduction of the disulfide under our conditions requires both hydrogen on the carbinol carbon and a free hydroxyl, neither one alone being sufficient. However we were unable to obtain unequivocal evidence for conversion of the alcohol to acetone. In one irradiation of the disulfide II in 2-propanol a derivative of acetone was obtained in about 20% yield but a blank irradiation of 2-propanol under similar conditions also led to acetone, isolated as the 2,4-dinitrophenylhydrazone. Furthermore, pinacol appears to be a major product, isolated in about 25% yield from irradiation of di-*n*-butyl disulfide in 2-propanol.

It is possible that this results in part from dimerization of radicals formed in the hydrogen abstraction process (3), in which case our failure to

$$\mathrm{RS\cdot + R^1_2CHOH \rightleftarrows RSH + R^1_2\dot{C}{-}OH} \qquad (3)$$

$$\mathrm{2R^1_2\dot{C}{-}OH \longrightarrow R^1_2C(OH)C(OH)R^1_2} \qquad (5)$$

observe reaction with the ether or ester is due either to less facile abstraction of hydrogen from these by the thiyl, or less facile dimerization, which may lead to reversal of reaction 3. On the other hand, the progress of the reaction may require formation of the ketone and mercaptan as intermediates, subsequent interaction of these two leading to the major part of the pinacol, this accounting for the lack of reaction with the ether and ester. The ketone might be formed by reaction of the intermediate radical either with thiyl radical or with disulfide, with the former, 4a,

$$\mathrm{R_2{}^1\dot{C}{-}OH + RS \rightleftarrows R_2C{=}O + RSH} \qquad (4a)$$

$$\mathrm{R_2{}^1\dot{C}{-}OH + RS{-}SR \longrightarrow R_2C{=}O + RSH + RS\cdot} \qquad (4b)$$

being favored on energetic grounds and likely to be quite rapid. Although it cannot be ruled out, it seems less likely that ketone may be formed by concomitant attack on the alcohol by two thiyl radicals or by a molecule of disulfide under the influence of light, leading in a single transition to two molecules of mercaptan and a carbonyl group.

That the reverse reaction, oxidation of the mercaptan by the ketone, takes place readily was indicated by experiments in which thiosalicylic acid was irradiated in acetone, the latter being an effective photosensitizer[24] for reactions of mercaptans, and in this case a reactant as well. Irradiation of thiosalicylic acid in a mixture of equal quantities of 2-propanol and acetone led to isolation of the disulfide in 83% yield, indicating that oxidation to the disulfide by acetone was favored. Irradiation of thiosalicylic in acetone which was free from 2-propanol led to 2-propanol isolated as its phenylurethan in 9% yield, to the disulfide in 80% yield and to pinacol in 14% yield, identified by oxidation to acetone by periodic acid.

A few additional experiments were carried out and may be mentioned. Irradiation of suspension of the disulfide II in benzene, toluene and chloroform led to recovery of II in 93–95% yield and little evidence of reaction. Strangely, irradiation of II in lactic acid did not lead to reduction of the disulfide, which was recovered in 96% yield. However, irradiation of a suspension of II in the ester, ethyl lactate, led to dissolution of the disulfide. The solution was distilled, and the disulfide was recovered in only 28% yield, while the presence of ethyl pyruvate was demonstrated in the forerun by formation of its 2,4-dinitrophenylhydrazone. Irradiation of ethyl pyruvate itself led to gross decomposition and this system was not investigated further.

Experimental

Anhydrous sodium acetate (5 g., 0.06 mole), 4 g. (0.024 mole) of α,α′-azo-bis-isobutyronitrile and 1 g. (0.009 mole) of α-thioglycerol were dissolved in 60 g. of glacial acetic acid and heated at 80–90° for three hours; loss in weight, 0.45 g.; calculated for nitrogen evolution, 0.68 g.

Hexaphenylethane was prepared[25] from triphenylmethyl chloride, magnesium and iodine, melting 140–150° dec.

Anhydrous sodium acetate (2 g., 0.024 mole), 4.8 g. (0.01 mole) of hexaphenylethane and 1 g. (0.009 mole) of α-thioglycerol in 30 g. of acetic acid were boiled under nitrogen for 40 hours. The product was concentrated in vacuum, the residue was extracted with water, and the extract was treated with barium hydroxide, leading to no barium succinate. The residue was treated with ethanol, leading to triphenylcarbinol, 2 g. (0.008 mole), m.p. and mixed m.p. 155–160°.

Thiosalicylic acid (I) (Eastman Kodak Co.) was crystallized from ethanol, m.p. 163–164°, reported[26] 164°–165°.

Bis-(2,2′-carboxyphenyl)disulfide (II) was prepared by treatment of 8 g. (0.05 mole) of thiosalicylic acid with 8 g. (0.063 mole) of iodine in 300 ml. of ether at room temperature with stirring for 20 hours. The solvent was evaporated and the residue was washed with cold 95% ethanol and crystallized from ethanol, 5 g., 63% yield, m.p. 287–290°, reported[26] 289°.

Di-*n*-butyl disulfide was obtained from Eastman Kodak Co. and used without further purification.

Ethyl Pyruvate.—A solution of 50 g. (0.57 mole) of pyruvic acid (Matheson) and 100 ml. of absolute ethanol was heated in a pressure bottle at 90° for 20 hours. The mixture was distilled and a fraction was collected, b.p. 144–147° (reported[27] 145–146°), 37.5 g., 57% yield.

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Irradiation Procedure.—Solutions or suspensions of the disulfides in the several solvents were placed in a Pyrex flask, evacuated with an oil-pump, closed and irradiated with a 275 watt G.E. sunlamp at 40–50° with magnetic stirring. The solvents were distilled off and the residues were worked up.

Irradiation of Bis-(*2,2'*-Carboxyphenyl) Disulfide (II). 1. In **Acetic Acid.**—A suspension of 1 g. of II in 80 ml. of acetic acid was irradiated for 92 hours, cooled and filtered, leading to recovery of II in 72% yield, m.p. and mixed m.p. 287–288°. The filtrate was concentrated and from the residue additional II was recovered, 3%. A gum was left, 0.2 g.

2. **Potassium Salt in Water.**—A solution of 3 g. (0.01 mole) of the disulfide II and 1.12 g. (0.02 mole) of potassium hydroxide in 100 ml. of water, *p*H about 7, was irradiated for 6 hours, made alkaline with sodium bicarbonate and extracted with two 40-ml. portions of ether. Evaporation of the ether extract led to no residue. The aqueous portion was brought to *p*H 4 with concentrated hydrochloric acid, leading to a white precipitate, 2.8 g., 94% yield, m.p. and mixed m.p. with starting disulfide, 275–292°.

3. **In Dioxane–Water.**—A solution of 4 g. of the disulfide II in 50 ml. of purified dioxane and 25 ml. of water was irradiated for 24 hours. The mixture was treated as above (2) leading to 3.6 g., 90% recovery of disulfide and to no ether-extractable residue.

4. **In Water.**—A suspension of 1 g. of the disulfide in II in 100 ml. of distilled water was irradiated for 10 days, leading to recovery of 0.94 g. of II, m.p. and mixed m.p. 285–287°.

5. **In Ethanol.**—A solution of 4 g. of the disulfide II in 100 ml. of absolute ethanol was irradiated for 150 hours, the color changing from light yellow to green. A small quantity, 0.031 g., of white solid was collected: it did not melt at 300°. The solution was distilled, no material boiling below ethanol being observed, and the dark residue was taken up in aqueous sodium bicarbonate and extracted with two 40-ml. portions of ether. The aqueous portion was acidified with dilute hydrochloric acid, leading to 0.9 g. of solid, sinter 150°, m.p. and mixed m.p. with thiosalicylic acid I, 160°. The ether extracts were dried over magnesium sulfate and concentrated, leading to 2 g. of yellow pasty residue. Treatment of this with benzene and petroleum ether led to 0.7 g. of yellow-green solid, sinter 130°, m.p. and mixed m.p. with I, 157°. Concentration of the filtrates led to 1.1 g. of oil which we failed to crystallize. Infrared spectra of the two solids and the oil fraction were quite similar to that of I. The yield of solid I recovered was 1.6 g., 40%. No starting disulfide II was found. In a control run, a solution of 4 g. of the disulfide in 100 ml. of ethanol was kept in the dark at 50° for 170 hours. The solution was concentrated under nitrogen and 3.5 g., at 88% of the disulfide was recovered, m.p. and mixed m.p. with II, 275–285°.

6. In **2-Propanol.**—A suspension of 3.2 g. of the disulfide in 100 ml. of 2-propanol, b.p. 82–83°, was irradiated for 90 hours, leading to a green solution. The solvent was distilled, 82–83°, leading to a brown residue, 6 g., which was dissolved in aqueous sodium hydroxide and extracted with ether. Evaporation of the ether led to a brown solid, 0.035 g., which did not melt at 300°. Acidification of the aqueous solution led to thiosalicylic acid (I), 2.91 g., 88% yield, m.p. and mixed m.p. 158–161°. Concentration of the filtrate led to the disulfide II, 0.155 g., 5% yield, m.p. and mixed m.p. 287–289°.

A suspension of 7.45 g. (0.025 mole) of disulfide II in 300 ml. of 2-propanol was irradiated for 6 days. The suspension was filtered leading to recovery of 1.80 g. (24%) of II, and the filtrate was distilled. The distillate was treated with 0.5 g. of dinitrophenylhydrazine and a few drops of concentrated hydrochloric acid, leading to acetone 2,4-dinitrophenylhydrazone, m.p. and mixed m.p. 124–126°. The treatment was repeated three times on the filtrate and on other fractions leading in all to 1.25 g. (0.005 mole), 20% yield, of the dinitrophenylhydrazone. In a blank run irradiation of 50 ml. of 2-propanol for six days led to recovery of 0.19 g. of acetone 2,4-dinitrophenylhydrazone. A blank test on the alcohol without irradiation led to no acetone derivative.

7. **In *t*-Butyl Alcohol.**—A solution of 4.0 g.of the disulfide in 250 ml. of *t*-butyl alcohol (Merck and Co., Inc., b.p. 82–83°) was irradiated for 96 hours and distilled. Distillation began at 80°, and was continued, leading to a gummy resdue, *ca.* 8 g. This was dissolved in 10% sodium hydroxide and extracted with ether, the ether extract leading on evaporation to no residue. The aqueous solution was acidified, leading to a crude yellow solid, melting 170–250°, which on recrystallization from chloroform–acetone led to 2.5 g., 63% yield of II, m.p. and mixed m.p. 275–290°, and to a small quantity of solid, melting 140–200°.

8. **In Diisopropyl Ether.**—A suspension of 2.22 g. of II in 200 ml. of di-isopropyl ether (Eastman Kodak Co., b.p. 67–68°, distilled over sodium) was irradiated for 92 hours with little apparent change. Residual II was filtered off, 1.98 g.; the filtrate was distilled leading to 0.08 g. more of II, total recovery 94%; treatment of the distillate with semicarbazide led to no semicarbazone.

9. In **Isopropyl Acetate.**—A suspension of 1.7 g. of II in 80 ml. of isopropyl acetate (Eastman Kodak Co., b.p. 86–87°) was irradiated for 96 hours and filtered, leading to II, 1.14 g., m.p. and mixed m.p. 285–290°. The filtrate was concentrated and the residue was triturated with methanol, leading to 0.19 g. more of II, and a gummy residue, which on treatment with 10% sodium hydroxide, extraction with benzene and acidification of the alkali led to 0.07 g. of II, total recovery 82%. A dark residual gum remained, 0.34 g.

10. **In Lactic Acid.**—A suspension of 1.09 g. of II in 40 ml. of lactic acid (Merck and Co., Inc., reagent grade, 85–90%) was irradiated for 96 hours with no apparent change, II being recovered in 96% yield, 1.04 g., m.p. 284–289°.

11. In **Ethyl Lactate.**—A suspension of 1.0 g. of II in 80 ml. of ethyl lactate (Eastman Kodak Co., b.p. 152–153°) was irradiated for 100 hours, leading to a green-yellow solution. This was distilled leading to foreruns boiling (i) 80–100°, 0.16 g.; and (ii) 100–151°, 0.865 g. The remainder of the ethyl lactate was distilled in vacuum, and the residue led to 0.28 g., 28%, of II, m.p. and mixed m.p. 280–286°. Forerun (i), one drop, was treated with 2,4-dinitrophenylhydrazine in alcohol, leading to the 2,4-dinitrophenylhydrazone of ethyl pyruvate, m.p. 135–137°, mixed m.p. 135–138°, authentic sample 136–138°. *Anal.*[28] Calcd. for $C_{11}H_{12}N_4O_6$: C, 44.59; H, 4.08; N, 18.91. Found: C, 44.27; H, 4.20; N, 18.84.

12. **In Benzene; Toluene; Chloroform.**—Suspensions of 1.0 g. of the disulfide II (i) in 80 ml. of benzene, (ii) in 100 ml. of toluene and (iii) in 30 ml. of chloroform were irradiated for 92 hours, leading to recovery of II in 95, 94 and 93% yield, respectively. The experiments in benzene and in toluene led to clean recovery and no residue. Concentration of the filtrate from the reaction in chloroform led to a trace of solid, melting 150–250°, and to an oily residue, the infrared spectrum of which in chloroform was quite similar to that of hexachloroethane in chloroform.

Irradiation of Di-*n*-butyl Disulfide in 2-Propanol.—A solution of 25 g. (0.14 mole) of di-*n*-butyl disulfide in 60 g. (1 mole) of 2-propanol was irradiated for 120 hours, the initially colorless solution becoming yellow. The solution was distilled, nothing appearing below 78°; the distillate was returned to the flask, 0.2 ml. of dilute hydrochloric acid was added and the distillation was resumed, nothing appearing below 78°; 20 ml. of water was added, the solution was boiled briefly and distilled, again with no sign of acetone. The residue was neutralized and cooled, leading to a white compound, 8 g. (0.035 mole), 25% yield, pinacol hydrate, m.p. 32–35°. This was treated with 10 ml. of water and 10 ml. of sulfuric acid, boiled for 10 minutes and distilled, leading to pinacolone, b.p. 105–106°.

Irradiation of Thiosalicylic Acid I in **Acetone.**—(1) A solution of 9.7 g. of thiosalicylic acid in 100 ml. of acetone and 100 ml. of 2-propanol was irradiated for 140 hours and concentrated. The disulfide II was isolated in several fractions, 8.0 g., 83% yield, m.p. and mixed m.p. 280–285°.

(2) A solution of 1.0 g. (6.5 mmoles) of thiosalicylic acid in 100 ml. of acetone, which had been distilled from potassium permanganate, was irradiated for 96 hours and fractionated. Fractions from which much of the acetone had been removed were treated with phenyl isocyanate, leading to isopropyl phenylcarbamate, m.p. (from alcohol) and mixed m.p. with an authentic sample, 75–76°, 0.055 g. (0.30 mmole), 9% yield. The residue was crystallized from ethanol leading to a low melting mixture, 0.050 g., melting over a wide range above 160°, and to the disulfide II, 0.80 g., 80% yield, m.p. and mixed m.p. 280–285°. The residues after isolation of the disulfide were concentrated and crystallized from alcohol,

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(28) Microanalysis by Dr. S. M. Nagy, Massachusetts Institute of Technology.

leading to a yellow solid, 1.3 g., which was chromatographed on alumina. The portion eluted by 95:5 ethanol–acetone was concentrated and dried in vacuum, washed with petroleum ether and treated with a small quantity of water, leading to white crystals, 0.102 g. (0.44 mmole), 14%, pinacol hydrate, m.p. 35–37°. A portion of this, 0.05 g., was dissolved in 10 ml. of water and treated with 0.25 g. of periodic acid in 40 ml. of water at room temperature overnight. The solution was distilled into a solution of dinitrophenylhydrazine in acidified ethanol–water, which was allowed to stand for two hours and then was evaporated, leading to acetone 2,4-dinitrophenylhydrazone, 0.017 g., m.p. and mixed m.p. with an authentic sample, 125–127°.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

Organoboron Compounds. X.[1,2] Popcorn Polymers and Highly Cross-linked Vinyl Polymers Containing Boron

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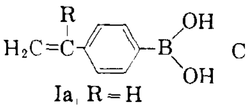
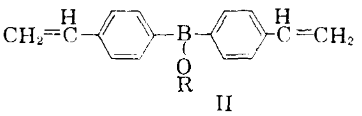
Several substituted styrene compounds possessing boron functional groups were synthesized and subjected to polymerization conditions. A popcorn-type copolymer was obtained from the ethyl tartrate ester of *p*-vinylbenzeneboronic acid, styrene and diallyl maleate. Although highly insoluble, this polymer reacted with phenylenediamine, alcohol and hydrogen peroxide. Copolymerization of 2-aminoethyl bis-*p*-vinylphenylborinate and styrene yielded a highly cross-linked, powdery solid, from which ethanolamine could be removed by hydrolysis. The resulting polymer readily adsorbed amino alcohols from solutions.

For studies on the catalytic action of organoboron compounds it was desirable to have a low density, porous, highly insoluble polymer that contained firmly bound $-B(OH)_2$ or $>B-OH$ groups. We undertook the preparation of two different types of polymers which held promise of exhibiting such properties. One was a "popcorn-type" polymer[3] derived from *p*-vinylbenzeneboronic acid (Ia). It should contain relatively few cross links. The other was a copolymer of styrene and an ester of bis-*p*-vinylphenylborinic acid (II), which should be highly cross-linked. The first section of this paper deals with the synthesis of the monomers, and the second, with the preparation and some properties of the polymers. Vinyl-type polymers containing boron have not previously been reported.

Monomer Synthesis.—Initial efforts were directed toward the preparation of *p*-vinylphenyllithium, from which the boron compounds should be obtainable by reaction with butyl borate. Unfortunately, all attempts to prepare this lithium compound were attended by extensive polymer formation. Thus, *p*-bromostyrene reacted with butyllithium in ether solution; however, the arylcarboxylic acids obtained on carbonation were all polymeric.[4] From the carbonation products of a similar interchange reaction which was carried out in pentane a small amount of *p*-vinylbenzoic acid was isolated, but the quantity was not of preparative significance.



Ia, R = H
Ib, R = CH_3

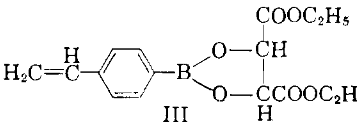


II

We next turned to *p*-bromo-α-methylstyrene, which polymerizes much less readily than *p*-bromostyrene. An interchange reaction with butyllithium proceeded satisfactorily to give, on carbonation, *p*-isopropenylbenzoic acid. With butyl borate the interchange products yielded *p*-isopropenylbenzeneboronic acid (Ib).

At this phase of the research the method of Leebrick and Ramsden for preparation of *p*-vinylphenylmagnesium chloride[5] appeared in the literature. Following their procedure, we prepared this Grignard reagent and treated it with butyl borate. A 60% yield of *p*-vinylbenzeneboronic acid was isolated from the reaction mixture.[6]

Compounds Ia and Ib rapidly decolorized bromine in carbon tetrachloride solution and yielded sharp melting dihydrobenzoboradiazole derivatives[7] with *o*-phenylenediamine. *p*-Vinylbenzeneboronic acid also furnished a solid ester (III) when heated in toluene with (+)-ethyl tartrate; the corresponding derivative of Ib did not crystallize.



III

The reaction of two mole equivalents of *p*-vinylphenylmagnesium chloride with butyl borate yielded bis-*p*-vinylphenylborinic acid, which was

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[1] This work was supported by the National Science Foundation, Grant G-2361.

[2] For the previous paper in this series see R. L. Letsinger and S. Dandegaonker, THIS JOURNAL, **81**, 498 (1959).

[3] For a review of popcorn polymerization see (a) E. H. Immergut, *Makromol. Chem.*, **10**, 193 (1953); (b) J. L. Amos, K. E. Coulter and F. M. Tennant in "Styrene," edited by R. H. Boundy and R. F. Boyer, Reinhold Publishing Corp., New York, N. Y., 1952, p. 729.

[4] Similar results were reported by G. B. Bachman, C. L. Carlson and M. Robinson, THIS JOURNAL, **73**, 1964 (1951).

[5] J. R. Lubrick and H. E. Ramsden, *J. Org. Chem.*, **23**, 935 (1958).

[6] A. Hoffman and W. M. Thomas recently prepared *p*-vinylbenzeneboronic acid by dehydrohalogenation and hydrolysis of *p*-(α-bromomethyl)-phenylboroxine, THIS JOURNAL, **81**, 580 (1959). Also, H. R. Snyder, M. S. Konecky and W. J. Lennarz, THIS JOURNAL, **80**, 3611 (1958), listed some frequencies at which *p*-vinylbenzeneboronic acid absorbs in the infrared, without however, giving any further information about the compound.

[7] R. L. Letsinger and S. B. Hamilton, *ibid.*, **80**, 5411 (1958).