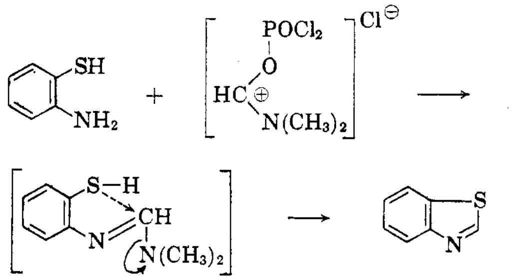
benzothiazole. The phosphorus oxychloride adduct of dimethylformamide reacted with 2-aminobenzenethiol to yield 85% benzothiazole.

It is known[2] that the phosphorus oxychloride adduct of dimethylformamide will react with amines to form *N,N,N'*-trisubstituted amidines. This amidine structure is probably an intermediate in this reaction.



Experimental

To a solution of phosphorus oxychloride (38.3 g., 0.25 mole) in anhydrous ether (40 ml.) was added dropwise a solution of dimethylformamide (18.2 g., 0.25 mole) in anhydrous ether (50 ml.). The addition was carried out at 15°. The dimethylformamide-phosphorus oxychloride adduct separated as an oil layer and the mixture was allowed to come to room temperature. The adduct was washed with three 50-ml. portions of anhydrous ether.

To the dimethylformamide-phosphorus oxychloride adduct was added 2-aminobenzenethiol (15 g., 0.125 mole) in anhydrous ether (50 ml.). The addition was accomplished dropwise with rapid stirring and cooling. After the addition was completed, the ether was evaporated and water (100 ml.) was added. The aqueous solution was extracted with ether and the ethereal solution dried over anhydrous sodium sulfate. The ether was evaporated and the residue distilled, b.p. 112-113/17 mm. (lit.,[3] b.p. 227°/765 mm.). The infrared spectrum of the product was in every way identical to commercial benzothiazole. Yield (based on 2-aminobenzenethiol) was 13.8 g. (85%).

Anal. Calcd. for C_7H_5NS: C, 62.19; H, 3.73. Found: C, 62.45; H, 3.41.

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Catalysis by Ion Exchange Resins. Improved Cyanoethylation and Carbamylethylation of Diols

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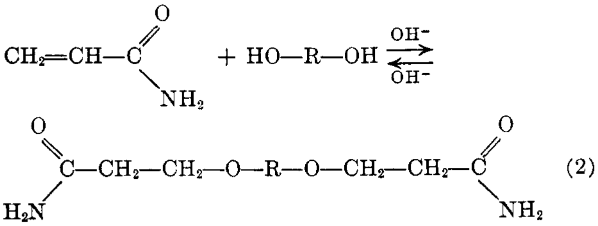
Catalysis by ion exchange resins has been reported for various reactions.[1-8] In general, ion-exchange resins were used in place of acids or bases as catalysts. This communication describes the advantageous use of ion exchange resins as catalysts in some reversible organic reactions. Cyanoethylation and carbamylethylation are base-catalyzed reactions[9]; such reactions of diols using conventional catalysts have been described.[10-12]

$$2\mathrm{CH_2{=}CH{-}CN} + \mathrm{HO{-}R{-}OH} \underset{\mathrm{OH^-}}{\overset{\mathrm{OH^-}}{\rightleftarrows}} \mathrm{NC{-}CH_2CH_2O{-}R{-}O{-}CH_2{-}CH_2{-}CN} \quad (1)$$



$$\mathrm{CH_2{=}CH{-}C({=}O)NH_2} + \mathrm{HO{-}R{-}OH} \underset{\mathrm{OH^-}}{\overset{\mathrm{OH^-}}{\rightleftarrows}} \mathrm{H_2N(O{=})C{-}CH_2{-}CH_2{-}O{-}R{-}O{-}CH_2{-}CH_2{-}C({=}O)NH_2} \quad (2)$$

In our experiments where Dowex-1 anion exchange resin, in its hydroxide form, was used in place of alkali or quaternary ammonium hydroxides, the yields of reactions 1 and 2 were 80-95% and 50-60%, respectively. The diols (OH—R—OH) used were ethylene glycol, diethylene glycol, 1,4-butanediol, and 1,5-pentanediol. Aside from the high yields obtained for reactions 1 and 2, it was also observed that considerably cleaner product mixtures were obtained at the end of the reactions. Furthermore, the polymerization of acrylonitrile and acrylamide was reduced.

The novel feature of insoluble polymeric catalysts (ion exchange resins) probably lies in the heterogeneous nature of the systems. In order for any reaction to take place, the reactants must diffuse into the ion exchange resins. This depends primarily on the swelling properties of the resins in the reaction mixtures. In our systems, because of the difference in size and functional groups between the reactants and the products, the reactant mixtures swell the resins to a much greater extent than the products. As a consequence, the reverse reaction is suppressed.

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[9] *Org. Reactions*, **V**, pp. **79**, 1949.

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[11] Unpublished work done by Dr. J. K. Magrane in these laboratories.

Experimental

The Cyanoethylation of Diols.—To a 1-l., round-bottom, three-neck flask equipped with a condenser, stirrer, and thermometer there was added 2 moles of a diol (HOROH) and 30 g. of Dowex-1 resin, X-8 (8% cross-linked), in its hydroxide form (approx. 90 meq.). The ion exchange resin was observed to swell 250–300% of its dry volume in diols. To this mixture, 4 moles of acrylonitrile was added dropwise, with stirring, keeping the reaction temperature between 28–38° by external cooling. The addition required approximately 2 hr. The reaction mixture was stirred overnight at room temperature. The ionexchange resin was filtered off and the filtrate was washed several times with saturated sodium chloride solution. The washed filtrate, which was now essentially the crude product, was a yellowish oil. It was purified by distillation in vacuum. The following compounds were prepared:

Bis(β-cyanoethoxy)ethane-1,2 was prepared from ethylene glycol, yield: 93.5%. It was a faintly yellow oil, b.p.: lit., 158°/2 mm.[12]; Found: 155–161°/0.2–0.3 mm.; infrared peaks: 1125 cm.$^{-1}$, 2250 cm.$^{-1}$.

Anal. Calcd. for $C_8H_{12}N_2O_2$: N, 16.67. Found: N, 16.97.

Bis(β-cyanoethoxy)butane-1,4 was prepared from butanediol-1,4,yield: 81.1%. It was a faintly yellow oil, b.p. 172–174°/0.05–0.1 mm.; infrared peaks: 1125 cm.$^{-1}$, 2250 cm.$^{-1}$.

Anal. Calcd. for $C_{10}H_{16}N_2O_2$: N, 14.28. Found: N, 14.49.

The Carbamylethylation of Diols.—In carbamylethylation, a solvent was used to dissolve the solid alkylating agent acrylamide. In order for the reaction to occur, the solvent must be a swelling agent for the ion exchange resin. *t*-Butyl alcohol was found to be suitable for this purpose since it was both inert to acrylamide and a swelling agent for Dowex-1 resin. Because of the initial diol content, the solution of the reactants in *t*-butyl alcohol was observed to swell the ion-exchange resin to a greater extent than that of the products.

To a 1-l., three-neck, round-bottom flask, fitted with condenser, thermometer, and stirrer there was charged 1 mole of a diol, 2 moles of acrylamide, and 100–200 g. of *t*-butyl alcohol. The mixture was warmed to 50° with stirring whereupon a solution was formed. To this solution there was added 30 g. of Dowex-1 resin, X-8, in its hydroxide form. After about 20 min. of stirring, the exothermic initial reaction raised the reaction temperature to 60–65°. The reaction mixture was held at 50–60° with stirring for an additional 20 hr. The solution was filtered with suction; the filtrate was concentrated *in vacuo;* and the residue, a yellow oil, was poured into excess acetone and chilled in a refrigerator overnight whereupon the product precipitated as white crystals. The crystals were collected, washed with acetone, recrystallized from dioxane or *t*-butyl alcohol, and dried. The following are the compounds prepared:

Bis(β-carbamylethoxy)diethyl ether was prepared from diethylene glycol. Yield: 60%; m.p.: lit., 103–104°[12]; Found: 94.5–96°.

Anal. Calcd. for $C_{10}H_{20}N_2O_5$: C, 48.39; H, 8.06; N, 11.28. Found: C, 48.55; H, 8.20; N, 11.4.

Bis(β-carbamylethoxy)pentane-1,5 was prepared from 1,5-pentanediol. Yield: 61%; m.p. 119.5–120°.

Anal. Calcd. for $C_{11}H_{22}N_2O_4$: C, 53.66; H, 9.00; N, 11.37. Found: C, 53.94; H, 9.13; N, 11.59.

Bis(β-carbamylethoxy)triethyl ether was prepared from triethylene glycol. Yield: 52%; m.p. 93.5–94.5°.

Anal. Calcd. for $C_{12}H_{24}N_2O_6$: C, 49.32; H, 8.22; N, 9.59. Found: C, 49.30; H, 8.38; N, 9.59.

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Pyrolysis of Dibenzyl Sulfones

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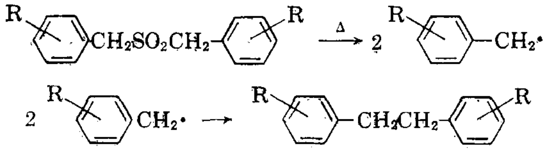
Sulfones are among the most stable organic compounds. Most sulfones can be distilled at atmospheric pressure with no decomposition. Since the sulfur atom is already fully oxidized, oxidations can be carried out at other sites on the molecule without affecting the sulfone group. The sulfone linkage is also not affected by acids and bases at moderate temperatures.

In spite of this stability, there are recorded examples of the decomposition of sulfones. Dibenzyl sulfone has been reported[1] to pyrolyze at 290° to yield stilbene and toluene as sole products. Ingold[2] has described the decomposition of dibenzyl sulfone. Once again the products isolated included stilbene and toluene. The cyclic sulfone formed by the reaction of two moles of a diazo compound with sulfur dioxide decomposes to form an olefin.[3] Cava[4] has reported that 1,3-dihydroisothianaphthene (I) on pyrolysis forms *o*-xylene, benzocyclobutene (II), and 1,2,5,6-dibenzo-1,5-cyclooctadiene (III).

Recently, LaCombe[5] at Union Carbide Chemicals Co. has pyrolyzed benzyl isopropyl sulfone and obtained a mixture of isobutylbenzene, sulfur dioxide, toluene, bibenzyl, and propylene.

In this laboratory, pyrolyses of dibenzyl sulfones at low pressures and temperatures of 600–700° have given high yields of the corresponding bibenzyls. The following sulfones have been prepared and pyrolyzed: dibenzyl sulfone, di-*p*-xylyl sulfone, bis(4-methylnaphthyl-1-methyl) sulfone, bis(4-isopropylbenzyl) sulfone, and bis(4-benzylbenzyl) sulfone. The mechanism of the reaction is believed to be cleavage of the sulfone to benzyl radicals with elimination of sulfur dioxide and subsequent coupling of the radicals:



This sulfone pyrolysis is a new method of synthesis of symmetrical diarylethanes. It is useful, also, for producing benzyl and substituted benzyl free radicals cleanly and in high yields.

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