constant stirring. It was quite thick at first but thinned rapidly. After heating for 3 hr., approximately one-half of the dimethylformamide was removed using reduced pressure; the residual very viscous material was taken up in 1.5 l. of water heated to 60°, and then acidified with hydrochloric acid. There was a slight evolution of carbon dioxide. The solution was allowed to stand at 4° overnight. Filtration gave 105.2 g. of crystalline material, m.p. 208–211°. An additional 18.5 g. were obtained from the mother liquors. Total yield was 123.7 g. (79% yield). Recrystallization from 50% ethanol gave 80.0 g. of white product, m.p. 194–195° (lit.,[4a] m.p. 193–194°), λ_{max} 268 mμ (0.1 *N* sodium hydroxide).

5-Ethyl-2,4,6-trichloropyrimidine.—By following essentially the procedure of Merkats, but with the addition of an equimolar amount of dimethylanaline, there was obtained an 85% yield of pure product, m.p. 76–79° (lit.,[4a] m.p. 75–77°), λ_{max}[1] 268.5 mμ, λ_{max} 223.5 mμ (ethanol).

6-Chloro-5-ethyl-2,4-dimethoxypyrimidine.—Using anhydrous sodium methoxide and the procedure of Merkats, there was obtained a 92% yield of crude, low-melting product [λ_{max} 267 mμ (ethanol)] which was used without further purification. The literature[4a] gives the melting point of this product as 33–34°.

2,4-Dimethoxy-5-ethylpyrimidine.—Reduction of the previous product using zinc dust[4a] was not too successful and a method[5] for its catalytic reduction was adapted. A mixture was made of 20.3 g. (0.1 mole) of the previous product, 20 g. of magnesium oxide, 2 g. of 5% palladium-on-charcoal, and 200 ml. of 50% ethanol. This was hydrogenated at 15 p.s.i. at 60°. The uptake of hydrogen virtually ceased after 2 hr. at which time approximately 70% of the theoretical amount had been taken up. The hydrogenation bottle was centrifuged and the supernatant decanted. The residue was washed twice with 150-ml. portions of 95% ethanol. Removal of solvents gave a highly volatile, pale yellow oil [λ_{max} 260 mμ (ethanol)] which could not be crystallized and was not purified further.

5-Ethyluracil.—The combined product from a number of reductions, 15.6 g., was refluxed with concd. hydrochloric acid for 6 hr. Water was added to dissolve the white precipitate which formed and the solution was filtered and allowed to cool. The product was recrystallized several times from 70% ethanol which effectively removed a more alcohol soluble impurity. There was obtained 8.4 g. (76% yield) of pure white crystalline material, m.p. 302–303°, λ_{max} 264.5 mμ (0.1 *N* hydrochloric acid), λ_{max} 289 mμ (0.01 *N* sodium hydroxide). The melting point of this compound has been variously reported as 300–303°,[4b] 300°,[2] 300–303°,[3] and 300–303°.[4a]

2-Thio-5-ethyluracil.—This reaction was performed as described[4b] previously except that sodium hydride was used as the condensing agent rather than sodium. This permitted an appreciably shorter reaction time with no decrease in yield. To a 1-l., three-necked flask equipped with a stirrer, condenser, and dropping funnel was added successively 14.4 g. (0.6 mole) of sodium hydride, 250 ml. of anhydrous ether, and 58.1 g. (0.5 mole) of ethylbutyrate. There was then added over a 3-hr. period 55.6 g. (0.75 mole) of ethyl formate in 100 ml. of ether, and the mixture was then refluxed overnight. Subsequent steps were as originally described. There was produced 10.7 g. (17% yield) of product, m.p. 190–191° (lit.,[2] 191–193°), λ_{max} 277 mμ (0.1 *N* hydrochloric acid), λ_{max}[2] 259 mμ, λ_{max}[3] 309 mμ (0.001 *N* sodium hydroxide), and the mother liquors yielded an additional 3.6 g. of material, m.p. 165–180°.

5-Ethyluridine.—To a solution of 1.73 g. (0.016 mole) of 5-ethyluracil in 100 ml. of 20% aqueous ethanol containing 0.64 g. (0.016 mole) of sodium hydroxide was added 5 g. of Celite, and the mixture was stirred vigorously at 70°. There was then added slowly a hot solution of 2.16 g. (0.008 mole) of mercuric chloride in 30 ml. of ethanol and then 200 ml. of hot water. The solution was filtered, the product was washed with hot water, and dried *in vacuo*.

To 350 ml. of a solution of anhydrous ether saturated at 0° with gaseous hydrogen chloride wax added 7.9 g. (0.0156 mole) of dry 1-*O*-acetyl-2,3,5-tri-*O*-benzoyl-D-ribofuranose[7] and 1 ml. of acetyl chloride. The solution was allowed to stand at 3° for 3 days and was then evaporated to dryness *in vacuo*. The residue was evaporated to dryness with several portions of benzene, dissolved in 25 ml. of xylene, and added to a refluxing suspension of the previously prepared di(5-ethyluracil)mercury in 200 ml. of xylene. The mixture was stirred at reflux for 3 hr., filtered through Celite, and evaporated to dryness *in vacuo*. The residue was dissolved in a mixture of 200 ml. of chloroform and 30 ml. of 30% aqueous potassium iodide and the layers were separated. The organic phase was washed with an additional 20 ml. of 30% aqueous potassium iodide and then with water. After drying over sodium sulfate, the solution was evaporated to dryness, taken up in 150 ml. of anhydrous ethanol, and the solution was saturated at 0° with ammonia. After several days standing, the solution was evaporated to dryness *in vacuo*, dispersed in 150 ml. of water and extracted three times with 50 ml. portions of ether. The aqueous phase was decolorized with charcoal and evaporated to dryness *in vacuo*. Attempts to crystallize the product from ethyl acetate and from ethanol were not successful. The residual material after removal of solvents was dissolved in 1 *N* ammonium hydroxide and passed through a 2.5 × 30 cm. column of Dowex 1-X8 in the formate form which had been pretreated with 1 *N* ammonium hydroxide. The column was washed with 1 *N* ammonium hydroxide until no further ultraviolet absorbing material was eluted and the product was then eluted with 500 ml. of 1 *N* formic acid. The formic acid was removed *in vacuo* and the residue was crystallized from absolute ethanol several times to give 0.8 g. (20% yield) of white crystalline material, m.p. 184–186° (uncorr.), λ_{max} 266.5 mμ (0.1 *N* hydrochloric acid or 0.001 *N* sodium hydroxide).

Anal. Calcd. for $C_{11}H_{17}O_6N_2$: C, 48.3; H, 6.26; N, 10.2. Found: C, 48.3; H, 6.03; N, 10.3.

Paper chromatography with 65% v./v. isopropyl alcohol–2 *N* hydrochloric acid[8] gave an R_f of 0.77. This compared with 0.84 for the free base, 0.76 for thymine, and 0.78 for thymidine.

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A Convenient Synthesis of Benzothiazole from Dimethylformamide

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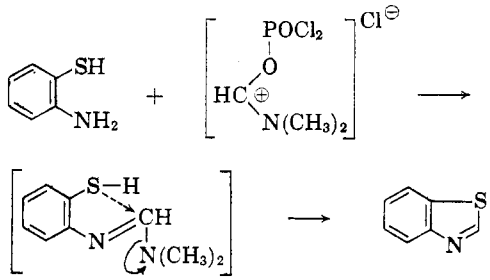
In 1880, Hofmann[1] reported the preparation of benzothiazole from 2-aminobenzenethiol and formamide. His synthesis required a high temperature and yielded only a small amount of benzothiazole. In this note, we wish to report a convenient synthesis using an amide which results in high yields of

(1) A. Hofmann, *Ber.*, **13**, 1223 (1880).

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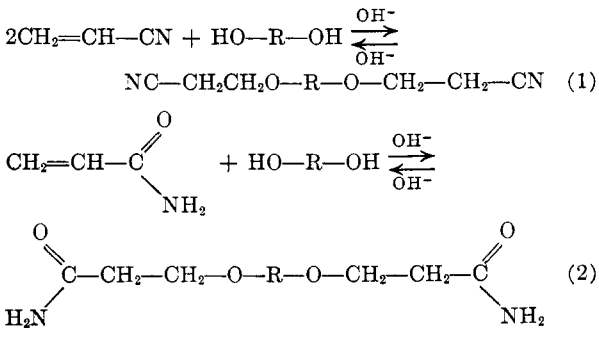
Catalysis by ion exchange resins has been reported for various reactions.[1-8] In general, ion-exchange resins were used in place of acids or bases as catalysts. This communication describes the advantageous use of ion exchange resins as catalysts in some reversible organic reactions. Cyanoethylation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



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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(3) B. A. J. Lister, *Ind. Chemist*, **32**, 257 (1956).

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(7) R. Glenat, *Chim. & Ind.* (Paris), **75**, 292 (1956).

(8) B. A. J. Lister, *Ind Chemist*, **32**, 257 (1956).

(9) *Org. Reactions*, **V**, pp. **79**, 1949.

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(11) Unpublished work done by Dr. J. K. Magrane in these laboratories.