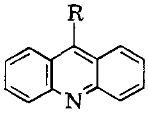
TABLE I

POLYPHOSPHORIC ACID-CATALYZED BERNTHSEN REACTION



R[a]	Yield,[b] %	M.p.[c]	Reported m.p.[d]	Reported yields[d]
C_6H_5	18[e]	184–185°[f]	184°	48
$C_6H_5CH_2$	11	170–173°	173°	50
$C_6H_5CH_2CH_2CH_2$	8	101–103°	104°	25
$CH_3(CH_2)_{16}$	Trace	66–68°	69–70°	?
p-BrC_6H_4	6	239–240°[g]	234°	?
p-$CH_3C_6H_4$	18	188–189°	189–190°	40
p-$NH_2C_6H_4$	24	270–272°[h]	. . .	0
p-$NO_2C_6H_4$	0	. . .	. . .	0

[a] All reaction were 0.03 mole acid to 0.06 mole amine with 230–250 g. PPA at 195–205° for 15 min. [b] Yield of material purified to within 2–3° of reported m.p. [c] M.p. of purified product (from ethanol or aqueous ethanol). [d] See ref. 2a for original literature reference. [e] 48% in a 0.1 mole run. [f] Phosphate salt, m.p. 194–196°. Calcd. for $C_{19}H_{16}NPO$: C, 64.58; H, 4.56; N, 3.97; P, 8.77. Found: C, 64.43, 64.64; H, 4.65, 4.63; N, 3.94, 4.04; P, 8.72. [g] Calcd. for $C_{19}H_{12}NBr$: C, 68.28; H, 3.62; N, 4.19. Found: C, 68.15; H, 3.81; N, 4.43. [h] Calcd. for $C_{19}H_{14}N_2$: C, 84.41; H, 5.22; N, 10.37. Found: C, 84.07; H, 5.40; N, 10.38.

In several instances a small amount of ketonic material, which is probably similar to the diacyldiphenylamine of Elston,[4] was noted.

Experimental[6]

Preparation of 9-Substituted Acridines.—A mixture of diphenylamine, a carboxylic acid, and polyphosphoric acid[7] was heated, with stirring, to the desired temperature and held at this temperature for the stated time. The reaction mixture was then poured onto ice and filtered or decanted. Examination of the infrared spectra of the gummy solid indicated that it contained mainly diphenylamine, a small amount of ketonic product,[8] and possibly some 9-substituted acridine.[9] Treatment of the solution with 25% sodium hydroxide solution caused the precipitation of a solid (while the solution was still acidic) which was apparently the phosphate salt of the 9-substituted acridine.[10] After filtration the solution was made strongly basic with sodium hydroxide and extracted with chloroform. Concentration of the chloroform generally gave a trace of the 9-substituted acridine. The phosphate salt was shaken with 25% sodium hydroxide and chloroform and the chloroform concentrated to give the 9-substituted acridine as listed in Table I.

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(6) All melting points are uncorrected. Analysis by Spang Microanalytical Laboratory, Ann Arbor, Michigan.

(7) Victor Chemical Co.

(8) In the case of the benzoic acid reaction, this fraction had peaks identical to those reported by Elston[4] for his dibenzoyldiphenylamine. In addition, in the case of stearic acid treatment of this gum with sodium hydroxide and chloroform gave, on evaporation of the chloroform, a solid, m.p. 107–108.5° (from absolute ethanol), which was apparently distearyldiphenylamine (Calcd. for $C_{48}H_{79}NO_2$: C, 82.11; H, 11.34; N, 2.00. Found: C, 82.41; H, 11.26; N, 1.98, 2.11).

(9) Since we were interested in the convenience of the method, no attempt was made to isolate this acridine and include it in the yield.

(10) In the case of 9-phenylacridine this salt was washed with water and alcohol to give analytically pure material (see Table I). The same salt could be obtained by reacting 9-phenylacridine with 85% phosphoric acid.

Apparent *meta* Rearrangement of Benzoylsulfuric Acid

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Benzoylsulfuric acid was reported by Oppenheim[1] to rearrange to m-sulfobenzoic acid. Elliott, *et al.*,[2] described the rearrangement as yielding chiefly o-sulfobenzoic acid. They suggested that the difference in products is due to direct sulfonation under Oppenheim's conditions as opposed to chiefly rearrangement under their own. Oppenheim either let benzoylsulfuric acid stand in the presence of sulfuric acid or warmed sulfuric acid with an excess of benzoyl chloride; details of time, temperature,[3] and amounts are lacking. Elliott, *et al.*, heated benzoylsulfuric acid *per se* at 100°. We have established that if the reaction mixture from sulfuric acid and a large or small excess of benzoyl chloride is heated at 100° then the predominant product is m-sulfobenzoic acid.

Our evidence indicates that this product is not due to direct sulfonation. The presence of unchanged sulfuric acid was avoided by the use of an excess of benzoyl chloride, the size of the excess evidently being immaterial, and by drawing out with dry air the hydrogen chloride produced in the initial reaction. Even should a trace of unchanged sulfuric acid have been present we could argue against direct sulfonation by sulfuric acid either of benzoyl chloride or of benzoylsulfuric acid from the observation that neither ethyl benzoate nor benzoic acid is sulfonated by sulfuric acid at our temperature. We consider the comparison applicable because of the similarity of the electronic environment in the several compounds of the carbon atom attached to the benzene ring. Ethyl benzoate reacts with sulfuric acid only by cleavage to benzoic acid, in consonance with the scheme of Newman, *et al.*[4]

The difference between our results and those of Elliott, *et al.*, is presumably to be sought in the difference in conditions. They heated purified benzoylsulfuric acid, which might undergo an intramolecular rearrangement—a self-sulfonation constrained to reaction at the *ortho* position by steric requirements—as indeed suggested by Elliott, *et al.*[2] Our conditions evidently cause intermolecular sulfonation (involving a sulfonating agent other

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(1) (a) A. Oppenheim, *Ber.*, **3**, 735 (1870); (b) Ador and Oppenheim, *ibid.*, 738.

(2) G. A. Elliott, L. L. Kleist, F. J. Wilkins, and H. W. Webb, *J. Chem. Soc.*, 1219 (1926).

(3) Elliott, *et al.*, ascribed a temperature of 150°, which Oppenheim did not mention.

(4) M. S. Newman, R. A. Craig, and A. B. Garrett, *J. Am. Chem. Soc.*, **71**, 869 (1949).

than sulfuric acid). Since alkanoylsulfuric acids act as sulfonating agents,[5] it is reasonable to ascribe a similar power to aroylsulfuric acids. The greater electronegativity of the aroyl group than of a proton suggests progressively greater sulfonating power in the series sulfuric acid, aroylsulfuric acids, diaroyl sulfates.

Identification of *m*-sulfobenzoic acid rests on two types of evidence: (a) negative results for attempted reactions known to occur with *o*-sulfobenzoic acid, *i.e.*, formation of an anhydride[2,6] and of Phenol Red,[2,7] and (b) direct evidence: identity of its bis(*S*-benzylisothiouronium) salt with an authentic sample, alkaline fusion to *m*-hydroxybenzoic acid, and identity of the infrared spectrum with that of authentic *m*-sulfobenzoic acid. Under our conditions rearrangement during alkaline fusion[8] does not occur.[9,10] Minor impurities of *o*-sulfobenzoic acid probably are present; traces of *p*-sulfobenzoic acid may also be present.

Under the influence of the initial hypothesis of an *ortho* rearrangement we wished to determine the effect of blocking groups in the *ortho* positions. Neither 2,6-dimethylbenzoyl chloride nor 2,4,6-trimethylbenzoyl chloride gave with cold sulfuric acid visible evidence of reaction comparable to the precipitate formed by benzoyl chloride. Furthermore in each of these cases the formation of a complex or of a mixed anhydride is belied by the fact that no major portion of the acyl moiety is extracted into the sulfuric acid phase nor of the sulfuric acid into the organic phase. (Cloudiness of the carbon tetrachloride solutions indicates that at least some of the sulfuric acid titrated for in that layer was mechanically carried over.) The reaction mixture from 2,4,6-trimethylbenzoyl chloride and sulfuric acid upon heating under the conditions used for benzoyl chloride once yielded a material which remained unidentified and could not be recrystallized, but which, on the basis of solubility characteristics, obviously was not a monomeric sulfonic acid. The absence of an absorption maximum near 5.8 μ indicates the loss of the carboxyl group.

Experimental

For the reactions with sulfuric acid all glassware was oven-dried. Infrared spectra were determined of material contained in potassium iodide pellets, using a Perkin-Elmer Infracord.

Reaction of Benzoyl Chloride with Sulfuric Acid. (A) Equimolar Amounts.—Typically 10.0 ml. (0.087 mole) of benzoyl chloride [b.p. 104–105° (66 mm.)] was placed with 10 ml. of carbon tetrachloride[11] (distilled from phosphorus pentoxide) into a three-necked round-bottomed flask fitted with a stirrer and a compensating dropping funnel and connected to a drying tower. Then 4.6 ml. (0.086 mole) of sulfuric acid (assay 99.3%) was dripped in. The reaction mixture gradually became yellow, then yellow-green, and, when about one half of the acid had been added, a white precipitate formed. A stream of dry air was sucked through the flask for 2 to 4 hr. The carbon tetrachloride (if any) was distilled, then the reaction mixture heated for 24 hr. at 100°; a dark red sirup remained. Warm water, 125 ml., was added and any undissolved benzoic acid filtered off and washed; the combined filtrate and washings were evaporated to 60 ml., let cool, and any additional benzoic acid was filtered off and washed. Sulfuric acid was precipitated with excess aqueous saturated barium hydroxide, then the barium removed by an exactly equivalent amount of 6 N sulfuric acid. The filtered solution was extracted with ether, then evaporated to dryness, and the off-white powder remaining was dried in a vacuum desiccator over concentrated sulfuric acid.[12] The product, obtained in a variable yield in the vicinity of 45%, melted over a wide range, the upper limit of which was not over 140°.

(B) Excess Benzoyl Chloride.—By the same procedure (without carbon tetrachloride) 10.0 ml. (0.087 mole) of benzoyl chloride reacted with 2.3 ml. (0.043 mole) of sulfuric acid. The product, which was water-soluble, showed the same infrared spectrum as the product from procedure A.

Attempts at Sulfobenzoic Anhydride. (A) Method of Elliott.[2]—Sulfobenzoic acid, 2.8 g. (0.014 mole), was refluxed with 3.3 g. (0.042 mole) of acetyl chloride for 2 hr., then the volatile material was distilled. The residue was thrice washed with dry benzene, the residual benzene distilled, then the residue exposed to moist air. A white film, too slight to collect, formed.

(B) Method of Remsen and Dohme.[6]—Sulfobenzoic acid, 1.0 g. (0.005 mole), was heated by a wax bath in a three-necked round-bottomed flask in a stream of dry air at 115–130° for 5 hr. With a 20-cm. long tube 2 cm. in diameter, topped by a drying tube, extending into the flask to the level of the external wax bath, the acid was then heated with phosphorus pentoxide for 2 days at 130°. A very slight film formed at the top of the flask; nothing collected in the tube.

Attempt at Phenolsulfonephthalein.[2,7]—Sulfobenzoic acid, 0.7 g. (0.0035 mole), was heated with 0.7 g. (0.007 mole) of phenol and 1.0 g. (0.007 mole) of zinc chloride. Insufficient dye formed to be collected, but one drop of aqueous 20% sodium hydroxide added to the reaction mixture produced a red color.

***S*-Benzylisothiouronium Salts of *m*-Sulfobenzoic Acid.**—Sulfobenzoic acid, 1.0 g. (0.005 mole), was dissolved in 10 ml. of water and heated to boiling. To the hot solution 10 ml. of aqueous 10% *S*-benzylisothiouronium chloride was added. Upon gradual cooling to room temperature nothing separated; at 0° a finely dispersed oil separated and resisted attempts at crystallization.[13] Upon first attempt the method of Veibel[14] also gave only an oil. The latter method applied to authentic *m*-sulfobenzoic acid again produced an oil, which began crystallizing after 4 days in a refrigerator and, after being left at room temperature for 7 hr. and returned to the refrigerator, could be filtered off crystalline after a total of 8 days. Recrystallization from aqueous ethanol again produced an oil which eventually crystallized, but which had a very wide melting range. Subsequent treatment of sulfobenzoic acid (from reaction of benzoyl chloride with sulfuric acid) gave the same results, except that the original oil began

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(5) A. J. van Peski, *Rec. trav. chim.*, **40**, 103, 736 (1921).

(6) I. Remsen and A. R. L. Dohme, *Am. Chem. J.*, **11**, 332 (1889).

(7) A. I. Vogel, "A Textbook of Practical Organic Chemistry," 3rd ed., Longmans, Green and Co., Ltd., London, 1956, p. 990.

(8) *Cf.*, *e.g.*, Paul Karrer, "Organic Chemistry," 4th English ed., Elsevier Publishing Co., Inc., Amsterdam, 1950, p. 429.

(9) J. N. Rây and M. L. Dey, *J. Chem. Soc.*, **117**, 1405 (1920).

(10) J. S. Reese, *J. Am. Chem. Soc.*, **54**, 2009 (1932).

(11) The carbon tetrachloride can be omitted without affecting the result.

(12) The method here described of isolating sulfobenzoic acid, despite the necessity of repeated filtration in order to see the end point of the barium sulfate precipitation, is less tedious than either of two alternative methods, which furthermore gave smaller yields.

(13) *Cf.* E. Campaigne and C. M. Suter, *J. Am. Chem. Soc.*, **64**, 3040 (1942).

(14) S. Veibel, *J. Am. Chem. Soc.*, **67**, 1867 (1945).

crystallizing within 1 day and could be filtered off after 3 days.

Authentic *m*-sulfobenzoic acid provided, by the method of Friediger and Pedersen,[15] the bis(*S*-benzylisothiouronium) salt as an oil which crystallized partly within 2 days and completely within 4 days, m.p. 136–137° (cor., lit.,[15] 130–133°). Subsequently sulfobenzoic acid by the same method yielded an oil which crystallized completely within 8 hr., m.p. 135–138°; mixed m.p. 135–138°.

m-**Hydroxybenzoic Acid.**—In a nickel crucible 1.0 g. (0.005 mole) of sulfobenzoic acid was fused with 9.0 g. (0.16 mole) of potassium hydroxide; the gently heated melt was stirred with an iron file for 10 min., during which time a gas was evolved. The melt was cooled, dissolved in water, and the solution acidified with 50% sulfuric acid. Potassium sulfate was filtered off.[16] The filtrate was extracted with ether, and an acid isolated, m.p. 170–180°. Recrystallization from water gave a 30% yield of off-white granular crystals, m.p. 197° (cor., lit.,[17] 200.8°), with a spectrum corresponding between 5 and 10 μ to that published[18] for *m*-hydroxybenzoic acid in this region. The infrared spectra of known salicylic acid and of known *p*-hydroxybenzoic acid differ at a number of wave lengths.

m-**Sulfobenzoic Acid.**—By the method of Reese[10] *m*-sulfobenzoic acid was obtained in 70% yield as a light tan solid with a wide melting range, the upper limit of which was 140°. The infrared spectrum was identical with that of the sulfobenzoic acid obtained by reaction of benzoyl chloride with sulfuric acid.

Attempted Sulfonation of Ethyl Benzoate with Sulfuric Acid. (A) Equimolar Amounts.—In the apparatus described for the reaction of benzoyl chloride with sulfuric acid 10.0 ml. (0.070 mole) of ethyl benzoate [$n^{17.3}\mathrm{D}$ 1.5069 (lit.,[19] $n^{17.3}\mathrm{D}$ 1.50682)] was heated with 3.6 ml. (0.068 mole) of 99.3% sulfuric acid at 100° for 24 hr. After adding water 4.3 g. (0.036 mole) of benzoic acid and 4.5 g. (0.030 mole) of ethyl benzoate were isolated.

(B) **Excess Sulfuric Acid.**—In the same apparatus 12.51 g. (0.0833 mole) of ethyl benzoate (C.P., The Coleman and Bell Co.) and 42.0 g. (0.425 mole) of 99.3% sulfuric acid were heated at 99–104° for 42 hr. After pouring the reaction mixture into 150 ml. of water 10.02 g. (0.0820 mole) of benzoic acid was isolated.

2-Bromo-1,3-dimethylbenzene. (A) Sandmeyer Reaction.—By a modification of the method of Hartwell[20] 20.0 ml. (0.16 mole) of 2,6-dimethylaniline (Eastman Kodak) was diazotized, then subjected to the Sandmeyer reaction: The diazonium salt, which separated as a yellow foamy solid, was spooned in portions into the solution of cuprous bromide, then the residual solution added. Product was collected with b.p. 200–205° (lit.,[21] *ca.* 206°); yield 4.7 g. (0.025 mole).

(B) *Via* **Mercuric Bromide Complex.**[22]—2,6-Dimethylaniline, 37.5 g. (0.310 mole), was diazotized as above, then 54.1 g. (0.150 mole) of mercuric bromide added either as an aqueous suspension[23] or dissolved in aqueous potassium bromide.[24] The pale yellow precipitate was filtered off and washed with water, acetone, and ether. The dry complex obtained by the latter method in a yield of 78.9 g. was immediately mixed with 292 g. (2.45 moles) of potassium bromide and pyrolyzed by being added in portions to a three-necked round-bottomed flask fitted with a reflux condenser. The reaction mixture was well extracted with benzene; the product was collected with b.p. 127° (88 mm.); yield 11.8 g. (0.064 mole).

2,6-Dimethylbenzoic Acid.—The method of Bowen[25] was used. The carbonated reaction mixture never became "granular" and was acidified while sticky. Based on 2-bromo-1,3-dimethylbenzene the yield was 56–58% of white powder, m.p. 115–116° (cor., lit.,[26] 116°).

2,6-Dimethylbenzoyl Chloride.—2,6-Dimethylbenzoic acid was refluxed for 2 hr. with excess thionyl chloride. Product was collected with a b.p. 108–110° (30 mm., lit.,[27] 217°) in 76% yield.

Attempted Reaction of 2,6-Dimethylbenzoyl Chloride with Sulfuric Acid.—In the apparatus described for the reaction of benzoyl chloride with sulfuric acid, 1.15 g. (0.0069 mole) of 2,6-dimethylbenzoyl chloride was dissolved in 10 ml. of carbon tetrachloride, then 0.36 ml. (0.0067 mole) of 99.3% sulfuric acid was slowly added. After 30 min. of additional stirring the reaction mixture was let stand for 1.5 hr. The not quite clear carbon tetrachloride layer was pushed by dry air pressure through a glass tube into another flask, fitted with a drying tube. The yellow sulfuric acid phase was washed three times with carbon tetrachloride, which was removed in the same manner. Evaporation of the carbon tetrachloride while exposed to air left a white solid which, after thorough washing with water and drying, weighed 0.63 g. (0.0042 mole), m.p. 114° (cor.). The water washings indicated 1.47 meq. of acid. From the sulfuric acid phase 0.20 g. (0.0013 mole) of 2,6-dimethylbenzoic acid, m.p. 113°, was precipitated by dilution with water. Titration of the filtrate showed 11.43 meq. of acid.

2,4,6-Trimethylbenzoic Acid.—By the method of Bowen[25] yields of 50–81% were obtained, m.p. 152.4–153.4° (cor., lit.,[25] 153.4–154.4°).

2,4,6-Trimethylbenzoyl Chloride.—By the method of Barnes[28] yields of 27–86% were obtained, b.p. 128–130° [40 mm., lit.,[28] 143–146° (60 mm.)].

Attempted Reaction of 2,4,6-Trimethylbenzoyl Chloride with Sulfuric Acid.—By the same method as for the attempt with 2,6-dimethylbenzoyl chloride, 1.10 g. (0.0060 mole) of 2,4,6-trimethylbenzoyl chloride was treated with 0.31 ml. (0.0058 mole) of 99.3% sulfuric acid. 2,4,6-Trimethylbenzoic acid was obtained, 0.8 g. (0.0049 mole) from the carbon tetrachloride phase and 0.1 g. (0.0006 mole) from the sulfuric acid phase. The wash water from the former portion of 2,4,6-trimethylbenzoic acid contained 1.86 meq. of acid.

Reaction of 2,4,6-Trimethylbenzoyl Chloride with Sulfuric Acid. (A).—In a manner analogous to the reaction of benzoyl chloride with sulfuric acid 0.58 g. (0.0032 mole) of 2,4,6-trimethylbenzoyl chloride, dissolved in carbon tetrachloride, was treated with 0.19 ml. (0.0034 mole) of 99.3% sulfuric acid. Distillation of the carbon tetrachloride left a homogeneous brassy yellow liquid, which was heated for 24 hr. at 100°. A chunk of brown solid remained. This solid dissolved in concentrated sulfuric acid and was recovered, evidently unchanged, upon dilution with water; it dissolved readily in cold cyclohexene; it was insoluble in the following solvents at their respective boiling points: water, aqueous 10% sodium hydroxide, absolute ethanol, methanol, ether,

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(15) A. Friediger and C. Pedersen, *Acta Chem. Scand.*, **9**, 1425 (1955).

(16) Identified by flame test and formation of an acid-insoluble precipitate with aqueous barium hydroxide.

(17) H. Offermann, *Ann.*, **280**, 1 (1894).

(18) R. B. Barnes, V. Liddel, and V. Z. Williams, *Ind. Eng. Chem., Anal. Ed.*, **15**, 695 (1943).

(19) K. Auwers and F. Eisenlohr, *J. Prakt. Chem.*, [2] **82**, 65 (1910).

(20) J. L. Hartwell, *Org. Syntheses*, Coll. Vol. III, 185 (1955).

(21) O. Jacobsen and W. Deike, *Ber.*, **20**, 903 (1887).

(22) H. C. Brown and M. Grayson, *J. Am. Chem. Soc.*, **75**, 20 (1953).

(23) M. S. Newman and P. H. Wise, *J. Am. Chem. Soc.*, **63**, 2847 (1941).

(24) H.-W. Schwechten, *Ber.*, **65**, 1605 (1932). This method proved more successful.

(25) D. M. Bowen, *Org. Syntheses*, Coll. Vol. III, 553 (1955).

(26) W. A. Noyes, *Am. Chem. J.*, **20**, 789 (1898).

(27) I. M. Heilbron and H. M. Bunbury, eds.-in-chief, "Dictionary of Organic Compounds," Vol. 1, Oxford University Press, New York, 1943, p. 895. No primary source for this value was found, either among the references cited by Heilbron and Bunbury for 2,6-dimethylbenzoic acid or by searching Beilstein's "Handbuch der organischen Chemie," 4th ed. plus two supplements, Springer-Verlag, Berlin, *Chem. Abstr.* indexes until June, 1960, and E. H. Huntress, "The Preparation, Properties, Chemical Behavior, and Identification of Organic Chlorine Compounds," J. Wiley and Sons, Inc., New York, 1948.

(28) R. P. Barnes, *Org. Syntheses*, Coll. Vol. III, 556 (1955).

dioxane, benzene, toluene, cyclohexane, carbon tetrachloride, chloroform, dichloromethane, glacial acetic acid, and nitromethane. After removal of nitromethane by boiling to dryness, the recovered brown solid no longer dissolved in cyclohexene. No material could be recovered from cyclohexene solution by dilution with chloroform or with carbon tetrachloride. The spectrum between 2.5 and 15 μ of the brown solid showed absorption maxima at 2.85 (weak), 3.3, 6.2, 6.35 (shoulder), 6.85, 7.2, 7.9, 8.4 (broad), 9.2 (very broad), 9.6 (broad), 11.4 (weak, broad), 11.65, 12.25 (broad), 13.0–13.2 (shoulder), and 14.2–14.5 μ (weak, very broad).

(B).—The same reaction was run with 5.5 g. (0.030 mole) of 2,4,6-trimethylbenzoyl chloride and 1.7 ml. (0.031 mole) of 99.3% sulfuric acid. The residue, after heating, was dissolved in water, and the sulfuric acid removed as after reaction of benzoyl chloride with sulfuric acid. Evaporation of the water left a brown tacky sirup, which did not solidify even after several weeks in a vacuum desiccator over concentrated sulfuric acid.

Selective Etherification of *p*-Hydroxybenzyl Alcohol

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Preparation of the simple *p*-(and *o*-)-alkoxymethylphenols has generally been attended by difficulties on account of their strong tendency to resinify on heating, particularly in the presence of acids or bases.[2] Substituted alkoxymethylphenols are rather more stable in this respect, and it was noted early by Auwers and Baum[3] that these ethers were formed with great ease by merely heating a substituted hydroxybenzyl alcohol with the required etherifying alcohol. This procedure was extended to unsubstituted *o*- and *p*-hydroxybenzyl alcohols by de Jonge and Bibo,[2] who showed that the reaction proceeded without appreciable resinification by heating the mixture in a sealed tube at 150° for several hours.

It has now been found that selective etherification of *p*-hydroxybenzyl alcohol can be carried out by treating its solution in an alcohol with a strong acid cation-exchange resin at room temperature. In this way *p*-methoxymethylphenol and the corresponding ethyl ether have been conveniently prepared in moderate yield on a small scale. When a methanol solution of *p*-hydroxybenzyl alcohol was refluxed with the exchange resin, however, rapid polymerization occurred with formation of a resinous product.

Experimental

***p*-Methoxymethylphenol.** Zeo-Karb 225 exchange resin in the hydrogen form was thoroughly washed with water, and then methanol. A solution of 1.7 g. of *p*-hydroxybenzyl alcohol[4] in 9 ml. of pure methanol was allowed to stand with 3.4 g. of the resin for 12 hr. at room temperature. The resin was separated, washed with methanol, and the combined filtrate and washings evaporated *in vacuo*. The oily residue soon crystallized, and was washed with cold water and dried. Recrystallization from benzene gave the phenol as compact prisms, yield 1.1 g. (60%), m.p. 81.5–82.5°, (lit.[2] m.p. 82.5–83.5°).

When the methanol solution was refluxed with the exchange resin for 1 hr., and the mixture worked up as before, a white, water-insoluble, resinous material was obtained.

***p*-Ethoxymethylphenol.**—Treatment of 1 g. of *p*-hydroxybenzyl alcohol with ethanol and Zeo-Karb 225 in the same way, followed by distillation, gave the phenol as an oil, yield 0.45 g. (37%), b.p. 118–120°/2 mm., which solidified on standing. It was recrystallized from benzene–petroleum ether, m.p. 50–51° (lit. m.p. 50–51°;[6] 56.5–57.5°[2]).

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[1] Present address: Department of Organic Chemistry, Weizmann Institute of Science, Rehovoth, Israel.

[2] J. de Jonge and B. H. Bibo, *Rec. trav. chim.*, **74**, 1448 (1955).

[3] K. Auwers and F. Baum, *Ber.*, **29**, 2329 (1896).

[4] *p*-Hydroxybenzyl alcohol was obtained by the lithium aluminum hydride reduction of ethyl *p*-hydroxybenzoate in the usual way.[5]

[5] R. F. Nystrom and W. G. Brown, *J. Am. Chem. Soc.*, **69**, 1197 (1947).

[6] H. Mitawa, *Bull. Chem. Soc. Japan*, **27**, 53 (1954).

Dehydrogenation of Alcohols by Lithium Metal–Ethylenediamine System

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Previous workers[2,3] have shown that lithium metal in ethylenediamine and in aliphatic monoamines can reduce aromatic compounds to monoolefins. It has been shown[2,3] also that phenol can be reduced to cyclohexanone in the presence of lithium metal in amines. In unpublished work from our laboratories, we have found that lithium metal in ethylenediamine will reduce a variety of phenols to saturated and unsaturated ketones and alcohols.

The proposed mechanism[2b] for this reduction reaction suggests a stepwise 1,4-addition of two moles of hydrogen to the aromatic ring. The addition of a third mole of hydrogen to the isolated double bond is so slow that the monoölefin may be isolated. It is reasonable to predict from this proposed mechanism that the ketones from the reduction of phenols arise from the isomerization of an enol intermediate. The alcohol products

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[1] American Chemical Society–Petroleum Research Foundation Undergraduate Fellow, 1961–1962.

[2] (a) R. A. Benkeser, R. E. Robinson, D. M. Sauve, and O. H. Thomas, *J. Am. Chem. Soc.*, **76**, 631 (1954); (b) R. A. Benkeser, C. Arnold, Jr., R. F. Lambert, and O. H. Thomas, *ibid.*, **77**, 6042 (1955).

[3] L. Reggel, R. A. Friedel, and I. Wender, *J. Org. Chem.*, **22**, 891 (1957).