only sucrose which crystallizes on the plants while the nectar from flowers of the Poinsettia (*Poinsettia sp.*) contained glucose, fructose, and sucrose.

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Cation Exchange Resins as Catalysts in the Alkylation of Phenols

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Both anion and cation exchange resins have been widely used as catalysts for reactions such as esterification, hydrolysis, and sucrose inversion[1,2]—reactions which involve only carbon-oxygen bonds. By comparison, reports of the use of resins (particularly cation exchange resins) as catalysts for reactions in which carbon–carbon bonds are formed, are few. Ion exchange resins are reported to catalyze cyanohydrin formation, aldol condensation,[3,4] and the various modifications of the Knoevenagel[5] and Michael[6] condensations. It seemed of interest to investigate other reactions which are normally catalyzed by strong acids, to see whether cation exchange resins could be used in place of the usual Lewis acids.

It has been found that the sulfonic acid type cation exchange resins are excellent catalysts for the alkylation of phenol with olefins such as isobutylene, diisobutylene, and nonene-1.

The resins investigated were Amberlite IR-112 and IR-120, Dowex 50 × 12, and Permutite Q; all were sulfonic acid type resins. The conversion[7] was a little lower when Amberlite IR-112 was used, but all other results were independent of the resin used.

The yields in these alkylations were essentially independent of the concentration of resin.

When phenol was alkylated with isobutylene using a cation resin there was generally no *ortho* isomer in the product.

The presence of water was deleterious, at least in the diisobutylene alkylation reactions, for when the resin was used after only air drying, no reaction occurred. The reaction required an oven-dried resin. Drying of the diisobutylene also increased the yield.

The use of a cation exchange resin as catalyst has the particular advantage over a mineral acid catalyst that at the conclusion of the reaction, a simple filtration of the molten reaction mixture leaves an acid-free solution ready for distillation. There is no chance of acid catalyzed rearrangement during the distillation, and the product is a high purity *p*-alkylphenol. In addition, the use of resins as catalysts eliminates by-products formed by reaction of the mineral acids with the phenol, and by by-products due to polymerization or degradation of the olefin.

Attempts to alkylate xylene and benzene using a resin catalyst were unsuccessful.

EXPERIMENTAL

Preparation of resin catalyst. The resins which are normally purchased in the salt form were converted to the acid form by washing with 5% H_2SO_4 until the wash water gave a negative flame test for sodium. The resin was then thoroughly washed with distilled water until the wash water was neutral, air dried for 24 hr., and then heated for 18 hr. in a vacuum oven at 100–120°.

The resin may be washed with acetone and ether, following the air drying, to remove traces of colored organic impurities. This treatment has no effect on the catalytic activity of the resin.

The resins were all commercial materials: Amberlite IR-112 and IR-120, 16 to 50 mesh (Rohm & Haas), Permutite Q, approx. 20 to 60 mesh (Permutite Corp.), and Dowex 50 × 12, 200–400 mesh (Dow Chemical).

p-tert-Octylphenol[8] (*p-diisobutylphenol or 1,1,3,3-tetramethylbutylphenol*). A typical preparation is given. Phenol (250 g., 2.6 moles), diisobutylene, (328 g., 219 moles), and 17.5 g. of Amberlite IR-112, prepared as described above, were heated together with vigorous stirring for 24 hr. at 70–75°.

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(7) For greater ease in discussing the results of these experiments, the terms "conversion" and "yield" are employed. Percent conversion represents the percent of theoretical value based on the amount of (limiting) starting material charged to the reaction. Percent yield represents the percent of the theoretical value based on the amount of starting material used up (or not recovered) during the reaction.

(8) As used here, *p-tert*-octylphenol refers to the alkyl group 1,1,3,3-tetramethylbutyl-, which results from the alkylation of phenols with diisobutylene (DIB). DIB is a mixture of two isomers, 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene which are assumed to give identical alkylation products.

TABLE I

Alkylation of Phenol with Isobutylene[a]

Catalyst	Resin,[b] %	Di-*tert*-Butylphenol, % conv.[c]	*o*-*tert*-Butylphenol, % conv.[c]	*p*-*tert*-Butylphenol, % conv.[c]	*p*-*tert*-Butylphenol, % yield[c]
Amberlite IR-112	6¹/₄	0	0	37	98
Permutite Q	6¹/₄	0	4	51	83
Amberlite IR-120	6¹/₄	0	0	57	87
Dowex 50 × 12	6¹/₄	0	0	49	77

[a] Reactions carried out as described in Experimental. [b] Wt. % based on total charge. [c] See ref. 8.

TABLE II

Alkylation of Phenol with Diisobutylene in the Presence of Amberlite IR-112

Temp., °C.	Time, Hrs.	Resin,[a] %	*tert*-Butylphenol, % Conv.[b]	*tert*-Octylphenol, % Conv.[b]	*tert*-Octylphenol, % Conv.[b]	
83	3	14	Trace	Trace	Trace	[c]
80	2³/₄	14	10	38	63	[d]
70–5	4¹/₄	1.4	6	49	100	[d,e]
70–5	8	0.4	4	53	97	[d,e]
70–5	24	3	4	73	95	[d,e]
70–5	24	7	3	88	100	[d,e]
100–5	4¹/₄	1.4	11	65	91	[d,e]
100–10	18	2	14	61	77	[d,e]

[a] Wt. % based on total charge. [b] See ref. 7. [c] Air dried resin used. [d] Heat dried resin. [e] DIB dried.

The resin was then filtered off. The pale yellow filtrate had a set point of 57–60°. On distillation, the following fractions were obtained. b.p. 78–110° (20 mm.), phenol, 63 g.; b.p. 140–153° (20 mm.), *p-tert*-octylphenol, 390 g. (73% conversion, 95% yield), colorless liquid which soon crystallized, m.p. 82–83° (lit.[9] b.p.$_{20}$ 163°, m.p. 84°).

p-tert-Butylphenol. In a typical preparation 94 g. (1.0 mole) of phenol and 10 g. of Amberlite IR-120, prepared as described above, were heated at 80° with vigorous stirring as 58.7 g. (0.92 moles) of isobutylene (Atlantic Refining Co.) was passed in beneath the surface of the liquid over a period of 3 hr. The isobutylene was completely absorbed. After the isobutylene had all been added, the temperature was raised to 120° for 4 hr. The resin was filtered off and the colorless filtrate was distilled giving the following fractions: b.p. 175–205°, phenol, 33.5 g.; b.p. 220–228°, *o*- and *p-tert*-butylphenol, 1.5 g.; b.p. 230–234°, *p-tert*-butylphenol, 73.8 g. (57.5% conversion, 88% yield), m.p. 92° (lit.[9] b.p. 237°, m.p. 100°).

Nonylphenol. Phenol (47 g., 0.5 mole), 63 g. (0.5 mole) of nonene-1 and 5 g. of prepared Amberlite IR-112 resin were heated at 100–10° for 24 hr. with vigorous stirring. The resin was removed by filtration and the filtrate distilled giving the following fractions: b.p. 130–160°, nonene-1, 7 g.; b.p. 182–183°, phenol, 10.6 g.; b.p. 297–305°, nonylphenyl, 75.2 g., n_{D}^{28} 1.5060 (68% conversion, 92% yield).

Attempted alkylation of xylene. The reaction was carried out as described under the preparation of *p-tert*-butylphenol, except that the isobutylene was fed in more slowly. No absorption of isobutylene occurred, and the xylene was quantitatively recovered.

Attempted alkylation of benzene. Benzene (80 g.), 84 g. of propylene tetramer and 5 g. of Amberlite IR-112 were heated at reflux, with stirring for 25 hr. No reaction had occurred for the propylene tetramer was quantitatively recovered on distillation.

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Metalation of Phenyl Benzyl Sulfide and Sulfone with *n*-Butyllithium

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The large activating effect of a sulfone group toward metalation at an adjacent C—H bond is well known. Thus Truce and co-workers[2] have demonstrated that diaryl sulfones are metalated readily with *n*-butyllithium at the positions *ortho* to the sulfone group. Gilman and Webb[3] observed the metalation of methyl phenyl sulfone with *n*-butyllithium on the methyl group, and Grignard reagents have been shown to metalate the same position.[4,5]

It was of interest to us to observe the position of metalation of phenyl benzyl sulfone since this molecule contains two different kinds of activated C—H bonds adjacent to the sulfonyl groups. The action of a *n*-butyllithium on an equimolar amount of benzyl phenyl sulfone followed by carbonation and hydrolysis allowed formation of 65% of α-phenylsulfonylphenylacetic acid (I) indicating metalation at the —CH_2— group. The structure of the acid from metalation is indicated by comparison of its decarboxylation temperature of 142–

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[1] Present address: The Koppers Co., Monaca, Pa.

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