phenol–DCC adducts (**1**) form faster than the alcohol–DCC adducts (**4**). However, the reversibility of **1**, already described by Vowinkel,[5] would allow a build-up of the 2-alkylpseudourea (**4**) proposed in path B. Once formed **4** would be vulnerable to SN2 attack by phenate ion.[6] The poor yields given by secondary or tertiary alcohols in this system may readily be explained by proposing steric hindrance to SN2 attack in path B (see **5**).

Cogent evidence in favor of one mechanism or the other can be obtained by incorporating ethanol-O^{18} into the phenol–*n*-alcohol–DCC system. As illustrated in Scheme I only "tagged" aryl alkyl ether **3** would result from attack of ethanol-O^{18} on **1** in path A, while only "tagged" DCU (**6**) would result if path B were followed.

Preliminary experiments included the reactions of ethanol-O^{18} with phenol and *p*-nitrophenol using DCC as a condensing agent. *p*-Nitrophenol would be expected to facilitate the mechanism outlined in path A; *viz.*, the "electron-withdrawing" effect of the *p*-nitro group should give additional stability to the transition state[7] resulting from nucleophilic attack by ethanol on the 2-(*p*-nitrophenyl)pseudourea, and the decreased nucleophilicity of the *p*-nitrophenate ion should slow up SN2 attack *via* path B.

One may conclude from the experimental data listed in Table I that aryl alkyl ether formation using DCC as a condensing agent *does not* proceed through path A. Although other mechanisms may be proposed path B seems to explain the results, *i.e.*, *SN2 attack by a phenate ion on a 2-alkylpseudourea intermediate.*

TABLE I

MASS SPECTROMETRIC ANALYSES OF ISOTOPIC PRODUCTS[a,b]

		—% of O^{18} predicted by—		
Expt. no.	Compd.	Path A	Path B	Found
1	Phenetole	1.9[c]	0	0[d]
	DCU	0	1.9[c]	1.8[e]
2	*p*-Nitrophenetole	1.9[c]	0	0[d]
	DCU	0	1.9[c]	1.4[e]

[a] A Consolidated Electrodynamics Corp. mass spectrometer, Model 21-103C, was used to determine O^{18} content. [b] All values reported are maximum values. [c] The ethanol used in this study contained 1.9% O^{18} (maximum value). [d] Trace amounts of O^{18} were not considered significant. [e] Both values are within the limit of experimental error.

Experimental[8]

Purification of Material.—Phenol (U.S.P., Mallinckrodt) and N,N′-dicyclohexylcarbodiimide (American Cyanamid) were used without further purification. *p*-Nitrophenol was obtained by acidifying the dihydrate of sodium *p*-nitrophenate. Two recrystallizations from benzene yielded pure *p*-nitrophenol, m.p. 114–115° (lit.[9] m.p. 113.8°).

General Procedure.—A mixture consisting of 6.6 g. (0.07 mole) of phenol, 14.4 g. (0.07 mole) of N,N′-dicyclohexylcarbodiimide, and 3.4 g. (0.07 mole) of ethanol (1.9% O^{18}) was sealed in a tube and heated to *ca.* 100°. After approximately 72 hr. the quasi-crystalline reaction mass was cooled to room temperature, triturated with three 50-ml. portions of ether, and filtered. The insoluble N,N′-dicyclohexylurea collected in this manner weighed 14.0 g. (91% yield). A sample of the urea derivative recrystallized twice from hot, glacial acetic acid[10] melted at 230–231° (lit.[11] m.p. 229–230°).

An excess of oxalic acid (1.8 g., 0.02 mole) was added to the ethereal filtrate and, after a brief evolution of gas,[12] the solution was decolorized using charcoal, filtered, and concentrated to a yellow oil. Distillation of the crude product using a spinning-band column gave a pure sample of phenetole boiling at 168–169° (765 mm.), lit.[13] b.p. 170° (760 mm.).

The reaction products purified as described above were submitted for mass spectrometric analysis (see Table I).

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[6] Precedents for the proposed SN2 reaction in path B are found in the formation of alkyl halides and N,N′-disubstituted ureas when aqueous, acidic solutions of N,N′-disubstituted 2-alkylpseudoureas are warmed: see F. B. Dains, *J. Am. Chem. Soc.*, **21**, 136 (1899); H. G. Khorana, *Can. J. Chem.*, **32**, 227 (1954).

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[10] N,N′-Dicyclohexylurea is insoluble in ordinary organic solvents.

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[12] Unreacted DCC is decomposed by oxalic acid to give a quantitative yield of DCU, CO_2, and CO.

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The Nitration of Toluene by Means of Nitric Acid and an Ion-Exchange Resin[1]

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When a dehydrated, sulfonic acid ion-exchange resin, instead of sulfuric acid, is used along with nitric acid to form the nitrating agent in the nitration of toluene, nitration does take place. Decreased *ortho–para* ratios, as low as 0.68, are obtained, indicating that this type of nitrating agent has a large steric effect. In addition to the normal mononitration products, 25–30% of phenylnitromethane is also sometimes produced. Evidence is presented that the nitronium ion is produced, and, when a nonpolar solvent is used, the ions are held as ion pairs on the surface of the resin, creating the steric effect.

The nitration of toluene has been investigated by many investigators, and, although some of the data in the literature appear to be in conflict,[2] the *ortho–para* ratios obtained by most investigators[3] is remarkably consistent at 1.57 ± 0.10. It is presumed from this that the steric effect of the nitrating agent is constant throughout most of the work and that the actual

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[1] This work was supported in part by Undergraduate Research Participation Grants from the National Science Foundation and from the Kansas City Association of Trusts and Foundations. Thanks is also extended to the Pittsburgh Chemical Co. for permission to publish the portion of the work done in their laboratories.

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agent for nitration is probably the nitronium ion, NO_2^+, or its hydrated species.

When a mixture of nitric acid, adsorbed on the surface of an anhydrous polystyrene polysulfonic acid ion-exchange resin (Rohm and Haas Amberlite IR-120), is used to nitrate toluene, *ortho–para* ratios are obtained which deviate considerably from the usual values. Depending upon the conditions of the reaction, *i.e.*, temperature and solvent, the stoichiometry, *i.e.*, the ratio of the resin to the nitric acid, and the amount of water present, *ortho–para* ratios between 0.68 and 1.40 have been obtained.

The acid form of the resin is available commercially, and normally contains about 50% water. This is removed by azeotropic distillation with toluene. The dried resin is then slurried in a mixture of toluene and solvent, and nitric acid is added dropwise to the slurry. The reaction is mild. The solvent color intensifies slowly as the reaction progresses, and only a small amount of the oxides of nitrogen can be seen. When the reaction is complete, the water formed may be removed azeotropically, and the solvent and the product can be filtered from the mixture, leaving the resin ready for another reaction. The product and solvent may be separated by distillation, or analyzed as such in the gas chromatograph.

Several reactions take place in the reaction mixture. In addition to the three nitrotoluenes, benzaldehyde, benzyl alcohol, and phenylnitromethane have also been identified. Some nitration takes place before the nitric acid has been adsorbed on the resin, and some reaction takes place before the nitric acid reacts with the resin after being adsorbed. The presence of nitrogen dioxide indicates that some oxidation has taken place, but there is not enough of the oxide to account for all of the three by-products formed. The contribution made by the nitronium sulfonate varies with the reaction parameters as shown by the variation in *ortho–para* ratio obtained. The formation of phenylnitromethane is temperature dependent. This by-product has been observed in as high as 30% of the total yield.

Even though the over-all product is the result of several reactions occurring simultaneously, there is evidence that one of the contributing reactions involves attack on the aromatic nucleus by a sterically hindered nitrating agent. The proposed mechanism for this contribution is as follows.

(1) Nitric acid reacts with the resin sulfonic acid in the same manner that it reacts with other strong acids.

$$HNO_3 + 2HClO_4 = NO_2^+ + H_3O^+ + 2ClO_4^-$$

$$HNO_3 + 2H_2SO_4 = NO_2^+ + H_3O^+ + 2HSO_4^-$$

$$HNO_3 + 2ResSO_3H = NO_2^+ + H_3O^+ + 2ResSO_3^-$$

(2) The ions, formed when the nitric acid reacts with the resin, form ion pairs with the resin when slurried in a nonpolar solvent and are not dissociated. The size of the salt, thus formed, is considerably greater than that of the nitronium ion.

The following data have been collected in support of these hypotheses.

(1) The reaction is definitely different when the resin is used and, although the phenomenon must begin with surface adsorption, there must also be some kind of chemical action on the surface of the resin. Three reactions were run. Toluene was nitrated with 90% nitric acid at 65–70° with no solvent and the *ortho–para* ratio was 1.65. When the same reaction was run in the presence of absorbent carbon granules of approximately the same size as the resin beads, *ortho–para* ratio was 1.72, but when a like amount of resin was used instead of the absorbent carbon in the same reaction at the same temperature, the *ortho–para* ratio was 0.68.

Toluene was nitrated in chloroform at five temperature ranges. The same series of reactions were carried out using the ion-exchange resin at the same temperature ranges. The results are tabulated in Table I.

TABLE I

NITRATION OF TOLUENE IN CHLOROFORM USING NITRIC ACID AND RESIN[a]

Temp., °C.	*ortho–para* ratio Without resin	 With resin
15–20	1.62	1.27
25–30	1.50	1.30
35–40	1.62	1.22
45–50	1.52	1.31
55–60	1.48	1.18

[a] The amounts used were toluene, 10 ml.; chloroform, 50 ml.; nitric acid, 90%, 5 ml.; and resin, 10 g.

(2) There is a relationship between the ratio of nitric acid to resin and the total yield. Using a constant amount of nitric acid the total yield of nitrated products depends upon the amount of resin used. A series of runs was made where the amount of toluene and the amount of nitric acid were kept constant while the amount of resin was varied. No solvent was used, and the reactions were all run for 1 hr. at 35–40° Data on these runs are in Table II.

TABLE II

NITRATION OF TOLUENE (184 G.) WITH 90% NITRIC ACID (70 G.) AND A VARIABLE AMOUNT OF RESIN

Resin, g.	Yield of nitrotoluenes G.	 Moles
100	50	0.365
100	42	0.307
158	73	0.532
158	77	0.561
200	117	0.854
200	116	0.847

(3) There is also a relationship between the ratio of nitric acid to resin and the *ortho–para* ratio. This is undoubtedly due to the available surface area of resin which may effect a quick adsorption of the nitric acid. The longer it takes to adsorb the nitric acid, the more the contribution of the liquid phase reaction, resulting in higher *ortho–para* ratios.

In one series of four runs 50 ml. of toluene was nitrated using a constant amount of the resin (10 g.) and variable amounts of nitric acid were added (Table III). In another series 250 ml. of toluene was used to suspend different amounts of the resin and 2 ml. of nitric acid was added to each (Table IV).

(4) It can be shown experimentally that the nitration attack on the methyl group is temperature dependent. The *ortho–para* ratio also appears to have

TABLE III

NITRATION OF TOLUENE (50 ML.) WITH RESIN (10 G.) AND A VARIABLE AMOUNT OF NITRIC ACID

90% HNO_3, g.	*ortho–para* ratio
3.0	0.87
3.75	0.92
4.5	0.99
7.5	1.06

TABLE IV

NITRATION OF TOLUENE (250 ML.) WITH A VARIABLE AMOUNT OF RESIN AND NITRIC ACID (2 ML.)

Resin, g.	Yield, g.	*ortho–para* ratio
5	1.52	1.19
20	3.98	0.81
100	4.14	0.68

some temperature dependence. Contrary to the usual pattern of behavior with other nitrating agents, however, the higher *ortho–para* ratios are obtained at the low temperatures, indicating again that this nitrating agent acts in a different manner to those which have been studied before.

A series of nitrations were carried out with 50 ml. of toluene, 15 g. of resin, and 2 ml. of 90% nitric acid. In all cases, the acid was added to a precooled (to 10°) slurry of the resin in toluene. This mixture was then stirred for 1 hr. after which the temperature was raised as rapidly as possible to a given range and maintained there for 1 hr. These reactions were run at nine different temperature ranges, as shown in Table V.

TABLE V

NITRATION OF TOLUENE (50 ML.) WITH RESIN (15 G.) AND 90% NITRIC ACID (2 ML.) AT DIFFERENT TEMPERATURES

Temp., °C.	*ortho–para* ratio	*ortho* ratio
25–30	1.36	No α
35–40	1.36	No α
45–50	1.30	Little α
55–60	1.26	100+
65–70	1.14	50+
75–80	1.06	4.0
85–90	0.98	1.2
95–100	0.90	1.0
105–110	0.90	0.90

Experimental

The ion-exchange resin used in this work was Rohm and Haas Amberlite IR-120. As it is commercially available in the acid form, it normally contains approximately 50% water. If the equivalent weight of the resin is figured at around 200, this would amount to about ten molecules of water per sulfonic acid group, which would be considered a dilute acid. This water can be removed quantitatively by azeotropically refluxing with toluene and removing the water in a Dean–Stark trap. The resin darkens in color and becomes preferentially toluene wetted. It is not immediately wetted by water in its dry state, but on standing reacts exothermically. The dried resin also reacts vigorously with alcohols.

The reactions were run in the usual glass apparatus, equipped for effective stirring, heating, and cooling. Although the resin, when dried, is hygroscopic, no drying tube precautions need be taken when it is slurried in the nonpolar solvent. The dried resin can be weighed in the open air without picking up a detectable amount of water.

The nitrations were carried out by adding 90% nitric acid dropwise to the toluene, or to a mixture of toluene and solvent. When the ion-exchange resin was used, it was mixed with toluene (and solvent) and stirred vigorously as the nitric acid was added. In some cases all the ingredients were mixed and stirred at a low temperature to ensure complete adsorption. Then the temperature was raised rapidly to an arbitrary level and maintained there for a prescribed amount of time.

Reaction samples were taken and treated with solid potassium carbonate. Analysis was made using an Aerograph 600 Hi Fy gas chromatograph which had a 6-ft. column packed with silicone wax on Chromosorb W. *ortho–para* ratios and *ortho–α* ratios were determined using the standard methods. Benzaldehyde, benzyl alcohol, and phenylnitromethane were identified by adding small amounts of authentic samples to the experimental samples.

Halogen Migration in the Reaction of Organic Dihalides with Aluminum Chloride[1]

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This paper comprises the Friedel–Crafts condensation of 1,5-dibromopentane and 1,6-dibromohexane with benzene[1,2] and the isomerization of 1,2-dichlorocyclohexane in the presence of aluminum chloride.

The reaction of 1,5-dibromopentane with benzene was carried out in the presence of a catalytic amount of anhydrous aluminum chloride at room temperature. The 1:1 (dihalide–benzene) condensates and the 1:2 products were separated by fractional distillation. The latter, higher boiling fraction was mainly 1,5-diphenylpentane (19% yield) accompanied by a small amount of isomeric diphenylpentane(s). 1,5-Diphenylpentane was identified by comparison with an authentic specimen.[3]

The lower boiling fraction, which contained 1:1 condensates, was obtained in about 44% yield and gave two peaks on gas–liquid chromatographic (g.l.c.) analysis. Preparative g.l.c. resulted in the isolation of *n*-amylbenzene[4] and 1-methyltetralin[5] in a ratio of 1:1.3, each being identified by comparison with authentic samples.

The reaction of 1,6-dibromohexane was analogously conducted. The 1:2 condensate consisted of 1,6-diphenylhexane[6] (13% yield) and a minor fraction which appeared to be isomeric diphenylhexane(s) (3.8% yield). The lower boiling 1:1 fraction (about 41% yield) was found to show three peaks on g.l.c. in a ratio of 1:14:26. The components were identified

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