

[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE COLLEGE]

Stereochemical Evidence for a Concerted Displacement Mechanism in Acidic Aromatic Alkylations. The Nuclear Alkylation of Phenols with α -Phenethyl Chloride¹

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α -Phenethyl chloride alkylated phenols nuclearily and spontaneously, without an added catalyst; optically active chloride gave products which were also optically active. An appreciable part of the observed loss of optical purity was due to racemization of the chloride *prior* to alkylation. *Ortho* alkylation (of *p*-cresol and *p*-chlorophenol) proceeded with retention of configuration, whereas *para* alkylation (of 2,6-xylenol) proceeded with inversion. The commonly accepted ionic alkylation mechanism is consistent with the stereochemistry of *para* alkylation, but cannot account for retention of configuration observed in *ortho* alkylation. A concerted nucleophilic displacement mechanism analogous to S_Ni, and possible only for *ortho* alkylation, is consistent with the data. An appreciable fraction of the reaction goes by this path, the remainder involving the ionization mechanism.

The mechanism of the Friedel-Crafts reaction has been discussed recently by Brown² and by Schmerling,³ and the extensive literature reviewed by those authors will not be discussed here. Suffice it to say that both Brown and Schmerling suggested that two alternative mechanisms appear necessary to account for the observed facts in Friedel-Crafts alkylations. The first is the generally accepted ionization mechanism⁴; the second is a concerted nucleophilic displacement mechanism, called for by lack of isomerization in certain instances where an ionization mechanism would predict isomerization,⁵ and by an aromatic substrate term in the third-order kinetics for benzyl halide alkylations, most conclusively demonstrated in the elegant work of Brown and Grayson.² It is the purpose of this paper to present for the first time stereochemical evidence which requires also the operation of a concerted mechanism, under favorable circumstances.

Previous studies⁶⁻⁸ on the stereochemistry of the Friedel-Crafts reaction have been consistent with the ionization mechanism. When benzene was alkylated with optically active *sec*-butyl alcohol^{6,7} or *sec*-butyl methyl ether,⁸ the product was extensively racemized. In at least one case,⁸ racemization occurred during (not prior to) the alkylation step, and the small (about 1%) activity in the product was caused by a slight predominance of inversion. This is the characteristic steric result of reactions which proceed by an ionization mechanism,⁹ although racemization was somewhat more drastic than usual. It was suggested⁸ that the extensive racemization may be connected with isomerization of the intermediate carbonium ion.

Since phenols can be alkylated by tertiary or ben-

zyl halides without an added catalyst,¹⁰ it was thought that α -phenethyl chloride would react similarly, and that one could study the stereochemistry of the reaction using optically active chloride. This halide appeared particularly promising because of the reported alkylation of phenol with styrene, using hydrogen iodide,¹¹ chloride¹² and bromide¹² as the catalysts. It was our purpose to avoid the use of the strong Lewis acids necessary to the alkylation of hydrocarbons. Furthermore, we have already established the configurational relationships of the anticipated products.¹ Accordingly, we studied the reaction of α -phenethyl chloride with phenol, *p*-cresol, *p*-chlorophenol and 2,6-xylenol.

Results and Discussion

The alkylation of phenol with α -phenethyl chloride proceeded more readily than had been anticipated. Although benzyl chloride alkylated phenol only one-twentieth as fast as *t*-butyl chloride,¹⁰ α -phenethyl chloride reacted more rapidly than *t*-butyl chloride. A 2:1 mixture of phenol and α -phenethyl chloride evolved hydrogen chloride *spontaneously at room temperature* in an exothermic reaction (*t*-butyl chloride required warming to 50° for rapid reaction). A good yield of mono- α -phenethylphenols was obtained, together with some dialkylate (the amount of dialkylate could be reduced by using an inert solvent, such as benzene). Spectrophotometric analysis¹³ of the monoalkylated phenols indicated about 55% *ortho* and 45% *para* isomer, consistent with the reported¹² products from the hydrogen chloride-catalyzed alkylation of phenol by styrene. *p*-Cresol, *p*-chlorophenol and 2,6-xylenol were alkylated similarly to give *o*- α -phenethyl-*p*-cresol, *o*- α -phenethyl-*p*-chlorophenol and 4- α -phenethyl-2,6-xylenol, respectively.

Alkylation with optically active α -phenethyl chloride gave optically active phenols. Some of the pertinent results are given in Table I. Although the rotations of the products were low, they were in fact real, and not due to the presence of unreacted optically active chloride. This conclusion is supported by the following data. With *p*-cresol and *p*-chlorophenol, the alkylation product had a rotation opposite in sign to that of the original chloride. With

(1) Paper IV in the series "Stereochemistry of Aromatic Alkylations." For previous papers, see H. Hart and R. Elia, *THIS JOURNAL*, **76**, 3031 (1954); H. Hart and H. S. Eleuterio, *ibid.*, **76**, 516, 519 (1954).

(2) H. C. Brown and M. Grayson, *ibid.*, **75**, 6285 (1953); H. C. Brown, H. W. Pearsall, L. P. Eddy, W. J. Wallace, M. Grayson and K. L. Nelson, *Ind. Eng. Chem.*, **45**, 1462 (1953).

(3) L. Schmerling, *ibid.*, **45**, 1447 (1953); L. Schmerling and J. P. West, *THIS JOURNAL*, **76**, 1917 (1954).

(4) C. C. Price, *Chem. Revs.*, **29**, 37 (1941); "Organic Reactions," Vol. 3, John Wiley and Sons, Inc., New York, N. Y., 1946, pp. 1-82.

(5) See, for example, V. Ipatieff, H. Pines and L. Schmerling, *J. Org. Chem.*, **5**, 253 (1940).

(6) C. C. Price and M. Lund, *THIS JOURNAL*, **62**, 3105 (1940).

(7) R. L. Burwell, Jr., and S. Archer, *ibid.*, **64**, 1032 (1942).

(8) R. L. Burwell, Jr., L. M. Elkin and A. D. Shields, *ibid.*, **74**, 4570 (1952).

(9) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 381.

(10) H. Hart and J. H. Simons, *THIS JOURNAL*, **71**, 345 (1949), and leading references cited there.

(11) R. Stoermer and O. Kippe, *Ber.*, **36**, 3992 (1903).

(12) R. P. Perkins and F. Brynes, U. S. Patent 2,247,402 (July 1, 1941).

(13) H. Hart, *Anal. Chem.*, **24**, 1500 (1952).

p-cresol and 2,6-xyleneol, a reversal in the sign of the product occurred when opposite enantiomorphs of α -phenethyl chloride were used. Furthermore, as will be shown below, any recovered unreacted chloride which might have been present would have been essentially racemic under the conditions used for most of the experiments in Table I. There can be no doubt, then that the observed rotations represent optical activity in the α -phenethylated phenols.

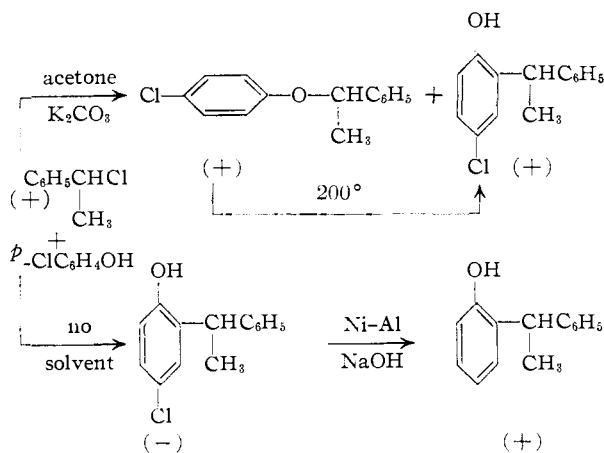
TABLE I

UNCATALYZED NUCLEAR ALKYLATION OF PHENOLS WITH OPTICALLY ACTIVE α -PHENETHYL CHLORIDE

Expt.	α^{25D}	α -Phenethyl chloride ^a Mole	Phenol ^b Mole	Time, min.	Temp., °C.	Alkylated phenol ^c α^{25D}	Alkylated phenol ^c Mole ^e
1	-46.5	0.064	0.213 P	45	70	-0.29	0.056
2	-41.6	.064	.213 P	75	55	-.35	.057
3	22.9	.070	.070 C	300	100	-.13	.042
4	-44.75	.070	.070 C	300	100	.23	...
5	77.37	.050	.100 C	60	<i>e</i>	-.44 ^d	.033
6	22.9	.070	.070 X	300	100	.09	.035
7	-44.75	.070	.070 X	300	100	-.11	...
8	29.5	.050	.100 Cl	60	<i>e</i>	-.24	.031

^a All rotations in this table are for homogeneous material, *l* 1 dm. ^b P = phenol, C = *p*-cresol, X = 2,6-xyleneol, Cl = *p*-chlorophenol. ^c Represents recovered, doubly-distilled product. ^d This rotation was checked at three temperatures: -0.44 at 25.8°, -0.42 at 23.3°, -0.41 at 21.4°. ^e Warmed over a low flame until hydrogen chloride evolution was complete.

Configurations.—The configurations of *o*- α -phenethyl-*p*-cresol and 4- α -phenethyl-2,6-xyleneol were related to α -phenethyl chloride previously.¹ From these assignments, it appeared that *alkylation of p-cresol went with retention of configuration, but the alkylation of 2,6-xyleneol involved inversion.*¹⁴ These results seemed odd, since we expected the mechanisms of *ortho* and *para* alkylation to be identical, and inversion was anticipated from previous work.⁶⁻⁸ In order to determine whether retention was general for *ortho* alkylation, we then examined *p*-chlorophenol (experiment 8, Table I). The configuration of the latter had not been previously determined, but we were able to demonstrate in three ways that here, too, alkylation proceeded with retention of configuration. The results are summarized in the flow sheet.



(14) In each case, the principal result was racemization; this will be discussed below.

Ether and C-alkylate formation both have been shown to proceed with inversion.¹ Furthermore, the thermal rearrangement of the ether was shown to involve retention.¹ Finally, removal of the chlorine from (-)-*o*- α -phenethyl-*p*-chlorophenol by reduction gave (+)-*o*- α -phenethylphenol, which had previously been shown to have the same configuration as (+)- α -phenethyl chloride. Thus the three independent methods are consistent, and indicate that *ortho* alkylation again proceeded with retention of configuration.

A Quantitative Estimate of Optical Purity.—

It was obvious from the rotations obtained by direct alkylation (Table I) and those assigned previously to optically pure products¹ that racemization was extensive. Experiments were first undertaken to determine whether it occurred during or prior to alkylation. In one experiment, an alkylation of phenol was interrupted when only a little more than 20% complete; the recovered chloride had only 44% of its initial rotation. Thus, racemization does indeed occur independently of alkylation, at a rate comparable with it. The kinetics of the alkylation and racemization were studied in detail, and the results will be reported in a separate communication.

As a consequence of this racemization of α -phenethyl chloride by phenols, it is necessary to know the rotation of the *initially formed* alkylated phenol, to make an estimate of the retention of optical purity associated with the alkylation step. This was obtained by running the alkylation for several time intervals and isolating the product. Extrapolation to zero time allowed a correction for the prior racemization of the chloride. Data for experiments of this type are given in Table II.

TABLE II

ALKYLATION OF *p*-CRESOL AND PHENOL BY α -PHENETHYL CHLORIDE IN BENZENE AT 50.0 ± 0.1°

Expt.	Phenol molarity ^a	Chloride mol-arity	Time, min.	Initial chloride	Optical rotations α^{25D} ^b Recovered chloride	Alkylated phenol
1	2.50 C	2.50	30	+55.55°	+42.06°	-0.84°
2	2.50 C	2.50	60	+55.55	+31.78	-.79
3	2.50 C	2.50	180	+55.55	+11.91	-.57
4	2.56 P	2.38	30	-47.7	-21.1	-.75
5	2.56 P	2.38	300	-47.7	-.25

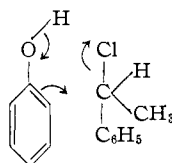
^a C = *p*-cresol, P = phenol. ^b All rotations are on homogeneous material, *l* 1 dm.

Extrapolating the data for *p*-cresol, we get *o*- α -phenethyl-*p*-cresol (-0.91°) from α -phenethyl chloride (+55.55°). From the experimental value of 109° for optically pure α -phenethyl chloride¹⁵ and the experimental value of 17.1° for optically pure *o*- α -phenethyl-*p*-cresol,¹ we calculate 10.4% retention of optical purity (and configuration). This is about ten times the activity obtained in the catalyzed alkylations of benzene.⁶⁻⁸ Experiments with phenol (experiments 4 and 5, Table II) indicate comparable retention of optical purity.¹⁶

(15) R. L. Burwell, Jr., A. D. Shields and H. Hart, *THIS JOURNAL*, **76**, 908 (1954).

(16) Although we do not have conclusive evidence, we believe that rotation in the products of experiments 4 and 5 is due mainly to the *ortho* isomer, and again indicate retention of configuration. The very

Mechanism.—The expected stereochemical result from the accepted ionic mechanism of the Friedel-Crafts reaction is extensive racemization due to planarity of the carbonium ion intermediate, with a slight predominance of inversion resulting from shielding.¹⁷ This is what was previously observed⁶⁻⁸ and what was found in the present instance for the alkylation of 2,6-xylenol. Alkylation of *p*-cresol or *p*-chlorophenol, on the other hand, gave retention of configuration and appreciably more retention of optical purity than is generally found in the ionization mechanism. We suggest that an important reaction path here involves a cyclic mechanism in which the *ortho* carbon of the phenol acts as a nucleophilic site. The hydroxyl group functions as the acid catalyst in removing the chlorine from the alkyl halide, and the whole



process is a concerted one, resulting in retention of configuration at the asymmetric carbon. The process is analogous to the S_Ni mechanism which has been used to explain retention of configuration in other reactions of α -phenethyl and similar groups.¹⁸ This concerted mechanism can only operate when alkylation occurs *ortho* to the hydroxyl group, and even then, the predominant mechanism is the ionic one, because the major stereochemical result is racemization. Reaction by the concerted path is appreciable, however, and constitutes evidence for a nucleophilic displacement mechanism in acidic aromatic alkylations. The stereochemical result is not that of inversion predicted by Brown's work, but that is only because the acid catalyst (hydroxyl group) and the aromatic component are a part of the same molecule. The displacement mechanism is presumably more important for primary than secondary halides but its stereochemical consequences cannot be tested in a primary halide without, say, resorting to deuterium to create the asymmetric center.

Experimental¹⁹

Alkylation of Phenol with α -Phenethyl Chloride.—In a 250-ml. round-bottomed flask equipped with a reflux condenser and a hydrogen chloride absorption trap, there was placed 94.0 g. (1.00 mole) of phenol and 70.2 g. (0.50 mole) of α -phenethyl chloride. Copious evolution of hydrogen chloride began immediately, and the temperature of the mixture rose spontaneously to 45°. The mixture was maintained at 60° for six hours, then subjected to vacuum dis-

small rotations for *para* alkylation (of 2,6-xylenol) suggest that the larger (0.75°) rotation here is due mainly to *ortho* alkylation. In one experiment, a portion of the *para* isomer crystallized out of the product mixture, and had little or no rotation compared with the residual oil, but this is only circumstantial evidence.

(17) C. C. Price, "Mechanisms of Reactions at Carbon-carbon Double Bonds," Interscience Publishers, Inc., New York, N. Y., 1946, p. 51.

(18) For a recent case, see H. Hart and H. S. Eleuterio, *This Journal*, **76**, 1379 (1954).

(19) All analyses are by Clark Microanalytical Laboratory, Urbana, Ill.

tillation, first with a water aspirator, and then with an oil pump. The material boiling up to 94° at 22 mm. solidified in the receiver, and was primarily recovered unreacted phenol (54.0 g.). The major product, boiling from 165–180° at 5–6 mm., weighed 62.5 g. (74.2% based on the phenol used) and was shown spectrophotometrically¹³ to contain about 55% *ortho* and 45% *para*- α -phenethylphenol. A third fraction, boiling at 235–240° at 6–7 mm., weighed 21.0 g. (16.4% based on phenol used). This was probably 2,4-di- α -phenethylphenol, but was not further characterized. A small amount (5.0 g.) of higher-boiling residue remained. In most subsequent experiments, the reaction was worked up by extracting the phenols from a benzene solution of the reaction mixture with aqueous or Claisen alkali, followed by acidification, extraction with benzene, drying and vacuum distillation.

A somewhat different procedure was followed with the optically active chloride (experiment 2, Table I). In a 100-ml. flask equipped with a stirrer, condenser and addition funnel there was placed 20 g. (0.21 mole) of phenol, which was heated to 55°, and 9.0 g. (0.064 mole) of α -phenethyl chloride (α^{25}_D -41.6°, homogeneous, *l* 1 dm.)^{16,20} was added dropwise over a period of 45 minutes. The mixture was stirred for an additional 30 minutes, and the product worked up as above. The alkylated phenols (11.0 g., 80.5%, b.p. 165–180° at 5–6 mm.) had a rotation α^{25}_D -0.35°, *l* 1 dm., homogeneous. The recovered, unreacted phenol (13.5 g.) was dissolved in 9.0 g. of benzene. The rotation of this solution in a 2-dm. tube was -0.02°. Most of the experiments listed in Table I were performed in this manner, or by simply mixing the reactants and warming on a steam-bath until hydrogen chloride evolution ceased.

Alkylation of *p*-Cresol in Benzene (Experiment 1, Table II).—In a 250-ml. glass-stoppered erlenmeyer flask there were placed 57 ml. each of 5 *M* α -phenethyl chloride (α^{25}_D +55.55°, *l* 1 dm., homogeneous), n^{25}_D 1.5250, and *p*-cresol in benzene. After 30 minutes in a bath at 50.0 ± 0.1°, the contents were cooled, diluted with 100 ml. of benzene, transferred to a separatory funnel with another 100 ml. of benzene, and extracted with Claisen solution. The alkali-insoluble product was dried over sodium sulfate and distilled, yielding 33.5 g. of recovered α -phenethyl chloride, α^{25}_D +42.06°, n^{25}_D 1.5248. The alkaline extract was acidified with hydrochloric acid, the phenols taken up in benzene, dried and distilled. There was recovered 25.2 g. of *p*-cresol and 4.8 g. of *o*- α -phenethyl-*p*-cresol, α^{25}_D -0.84°, whose infrared spectrum was identical with that of an authentic sample.²¹ The remaining experiments described in Table II were performed in a similar manner, and the infrared spectra of all products on which rotations were determined were identical with those of authentic specimens.

Alkylation of 2,6-Xylenol.—The procedure was similar to those described above. The product boiled at 143–145° at 1 mm. The stereochemical results are given in Table I. In experiment 6, recovered α -phenethyl chloride had a rotation α^{25}_D +1.05°, *l* 1 dm., homogeneous.

Anal. Calcd. for $C_{16}H_{18}O$: C, 84.8; H, 8.0. Found: C, 84.8; H, 8.4.

Alkylation of *p*-Chlorophenol.—Equimolar amounts of *p*-chlorophenol and α -phenethyl chloride gave, on warming for one hour on a steam-bath and working up in the usual manner, *o*- α -phenethyl-*p*-chlorophenol, b.p. 155° at 2 mm., in 75% yield.

Anal. Calcd. for $C_{14}H_{13}OCl$: C, 72.1; H, 5.62; Cl, 15.42. Found: C, 72.4; H, 5.56; Cl, 15.13.

***p*-Chlorophenyl α -Phenethyl Ether.**—*p*-Chlorophenol was alkylated according to the acetone-potassium carbonate procedure described previously.¹ From α -phenethyl chloride (α^{25}_D +32.1°) there was obtained a 60% yield of *p*-chlorophenyl α -phenethyl ether, m.p. 66.4–67.0° when recrystallized from petroleum ether; $[\alpha]^{25}_D$ +1.31°, *c* 32 in benzene. (There was also obtained a 4% yield of *o*- α -phenethyl-*p*-chlorophenol, α^{25}_D +2.60°, *l* 1 dm., homogeneous.)

Anal. Calcd. for $C_{14}H_{13}OCl$: C, 72.1; H, 5.62; Cl, 15.42. Found: C, 72.0; H, 5.65; Cl, 15.09.

(20) A. McKenzie and G. W. Clough, *J. Chem. Soc.*, **103**, 687 (1913).

(21) Ng. Ph. Buu-Hoi, H. LeBihan and F. Binon, *J. Org. Chem.*, **17**, 246 (1952).

Rearrangement of *p*-Chlorophenyl α -Phenethyl Ether.—This ether was rearranged according to a procedure described previously.¹ From 10 g. of ether prepared above, there was obtained 1.5 g. of *o*- α -phenethyl-*p*-chlorophenol, $\alpha^{25D} +0.80^\circ$.

Reduction of *o*- α -Phenethyl-*p*-chlorophenol.—*o*- α -Phenethyl-*p*-chlorophenol (10.0 g., $\alpha^{25D} -0.24^\circ$, 1 l dm., homogeneous) was reduced with nickel-aluminum alloy and aqueous

alkali, according to the procedure of Papa and Schwenk.²² The product was 6.9 g. (81%) of *o*- α -phenethylphenol, $\alpha^{25D} +0.064 \pm 0.005^\circ$, infrared spectrum identical with that of an authentic sample.

(22) D. Papa, E. Schwenk and B. Whitman, *ibid.*, **7**, 587 (1942).

EAST LANSING, MICHIGAN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TEXAS]

Phosphorus Acids in Organic Systems. I. Intermolecular Condensations Catalyzed by Polyphosphoric Acid

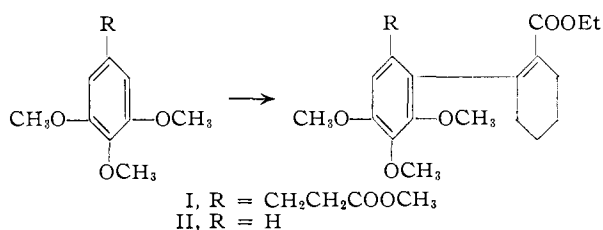
BY PETE D. GARDNER

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The reaction of anisole and trimethylpyrogallol with acetic acid, acetic anhydride, benzoic acid and β -carbomethoxypropionic acid is described. The product in all cases was the expected Friedel-Crafts adduct; but unlike the aluminum chloride catalyzed reaction, no ether cleavage was observed. Alkylation of anisole with 2-propanol and cyclohexanol and of phenol with cyclohexanol by means of this catalyst is also described.

The utility of polyphosphoric acid as a catalyst in the intramolecular acylation reaction with acids and anhydrides has been adequately demonstrated.¹⁻⁵ Further, the work of Horning and his associates⁶ has shown it to be extremely effective in the Bougault type of cyclization. With the exception of one rather unsatisfying example,⁷ nothing has been reported regarding the effectiveness of this Lewis acid in intermolecular acylations. This paper⁷ also describes the only reported successful alkylation reaction using the catalyst.

The need for generalization of the reaction to intermolecular systems arose in connection with a projected synthesis of I in which the ester group may be considered a non-reactive function at moderate temperatures in the catalyst as a medium.⁸ It should be recognized that this reaction would be the intermolecular equivalent of some of those effected by others.⁶



When either anisole or trimethylpyrogallol was treated with acetic anhydride (or acetic acid), benzoic acid or β -carbomethoxypropionic acid the corresponding ketone or keto ester was obtained in excellent yield (75-100%). With these condensations, as with others, the catalyst itself proved to be the only suitable solvent found. This method appears to offer a serious limitation to the scope of

the reaction by virtue of the insolubility of hydrocarbons in the system. Thus far, only phenols and phenyl esters and ethers appear to be useful as the aromatic component but the solvent might be expected to be equally useful with any substance possessing a center of electron density sufficiently high to serve as a solubilizing influence (subject, of course, to the usual activation restrictions characteristic of all aromatic electrophilic substitutions). Attempted condensations with benzene, toluene and cyclohexene failed completely and recovery of the hydrocarbon was above 90% in all cases. Solubility is not a problem in cyclization reactions because of the solubilizing effect of the carboxyl group.

The preparation of chloroacetomesitylene (16%) reported by Snyder and Roeske⁷ used a 2:1 catalyst to hydrocarbon ratio and a reaction time of 5 hr. at reflux temperature. It was found in the present study that, due to the enhanced reactivity of the aromatic components used, long reaction times and, more particularly, high temperatures were not required. The substituted benzoylpropionic esters required temperatures of only 30-45° and in this range, prolonged reaction times did not appear to be particularly detrimental. Temperatures of 40-50° were optimum for the acetophenones and 70-80° most satisfactory for the two benzophenones studied. Higher temperatures (80-100°) gave slightly lower yields of the acetophenones but drastically lower yields in the case of the esters. The ratio of catalyst to aromatic did not determine the yield in any case until it was reduced to 6:1.

In addition to the simplicity of the method and the high yields obtained, the absence of ether cleavage products makes the reaction the one of choice for this type of compound. The usual Friedel-Crafts technique utilizing an acid chloride in conjunction with aluminum chloride as a catalyst invariably results in total or partial ether cleavage when the acyl function enters *ortho* to a methoxyl group.⁹

To further generalize the catalyst, the alkylation of anisole and phenol with 2-propanol and cyclohexanol was studied. Although these proceeded nor-

(9) E. Berliner in "Organic Reactions," Vol. V, John Wiley and Sons, Inc., New York, N. Y., 1949, Table VII, p. 271.

- (1) A. Koebner and R. Robinson, *J. Chem. Soc.*, 1994 (1938).
- (2) W. E. Bachmann and W. J. Horton, *THIS JOURNAL*, **69**, 58 (1947).
- (3) H. R. Snyder and F. X. Werber, *ibid.*, **72**, 2965 (1950).
- (4) P. D. Gardner, W. J. Horton, G. Thompson and R. R. Twelves, *ibid.*, **74**, 5527 (1952).
- (5) P. D. Gardner and W. J. Horton, *ibid.*, **75**, 4976 (1953).
- (6) For leading references see J. Koo, *ibid.*, **75**, 2000 (1953).
- (7) H. R. Snyder and R. W. Roeske, *ibid.*, **74**, 5820 (1952).
- (8) Unpublished data obtained in this Laboratory.