

Anal. Calcd. for $C_{10}H_{11}NO_2$: N, 7.25. Found: N, 7.41, 7.27.

$\Delta^{607a, 1a, 12a}$. **Tetradecahydrochrysen-5,6,11,12-tetracarbox-diimide.**—One gram (0.01 mole) of maleimide was suspended in a solution of 1.0 g. (0.0053 mole) 1,1'-dicyclohexylacetylene and 15 cc. of xylene. A few crystals of hydroquinone were added and the mixture was refluxed for seven hours. On

cooling and filtering 1.0 g. of crude product was obtained. Recrystallization from aqueous methyl cellosolve gave 0.6 g. of colorless microcrystals melting at 357–358° with gas evolution (placed in bath at 350°).

Anal. Calcd. for $C_{22}H_{24}N_2O_4$: N, 7.36. Found: N, 7.25, 7.34.

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RECEIVED APRIL 23, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ROCHESTER]

The Action of Aluminum Bromide on Allyl Phenyl Ether

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Both allyl phenyl ether (I) and *o*-allylphenol have been found to be converted very rapidly by aluminum bromide in chlorobenzene solution to 51 and 50%, respectively, of 1-(*o*-hydroxyphenyl)-1-(*p*-chlorophenyl)-propane (II). This compound (II) in the presence of aluminum bromide is converted at a slower measurable rate to 65–75% of phenol and a corresponding amount of $ClC_6H_4CH(C_2H_5)_2$; in addition a side reaction occurs in which II is isomerized to 1-(*o*-hydroxyphenyl)-2-(*p*-chlorophenyl)-propane. The latter compound is not readily converted to phenol. The formation of II is thought to proceed by the intramolecular path, in which allyl phenyl ether is converted first to *o*-allylphenol; the latter is isomerized to the propenyl compound, which then adds chlorobenzene to form II.

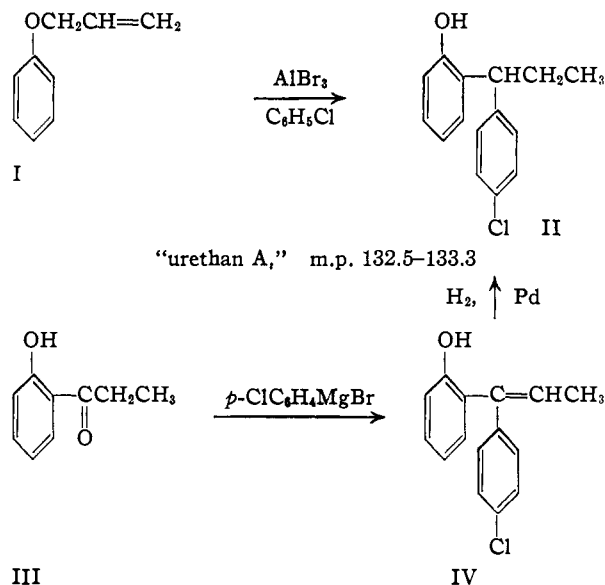
It was reported previously² that benzyl phenyl ether was converted by aluminum bromide in an extremely rapid intramolecular reaction to *o*-benzylphenol, with no evidence for the formation of *p*-benzylphenol.

Anisole has been found not to undergo this type of reaction; it forms no detectable amount of *o*-cresol, although it is demethylated, as would be expected.³ It appeared that, for the intramolecular rearrangement to occur, a group with greater tendency for carbonium ion formation than the methyl group was required. The present paper describes the behavior of allyl phenyl ether with aluminum bromide in chlorobenzene solution.

Treatment of the ether (I) with two moles of aluminum bromide in dilute solution in chlorobenzene, followed by immediate quenching with water, led to 51% of 1-(*p*-chlorophenyl)-1-(*o*-hydroxyphenyl)-propane (II); the remainder of the starting material was converted into a non-volatile neutral material (possibly a polymer of I) and an alkali-soluble polymer, possibly a polymer of 2-allylphenol. The structure of II was inferred from the fact that permanganate oxidation gave *p*-chlorobenzoic acid in 50% yield, and that the Liebermann nitroso reaction⁴ was positive, indicating a free position *para* to the phenolic hydroxyl group. The structure of II was proved by synthesis as indicated below; the synthetic product was compared to the reaction product through the crystalline phenylurethan m.p. 132.5–133.3° ("urethan A").

It is noteworthy that in contrast to benzyl phenyl ether,² there was no initial formation of phenol itself; in analogy to the previous case, however, there was no isolatable amount of the *para* isomer of II.

In the presence of aluminum bromide in chlorobenzene, *o*-benzylphenol was quantitatively con-



verted at a measurable rate to phenol.² Similarly, II was converted to phenol. However, the reaction appeared not to be quantitative and ceased after a production of 65–75% of phenol. The data are listed in Table I.

These results implied that in addition to the reaction causing the phenol formation, a simultaneous isomerization reaction must be taking place. This was proved by an isolation run in which synthetic II was treated with aluminum bromide in chlorobenzene for three hours at 25°. It was found that the major portion of II was converted to phenol and 24% was converted to a mixture of isomers of II. This mixture was shown to contain some 1-(*o*-hydroxyphenyl)-2-(*p*-chlorophenyl)-propane (V), which was characterized through its crystalline phenylurethan, m.p. 93.5–94° ("urethan B"). In addition, a small amount of a phenylurethan ("urethan C," m.p. 148–149°) was obtained, which was probably derived from a *para*-substituted phenol, such as $p\text{-HOC}_6\text{H}_4\text{CH}_2\text{CH}(\text{C}_6\text{H}_4\text{Cl})\text{CH}_3$.

The structure of V was established by synthesis from the readily available *o*-methoxyphenylacetic

(1) Abbott Laboratories Fellow, 1951–1952.

(2) D. S. Tarbell and J. C. Petropoulos, *THIS JOURNAL*, **74**, 244 (1952).

(3) P. Pfeiffer and E. Haack, *Ann.*, **460**, 156 (1928); P. Pfeiffer and W. Loewe, *J. prakt. Chem.*, **147**, 298 (1937); R. Adams and J. Mathieu, *THIS JOURNAL*, **70**, 2120 (1948).

(4) J. Houben, "Die Methoden der organischen Chemie," Georg Thieme, Leipzig, 1930, Vol. III, p. 30.

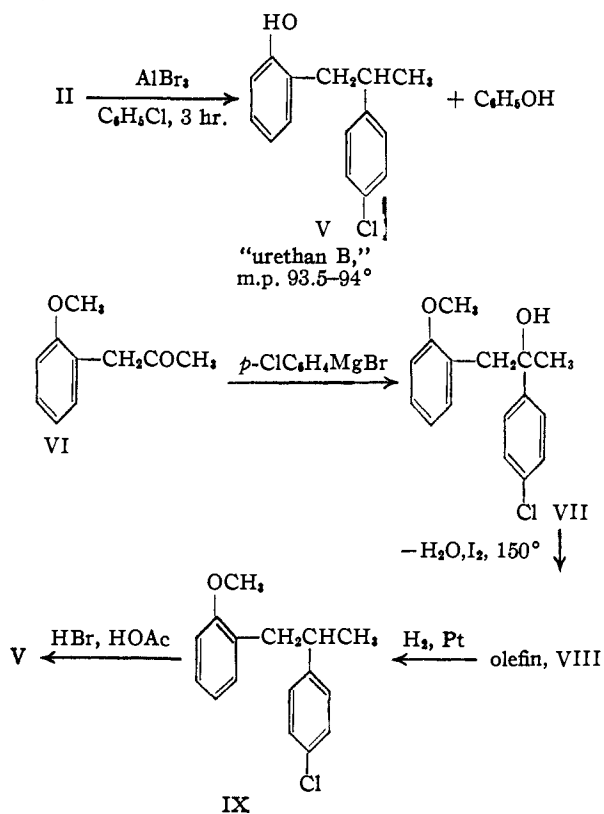
TABLE I

THE ACTION OF ALUMINUM BROMIDE ON 1-(*p*-CHLOROPHENYL)-1-(*o*-HYDROXYPHENYL)-PROPANE (II)

[II], ^a m./l.	[AlBr ₃], ^a m./l.	Time, ^b hours	Phenol, ^c %
0.0245 ^e	0.11	0.0017 ^d	2.7
		1.0 ^d	64.6
		3.25 ^d	64.1
.0265 ^e	.075	7	60
		24 ^f	80.5
.0261 ^e	.075	7	59.2
		23	73.6
.0246 ^h	.075	6.5	70.8
		12	83.7

^a Solvent chlorobenzene. ^b Temperature 0° unless specified. ^c Figures determined by the titration method previously described.³ ^d Reaction temperature 25°. ^e Allyl phenyl ether, which has been shown to be rapidly converted to II by the action of aluminum bromide in chlorobenzene solvent. ^f With an additional 24 hours at 25°. ^g II isolated from the initial rapid rearrangement of allyl phenyl ether. ^h Synthetic II.

acid,⁵ which was converted to *o*-methoxyphenylacetone (VI) by the excellent general method of Hauser⁶; VI was converted to V by the steps indicated, and the identity was proved through the phenylurethan.



The fact that V is more stable to aluminum bromide than II was shown by the observation that after exposure to aluminum bromide under the same conditions as above for three hours, 82% of V was recovered unchanged. These relative stabilities of II and V are those which would be predicted for the

(5) J. Levine, T. E. Eble and H. Fischback, *THIS JOURNAL*, **70**, 1980 (1948).

(6) H. G. Walker and C. R. Hauser, *ibid.*, **68**, 1886 (1946); G. A. Reynolds and C. R. Hauser, *Org. Syntheses*, **30**, 70 (1950).

carbonium ions $\oplus\text{CH}(\text{C}_6\text{H}_4\text{Cl})\text{CH}_2\text{CH}_3$ and $\oplus\text{CH}_2\text{CH}(\text{C}_6\text{H}_4\text{Cl})\text{CH}_3$.

The neutral product obtained from allyl phenyl ether and aluminum bromide after three hours in chlorobenzene was found to be $\text{ClC}_6\text{H}_4\text{CH}(\text{C}_2\text{H}_5)\text{C}_6\text{H}_4\text{Cl}$ (X), which was oxidized by chromic acid to the same eutectic mixture of 3,3'- and 3,4'-dichlorobenzophenones, which had been obtained from oxidation of the mixed dichlorodiphenylmethanes in the previous work.² The products extracted by aqueous alkali included 33% of phenol, and 8% of a higher molecular weight phenol, probably a dimer of *o*-allylphenol.

The material (VA, 17%) extracted by Claisen alkali, on additional treatment with aluminum bromide in chlorobenzene for 24 hours at 0° gave only 3.8% of phenol, implying that this phenolic material (VA) contained the $-\text{CH}_2\text{CH}(\text{C}_6\text{H}_4\text{Cl})\text{CH}_3$ type side chain. It is noteworthy, however, that in the presence of aluminum bromide at 60° for 24 hours, VA did yield phenol in 84% yield.

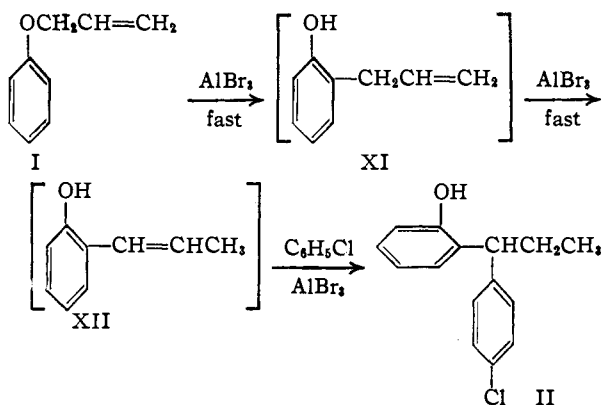
Treatment of VA with phenyl isocyanate gave a mixture of urethans from which was isolated some of "urethan C," m.p. 148-149°, and two new urethans, "D," m.p. 72-73° and "E," m.p. 128-129°. These urethans have not been characterized; however, their analyses are compatible with the empirical formula for "urethan B." In view of this and the data presented above, it is reasonable to assume that they are isomeric with "urethan B."

The $-\text{CH}(\text{C}_6\text{H}_4\text{Cl})\text{CH}_2\text{CH}_3$ side-chain of II is thus seen to be transferred in part to the solvent by aluminum bromide, just as the benzyl group in *o*-benzylphenol is, and it is in part isomerized to $-\text{CH}_2\text{CH}(\text{C}_6\text{H}_4\text{Cl})\text{CH}_3$, forming V, and perhaps also other isomers of V.

Runs on the rate of phenol formation from II gave a falling first-order "constant," but the rate was similar to that which was observed starting with allyl phenyl ether itself; the "constants" in this case fell more rapidly than when pure II was the starting material, probably due to the complicating effect of the side-products. The rate of formation of phenol from II with aluminum bromide was greater than that from *o*-benzylphenol²; this would be expected, because the group $-\text{CH}(\text{C}_6\text{H}_4\text{Cl})\text{CH}_2\text{CH}_3$ can form a secondary carbonium ion, whereas $-\text{CH}_2\text{C}_6\text{H}_5$ can form only a primary carbonium ion.

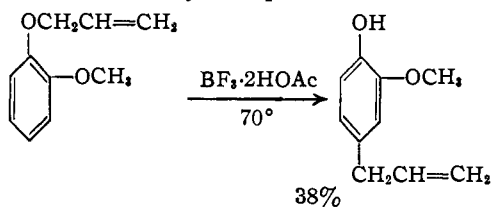
The path by which II is formed from I is probably the following: I is converted to *o*-allylphenol by the intramolecular path, and the latter is isomerized to the propenyl compound, or its carbonium ion equivalent, which then adds solvent to form II. Supporting evidence for the above scheme was obtained by the isolation of 50% of II from the reaction of *o*-allylphenol and aluminum bromide in chlorobenzene solution.

The isomerization of the *o*-allylphenol (XI) to the propenyl isomer XII must be more rapid than the addition of chlorobenzene to the allyl compound XI, because the latter process would lead to compound V; as shown above, V is stable under these conditions. Since V is not isolated among the initial products, it must not be formed in the initial rapid reaction.



Another scheme which has not been ruled out is the conversion of I to the propenyl ether C₆H₅-OCH=CHCH₃, which might then be isomerized to XI or XII, or which might add chlorobenzene and then isomerize.

The only other case involving acid rearrangement of allyl aryl ethers of which we are aware is illustrated below⁷; in this case the allyl group goes mainly to the para position, along with formation of guaiacol and diallylated products.



Experimental⁸

Preparation of Materials.—Chlorobenzene and aluminum bromide were purified as described previously.² Allyl phenyl ether was prepared from allyl bromide and phenol by the usual method.⁹

Cleavage of Anisole with Aluminum Bromide in Chlorobenzene Solvent.—Phenol and no *o*-cresol was found to result from a slow cleavage of anisole (0.0302 mole) with aluminum bromide (0.11 mole) in chlorobenzene solvent. A reaction time of 18 hours at 26° produced only 11% of phenol while 23 hours at 26° followed by 18 hours at 60° produced 92% phenol. The procedure used for this run has been previously described.² Phenol was identified as the crystalline tribromophenol.

1-(*p*-Chlorophenyl)-1-(*o*-hydroxyphenyl)-propene (IV).—*o*-Hydroxypropiophenone (III) was prepared by the method of Miller and Hartung¹⁰ with the following modifications: the reaction was heated to 180–190° for two hours, and after hydrolysis, the mixture was steam distilled. The oily *o*-isomer (190 g.) was separated from the distillate, and the latter was extracted with ether, which yielded 16 g. of additional product. Distillation of the combined oil gave 195 g. (52%) of the *o*-isomer, b.p. 95–109° (15 mm.).

To the Grignard reagent prepared from 138 g. of *p*-chlorobromobenzene, 16.6 g. of magnesium and 300 cc. of dry ether in a nitrogen atmosphere, was added over a period of an hour a solution of 45.8 g. of *o*-hydroxypropiophenone in 200 cc. of ether; the reaction mixture was allowed to reflux for three hours. The magnesium complex was hydrolyzed with saturated ammonium chloride, the solution was extracted with ether, the ether solution was dried and the solvent was removed. Distillation of the residual viscous oil yielded 40 g. (55%) of the olefin IV, with the following properties: b.p. 165–168° (3 mm.); *n*²⁰_D

1.6182. The compound absorbed bromine from a carbon tetrachloride solution rapidly, with no evolution of hydrogen bromide; *o*-benzylphenol, used as a control, did not absorb bromine under these conditions.

The phenylurethan was prepared, using pyridine as a catalyst, and melted, after crystallization from heptane, at 145°.

Anal. Calcd. for C₂₂H₁₉ClNO₂: C, 72.62; H, 4.99. Found: C, 72.55; H, 5.06.

1-(*p*-Chlorophenyl)-1-(*o*-hydroxyphenyl)-propane (II).—The above olefin (IV, 5.05 g.) was reduced in 40 cc. of methanol at room temperature and atmospheric pressure with hydrogen and palladium; 19 hours were required for the quantitative absorption of the hydrogen. The product (4.0 g., 80%) after removal of the catalyst and solvent, was obtained by distillation as a light yellow oil, b.p. 154–155° (0.8 mm.), *n*²⁰_D 1.5903. The analysis is given below.

The phenylurethan ("urethan A") melted at 132.5–133.3° and gave no depression with the sample prepared below from the rearrangement product. The analysis is given below.

***o*-Methoxyphenylacetone (VI).**—*o*-Methoxyphenylacetic acid⁵ (35 g.) and 75 cc. of thionyl chloride were refluxed until no more hydrogen chloride was evolved. The excess thionyl chloride was removed with a water-pump and the residue was distilled to yield 24.1 g. (69%) of *o*-methoxyphenylacetyl chloride, as a yellow oil, b.p. 132–133° (15 mm.).

This acid chloride was converted to *o*-methoxyphenylacetone (VI), according to the procedure of Hauser⁶ for making *o*-nitroacetophenone. The yield was 60% of material boiling at 128–130° (16 mm.), *n*²⁰_D 1.5225.

The semicarbazone melted, after crystallization from benzene-heptane at 146–147° (taken in a sealed tube).

Anal. Calcd. for C₁₁H₁₃N₂O₂: C, 59.71; H, 6.83. Found: C, 60.05; H, 6.95.

A mixture of 3.5 g. of the pure semicarbazone and 4.1 g. of phthalic anhydride in 30 cc. of water was heated to reflux, and the regenerated ketone was removed by steam distillation. The distillate was extracted with ether and the combined extracts were washed with a solution of sodium bicarbonate followed by water. The ether solution was dried, the solvent was removed with subsequent vacuum distillation of the oily residue to give 1.67 g. (64%) of pure *o*-methoxyphenylacetone (VI), *n*²⁰_D 1.5222.

Anal. Calcd. for C₁₀H₁₂O₂: C, 73.14; H, 7.37. Found: C, 73.02; H, 7.48.

1-(*o*-Methoxyphenyl)-2-(*p*-chlorophenyl)-propanol-2 (VII).—To a solution of *p*-chlorophenylmagnesium bromide prepared from 6.9 g. of *p*-chlorobromobenzene and 0.83 g. of magnesium in 40 cc. of dry ether was added slowly a solution of 5.0 g. of *o*-methoxyphenylacetone in 30 cc. of dry ether. After stirring for two hours, the reaction was decomposed with saturated ammonium chloride solution, and the aqueous layer was extracted with ether. Evaporation of the combined dried ether extracts gave 7.1 g. (84.5%) of a yellow solid, which was purified by recrystallization from heptane to give white crystals, m.p. 68–69°.

Anal. Calcd. for C₁₈H₁₇ClO₂: C, 69.43; H, 6.19. Found: C, 69.50; H, 6.17.

1-(*o*-Methoxyphenyl)-2-(*p*-chlorophenyl)-propane (IX).—The carbinol VII (6.0 g.) was heated with a few crystals of iodine for 15 minutes in an oil-bath at 150–160°. After cooling, ether was added, and the resulting solution was washed with sodium bisulfite solution to remove the iodine. The ether solution was dried and evaporated to dryness; the residual oil was distilled in a cold finger distilling apparatus to give 5.27 g. (95%) of a light colored oil, b.p. 165–170° (bath temperature) (0.5 mm.), *n*²⁰_D 1.6295.

The above olefin (5.27 g.) was reduced with hydrogen and platinum oxide catalyst (0.1 g.) in 40 cc. of ethyl acetate. After six hours, the theoretical amount of hydrogen had been absorbed and the reaction was stopped. Some of the chlorine must have been removed by reduction since the ethyl acetate solution was acidic to moist litmus paper. The catalyst and solvent were removed by filtration and evaporation leaving an oil, which was distilled once in a cold finger distilling apparatus to give 4.45 g. (84%) of a colorless oil, b.p. 165–170° (bath temperature) (0.5 mm.). The oil was fractionally distilled five times for analysis, b.p. 142° (0.8 mm.), *n*²⁰_D 1.5663.

(7) L. Ya. Bryusova and M. L. Ioffe, *J. Gen. Chem.*, (USSR), 11, 722 (1941); *C. A.*, 36, 430 (1942).

(8) Melting points corrected; analyses by Miss Claire King.

(9) D. S. Tarbell, "Organic Reactions," Vol. II, p. 26.

(10) "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., p. 543.

Anal. Calcd. for $C_{16}H_{17}ClO$: C, 73.69; H, 6.52. Found: C, 73.87; H, 6.62.

1-(*o*-Hydroxyphenyl)-2-(*p*-chlorophenyl)-propane (V).—The above methoxy compound IX (1.67 g.) was refluxed with a mixture of 15 cc. of glacial acetic acid and 5 cc. of 48% hydrobromic acid for ten hours. The resulting red homogeneous solution was added to cold water and the aqueous mixture was extracted several times with benzene. The combined benzene extracts were washed with Claisen alkali to remove the acidic material. Recovery of the substituted phenol was accomplished by acidification followed by ether extraction of the combined Claisen alkali washings. Evaporation of the ether from the dried solution yielded an oil which, when distilled in a cold finger distilling apparatus, gave 0.96 g. of a light yellow colored viscous oil (V) b.p. 165–170° (bath temperature) (0.5 mm.), n_D^{25} 1.5783.

Anal. Calcd. for $C_{16}H_{16}ClO$: C, 73.02; H, 6.13. Found: C, 73.55; H, 6.23.

A phenylurethan derivative was prepared employing dry pyridine as a catalyst. Recrystallization of the solid material from the hexane gave needles melting at 93.5–94° ("urethan B").

Anal. Calcd. for $C_{22}H_{20}ClNO_2$: C, 72.22; H, 5.51. Found: C, 72.59; H, 5.83.

The phenylurethan melts with slow heating at 93.5–94°; it melts immediately however, if placed on the hot stage at approximately 80°.

The Reaction between Allyl Phenyl Ether and Aluminum Bromide in Chlorobenzene. A. The Initial Products.—To a solution of allyl phenyl ether (13.4 g.) in chlorobenzene (500 cc.) was added a solution of 59.4 g. of aluminum bromide in 500 cc. of chlorobenzene. Immediately after mixing the two solutions, 300 cc. of water was added to quench the reaction. Heptane (1 l.) was added to facilitate the removal of the water layer and the organic layer was extracted twice with 400-cc. portions of 20% aqueous sodium hydroxide, followed by three extractions with 200-cc. portions of Claisen alkali. The solution was dried, and the chlorobenzene and heptane were removed by distillation using a fractionating column. A residue was obtained which could not be distilled, but decomposed when heated *in vacuo*. This alkali-insoluble residue is thought to be a dimer or trimer of allyl phenyl ether.

The aqueous alkaline layer was extracted four times with 200-cc. portions of ether and the combined ether extracts were dried. Removal of the ether gave 2.17 g. of a light brown viscous oil which could not be converted into a phenylurethan derivative. This residue probably consisted mainly of polymers of 2-allylphenol. Acidification of the aqueous alkaline solution followed by extraction with ether and removal of the ether yielded 0.60 g. of a dark resinous oil which was not identified.

The combined Claisen alkali extracts were acidified with hydrochloric acid, extracted three times with 200-cc. portions of ether and dried. Removal of the ether gave a light brown oil which, when distilled, gave 10.65 g. (51%) of II as a light yellow oil, b.p. 135–142° (0.3 mm.), n_D^{25} 1.5865. Elementary analysis showed chlorine to be present.

Anal. Calcd. for $C_{16}H_{15}ClO$: C, 73.02; H, 6.13. Found: C, 73.39; H, 6.23.

The phenylurethan of this material was prepared with pyridine catalyst and was recrystallized from heptane to give small needles, m.p. 132–133°.

Anal. Calcd. for $C_{22}H_{20}ClNO_2$: C, 72.22; H, 5.51. Found: C, 72.51; H, 5.71.

The phenylurethan was shown by a mixed m.p. to be identical with the phenylurethan of synthetic 1-(*o*-hydroxyphenyl)-1-(*p*-chlorophenyl)-propane (II) described above. For the oxidation experiment, II (1 g.) was dissolved in 40 cc. of 10% aqueous sodium hydroxide and 60 cc. of water. Powdered potassium permanganate (10 g.) was added slowly and the solution was allowed to react for 30 minutes. The solution was acidified with hydrochloric acid and the manganese dioxide, which formed from the oxidation, was removed by reduction with sodium bisulfite. Extraction with ether with subsequent removal of the ether yielded a yellow solid, which was sublimed at 0.3 mm. to give 0.3 g. (51%) of *p*-chlorobenzoic acid, identified by a mixed m.p. with an authentic sample.

Liebermann's reaction⁴ demonstrated that II was a

phenol with an unsubstituted para position; *o*-benzylphenol and *p*-benzylphenol were used as controls.

B. The Final Products.—The quantities of reactants and procedure were those described above, except that the reaction was allowed to proceed for three hours at room temperature, and then was hydrolyzed with 300 cc. of water. Pentane (700 cc.) was added to facilitate the separation of layers. After three extractions with 200-cc. portions of Claisen alkali, the chlorobenzene-pentane layer was dried and evaporated to dryness. The neutral viscous oil which remained was distilled at reduced pressure to give 11.81 g. (44.6%) of product, b.p. 180–185° (12 mm.), n_D^{25} 1.5773.

Anal. Calcd. for $C_{16}H_{14}Cl_2$: C, 67.94; H, 5.32. Found: C, 68.29; H, 5.29.

This oil was shown to be a mixture of 1-(*m*-chlorophenyl)-1-(*p*-chlorophenyl)-propane and 1,1-bis-(*m*-chlorophenyl)-propane by oxidation. The oil (0.5 g.) was dissolved in a mixture of 15 cc. of glacial acetic acid and 2 cc. of concd. sulfuric acid.¹¹ Chromic acid (1.0 g.) was added slowly and the reaction was allowed to continue for 12 hours at room temperature, and it was then added to a beaker of cold water containing ferrous sulfate. After the aqueous mixture remained in a refrigerator for a week, a solid precipitated, which, after crystallization from methanol, melted at 90.5–92°; it showed no depression on mixed m.p. with the eutectic mixture of 3,3'- and 3,4'-dichlorobenzophenone previously described.² In addition the infrared absorption curves of both samples were identical.

The combined Claisen alkali extracts were acidified and extracted three times with ether; removal of solvent and distillation of the residual oil yielded the following fractions: (1) 3.14 g. (33%), b.p. 179–181° (760 mm.) (identified as phenol); (2) 4.2 g. (17%) (VA), b.p. 148–150° (0.5 mm.), n_D^{25} 1.5857; (3) 2.0 g. (7.5%), b.p. 185–215° (0.5 mm.) (probably a dimer of *o*-allylphenol).

Treatment of fraction 2(VA) with phenyl isocyanate and a drop of dry pyridine, gave a crude oily urethan, which was dissolved in hexane. After several days had elapsed, small clusters of needles appeared, which, after several crystallizations from hexane, melted at 128–129° ("urethan E"). Mixed m.p. with "urethan A" (m.p. 132.5–133.3°) gave a depression.

Anal. Calcd. for $C_{22}H_{20}ClNO_2$: C, 72.22; H, 5.51. Found: C, 72.45; H, 5.55.

Concentration of the original mother liquor produced a second solid ("urethan D") whose m.p. remained constant at 72–73°, after several crystallizations from pentane.

Anal. Calcd. for $C_{22}H_{20}ClNO_2$: C, 72.22; H, 5.51. Found: C, 72.49; H, 5.74.

Another run, in which the crude urethans were chromatographed on a "Florisil" column using benzene as the eluate, led to the isolation of a small quantity of "urethan C," m.p. 148–149°.

Anal. Calcd. for $C_{22}H_{20}ClNO_2$: C, 72.22; H, 5.51. Found: C, 72.36; H, 5.64.

Urethans "C," "D" and "E" were not characterized.

Isomerization of 1-(*o*-Hydroxyphenyl)-1-(*p*-chlorophenyl)-propane (II).—To the above synthetic phenolic material (4.1 g.) dissolved in 83 cc. of chlorobenzene, was added a solution of 9.75 g. of aluminum bromide dissolved in 83 cc. of chlorobenzene. The resulting solution is approximately 0.1 mole in phenolic material concentration and about 0.22 mole in aluminum bromide concentration. After a three-hour reaction time at room temperature, water (30 cc.) was added to hydrolyze the reaction. Pentane (200 cc.) was added and the organic solution was extracted three times with 20-cc. portions of 20% sodium hydroxide solution to remove phenol which is the major product. The pentane-chlorobenzene layer was extracted three times with 20-cc. portions of Claisen alkali to remove the remaining substituted phenol. The combined Claisen alkali extracts were acidified and extracted with ether. Evaporation of the ether from the dried solution left an oily residue which, when distilled in a cold finger distilling apparatus, gave 1.0 g. (24%) of a light yellow oil, b.p. 165–170° (0.5 mm.) (bath temperature), n_D^{25} 1.5875.

The above oil was converted into a phenylurethan derivative with dry pyridine as a catalyst. One recrystallization from hexane gave a solid which melted at 78–80°.

(11) R. Slack and W. A. Waters, *J. Chem. Soc.*, 1666 (1948).

The mother liquor, on remaining overnight, gave a small quantity of needles which, after two crystallizations from hexane, melted at 148°. This was shown by a mixed m.p. to be identical with "urethan C" above.

Seven crystallizations from hexane of the first solid isolated (78–80°) raised its m.p. to 91°; a mixed m.p. with the phenylurethan derivative of 1-(*o*-hydroxyphenyl)-2-(*p*-chlorophenyl)-propane (V) (m.p. 91.5–92°, "urethan B") gave no depression.

The treatment of 1-(*o*-hydroxyphenyl)-2-(*p*-chlorophenyl)-propane (V) (680 mg.) with aluminum bromide and chlorobenzene employing the same mole ratios and isolation procedure as given above, resulted in the recovery of 560 mg. (82%) of starting material, identified as the phenylurethan.

The Initial Reaction between *o*-Allylphenol and Aluminum Bromide in Chlorobenzene.—To a solution of 13.4 g.

of *o*-allylphenol in 500 cc. of chlorobenzene was added a solution of 59.4 g. of aluminum bromide in 500 cc. of chlorobenzene. Immediately after mixing the two solutions, 300 cc. of water was added to quench the reaction. Hexane (300 cc.) was added to facilitate the removal of the water layer and the organic layer was extracted three times with 100-cc. portions of 20% aqueous sodium hydroxide followed by three extractions with 100-cc. portions of Claisen alkali.

The combined Claisen alkali extracts were acidified with hydrochloric acid, extracted three times with 200-cc. portions of ether and dried. Removal of the ether gave a viscous red oil which, when distilled, gave 10.5 g. (50%) of II as a light yellow oil, b.p. 180–185° (2 mm.), n_D^{20} 1.5869.

The phenylurethan of this material was identical in all respects with "urethan A."

ROCHESTER, NEW YORK RECEIVED SEPTEMBER 2, 1951

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

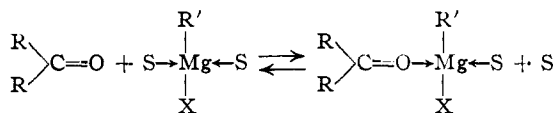
Solvent Effects in the Grignard Reaction¹

BY RICHARD N. LEWIS² AND JAMES R. WRIGHT

The effect of the basicity of the solvent on the course of the Grignard reaction has been investigated. A strongly basic solvent (pyridine) retards the reaction between a Grignard reagent and a ketone, while a weakly basic solvent (anisole, phenetole) permits a rapid reaction. A solvent of intermediate basicity (tetrahydrofuran) results in abnormal products. It appears that a basic solvent retards the formation of the ketone-Grignard coordination compound which is an intermediate in both normal and abnormal reactions. It also retards the second step in the normal reaction. Both steps require the displacement of a solvent molecule from the Grignard reagent. Reactions studied include one in which steric hindrance is small (benzophenone-ethylmagnesium bromide) and four in which it is large. Yields of normal products were uniformly higher in anisole than in ether.

The effect of solvents in the Grignard reaction should be discussed in the light of the mechanism of the reaction. When a Grignard reagent reacts with a ketone the first step appears to be the formation of a coordination compound, in which one of the coordination points of the magnesium is taken up by the carbonyl oxygen. Pfeiffer and Blank³ have actually isolated such compounds as solids or oily liquids which separated from ether solution; treatment with water regenerated the ketone.

It is unlikely for steric reasons that the magnesium atom in these compounds could coordinate more than two molecules of solvent or ketone. Thus, when a Grignard reagent coordinates with a ketone, there must be a simultaneous displacement of a solvent molecule, possibly in a manner similar to nucleophilic displacement on a carbon atom. The extent of ketone coordination at equilibrium will depend on the relative nucleophilic character of ketone and solvent. This step may be represented by the following equation, where S is a solvent molecule.⁴

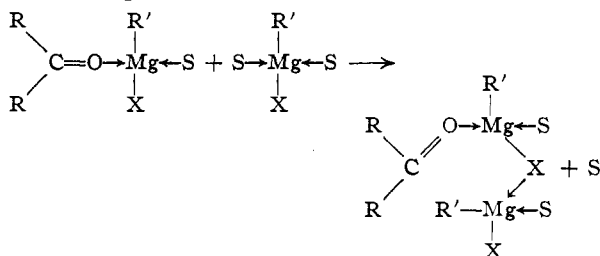


The coordinating power of a solvent for a light atom like magnesium is, in general, a function of the base strength of the solvent. In comparison with ether, a strongly basic solvent, which forms a

strong bond with the metal, should retard the Grignard reaction by retarding the formation of the ketone-complex. A feebly basic solvent, on the other hand, should facilitate the reaction.

The second step in the reaction appears not to take place through an internal rearrangement of the addition compound but through the approach of a second molecule of Grignard reagent. Thus, Pfeiffer and Blank obtained no tertiary alcohol from benzophenone and ethylmagnesium bromide in the absence of excess Grignard reagent. An interesting cyclic intermediate involving two molecules of the Grignard reagent has been proposed by Swain and Boyles,⁵ on the basis of the favorable effect of magnesium bromide in the reaction of propylmagnesium bromide with diisopropyl ketone. Magnesium bromide, because of its stronger coordinating power, displaces the Grignard reagent in the first addition compound, and is more effective than the Grignard reagent in polarizing the carbon-oxygen double bond.

The formation of such a cyclic intermediate again requires the displacement of a solvent molecule, and is therefore affected by the basicity of the solvent in the same way as the first step. The second step can be formulated as



(1) From the Ph.D. thesis of James R. Wright, June, 1951. Presented at the Southwest Regional Meeting, A.C.S., Austin, Texas, October, 1951.

(2) Olin Industries, New Haven, Conn.

(3) P. Pfeiffer and H. Blank, *J. prakt. Chem.*, **163**, 242 (1939).

(4) J. R. Johnson in "Organic Chemistry," 2nd ed., edited by H. Gilman, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 1880.

(5) C. G. Swain and H. B. Boyles, *THIS JOURNAL*, **73**, 870 (1951).