

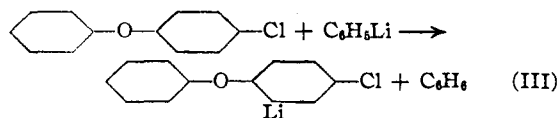
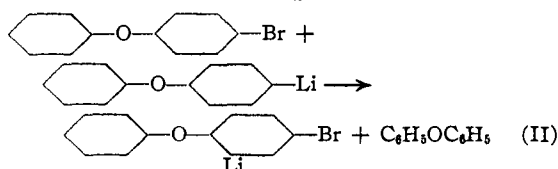
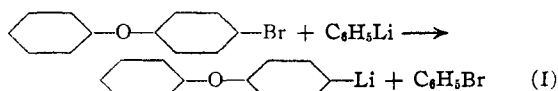
[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF OKLAHOMA PANHANDLE A. AND M. COLLEGE, KANSAS UNIVERSITY AND IOWA STATE COLLEGE]

Metalation and Halogen-Metal Interconversion Reactions of Some Halogenated Phenyl Ethers

BY WRIGHT LANGHAM, R. Q. BREWSTER AND HENRY GILMAN

The extensive application of the halogen-metal interconversion reaction to aryl halides and the two-stage metalation of a number of halogenated aryl ethers [reactions (I) and (II)] have suggested a study of the effect of orientation, the kind of halogen and the nature of the RLi compound on the reactions of some halogenated phenyl ethers.

Orientation.—The first illustrations of the halogen-metal interconversion reaction with bromoaryl ethers^{1a,b,c} involved bromine *ortho* to the ether linkage [reaction (IV)]. In subsequent studies,^{1d,e} however, it was found that it is not necessary to have bromine in the *ortho* position. It has been shown also that the metal enters the position *ortho* to the ether linkage in *hydrogen*-metal interconversion reactions of aryl ethers,^{1f} and invariably a nucleus having a negative substituent has been found to be metalated in preference to a nucleus without a substituent^{1c,g} [reaction (III)].



Under mild conditions we have found interconversion to be the primary reaction of iodo- and bromophenyl phenyl ethers with *n*-butyllithium and phenyllithium when the halogen is not only *ortho*, but also *meta* and *para* to the ether linkage. Under more drastic conditions, however, the *p*-halogenophenyl phenyl ethers

undergo appreciable metalation with methyl-lithium, *n*-butyllithium and phenyllithium. In all cases the metal enters the position *ortho* to the ether linkage in the halogenated nucleus. No conclusive evidence of metalation of *o*- and *m*-halogenophenyl phenyl ethers has been obtained.

The Kind of Halogen.—The nature of the halogen attached to the aromatic nucleus has a pronounced effect on both halogen-metal interconversion and metalation. Iodides have been shown to undergo exchange more readily than bromides and only two examples of a chlorine-lithium interconversion have been reported.^{2a,b} The effect of the kind of halogen on metalation is demonstrated by the *p*-halogenoanisoles. *p*-Chloroanisole^{2a} and *n*-butyllithium undergo a direct hydrogen-metal interconversion to give 2-methoxy-5-chlorophenyllithium with no indications of a two-stage process, such as occurs with *p*-iodo- and *p*-bromoanisoles.^{2c}

We have observed that *o*- and *p*-iodophenyl phenyl ethers and *n*-butyllithium and phenyllithium give larger yields of interconversion products than do the corresponding bromo compounds, while the chloro compounds give no indications of interconversion. Under more drastic conditions *p*-bromophenyl phenyl ether reacts with phenyllithium and *n*-butyllithium to give 2-phenoxy-5-bromophenyllithium and phenyl ether [reactions (I) and (II)]. We have found no conclusive evidence, however, that metalations of *p*-chlorophenyl phenyl ether proceed by such a two-stage process. From one reaction of *p*-chlorophenyl phenyl ether with phenyllithium a 17% yield of benzene was isolated [reaction (III)]. With *n*-butyllithium, *p*-chlorophenyl phenyl ether gave no indications of halogen-metal interconversion and at the end of a fifteen-minute reaction period at room temperature, there was obtained a 16% yield of crude 2-phenoxy-5-chlorobenzoic acid subsequent to carbonation.

It was reported in earlier studies^{2a,3} that inter-

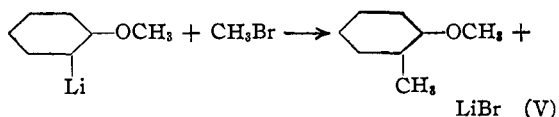
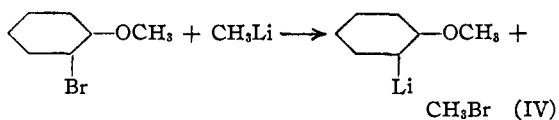
(1) (a) Gilman and Jacoby, *J. Org. Chem.*, **3**, 108 (1938); (b) Wittig, Pockels and Dröge, *Ber.*, **71**, 1903 (1938); (c) Gilman, Langham and Jacoby, *This Journal*, **61**, 106 (1939); (d) Gilman, Willis and Swislowsky, *ibid.*, **61**, 1371 (1939); (e) Gilman, Swislowsky and Brown, *ibid.*, **62**, 348 (1940); (f) Gilman and Young, *ibid.*, **56**, 1415 (1934); **57**, 1121 (1935); Gilman and Bebb, *ibid.*, **61**, 109 (1939); (g) Gilman, Cheney and Willis, *ibid.*, **61**, 981 (1939).

(2) (a) Gilman, Langham and Moore, *ibid.*, **62**, 2327 (1940); (b) see Footnote 1c of Ref. 2a for studies by Messrs. Melstrom and Haubein; (c) Gilman, Langham and Willis, *ibid.*, **62**, 346 (1940).

(3) Gilman and Moore, *ibid.*, **62**, 1843 (1940).

conversion seems to precede coupling reactions between alkyl lithium compounds and aryl halides. The results reported in this paper indicate that the rate of such coupling reactions may be influenced by the kind of halogen, its orientation and the kind of RLi compound.

At the end of a fourteen-hour reaction period, methyl lithium and *o*-bromo- and *o*- and *p*-iodoanisoles gave good yields of methyl tolyl ethers along with definite indications of halogen-metal exchange; presumably the methyl tolyl ethers were formed subsequent to the interconversion.



Under the same conditions methyl lithium and *p*-chloroanisole gave no indications of halogen-metal exchange and no conclusive evidence of secondary coupling products. It is doubtful, however, that interconversion is necessarily a prelude to coupling reactions between aryl fluorides and chlorides and alkyl lithium compounds.⁴ Under conditions which produced metalation of *p*-chlorophenyl phenyl ether, *o*-chlorophenyl phenyl ether and *n*-butyllithium underwent a vigorous reaction and gave only a trace of acidic gum. Hydrolysis and titration of an aliquot of the reaction mixture showed that almost all of the organometallic compounds had been used up, presumably in coupling reactions. Under similar conditions *o*-iodo- and *o*-bromophenyl phenyl ethers gave interconversion with *n*-butyllithium.

The Kind of Organolithium Compound.—That the nature of the RLi compound can be highly significant in the metalation of aryl ethers has been pointed out previously.^{1f,2a} Its effect on halogen-metal interconversion has also been amply demonstrated with α -bromonaphthalene.³

With the *p*-halogenophenyl phenyl ethers, we find phenyllithium gives slightly larger yields of metalation products than does *n*-butyllithium; this may be a result of higher rates of secondary coupling reactions in the latter case or a greater tendency for phenyllithium to produce metalation directly instead of by a two-stage mechanism.

(4) Wittig, *Angew. Chem.*, **53**, 241 (1940).

With methyl lithium, *p*-chloro- and *p*-bromophenyl phenyl ethers and *p*-fluoro-, *p*-chloro- and *p*-bromoanisoles give metalation to the extent of 14–20%. The absence of any indications of halogen-metal interconversion favors a direct mechanism for these metalations. Under milder conditions, *p*-bromophenyl phenyl ether and *n*-propyllithium gave more interconversion than did *n*-butyllithium, which in turn gave a higher per cent. of interconversion than did phenyllithium. No halogen-metal exchange was observed, under customary conditions, between *p*-halogenophenyl phenyl ethers and methyl lithium. Under forced conditions, however, methyl lithium gave appreciable interconversion with *o*-bromoanisole, *o*- and *p*-iodoanisoles and *o*-iodophenyl phenyl ether.

Experimental Part

The general procedure for carrying out the interconversion and metalation reactions reported in this work was essentially that described in preceding reports. The organic halide was dissolved in a small quantity of diethyl ether and added rapidly to the desired amount of organolithium compound, which was also in ether solution. When halogen-metal interconversion was the desired reaction, the mixture was allowed to stand at room temperature for fifteen minutes or less. In order to produce metalation, a long period of reaction was used and in some cases heat was applied. At the end of the reaction period, the mixture was carbonated by pouring it upon powdered solid carbon dioxide. The acidic material formed was isolated by extraction with 5% sodium hydroxide.

The results obtained with halogenophenyl phenyl ethers and various organolithium compounds are reported in Table I and its accompanying footnotes. The results obtained with methyl lithium and some halogenoanisoles are given in Table II.

4-Methoxyphenyl Phenyl Ether with *n*-Butyllithium.—When 0.02 mole of 4-methoxyphenyl phenyl ether was mixed with 0.031 mole of *n*-butyllithium in ether solution and the reaction mixture carbonated after standing at 20° for thirty hours, there was obtained 1.88 g. (38.5%) of acidic material melting at 90–95° and having a *neutral equivalent* of 240 (calcd. for C₁₄H₁₂O₄, 244). Repeated recrystallization from petroleum ether (b. p. 50–100°) gave 1.4 g. (29%) of 2-methoxy-5-phenoxybenzoic acid, m. p. 108–110°. The product was shown by means of a mixed m. p. determination to be the same as that prepared by the hydrolysis of 2-methoxy-5-phenoxybenzotrile. Also, a mixed melting point with the product obtained from the halogen-metal interconversion reaction of *n*-butyllithium and 3-bromo-4-methoxyphenyl phenyl ether showed no depression. [See Table I, Footnote (q).] Though the crude metalation product apparently was a mixture of isomeric methoxyphenoxybenzoic acids, only the 2,5-isomer was isolated.

Starting with 0.02 mole of 4-methoxyphenyl phenyl ether and 0.03 mole of *n*-butyllithium, a second reaction mixture which was refluxed for twenty-four hours gave a

TABLE I
 REACTION BETWEEN HALOGENOPHENYL PHENYL ETHERS AND RLi COMPOUNDS

Phenyl ether	Mole	RM compound	Mole	Reaction temp., °C.	Reaction time, hours	RCO ₂ H	Yields, %	
2-Iodophenyl	0.01	<i>n</i> -C ₄ H ₉ Li	0.02	26	0.25	2-C ₆ H ₅ OC ₆ H ₄ CO ₂ H	79 ^a	
	.01	C ₆ H ₅ Li	.02	26	.25		56 ^b	
	.01	C ₆ H ₅ Li	.02	18-20	24		79	
	.01	CH ₃ Li	.01	26	0.25		14 ^c	
3-Iodophenyl	.01	<i>n</i> -C ₄ H ₉ Li	.02	26	.25	3-C ₆ H ₅ OC ₆ H ₄ CO ₂ H	75 ^d	
	.01	C ₆ H ₅ Li	.01	26	.25		37 ^e	
4-Iodophenyl	.01	<i>n</i> -C ₄ H ₉ Li	.02	26	.25	4-C ₆ H ₅ OC ₆ H ₄ CO ₂ H	93 ^f	
	.02	<i>n</i> -C ₄ H ₉ Li	.01	20-22	26		2,5-(C ₆ H ₅ O)IC ₆ H ₃ CO ₂ H	30 ^g
	.01	C ₆ H ₅ Li	.01	26	0.25		4-C ₆ H ₅ OC ₆ H ₄ CO ₂ H	33 ^h
4-Iodophenyl-4'-methoxy	.02	C ₆ H ₅ Li	.02	34	15	2,5-(C ₆ H ₅ O)IC ₆ H ₃ CO ₂ H	32 ⁱ	
	.01	<i>n</i> -C ₄ H ₉ Li	.02	26	0.25	4-(4'-CH ₃ OC ₆ H ₄ O)C ₆ H ₄ CO ₂ H	61 ^j	
	.01	C ₆ H ₅ Li	.01	26	.25		47 ^k	
	.01	<i>n</i> -C ₄ H ₉ Li	.02	26	.25	2-C ₆ H ₅ OC ₆ H ₄ CO ₂ H	65 ^l	
2-Bromophenyl	.01	<i>n</i> -C ₄ H ₉ Li	.02	26	.25	4-C ₆ H ₅ OC ₆ H ₄ CO ₂ H	36 ^m	
4-Bromophenyl	.01	<i>n</i> -C ₄ H ₉ Li	.01	26	.033	2,5-(C ₆ H ₅ O)BrC ₆ H ₃ CO ₂ H	80	
	.01	<i>n</i> -C ₂ H ₅ Li	.02	26	.083		7 ⁿ	
	.01	C ₆ H ₅ Li	.01	26	.25		35 ^o	
	.15	C ₆ H ₅ Li	.08	20	24		14 ^p	
3-Bromo-4-methoxyphenyl	.01	CH ₃ Li	.01	20	24	2,5-(CH ₃ O)(C ₆ H ₅ O)C ₆ H ₃ CO ₂ H	66 ^q	
	.01	<i>n</i> -C ₄ H ₉ Li	.02	26	0.25		0 ^r	
2-Chlorophenyl	.01	CH ₃ Li	.01	20	24	2,5-(C ₆ H ₅ O)ClC ₆ H ₃ CO ₂ H	16 ^s	
4-Chlorophenyl	.005	<i>n</i> -C ₄ H ₉ Li	.008	26	0.25		23 ^t	
	.015	<i>n</i> -C ₄ H ₉ Li	.02	34	10		36 ^u	
	.02	C ₆ H ₅ Li	.01	20	26		14 ^v	
	.01	CH ₃ Li	.01	20	24			

^a After crystallization of the product from petroleum ether (b. p. 50-100°) the yield of purified acid was 71%. Identification was made by means of a mixed melting point determination. From a check experiment there was obtained a 75% yield of crude 2-phenoxybenzoic acid. ^b The product was separated from a large quantity of benzoic acid by crystallization from hot water. ^c No acidic material was isolated from a second reaction mixture which was carbonated after standing twenty-four hours at 18-20°. ^d Recrystallization of the 3-phenoxybenzoic acid from petroleum ether (b. p. 70-80°) gave a 65% yield of product melting at 145-146°. The acid was identified by a mixed melting point determination with a specimen prepared by carbonating the Grignard reagent from 3-iodophenyl phenyl ether. A second experiment gave a 70% yield of the crude acid. ^e Recrystallization of the acid from petroleum ether (b. p. 70-80°) gave a 28% yield of purified product. From a second experiment in which carbonation was carried out after standing for thirty hours at 20° there was obtained a small quantity of acidic gum and a large quantity of neutral reddish oil. No acidic material was obtained when methyl lithium was used as the metalating agent and the reaction mixture carbonated after standing thirty hours at 20°. ^f When this product was recrystallized from petroleum ether (b. p. 50-100°), there was obtained a 70% yield of purified acid melting at 158°. The acid was identified by means of a mixed melting point with a specimen obtained by carbonating the Grignard reagent from 4-bromophenyl phenyl ether. A second reaction gave an 80% yield of crude material. ^g The yield of acid was calculated on the basis of a two-stage metalation. The crude product melted at 142-144°, and when recrystallized from petroleum ether melted at 146°, yield 24%. The melting point reported for 2-phenoxy-5-iodobenzoic acid is 148° [Brewster and Strain, THIS JOURNAL, 56, 117 (1934)]. The acid was identified by a mixed melting point with a specimen prepared from 2-phenoxy-5-aminobenzoic acid by the Sandmeyer reaction. ^h It was necessary to separate the 4-phenoxybenzoic acid from a quantity of benzoic acid by crystallization from petroleum ether (b. p. 50-100°). ⁱ The yield was calculated on the basis of the recrystallized material (m. p. 142-144°) and a two-stage metalation mechanism. From a second experiment there was obtained a 30% yield of acid. With 0.01 mole of 4-iodophenyl phenyl ether and 0.02 mole of methyl lithium and a fifteen-minute period of reaction a trace of acidic gum was obtained. Only a trace of acidic gum was obtained when a second reaction mixture prepared with methyl lithium was carbonated after a seventeen-hour period of heating. From the neutral fraction there was obtained a quantity of reddish oil. ^j The yield was calculated on the basis of the purified product (m. p. 174-176°). The acid was identified by a mixed m. p. determination with a specimen prepared by carbonating the Grignard reagent from 4-iodophenyl 4'-methoxyphenyl ether. The m. p. reported for 4-(4'-methoxyphenoxy)-benzoic acid is 177° [Harrington, Biochem. J., 20, 300 (1926)]. From a second experiment there was obtained a 63% yield of purified acid. ^k When the product was crystallized from petroleum ether (b. p. 50-100°), there was obtained a 40% yield of purified acid (m. p. 176°). ^l Crystallization from petroleum ether (b. p. 50-100°) gave a 60% yield of purified acid. ^m There was recovered 32% of unreacted *p*-bromophenyl phenyl ether from the neutral fraction of this experiment. In an earlier experiment^{2a} carbonation of the reaction mixture after fifteen minutes gave 70% of 4-phenoxybenzoic acid while carbonation after 20 hours of heating gave a 21% yield of 2-phenoxy-5-bromobenzoic acid.^{1e} ⁿ In addition there was isolated a 40% yield of benzoic acid. ^o The crude product melted at 110-124°. Crystallization from petroleum ether gave 35% of 2-phenoxy-

5-bromobenzoic acid (m. p. 133°). The yield was calculated on the basis of the phenyllithium used. From the neutral fraction there was obtained 1.7 g. of bromobenzene, 14.7% of phenyl ether, 34% of 4-bromophenyl phenyl ether, and 6.6 g. of tarry residue. From a check experiment using 0.08 mole of phenyllithium and 0.13 mole of *p*-bromophenyl phenyl ether there was obtained a 46% yield of 2-phenoxy-5-bromobenzoic acid, a 5% yield of benzene, 18% of phenyl ether and a 24% yield of bromobenzene in addition to a 19% recovery of *p*-bromophenyl phenyl ether. ² The yield after crystallization from petroleum ether was 10%, and the m. p. 132–133°. From a second reaction mixture which was carbonated after fifteen minutes only a trace of acidic oil was obtained in addition to acetic acid. ³ The acid melted at 110–111° and was shown by a mixed m. p. determination to be the same as that obtained by carbonating the product of a hydrogen-metal interconversion reaction between 4-methoxyphenyl phenyl ether and *n*-butyllithium. ⁴ Only a trace of acidic gum could be obtained from 2-chlorophenyl phenyl ether when the metalating agent was methyllithium, *n*-butyllithium or phenyllithium. In every case a vigorous reaction occurred and the solution became colored. Hydrolysis and titration of an aliquot of each reaction mixture showed that coupling reactions had predominated, resulting in the essential disappearance of RLi compound. ⁵ The crude product was recrystallized from petroleum ether, yield 8% (m. p. 110–111°). Identification was made by means of a mixed m. p. with a specimen prepared from 2-phenoxy-5-aminobenzoic acid by the Sandmeyer reaction. ⁶ From another reaction mixture which was carbonated after standing for 26 hours at 18–20° there was obtained a large quantity of acidic gum which yielded 20.3% of acid (m. p. 110–111°) on crystallization from petroleum ether (b. p. 50–100°). In a third experiment petroleum ether was used as the solvent and the reaction mixture was carbonated after standing thirty hours at 20°. The yield of crude acid (m. p. 105–108°) was 22%. ⁷ The yield was calculated on the basis of the recrystallized product (m. p. 110–111°) and on the quantity of phenyllithium used in the reaction. From the neutral fraction there was recovered 41% of unreacted 4-chlorophenyl phenyl ether. From a check experiment using 0.065 mole of *p*-chlorophenyl phenyl ether and 0.043 mole of phenyllithium there was obtained a 35% yield of 2-phenoxy-5-chlorobenzoic acid and a 16.7% yield of benzene in addition to a 45% recovery of *p*-chlorophenyl phenyl ether. No indications of the presence of chlorobenzene and phenyl ether were observed. From another reaction mixture which was carbonated after fifteen minutes at room temperature there was obtained an 82% yield of benzoic acid only. ⁸ The yield of purified acid (m. p. 111°) was 8%. When the reaction mixture was refluxed for seventeen hours the yield of crude acid was 13.5%.

TABLE II
REACTIONS OF HALOGENOANISLES WITH METHYLLITHIUM AT 34° FOR FOURTEEN HOURS

Anisole	Mole	CH ₃ Li mole	RCO ₂ H	Yield, %
<i>p</i> -Fluoro-	0.03	0.05	2,5-(CH ₃ O)FC ₆ H ₃ CO ₂ H	17.7 ^a
<i>p</i> -Chloro-	.03	.05	2,5-(CH ₃ O)ClC ₆ H ₃ CO ₂ H	21.6 ^b
<i>p</i> -Bromo-	.02	.03	2,5-(CH ₃ O)BrC ₆ H ₃ CO ₂ H	21.7 ^c
<i>p</i> -Iodo-	.03	.05	4-CH ₃ OC ₆ H ₄ CO ₂ H	13.1 ^d
<i>o</i> -Chloro-	.02	.03		0.0 ^e
<i>o</i> -Bromo-	.02	.03	2-CH ₃ OC ₆ H ₄ CO ₂ H	16.6 ^f
<i>o</i> -Iodo-	.013	.03	2-CH ₃ OC ₆ H ₄ CO ₂ H	12.5 ^g
<i>m</i> -Bromo-	.02	.03		0.7 g. ^h

^a From this reaction there was recovered 38.5% of unreacted *p*-fluoroanisole (b. p. 155–157°) and a quantity of reddish oily residue. ^b In addition, there was recovered 57% of unreacted *p*-chloroanisole, b. p. 78–80° at 12 mm. ^c From another experiment there was obtained a 16% yield of acid and a 50% recovery of unreacted *p*-bromoanisole. ^d Upon vacuum distillation of the neutral fraction there was obtained 1.8 g. (48.6%) of methyl *p*-tolyl ether (b. p. 176°, sp. g. 0.976) in addition to a small amount of oily residue. The methyl *p*-tolyl ether was identified by oxidation to *p*-methoxybenzoic acid with potassium permanganate. From a second experiment the yield of *p*-methoxybenzoic acid was 5% and the yield of methyl *p*-tolyl ether was 52%. ^e In addition to acetic acid, a 64% recovery of *o*-chloroanisole (b. p. 85–86° at 11 mm.) was obtained. ^f From the neutral fraction of this reaction there was obtained a 43.5% yield of methyl *o*-tolyl ether, b. p. 170°. The product was identified by oxidation to *o*-methoxybenzoic acid. ^g In addition there was obtained a 75% yield of methyl *o*-tolyl ether, b. p. 170°, sp. g. 0.985. The product was identified by oxidation to *o*-methoxybenzoic acid. ^h This product was an acidic gum from which nothing has been identified. From the neutral portion there was obtained 0.32 g. (13%) of methyl *m*-tolyl ether, b. p. 62–64° at 9 mm., and 0.43 g. of an unidentified product, b. p. 79–81° at 9 mm. The methyl *m*-tolyl ether was identified by oxidation to *m*-methoxybenzoic acid.

30% yield of impure 2-methoxy-5-phenoxybenzoic acid, m. p. 107–109°.

Summary

The reactions of some halogen derivatives of phenyl ether with methyllithium, *n*-butyllithium and phenyllithium have been studied. When the halogen is iodine or bromine, halogen-metal interconversion has been found to be the predominant

reaction. Iodophenyl phenyl ethers undergo interconversion more readily than bromophenyl phenyl ethers, and chlorophenyl phenyl ethers are essentially not affected.

During long periods of reaction or upon refluxing in ether solution, *p*-bromo- and *p*-chlorophenyl phenyl ethers are metalated by methyllithium, *n*-butyllithium and phenyllithium. Under the

same conditions *p*-iodophenyl phenyl ether is metalated in reactions with *n*-butyllithium and phenyllithium.

p-Fluoro-, *p*-chloro- and *p*-bromoanisoles are metalated by methyllithium. Under the same conditions *o*- and *m*-bromo- and *o*- and *p*-iodo-

anisoles undergo some halogen-metal interconversion followed by coupling, which results in appreciable yields of methyl tolyl ethers.

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[A COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

The Products of the Hydrogenation of Lignin¹

BY HOMER ADKINS, ROBERT L. FRANK AND EDWARD S. BLOOM

The first paper of this series described experimental work in which lignin, extracted from freshly cut aspen, was converted by hydrogenation over copper chromite to a mixture of saturated, colorless compounds.^{2,3} At least 75% of the lignin was converted to water, methanol and derivatives of propylcyclohexane. The predominance of hydroxy derivatives of propylcyclohexane among the products of the hydrogenation supported the hypothesis that lignin is a polymer in which the primary unit contains nine carbon atoms. However, the isolation of compounds of such low molecular weight does not show how they were joined together in the lignin molecule. It therefore seemed of importance to study the products of the hydrogenation of types of lignin which gave larger proportions of compounds containing more than nine carbon atoms to the molecule.

A survey in this Laboratory of the behavior of different types of lignin has shown that lignins obtained from either hard or soft woods, by either the soda or sulfite process, give a much lower yield of nine carbon atom compounds than did the lignin extracted with methanol from freshly cut aspen. Attention has therefore been concentrated upon a sample of lignin produced by the Meade Company of Chillicothe, Ohio, from a mixture of hard woods, using the soda process.⁴

(1) This investigation was supported in part by funds given by the Wisconsin Alumni Research Foundation.

(2) Harris, D'Ianni and Adkins, *THIS JOURNAL*, **60**, 1467 (1938).

(3) Credit should have been given in the first paper to Dr. Harold Hibbert of McGill University, who supplied the sample of lignin on which the first successful hydrogenation of lignin over copper chromite was accomplished. The mixture of products resulting from the hydrogenation was returned to him. The method and process used by me on the sample of lignin submitted by Dr. Hibbert was the same as that used almost a year later on a sample prepared by Dr. Harris. A patent has been obtained by Messrs. Earl C. Sherrard and Elwin E. Harris (application May 10, 1938, issued February 7, 1939, number 2,146,655) which attempts to cover the process of hydrogenating lignin over copper chromite.—H. A.

(4) We are indebted to Mr. Gaston DuBois of the Monsanto Chemical Company for our supply of Meade lignin.

The Meade lignin is a cocoa-like reddish-brown powder which according to an analysis by Dr. Carl Tiedcke of New York City contains 23.3% methoxyl, 65.65% carbon, 6.37% hydrogen, and so corresponds to the formula $(C_{48}H_{27}O_9(OCH_3)_7)_n$. These values were calculated after making allowance for the fact that the sample contained 3.1% ash.

About 80% of the lignin is soluble in cold dry dioxane to give a solution which, when saturated, contains about 15% lignin. Solution takes place rather slowly but may be accomplished by stirring the lignin (25 g.) with dioxane (150 ml.) for eight hours at room temperature. The portion of the lignin insoluble in cold dry dioxane may be readily suspended in the solution, but it is thrown out when centrifuged at 2500 r. p. m. in a no. 2 International Centrifuge.

Hydrogenation of Meade Soda Lignin.—There is a good deal of variation in the rate and extent of hydrogenation of a sample of lignin, depending upon the concentration of lignin in the solution and the temperature of hydrogenation. A few typical experiments carried out in reaction vessels of various sizes will be described below. The pressure of hydrogen during reaction was from two hundred to three hundred and fifty atmospheres.

(a) A solution (125 ml.) of lignin (15 g.) in dioxane with 6 g. of copper chromite in a steel reaction vessel of 270 ml. capacity required twelve hours at 260° or four and one-half hours at 290° for complete hydrogenation. In each case the solution of the product was colorless and one mole of hydrogen was absorbed by 27 to 28 g. of lignin.

(b) A solution (900 ml.) of lignin (85 g.) in dioxane with 30 g. of copper chromite in a steel reaction vessel of 1880 ml. capacity required twelve hours at 290° for complete hydrogenation.