of furfural, and 40 ml. of 33% sodium hydroxide solution in a three-necked flask fitted with a thermometer, a mechanical stirrer, an inlet tube for nitrogen, and a small exit passage for gas. *m*-Nitrobenzaldehyde was dissolved in furfural by gently warming the mixture, and this solution was added to the sodium hydroxide solution in the flask cooled in an ice bath at such a rate that the temperature of the reaction mixture did not rise above 45°; this required 15–20 min. The mixture was semisolid by the time all of the aldehyde solution had been added even though constant stirring had been maintained. The ice bath was replaced by a 40–45° water bath. Stirring was continued, and 20 ml. of water was added in small amounts over a period of 1 hr. Thereafter, the mixture was permitted to stand for 2 hr. before separation of reaction products was undertaken.

Furfural and *p*-Bromobenzaldehyde.—For reactions 3 and 4, 4.8 g. (0.05 mole) of furfural, 9.23 g. (0.05 mole) of *p*-bromobenzaldehyde, and 5 ml. of 33% sodium hydroxide solution were used; for reaction 5, twice the foregoing amounts were used. Ethereal solutions of alcohol mixtures were dried with anhydrous sodium sulfate; thereafter, most of the ether was removed by distillation through a 50-cm. Vigreux column, and the last traces of the solvent were removed at reduced pressure (*ca.* 18 mm.), in an atmosphere of nitrogen, from a Claisen flask with a 25-cm. column. Ethereal solutions of acids were washed with water (3 × 25 ml.); the major portion of ether was removed by distillation through a 50-cm. Vigreux column.

***m*-Nitrobenzaldehyde and Benzaldehyde.**—The same molar quantities of materials and the same procedures as those recorded above for *m*-nitrobenzaldehyde–furfural mixtures were used for the reations with this mixture of aldehydes.

Benzaldehyde and *p*-Anisaldehyde.—Because the reaction rate for this mixture of aldehydes with aqueous alkali was extremely slow, some methanol was introduced to overcome the difficulty. The reaction was carried out with 21.2 g. (0.2 mole) of benzaldehyde, 27.2 g. (0.2 mole) of *p*-anisaldehyde, and 9 g. of sodium hydroxide dissolved in 13.5 ml. of water and 5.7 ml. of methanol.

Furfural and *p*-Anisaldehyde.—With 19.2 g. (0.2 mole) of furfural, 27.2 g. (0.2 mole) of *p*-anisaldehyde, and 40 ml. of 33% sodium hydroxide solution, the reaction was carried out as described above for mixtures of furfural and *p*-bromobenzaldehyde. The alcohol mixture was distilled at reduced pressure (2 mm.) prior to analysis.

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Aluminum Chloride-Induced Isomerization of Chlorinated Biphenyls[1]

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Chlorinated biphenyls were found to isomerize in the presence of hydrogen chloride and aluminum chloride. The transformation appears to be intramolecular with phenyl migration predominating over chlorine migration.

In the course of related work[2] we observed the various chlorinated biphenyls to be readily isomerized in the presence of aluminum chloride. Since only halobenzene[3] and halonaphthalene[4–6] isomerizations have been reported in the literature, we decided to examine the chlorinated biphenyl system in more detail.

Results and Discussion

We observed that the three monochlorobiphenyls upon treatment with hydrogen chloride and aluminum chloride at 160° gave the same, presumably thermodynamic, mixture described in example 1, Table I. This isomeric distribution agrees fairly well with the thermodynamic distribution reported for other aromatic systems.[7] The results were particularly interesting when we discovered appreciable isomerization rates at temperatures as low as 100°.

TABLE I

	Compound	Conditions	Products		
			% *o*	% *m*	% *p*
(1)	*o*, *m* or *p*-Chlorobiphenyl	160°, 30 min.	3[a]	64	33
(2)	*o*-Chlorobiphenyl	100°, 15 min.	82[b]	18	<1
(3)	*p*-Chlorobiphenyl	100°, 15 min.	0.2[c]	14.8	85
(4)	*m*-Chlorobiphenyl	100°, 10 min.	3[d]	90	7
(5)	*o*-Bromobiphenyl	50°, 5 min.	69[e]	2	29

[a] Product contains 3 to 6% biphenyl. [b] Contains trace biphenyl. [c] Contains 1% biphenyl. [d] Contains trace biphenyl. [e] Contains 20% biphenyl.

We first sought to establish experimentally the inter- or intramolecular character of the transformation. To accomplish this the three monochlorobiphenyls were isomerized under very mild conditions for a short period of time. This allowed

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(1) Presented at the 140th Meeting of the American Chemical Society, Chicago, Ill., September, 1961, abstract p. 56Q.

(2) H. Weingarten, *J. Org. Chem.*, **26**, 4347 (1961).

(3) J. T. Fitzpatric, U. S. Patent 2,666.085 (1954).

(4) N. N. Vorozhtsov, Jr., and V. A. Koptyug, *Zhur. Obshchei Khim.*, **28**, 372 (1958).

(5) H. E. Fisher and R. H. Clark, *Can. J. Research*, **17B**, 251 (1939).

(6) Y. Zalkind and Z. Stezuro, *Ber.*, **64B**, 953 (1931).

(7) R. H. Allen, L. D. Yats, and D. S. Erley, *J. Am. Chem. Soc.*, **82**, 4853 (1960).

TABLE II

	Compound	Conditions	Products
(1)	3,5-Dichlorobiphenyl	160°, 30 min.	94% 3,5-dichlorobiphenyl, 5% 2,4-dichlorobiphenyl, 0.5% 2,5-dichlorobiphenyl[a]
(2)	3,4-Dichlorobiphenyl	160°, 10 min.	94% 3,4-dichlorobiphenyl, 5% 2,3-dichlorobiphenyl, 0.6% 2,4- and 3,5-dichlorobiphenyl[b]
(3)	2,5-Dichlorobiphenyl	162°, 60 min.	65% 2,5-dichlorobiphenyl, 2% 2,6-dichlorobiphenyl, 1.7% 2,4-dichlorobiphenyl, 9.5% 3,5-dichlorobiphenyl, 0.6% 2,3 and 3,4-dichlorobiphenyl, 4% X,X′-dichlorobiphenyl, 8.2% mono-, and 8.7% trichlorobiphenyl[c]

[a] Contains traces of monochlors. [b] Contains 7% monochlors. [c] Contains trace biphenyl.

us to examine the first isolable products of isomerization. Examples (2), (3), and (4) of Table I represent our results which we interpret to mean an intramolecular reaction proceeding *via* 1–2 shifts. Products of intermolecular isomerization would be expected to favor *ortho* and *para* substitution in the first few percent of reaction as is actually the case with bromobiphenyls [example (5), Table I].

Our second aim was to distinguish chlorine migration from phenyl migration since either could account for our results. To this end the 3,5- and 3,4-dichlorobiphenyls were subjected to partial isomerization and found to yield 2,4- and 2,3-dichlorobiphenyl, respectively, along with small amounts of other dichlorobiphenyls [examples (1) and (2), Table II]. These results are intelligible only if we assume phenyl to be the migrating unit.[8] It seems reasonable to suppose phenyl migration taking place *via* the intermediate or transition state pictured in Fig. 1. We expect this intermediate to be analogous to the bridged phenonium ion postulated in aliphatic chemistry.[9]

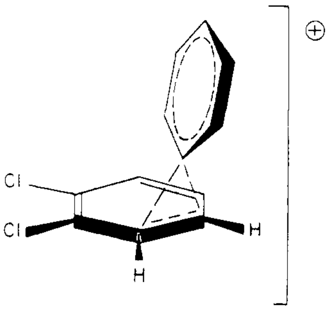

Figure 1

When we realized the phenyl group was migrating we examined several more obvious examples, namely, *o*-terphenyl and α-phenylnaphthalene. Both of these compounds isomerize easily under our conditions. Furthermore, both have been reported in the literature to isomerize under similar or related conditions.[10,11] The mixture obtained on phenylnaphthalene isomerization was specifically examined by gas chromatographic techniques for possible intermolecular migration products (naphthalene, diphenylnaphthalene) and none were observed.

Our final objective was to examine the possibility of intramolecular chlorine migration. Products of intramolecular chlorine migration are observed in the isomerization of 3,5- and 3,4-dichlorobiphenyl [examples (1) and (2), Table II] but their concentration is so low as to make their significance doubtful. We therefore chose 2,5-dichlorobiphenyl as the system most likely to answer the above question since phenyl migration would not interfere with the result. The data recorded in Table II, example (3), clearly show intermolecular and intramolecular chlorine migrations occurring at similar rates. The products 2,6- 2,4-, and 3,4-dichlorobiphenyl could not arise in major amounts *via* an intermolecular path since their formation could not compete favorably with the formation of X,X′-isomers.[2] The fact that the chlorine atoms of the 2,6-, 2,4, and 3,4-isomers have not only remained in the ring to which they were originally attached but have shifted only one position to the virtual exclusion of the 2,3- and 3,4-isomers also argues in favor of their arising *via* an intramolecular path. The intramolecular chlorine migration presumably takes place through the intermediate or transition state pictured in Fig. 2.[12]

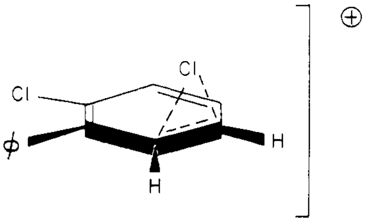

Figure 2

Experimental

All of the monochloro- and most of the dichlorobiphenyls have been adequately characterized and reported in the literature. Samples of 2,3′-, 2,4′-, and 4,4′-dichlorobiphenyls were kindly supplied by Dr. A. M. Ellenburg, Monsanto Chemical Co., St. Louis. All others were prepared by Gomberg techniques.[13,14]

The 2,5-dichlorobiphenyl previously reported as a liquid is here reported as a solid, m.p. 22–23°.

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[8] The bromobiphenyl example must involve intermolecular halogen migration and little if any phenyl migration.

[9] D. J. Cram, *J. Am. Chem. Soc.*, **71**, 3863 (1949).

[10] R. D. Swisher, U. S. Patent 2,363,209 (1944).

[11] F. Mayer and R. Schiffner, *Ber.*, **67B**, 67 (1934).

[12] N. N. Vorozhtsov and V. A. Koptyug have suggested the same type of intermediate in the chloronapththalene isomerization, ref. 4.

[13] H. Weingarten, *J. Org. Chem.*, **26**, 730 (1961).

[14] H. Weingarten *et al.*, *Anal. Chim. Acta*, **26**, 391 (1962).

Anal. Calcd. for $C_{12}H_8Cl_2$: C, 64.6; H, 3.6. Found: C, 64.8; H, 3.7.

The monobromobiphenyls were purchased from K and K Laboratories. The terphenyls were purchased from Eastman. The α-phenylnaphthalene was purchased from the Aldrich Chemical Co. All compounds used as starting materials in the isomerizations were purified until gas chromatographically pure.

Isomerization of Halogenated Biphenyls.—A mixture of 1 g. of compound and 0.01 g. of aluminum chloride (B and A, anhydrous, sublimed) in a 6-in. test tube was placed in an oil bath. Anhydrous hydrogen chloride was bubbled through the mixture throughout the reaction. The reaction time and temperature are described in Tables I and II. After cooling, *n*-pentane was added to the mixture and the organic phase washed with water. The organic layer was dried over magnesium sulfate, filtered, and evaporated to an oily residue which was analyzed directly by gas chromatography as described in ref. 14.

Isomerization of α-Phenylnaphthalene. Anhydrous hydrogen chloride was bubbled through a solution of 0.01 mole of α-phenylnaphthalene in 10 ml. of benzene to which had been added 0.05 g. of aluminum chloride. The reaction time was 15 min. at 70°. The product was prepared for analysis as described above. Gas chromatography indicates an equilibrium distribution of 3% α-phenylnaphthalene and 97% β-phenylnaphthalene. The same mixture is obtained starting with β-phenylnaphthalene.[15]

No naphthalene or diphenylnaphthalene peaks were observed on the gas chromatograms.

Isomerization of *o*-Terphenyl.—Anhydrous hydrogen chloride was bubbled through a mixture of 1 g. of *o*-terphenyl and 0.01 g. of aluminum chloride held at 160° for 30 min. The product was prepared for analysis as described above. Gas chromatographic analysis indicated an equilibrium mixture of 64% *m*-terphenyl and 36% *p*-terphenyl.

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[15] β-Phenylnaphthalene was obtained from the α-phenylnaphthalene isomerization after sublimation and recrystallization, m.p. 102.4–102.7°.

Anal. Calcd. for C, 93.8; H, 6.0. Found: C, 94.0; H, 6.1.

The Friedel-Crafts Isopropylation of Benzo[*b*]thiophene[1]

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Benzo[*b*]thiophene has been isopropylated with several reagents using various methods and catalysts. In each case, a mixture of the 2- and 3-substituted products was obtained in which the 2-isomer predominated. The authentic compounds, 2-isopropyl- and 3-isopropylbenzo[*b*]thiophene, were each synthesized by two different routes and were, in addition, degraded to known compounds. The results are discussed.

The Authentic Compounds.—For a study of this type, the identity and purity of the authentic compounds are extremely important. Thus, 2-isopropyl-(I) and 3-isopropylbenzo[*b*]thiophene (II), the major compounds which would result from the monoalkylation of benzo[*b*]thiophene, were synthesized by two different routes, each thought to be unequivocal. The isomers were prepared by ring closure methods to ensure purity, but a second synthesis from the known 2- and 3-carboxylic acid esters was used to ensure identity. The synthetic reactions are outlined in the chart. In each case, the isomers derived from the different paths were identical.

The syntheses were reconfirmed by the desulfurization[11] of the 2- and 3-isomers to the corresponding hydrocarbons, 3-methyl-1-phenylbutane, (XVI), and 2-methyl-3-phenylbutane (XVII). The reference hydrocarbons XVI and XVII were synthesized by the procedures of Gilman and Beaber[12] and Klages,[13] respectively. The infrared spectra and physical constants of the prepared hydrocarbons were identical with those of the hydrocarbons derived from the benzo[*b*]thiophene derivatives. 2-Isopropyl- and 3-isopropylbenzo[*b*]thiophene were characterized as 2,4,7-trinitrofluorenone derivatives.[14]

Alkylation Experiments.—Benzo[*b*]thiophene was isopropylated using a variety of Lewis acid catalysts and alkylating agents. The alkylation procedures were dictated by the physical constants of the reactants and the desired temperatures, were of seven types and are described in the Ex-

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[1] This investigation was partially supported by a Frederick Gardner Cottrell Grant from the Research Corporation.

[2] Abstracted in part, from the Ph.D. thesis of S. F. Bedell, University of Connecticut, 1959. Present address: Monsanto Chemical Company, Research and Engineering Division, Special Products Department, Everett, Mass.

[3] To whom inquiries should be sent.

[4] H. D. Hartough and A. I. Kosak, *J. Am. Chem. Soc.*, **68**, 2639 (1946).

[5] The experiments, III to VI, were carried out as a modification of the experiments first performed by C. B. Germain, Ph.D. dissertation, University of Connecticut, 1953.

[6] The conversions, VI to I, were carried out in a manner analogous to the preparation of 4-hydroxybenzo[*b*]thiophene; L. F. Fieser and R. G. Kennelly, *J. Am. Chem. Soc.*, **57**, 1611 (1935).

[7] R. Weissgerber and O. Kruber, *Ber.*, **53**, 1551 (1920).

[8] The major route (through XV) was the general method of E. G. G. Werner, *Rec. trav. chim.*, **68**, 519 (1949).

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[11] F. F. Blicke and D. G. Sheets, *J. Am. Chem. Soc.*, **71**, 4010 (1949).

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[13] A. Klages, *Ber.*, **36**, 3688 (1903).

[14] N. D. Cheronis and J. B. Entrikin, "Semimicro Qualitative Organic Analysis," 2nd ed., Interscience Publishers, Inc., New York, 1957, p. 487.