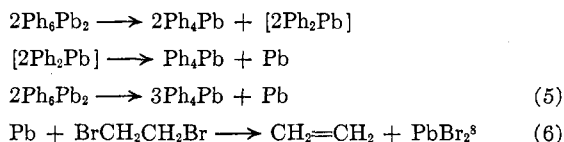


larly as it applies to the decomposition of hexaphenyldilead (reaction 1).

As final evidence for decomposition of hexaphenyldilead into tetraphenyllead and diphenyllead, we studied the reaction of hexaphenyldilead with 1,2-dibromoethane. Recent studies have shown that hexaethyldistannane when treated with 1,2-dibromoethane yields as the main products triethyltin bromide and ethylene.⁷ When hexaphenyldilead reacted with 1,2-dibromoethane, the only nonvolatile products were tetraphenyllead (81%) and lead bromide (98%) based upon the assumed disproportionation of diphenyllead to tetraphenyllead and elemental lead followed by the reaction sequence shown.



It seems consistent with the experimental data now available that hexaphenyldilead undergoes an initial decomposition to tetraphenyllead and elemental lead via the unstable intermediate diphenyllead. In the presence of acids this initially formed diphenyllead reacts to form lead acetate and benzene (reaction 4).

This reaction scheme would also explain why, in the presence of acids, the combined yields of triphenyllead halide and diphenyllead dihalides are stoichiometrically limited to 50%.

Experimental

All reactions were followed and products identified by thin layer chromatographic techniques using silica gel G as a solid phase and either carbon tetrachloride or benzene-hexane mixtures as solvents. A dithizone spray (6 mg./100 ml. of chloroform) was used. Triphenyllead compounds gave yellow spots, diphenyllead compounds gave red spots, and tetraphenyllead gave no color reaction with dithizone. Tetraphenyllead gave a yellow spot using a permanganate spray.

Melting points were determined with a Thomas-Hoover melting point apparatus. Where possible, mixture melting points with authentic samples and comparison of infrared spectra with those of authentic samples were used as confirmatory identification of the products.

Hexaphenyldilead was prepared by the established Grignard method. Careful purification by successive recrystallizations resulted in thin layer chromatograms in which the complete absence of tetraphenyllead was demonstrated.

Hexaphenyldilead-Acetic Acid (Ratio 1:2).—Hexaphenyldilead, 4.38 g. (5.0 mmoles), and glacial acetic acid, 0.60 g. (10 mmoles), dissolved in 50 ml. of *n*-heptane was refluxed for 3 hr. No visible evolution of hydrogen was noted during the reaction. During the 3-hr. period, the reaction was followed by thin layer chromatographic techniques as described. Periodic sampling showed the disappearance of hexaphenyldilead and the formation of tetraphenyllead, lead(II) acetate, and triphenyllead acetate. After completion of the reaction, the liquid phase was distilled and investigated using v.p.c. techniques. Vapor phase chromatography indicated the liquid phase to contain only *n*-heptane and benzene and by comparison of peak sizes, the amount of benzene obtained in the reaction was calculated to be 0.7 g. (90%). The solid residue remaining after the removal of the solvent (4.11 g.) was extracted with boiling chloroform. The insoluble residue (1.31 g.) consisted of lead acetate, identified by its solubility in water and black precipitate with hydrogen sulfide. From the

chloroform extract, 1.27 g. of tetraphenyllead was precipitated by adding alcohol and identified by mixture melting point. The mother liquor contained 0.87 g. of triphenyllead acetate and 0.13 g. of unchanged hexaphenyldilead, identified by mixture melting point and infrared spectra.

Hexaphenyldilead-Acetic Acid (Excess).—A solution of hexaphenyldilead, 2.20 g. (2.5 mmoles), was refluxed in 20 ml. of glacial acetic acid for 5 min. During the reaction period, a white precipitate formed which, after the reaction was complete, was filtered and extracted with chloroform. The residue (0.81 g.) was shown to be lead(II) acetate (99%), identified as before; the filtrate was evaporated under vacuum; the residue, m.p. 203–206°, recrystallized from benzene-acetic acid to yield 1.41 g. (94%) of diphenyllead diacetate, m.p. 208–209°. Mixture melting point with an authentic sample gave no depression.

Hexaphenyldilead with Excess Thioloacetic Acid.—A solution of 2.20 g. (2.5 mmoles) of hexaphenyldilead was dissolved in 20 ml. of thioloacetic acid and refluxed for 5 min. During the reaction 0.50 g. of a black precipitate of lead sulfide formed, apparently from decomposition of lead (II) thioloacetate. This corresponds to an 89% yield of the latter compound. From the filtrate, after removal of the excess thioloacetic acid, there was obtained 1.58 g. of residue which was recrystallized from ethanol to yield 0.90 g. (70%) of diphenyllead dithioloacetate, m.p. 94–95°. Thin layer chromatography of the mother liquor showed some triphenyllead thioloacetate and possibly diphenyllead sulfide [(C₆H₅)₂PbS]_n.

Hexaphenyldilead with Sulfur.—A benzene solution of 64 mg. (2 mmoles) of sulfur was added to a benzene solution containing 1.75 g. (2 mmoles) of hexaphenyldilead and left to stand for 10 days at room temperature. After 1 hr., the clear solution had become turbid. After 10 days, 20 mg. of precipitate was filtered and the solvent evaporated under vacuum to leave a residue of 1.68 g. The residue was dissolved in chloroform, alcohol added, and, after a few minutes, a colorless precipitate, 0.43 g. (24%) of hexaphenyldilead, settled out of solution (identified by infrared spectra). Some tetraphenyllead could be detected in this precipitate using thin layer chromatography techniques. The solvent was partially removed from the mother liquor; the precipitate that formed was filtered and recrystallized from ethanol. The yield was 1.02 g. (59%) of bis(triphenyllead) sulfide, m.p. 139–140°, identified by mixture melting point with an authentic sample. The remaining mother liquor contained some diphenyllead sulfide and bis(triphenyllead) sulfide according to thin layer chromatography experiments.

Hexaphenyldilead with 1,2-Dibromoethane.—Hexaphenyldilead, 4.39 g. (5 mmoles), dissolved in 30 ml. of warm 1,2-dibromoethane was refluxed for 15 min. The solution turned yellow followed by the formation of a white precipitate. The precipitate was filtered (3.83 g.), washed with solvent, and ether extracted with hot chloroform and the insoluble portion filtered. The insoluble residue (0.9 g., 98%) was identified as lead bromide by classical techniques. The chloroform and original 1,2-dibromoethane filtrates were combined, the solvents removed under vacuum, and the residue recrystallized from chloroform to yield 3.14 g. (81% yield) of tetraphenyllead, m.p. 226–228°. The filtrate contained some unchanged hexaphenyldilead as shown by thin layer chromatography experiments.

Friedel-Crafts Isomerization. VI. Aluminum Chloride-Catalyzed Isomerization of Fluorobiphenyls

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Examples of phenyl group migration in substituted aromatics under Friedel-Crafts isomerization conditions are not numerous. Weingarten¹ reported re-

(7) G. A. Razuvaev, N. S. Vyazankin, and Yu I. Dergunov, *J. Gen. Chem. (Eng. Transl.)*, **30**, 1339 (1960).

(8) Razuvaev⁷ has carried out the analogous reaction with hexaethyldilead and obtained similar results. Their explanation of the formation of tetraethyllead as a consequence of the disproportionation of triethyllead bromide appeared to be inconsistent with their prior description of the thermal stability of triethyllead bromide.

(1) H. Weingarten, *J. Org. Chem.*, **27**, 2024 (1962).

cently on the aluminum chloride-induced isomerization of chlorinated biphenyls. Investigating the isomerization of mono- and dichlorobiphenyls he assumed the transition state of phenyl migration to consist of a bridged phenonium ion as postulated by Cram.² In the isomerization of chlorobiphenyls, however, the data do not permit an unambiguous decision whether or not isomerization takes place exclusively by phenyl migration without chlorine migration also being involved.

In the previous paper of this series³ we reported on the aluminum chloride-induced isomerization of terphenyls. Results were explained by an intramolecular 1,2-phenyl-shift mechanism. The equilibrium composition of terphenyl contained 63% *meta* and 37% *para* isomer. The absence of *ortho*-terphenyl from the equilibrium mixture was explained on the basis of steric hindrance.

Results and Discussions

It seemed to be of interest to extend our investigations to the aluminum chloride-catalyzed isomerization of fluorobiphenyls. It was hoped that the results would give (a) an unambiguous example of phenyl migration in the isomerization of halobiphenyls, as it was established previously that ring bonded fluorine is unable to undergo intra- or intermolecular migration under Friedel-Crafts conditions,¹⁻⁴ and (b) to obtain information on the steric *ortho* effect in the formation of *ortho*-halobiphenyls by comparing previous results involving chloro and phenyl substituents to the much smaller fluorine substituent.

Isomerization of *ortho*-, *meta*-, and *para*-fluorobiphenyls with water-promoted aluminum chloride catalysts was carried out under similar conditions to those described previously.³ The results are summarized in Table I.

The equilibrium mixture obtained starting with any one of the isomers contained about 13% *ortho*-, 58% *meta*-, and 29% *para*-fluorobiphenyl. There is little variation in the composition of final mixture with temperature and time. The isomer distribution does not appear to be influenced by halogen exchange and electrophilic arylation reactions which usually accompany Friedel-Crafts isomerizations,⁵ and the experimental isomer distribution is believed to be close to thermodynamic equilibrium. In all runs besides some chlorobiphenyls and biphenyl (3-10%) there were formed varying amounts of insoluble material of higher molecular weight. The inability of ring bonded fluorine to undergo migration, as found in previous work,³ was confirmed in the present case. From Table I it appears that *ortho*- and *para*-fluorobiphenyl isomerize by an intramolecular 1,2-phenyl shift, the other isomer appearing only after the formation of a substantial amount of *meta*. A 1,2-shift is also assumed in the isomerization of *meta*-fluorobiphenyl.

A comparison of the isomer distribution of fluorobiphenyls with that reported for chlorobiphenyls and terphenyls gives the following information on the amount of *ortho* isomer and, consequently, on the steric requirements of the substituent group (Table II).

(2) D. J. Cram, *J. Am. Chem. Soc.*, **71**, 3863 (1949).

(3) G. A. Olah and M. W. Meyer, *J. Org. Chem.*, **27**, 3682 (1962).

(4) G. A. Olah, W. S. Tolgyesi, and R. E. Dear, *ibid.*, **27**, 3441, 3449, 3455 (1962).

(5) G. A. Olah and M. W. Meyer, *ibid.*, **27**, 3464 (1962).

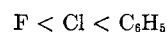
TABLE I
ISOMERIZATION OF FLUOROBIPHENYLS WITH WATER-PROMOTED ALUMINUM CHLORIDE

Reaction time	Temp., °C	% Fluorobiphenyl isomer distribution		
		<i>ortho</i>	<i>meta</i> normalized	<i>para</i>
2-Fluorobiphenyl				
5 min.	140	95.7	3.8	0.5
7		59.3	30.8	9.9
10		42.7	43.5	13.8
15		23.8	54.6	21.6
30		20.0	56.6	23.4
60		18.9	57.5	23.6
24 hr.		12	57	31
275		13	58	29
5 min.	200	14.4	59.4	26.2
10		18.0	51.1	23.9
15		16.5	57.5	26.0
20		15.8	57.5	26.7
25		15.8	57.9	26.3
30		14.2	59.4	26.4
60		13	57	30
3-Fluorobiphenyl				
60 min.	140	14.6	59.1	26.3
180		14	60	26
30	200	12	58	30
60		13	59	28
4-Fluorobiphenyl				
2 min.	140	0	1.5	98.5
4		0	10.5	89.5
6		0	23.6	76.4
10		5.2	48.3	46.5
15		6.3	51.7	42.0
30		7.5	58.2	34.3
60		9.0	60.3	30.7
120		10.5	59.9	29.6
240		10.2	58.8	31.0
5 min.	200	10.5	58.0	31.5
10		9.9	60.6	29.5
15		11.2	58.4	30.4
20		12.1	57.4	30.5
25		11.9	58.5	29.6
30		12.6	56.4	31.0
60		11.5	58.0	30.5

TABLE II
ISOMER DISTRIBUTION OF SUBSTITUTED BIPHENYLS
R-C₆H₄-C₆H₅

R	% Isomer in equilibrium mixture		
	<i>ortho</i>	<i>meta</i>	<i>para</i>
F	13	58	29
Cl	3	64	33
C ₆ H ₅	0	63	37

The decreasing amount of *ortho* isomer is in accordance with the increasing steric requirement of the following groups.



Experimental

Materials.—*ortho*- and *para*-fluorobiphenyl were obtained from Columbia Organic Chemicals Co., Columbia, S. C. *meta*-Fluorobiphenyl was prepared using the procedure as given by Elks, Haworth, and Hey.⁶

Isomerization Procedure.—The amounts of substrate and catalyst in each experiment were 2.0 g. of fluorobiphenyl and 0.3 g. of Al₂Cl₆. To this mixture 0.01 ml. of water was added from a syringe. Isomerizations were carried out in sealed tubes. Prod-

(6) J. Elks, J. W. Haworth, and D. H. Hey, *J. Chem. Soc.*, **1940**, 1284.

ucts were recovered by extraction with boiling carbon disulfide in the presence of water. After drying with calcium chloride the extract was submitted to gas-liquid chromatographic and infrared analysis. The infrared analysis was carried out using the following bands.

<i>ortho</i> -Fluorobiphenyl.....	1110 cm. ⁻¹
<i>meta</i> -Fluorobiphenyl.....	879 cm. ⁻¹
<i>para</i> -Fluorobiphenyl.....	837 cm. ⁻¹
Biphenyl.....	737 cm. ⁻¹

The accuracy of the infrared analyses based on mixtures of known composition is within ± 3 relative %. The gas-liquid chromatographic analysis has been reported previously.⁷

Separation of the *ortho* isomer from the *meta-para* isomer was good, that of *meta* from *para* reasonable with a higher error of determination when the *meta* isomer was present only in small amounts. Separation of *para* and *meta* isomers on more loosely packed columns than those used in previous work⁷ gave shorter retention times and poorer separation. It was possible to obtain partial separation of *meta-para* isomers by lowering the column temperature to 160° with retention times of *meta* isomer of 55.6 and *para* isomer of 56.5 min. (Previous retention times at 190° were 38 and 40 min. on the tightly packed columns used, but only 18 min. under the same conditions, without separation, on presently used looser column.) As these conditions were unsatisfactory, isomer mixtures were analyzed by combining gas chromatography and infrared analyses. The *ortho* isomer was well separable from the combined *para-meta* isomers by gas chromatography and the *para* and *meta* isomers could be determined by infrared analysis. Gelay columns (polypropylene glycol) were tried and found unsuitable for the *para-meta* separation.

The normalized per cent isomers in Table I are believed to be correct to within ± 1 unit, based on treatment and analysis of mixtures of known composition.

Acknowledgment.—We thank Dr. D. S. Erley of the Chemical Physics Research Laboratory, The Dow Chemical Co., Midland, Michigan, for carrying out the infrared analyses.

(7) G. A. Olah and W. S. Tolgyesi, *J. Org. Chem.*, **26**, 2053 (1961).

Molecular Weight Determination by N.m.r. Spectroscopy

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In contrast to other types of spectroscopy used in organic chemistry, nuclear magnetic resonance spectroscopy can be used for quantitative analytical measurements without the knowledge of extinction coefficients, since such a coefficient is constant and independent of the chemical environment of the nuclei under inspection. This makes n.m.r. spectroscopy a very powerful quantitative tool. So far, its application¹ includes the measurement of extent of isotope substitution, the analysis of mixtures, per cents of hydrogen, proton counting, and interpretation of spectra in general, where integration is combined with chemical shift and splittings measurements.

We propose to apply n.m.r. integration for the determination of molecular weights. The method consists of comparing the integrated intensities of an added standard and a recognizable peak or group of

peaks of the unknown in a solution containing a known weight of standard and unknown. The molecular weight is then given by the following formula.

$$M = \frac{I_s n W M_s}{I n_s W_s}$$

- M = the molecular weight of the unknown
 I_s = the intensity of the standard
 I = the intensity of the unknown
 n = the number of protons in the recognizable peak or group of peaks of the unknown
 n_s = the number of protons of the standard peak
 W = the weight of the unknown
 W_s = the weight of standard
 M_s = the molecular weight of standard

The method can be combined with taking the n.m.r. spectrum of the unknown; the only extra work required is the weighing of sample and standard, and the calculation. The values are not affected by dissociation and solvent interaction phenomena or various other effects that cause great errors in methods dependent on ideality in colligative properties of liquids. The error resulting from impurities is proportional to their weight and not to the molar amount. On the assumption that most impurities are smaller molecules than the unknown, this method gives smaller errors than the cryoscopic, etc., methods. The standard also serves as a marker for chemical shift calibration. Hopefully, in the future n.m.r. tubes and spectrometers can be standardized, stabilized, and precalibrated well enough, so that precise integrations can be performed without the use of a standard, similarly to our present-day ultraviolet intensity measurements.

On the other hand the method requires that at least one peak or group of peaks of the unknown be recognized as to the number of protons it contains; this absorption should not overlap with others, since otherwise the integration is very subjective. Molecules related as monomers and symmetrical dimers cannot easily be distinguished by the n.m.r. method, since they show very similar spectra. In some other cases too, difficulties arise in assigning a chosen absorption the number of hydrogens it represents. In general, however, one knows which hydrogens of a known starting material should end up unchanged in an unknown product under given reaction conditions, and use those for the determination. The choice can best be made once the n.m.r. spectrum is taken and perhaps integrated.

Experimental

The Standard.—Based on our experience the most suitable standard is hexamethyl cyclotrisiloxane, m.p. 64.5°, b.p. 133°, a very soluble inert solid, which can be removed by sublimation. There is no loss by sublimation if it is weighed last and dissolved and stoppered immediately. Its absorption at 9 c.p.s. is conveniently outside other absorptions. Any other (preferably) single peak pure material can be used as standard if its absorption can be separately seen in the spectrum. All these standards mark the chemical shift scale at the same time, and no tetramethylsilane is needed. Other possible standards include: iodoform at 294, benzoquinone at 406, *p*-dinitrobenzene at 507, and 1,3,5-trinitrobenzene at 566 c.p.s. The nitroaromatic standards should be used with caution, since occasional complex formation with aromatic unknowns offsets the results.

Procedure.—The unknown and standard should be weighed into the n.m.r. tube to give about equal intensities, completely homogenized with solvent, the spectrum taken, integrated, the chosen absorption and standard individually integrated accurately, utilizing the full chart range for the bigger of the two,

(1) "Quantitative Measurements by High Resolution NMR," Varian Associates technical information bulletin, Vol. 3, No. 1.