TABLE I

			Calcd.				Found				Fluoroborates[a]	
Anthraquinone	Yield, %	M.p., °C.	C	H	F	Cl	C	H	F	Cl	Yield, %	Dec. temp., °C.
1-Fluoro-	57	226–227	74.4	3.1	8.42	. . .	74.35	3.13	8.37	. . .	85[b]	146–147
2-Fluoro-	68.5	203–204	74.4	3.1	8.42	. . .	74.45	3.07	8.31	. . .	95[c]	113–114
1,5-Difluoro-	53.5	230–231	68.8	2.46	15.57	. . .	69.1	2.47	15.24	. . .	95[d]	180–181
2,6-Difluoro-	65	228–229	68.8	2.46	15.57	. . .	69.2	2.44	15.46	. . .	98[c]	115–118
1-Fluoro-4-chloro-	. . .	164–166			7.3	13.65			7.21	13.7	82[e]	180–182
1-Fluoro-5-chloro-	42	215–216	64.5	2.3	7.3		64.3	2.3	7.17		87[f]	165–167
1-Fluoro-2-carboxylic acid-	. . .	219–222	66.7	2.59	7.04		66.8	2.56	6.97	. . .	45[e]	165–166
1-Fluoro-4-chloro-2-carboxylic acid-	. . .	224–225			6.23	11.65			6.1	11.8	51[e]	160–162
1-Chloro-2-fluoro-	54	183–184			7.3	13.65			7.32	13.5	77[d]	193–194
1-Fluoro-4-methoxy-	33	208–209	70.3	3.52	7.42		70.25	3.51	7.36		76[b]	188–189
1-Fluoro-2-methyl-	53	177–178	75	3.75	7.92		74.9	3.76	7.56		90[b,g]	160–161
1-Fluoro-2-methyl-4-chloro-	52	191–192	65.6	2.92	6.93	12.93	65.7	2.94	6.84	13.0	79[b]	179–180

[a] Mono- or bis- corresponding to the fluoroanthraquinones listed; precipitated from water solution of the corresponding diazonium sulfate unless indicated otherwise. Decomposition performed: [b] In *o*-dichlorobenzene. [c] In chlorobenzene. [d] In trichlorobenzene. [e] Without solvent. [f] In nitrobenzene. [g] Precipitation from water suspension.

at a temperature of 10 to 15°, a solution of 15 g. of sodium nitrite in 150 ml. of concentrated sulfuric acid was added. The gray diazonium salt solution which resulted was further stirred for 2 hr. and then poured into the necessary amount of ice. The gray precipitate formed was passed through a glass filter and when still wet dissolved in about a liter of water at 15–20°, and filtered from the impurities to yield a brownish filtrate. A 60-ml. aliquot of 40% fluoroboric acid solution was then added with stirring and yielded a heavy yellowish precipitate of **anthraquinone 1-diazonium fluoroborate.** It was filtered, washed with water to neutral, then further treated with methanol and dried *in vacuo;* yield 24.2 g. (85%). Dec. temp. 146–147°. If the diazonium sulfate removed by filtration is added to less water, a suspension is obtained. The addition of fluoroboric acid solution to such a suspension followed for 1 hr. by stirring, transforms the gray diazonium sulfate to the yellowish diazonium fluoroborate. The salt prepared in this way is produced in higher yield than in the first case (91%) but possesses a lower decomposition temperature (137–138°).

A 24.2-g. portion of the prepared salt was suspended in 150 ml. of *o*-dichlorobenzene. The suspension was slowly heated to reflux with stirring, so to avoid violent decomposition. Then after the evolution of boron trifluoride had ceased (*ca.* 1 hr.) some decolorizing carbon was added. The solution was filtered hot, and the **1-fluoroanthraquinone** crystallized from the filtrate on cooling. The crystals were filtered off and washed with methanol, until the *o*-dichlorobenzene was completely removed, and then dried. A yellow crystalline product with a m.p. of 219–221° was obtained; it was recrystallized from chlorobenzene, m.p. 234–235°, and further purified by sublimation, m.p. 234–236°.

2,6-Difluoroanthraquinone.—A 20-g. sample of 2,6-diaminoanthraquinone was added with stirring to 250 ml. of concentrated sulfuric acid. To the solution, at a temperature of 10–15° a solution of 28 g. of sodium nitrite in 250 ml. of sulfuric acid was slowly added. The gray solution resulted was further stirred for 1 hr. and then poured over ice. The precipitated bisdiazonium sulfate was filtered off and then dissolved into 2 l. of water. To the orange solution being filtered from the insolubles, 70 ml. of 40% fluoroboric acid was added. A 35-g. sample of **anthraquinone, 2,6-bisdiazonium fluoroborate** was obtained (98% yield); dec. temp. 115–116°.

The decomposition was carried out in 300 ml. of chlorobenzene. The **2,6-difluoroanthraquinone** crystallized after cooling and had a m.p. of 225–226° which after recrystallization from chlorobenzene, increased to 228–229°; yield 13 g. (65%).

Friedel-Crafts Isomerization. V.[1a] Aluminum Chloride-Catalyzed Isomerization of Terphenyls

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Examples of the migration of phenyl groups in substituted aromatics are not as numerous as for alkyl or halogen substituents.

A number of thermal rearrangements are known: the rearrangement of 1-phenyl indene to the 2-phenyl isomer,[1b] the isomerization of 1-phenyl naphthalene to 2-phenyl naphthalene,[2] and the formation of 2,3-benzfluorene from 1-*o*-anisyl naphthalene.[3] In a patent, Swisher[4] reported the isomerization of the terphenyls using varying amounts of aluminum chloride at temperatures ranging from 140 to 220° and reported the formation of 65 to 70% *m*-terphenyl. Weingarten[5] reported intra- and intermolecular halogen migration as well as intramolecular phenyl migration in the aluminum chloride–

(1a) Part IV, G. A. Olah and M. W. Meyer, *J. Org. Chem.*, **27**, 3464 (1962); (1b) I. v. Braun and G. Manz, *Ber.*, **62**, 1059 (1929).

(2) F. Mayer and R. Schiffner, *ibid.*, **67**, 67 (1934).

(3) M. Orchin and L. Reggel, *J. Am. Chem. Soc.*, **70**, 1245 (1948).

(4) R. D. Swisher, U. S. Patent 2,363, 209 (1944) (Monsanto Chemical Co.).

(5) H. Weingarten, Abstract of Papers, American Chemical Society, 140th National Meeting, Chicago, Illinois, p. 56-Q.

hydrogen chloride-catalyzed rearrangement of mono- and dichlorobiphenyls and assumed the transition state of the phenyl migration to consist of a bridged phenonium ion as postulated by Cram.[6]

To obtain information on the migration of phenyl groups under Friedel-Crafts' conditions, the isomerization of *o*-, *m*-, and *p*-terphenyl with water-promoted aluminum chloride was investigated. In order to be independent of traces of moisture present in substrate and catalyst, as well as to promote the reaction (which in the absence of added water as co-catalyst is much slower and under strictly anhydrous conditions might not take place) a known, constant amount of water was added as cocatalyst in each experiment. The results are summarized in Table I.

TABLE I

ISOMERIZATION OF TERPHENYLS WITH WATER-PROMOTED ALUMINUM CHLORIDE

Terphenyl	Reaction time, hr.	Temp., °C.	% terphenyl isomer distribution *ortho*	*meta* normalized	*para*
ortho	2	140	70	30	0
	4	140	59	32	9
	19	140	7	70	23
	2.5	210	0	75	25
	4.5	210	0	62	38
	4.5	210	0	63	37
meta	2	140	0	84	16
	4	140	0	71	29
	19	140	0	63	37
	1.5	210	0	64	36
	4.5	210	0	63	37
para	5 min.	180	0	25	75
	10 min.	180	0	36	64
	15 min.	180	0	52	48
	20 min.	180	0	65	35
	1.25	200	0	63	37
	2.5	200	0	64	36
	1.25	210	0	63	37
	2.5	210	0	62	38

The equilibrium mixture obtained starting with any one of the isomers consists of about 63% *m*- and 37% *p*-terphenyl with no *ortho* isomer present. There is little variation in the composition of the final mixtures with temperature and time, and they are believed to be corresponding to thermodynamic equilibrium. From the figures for the rearrangement of *o*-terphenyl it appears that the migration of the phenyl group takes place by intramolecular 1,2-shift, the *para* isomer appearing only after the formation of a substantial amount of *meta*. A 1,2-shift is also assumed in the isomerization of *m*- and *p*-terphenyl. In all experiments the terphenyls accounted for 70 to 85% of the material balance, the rest being high molecular weight tarry materials which were not further investigated.

The absence of *o*-terphenyl in the equilibrium mixture is not surprising for steric reasons. X-ray diffraction studies showed the arrangement of the rings to be nonplanar, the two outer phenyl groups being rotated through approximately 45° in the same direction which brings them into a position roughly orthogonal to the central ring.[7] Assuming the compound to have a similar configuration under our experimental conditions, it appears that the steric requirements for the formation of *o*-terphenyl from the *meta* isomer are unfavorable. Models show that the spatial arrangement of the phenyl groups in *m*-terphenyl must be nearly co-planar and not too different from that of *p*-terphenyl which is known to be co-planar in the solid state.[8]

Experimental

Isomerizations were carried out in sealed Pyrex glass tubes at temperatures and periods of time given in Table I. The amounts of substrate and catalyst in each experiment were 3.0 g. of appropriate terphenyl isomer and 0.3 g. of Al_2Cl_6 ($\sim$8 mole %). To this mixture 0.015 ml. of water was added from a syringe. Products were recovered by extraction of the reaction mixtures with boiling carbon disulfide, in the presence of water. After drying with calcium chloride, the extract was submitted to infrared analysis using the following bands: 11.90 μ for *o*-terphenyl, 12.55 and 11.25 μ for *m*-terphenyl, and 11.95 μ for *p*-terphenyl. The accuracy of measurement is believed to be within ±3 relative per cent (as checked on mixtures of known composition). The terphenyls were Eastman grade laboratory chemicals. No impurity bands could be detected and purity of 99+% was assumed.

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

[7] I. L. Karle and L. O. Brockway, *ibid.*, **66**, 1974 (1944).

[8] L. W. Pickett, *Proc. Roy. Soc.* (London), **A142**, 333 (1933).

Cyclization of 2,4-Dinitrophenylacetic Acid

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During the course of investigation on reactive methylene compounds,[2-4] it was noticed that 2,4-dinitrophenylacetic acid, when heated in sulfuric acid for two hours at 120–130°, cyclized to a bicyclic compound (I), $C_7H_4N_2O_3$. I formed a salt with hydrazine hydrate and could be regenerated by hot water. It reduced Tollen's reagent and decolorized potassium permanganate solution. This compound on heating with sodium dichromate and sulfuric acid was oxidized to 5,5′-dinitroazoxybenzene-2,2′-dicarboxylic acid (II) and was hydrolyzed with sodium carbonate solution to 2-amino-4-nitrobenzoic acid. The properties and transformations indicate that the compound (I) is probably 6-

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[2] H. G. Garg and S. S. Joshi, *J. Org. Chem.*, **26**, 946 (1961).

[3] H. G. Garg, *ibid.*, **26**, 948 (1961).

[4] H. G. Garg, *ibid.*, **27**, 1045 (1962).