

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF MCGILL UNIVERSITY AND THE B. F. GOODRICH CO.]

Aryliododihalides as Halogenating Agents

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The purpose of the work outlined in this paper was to investigate the use of aryliododifluorides as fluorinating agents. As a preliminary study the chlorinating action of phenyliododichloride was compared with that of chlorine gas.

Chlorination of ethylenic compounds with phenyliododichloride gave either the same products as chlorine gas or no chlorinated product. In all cases the reaction was less vigorous than with chlorine. The milder reaction and the convenience of handling a solid are the possible advantages of phenyliododichloride as a chlorinating agent

For fluorination *p*-tolyliododifluoride was used because it is an easily purified solid, it can be prepared and used in glass apparatus, and its chloroform solution is stable for several days. With this chloroform solution the simple olefins and stilbene gave mixtures. Rubber gave with evolution of hydrogen fluoride a white, amorphous powder, apparently a monofluoro derivative of rubber. While these products were not identified definitely due to difficulties in purification, the indications were that the iododifluoride acted as a direct fluorinating agent at the double bond and that the resulting olefin difluoride decomposed with evolution of hydrogen fluoride. This interpretation received confirmation when Henne and Midgley¹ showed that 1,2-olefin difluorides readily lose hydrogen fluoride.

p-Tolyliododifluoride reacted with certain aromatic polynuclear hydrocarbons and ketones to give two types of product, one formed by the substitution of hydrogen by fluorine and the other by a coupling reaction. Acenaphthene gave diacenaphthene. Anthrone formed dianthrene. Pyrone gave a monofluoropyrene and a dipyrenyl. Anthracene and benzanthrene gave only monofluoro derivatives, Bockemüller² has reported that diethylaniline gave *p*-fluorodiethylaniline and tetraethylbenzidine.

Experimental

I. Preparation of Iododihalides.—Dry chlorine was passed into 50 g. of iodobenzene in 500 cc. of chloroform, with external cooling to keep the temperature below 25°, as

long as a precipitate formed. The yellow, air-dried product weighed 65 g. (95% yield). In the chlorination of *p*-iodotoluene, cooling was avoided, since the product that separated from a warm solution was much easier to filter; the yield was 90%, this dichloride being more soluble in chloroform.

The iodoso compounds were secured by adding either of the above to a solution of 15 g. of sodium hydroxide in 800 cc. of water, with vigorous stirring for an hour. The next day, the pale yellow precipitate was filtered, washed well, and air-dried; the dry substance was then washed twice with chloroform. The yields were 95 and 85%, respectively.

To secure the difluoride, 100 g. of *p*-iodosotoluene was dissolved in 400 cc. of glacial acetic acid at room temperature (a solid separates on standing) and 100 cc. of technical 46% hydrofluoric acid added with stirring. A small amount of solid soon separated, and on adding water to make the total volume 800 cc. a crystalline precipitate formed. Since the solid is unstable, it was filtered and at once dissolved in chloroform; such solutions could be kept for two days and were used in the fluorination experiments.

All reactions were carried out in Pyrex glass apparatus; etching was not as great as might be expected. An excess of the reagent was used in all cases.

II. Experiments with Phenyliododichloride.—A mixture of 13 g. of the freshly prepared reagent, 10 g. of benzalacetophenone, and 600 cc. of ethylene dichloride was heated slowly to the boiling point; the solution became clear after thirty minutes of refluxing. The solvent and iodobenzene were recovered by steam distillation, the residue taken up in ether, and dried with calcium chloride. After removal of the solvent, 12.7 g. (95.5%) of mixed dichlorides was left. These were separated by fractional crystallization into the two stereoisomers, m. p. 113 and 86°, as described in the literature.³

In a similar manner, stilbene, dibenzalacetone, and *trans*-dibenzoyl ethylene were converted into chlorides. In each instance a check was secured by carrying out a direct chlorination; the yields and melting points were essentially the same. Cinnamic acid was not affected by the reagent. Of the aliphatic hydrocarbons, only pentene-2 gave a satisfactory product; caprylene and cyclohexene gave dichlorides, but the boiling points were so near that of iodobenzene that a complete separation was not accomplished. Styrene gave a polymer on attempted distillation of the reaction product. Benzene was unattacked.

III. Reactions with *p*-Tolyliododifluoride.—As stated in the introduction, these gave coupling and/or substitution products in most instances where a reaction occurred. The general procedure was the same with all substances; a chloroform solution containing 8.5 g. of the reagent (assuming a quantitative yield in its preparation) was added to 6 g. of the substance in 50 cc. of chloroform. Any vis-

(1) Henne and Midgley, *This Journal*, **58**, 882 (1936).

(2) Bockemüller, *Ber.*, **64B**, 522 (1931).

(3) Some of the preliminary experiments were performed by Mr. James C. McGuire; his assistance is gratefully acknowledged.

TABLE I
 PROPERTIES OF THE NEW SUBSTANCES

No.	Name	M. p., °C.	Formula	Crystal form	Solvent	Yield, %
1	Diacenaphthyl	174	C ₂₄ H ₁₈	Needles	Acetone-methanol	17 ^a
2	Fluoropyrene ^b	113	C ₁₆ H ₉ F	Bronze plates	Methanol	40
3	Dipyrenyl ^b	...	C ₃₂ H ₁₈	Fine prisms	Trichlorobenzene	50
4	Difluoroanthyl ^c	360	C ₃₂ H ₁₈	Plates	Acetic acid	1
5	9-Fluoroanthracene ^d	110	C ₁₄ H ₉ F	Prisms	Hexane	18 ^a
6	Bz- <i>x</i> -Fluorobenzanthrone	186	C ₁₇ H ₁₀ OF	Rods	Acetic acid	56 ^a

ANALYSES

No.	C	Calcd. H	F	Mol. wt.	C ^e	Found H	F ^f	Mol. wt.
1	94.1	5.9		306	94.0	6.0		295
2	95.5	4.5		402	95.6	4.4		412
3	87.3	4.1	8.7		87.0	4.2	4.3	8.8
4	95.5	4.5			95.3	4.3		
5	85.7	4.6	9.7		85.4	4.8	9.1	
6	82.3	3.7	7.7		82.2	3.6	8.0	

^a This represents the amount of analytically pure material; the actual yields were, doubtless, greater, but quantitative separations were not attempted. ^b After steam distillation, the residual solid was dissolved in technical trichlorobenzene, filtered, treated with animal charcoal, and the solvent steam distilled. The residue was extracted with acetone, but could not be crystallized satisfactorily from any available solvent; it was analyzed and assumed to be dipyrenyl. It softened at about 250°, and was all liquid at 300°. The acetone extract deposited the fluoropyrene. ^c This reaction was successful only once, the hydrocarbon being recovered unchanged in all other attempts. ^d An immediate evolution of hydrogen fluoride was noticed; after five days the solution was worked up as above. Ten grams of anthracene gave 7 g. of a mixture, composed of unchanged hydrocarbon and the fluoro derivative. Separation was accomplished by fractional solution in hexane (60–68° fraction of petroleum ether.) ^e Satisfactory combustions were accomplished using a Pyrex tube containing both copper oxide and lead chromate, and mixing the sample with copper oxide in the boat. ^f General procedure of Hahn and Reed [THIS JOURNAL, 46, 1645 (1924)] but with the substitution of 1 g. of sodium perchlorate for 1 g. of starch; 0.4 g. of sample required 12–14 g. of sodium peroxide. For the loan of the bomb and use of facilities we are indebted to Drs. J. T. Donald and S. G. Lipsett of J. T. Donald & Co., Ltd., Montreal.

ible change (darkening, warming) was noted, and, after being allowed to stand for forty-eight hours, the solution was worked up by an appropriate procedure. If there was no visible evidence of reaction, the solution was refluxed on the steam-bath for a half hour. Steam distillation removed the solvent, aryl iodide, and, in some cases, unreacted starting material. The residual solid was then removed, taken up in a suitable solvent, treated with a decolorizing carbon and purified.

By this procedure monofluorides were obtained from pyrene, anthracene, and benzanthrone; coupling products resulted with acenaphthene, pyrene, fluoranthene, and anthrone.⁴

Ten grams of the reagent in 100 cc. of benzene was added to 2.6 g. of rubber in 50 cc. of benzene. The solution slowly became lighter in color and fumed somewhat. After standing for five days the benzene solution was poured into 500 cc. of alcohol. The colorless, amorphous precipitate was filtered, washed with fresh alcohol, and dried. The analysis for fluorine showed 17.3%. The theoretical for one atom of fluorine to each C₆H₈ unit is 22%.

It was impossible to determine the nature of the products from stilbene, pentene-2, caprylene and cyclohexene, owing to the difficulties of purification. Aniline, the three toluidines, and phenol gave tars. There was no reaction with naphthalene, fluorene, phenanthrene, 1-phenylcyclohexene, 1,4-diphenylbutadiene, anisole, acetanilide, ben-

zalacetophenone, *trans*-dibenzoyl ethylene, benzoylphenylacetylene, anthraquinone and β -methylanthraquinone. The properties of the new substances are summarized in Table I.

The structure of the 9-fluoroanthracene was shown by oxidation, when anthraquinone resulted; the fluorine atom is thus on the *meso* carbon atom. In the case of the fluorobenzanthrone oxidation gave anthraquinone- α -carboxylic acid, identified as the methyl ester.⁵ Thus the fluorine atom is in the *benz* ring. A direct comparison with Bz-1-fluorobenzanthrone, m. p. 192–193°, prepared as directed⁶ showed their non-identity. Thus, it is *benz*-2 or 3-fluorobenzanthrone.

The fluorine atom in these substances is characterized by its complete inactivity. Thus, the Beilstein test is negative; further, when *p*-fluoroacetophenone was heated in a sealed tube for eight hours, with potassium and cuprous cyanides, it was recovered unchanged.⁷

Summary

Phenyl iododichloride as a chlorinating agent gave the same products as chlorine gas, but the reaction was milder.

p-Tolyliododifluoride acts as a fluorinating agent. The reaction is not general. With a few

(5) Allen and Overbaugh, THIS JOURNAL, 57, 744 (1935).

(6) Lüttringhaus and Neresheimer, Ann., 473, 186 (1929).

(7) Method of Rosenmunde and Struck, Ber., 52, 1749 (1919).

(4) Anthrone gave some anthraquinone unless air was excluded.

polynuclear aromatic substances it acts as a coupling agent.

The fluorine atom in fluorobenzanthrone is in the 2- or 3- position of the *benz* ring. This is un-

usual since most reagents substitute in the 1-position in this ring.

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Vapor-Liquid Equilibria of Methylcyclohexane-Toluene Mixtures

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During the course of work on the fractionation and composition of straight-run gasolines, efficient large scale fractionating columns have been developed. It has been found that binary mixtures of hydrocarbons are most suitable for determining the efficiencies of such columns. The equilibria of a number of binary hydrocarbon mixtures have already been presented.^{1,2} However, in selecting a pair of hydrocarbons for such efficiency tests, particularly on large scale columns taking a charge of many gallons of material, consideration must be given to the ease of analyzing the equilibrium mixtures obtained, the purity possible of the starting materials, the ease with which they may be further purified if necessary, and their cost and availability. Because methylcyclohexane and toluene seemed to be a pair of hydrocarbons which fulfilled these prerequisites, their vapor-liquid equilibria have been obtained at normal pressures.

Properties of Materials

The methylcyclohexane was a technical grade obtained from the Eastman Kodak Company. It was purified by shaking with concentrated sulfuric acid, neutralizing with sodium carbonate, washing with water, and fractionating. Two different lots of methylcyclohexane were used and they had the following properties:

	No. 1	No. 2
Boiling point at 760 mm., °C.	100.85	100.85
Density, d^{20}_4	0.7695	0.7692
Refractive index, n^{20}_D	1.4234	1.4235

Later work in this Laboratory has shown that methylcyclohexane of sufficient purity without any treatment, for testing fractionating columns, may be obtained from the Rohm and Haas Company of Philadelphia.

The toluene for equilibrium determinations was obtained by carefully fractionating a nitration grade obtained from the Barrett Company of New York. Two different lots were used and had the following properties.

	No. 1	No. 2
Boiling point at 760 mm., °C.	110.6	110.6
Density, d^{20}_4	0.8658	0.8663
Refractive index, n^{20}_D	1.4965	1.4965

For test purposes the nitration grade of toluene as purchased is not of sufficient purity. Experience has shown that its fractionation in batch columns having up to 75 perfect plates yields only 50 or 60% of suitable material, the first 20-30% and the last 15-20% being unsuitable. A high reflux ratio should be maintained during the separation of the initial undesirable material, though it may be reduced appreciably when the middle portion is being fractionated.

Procedure

The equilibrium mixtures were obtained at ordinary barometric pressure by means of the Othmer equilibrium still³ used in previous work.² Analyses of these mixtures were made by density, refractive index, and boiling point determinations as before.² Density and refractive index measurements are probably accurate to within ± 0.0002 while boiling point measurements are probably accurate to no better than ± 0.05 to $\pm 0.1^\circ$. Because of the possible inaccuracy of the latter it cannot be too strongly stressed that definite conclusions as to the validity of equilibrium data should not be drawn from this property alone as has been done by Beatty and Calingaert.¹

Results

The equilibrium data obtained on mixtures of methylcyclohexane and toluene are the result of two entirely separate investigations by different experimenters. The 69 points of equilibria obtained from density, refractive index, and boiling point measurements were plotted on a large curve 100 cm. square similar to the smaller curve shown in Fig. 1 and the best representative curve was drawn. Because the refractive index and density determinations were more accurate than the boiling points, greater weight was given to them in drawing the equilibrium curve. The data presented in Table I are points taken from this large smoothed curve. The refractive index,

(1) Beatty and Calingaert, *Ind. Eng. Chem.*, **26**, 504, 904 (1934).

(2) Bromley and Quiggle, *ibid.*, **26**, 1136 (1933).

(3) Othmer, *Ind. Eng. Chem.*, **20**, 743 (1928); *ibid.*, *Anal. Ed.*, **4**, 233 (1932).