

UNITED STATES PATENT OFFICE

EDGAR C. BRITTON AND WESLEY C. STOESSER, OF MIDLAND, MICHIGAN, ASSIGNORS
TO THE DOW CHEMICAL COMPANY, OF MIDLAND, MICHIGAN, A CORPORATION OF
MICHIGAN

HALOGENATION OF MULTINUCLEAR AROMATIC HYDROCARBONS

No Drawing.

Application filed June 24, 1929. Serial No. 373,473.

The present invention relates to methods for chlorinating or halogenating multinuclear aromatic hydrocarbons of the type represented by diphenyl, and has particular regard to such methods wherein the reaction is carried out in an organic solvent medium.

solvents the lower chlorinated derivatives of the aforementioned aromatic hydrocarbons are likewise well suited, examples of such being chlorbenzene, o-dichlor-benzene, the chlor-toluenes, etc.

Taking diphenyl, for example, as the simplest compound of the type in question, this compound has been chlorinated directly by passing chlorine into the molten material, using a catalyst such as antimony pentachloride or iodine. Such method, however, is difficult to control, especially when it is desired to prepare the mono-chlor derivative, due to the strong tendency to formation of dichlor- and higher chlorinated derivatives at the temperature above 70° C. necessarily employed. The use of solvents in which to carry out the chlorination or halogenation has been proposed, for example, carbon bisulphide. The latter, however, suffers from a serious objection because of its volatility and the very inflammable nature of its vapors. The use of carbon bisulphide for such a reaction, therefore, involves considerable hazards, particularly for operations to be conducted in large scale commercial apparatus. A safer and more easily controlled solvent for the present reaction is much to be desired.

It is well known that benzene and related aromatic hydrocarbons, such as toluene, the xylenes and the like, are readily halogenated at ordinary temperatures. For this reason it was to be expected that the use of such hydrocarbons as solvents for carrying out the halogenation of other organic compounds would be out of the question. We have made the unexpected discovery, however, that certain organic compounds when dissolved in benzene, toluene or the like and subjected to the action of a halogen are preferentially halogenated. In fact, the reaction is so selective that the solvent remains substantially unattacked by the halogen until the dissolved compound has been entirely halogenated at least to the corresponding dihalogenated derivatives. Among the compounds capable of being thus selectively halogenated are diphenyl, naphthalene, the phenols, etc. As

In a pending joint application of E. C. Britton and W. R. Reed, Serial No. 158,818, filed January 3, 1927, now Patent No. 1,784,267, is disclosed a method of chlorinating naphthalene in accordance with the present general method of procedure. The present application specifically describes the procedure as applied to the halogenation of diphenyl and related multinuclear aromatic hydrocarbons. To the accomplishment of the foregoing and related ends, the invention, then, consists of the steps hereinafter fully described and particularly pointed out in the claims, the following description setting forth in detail but a few of the various ways in which the principle of the invention may be used.

For the purpose of illustrating the application of our improved method we shall describe it more particularly with reference to the chlorination of diphenyl, but the method is equally adapted to the chlorination of related multinuclear aromatic hydrocarbons, such as ditolyl, phenyl-tolyl and the like, as well as to the bromination thereof.

Diphenyl may be chlorinated by passing chlorine into the benzene solution thereof at temperatures varying from about -10° to 40° C., and preferably in the presence of a catalyst such as finely divided metallic iron, anhydrous ferric chloride or the anhydrous chlorides of other metals such as cobalt, aluminum, antimony, etc. The principal products formed consist of the ortho- and para-chlor-diphenyl as well as various isomeric dichlor-diphenyls. At the lower temperatures mentioned, the tendency is greater toward the formation of para-chlor-diphenyl while at higher temperatures there is greater tendency toward the formation of the ortho-chlor-derivative. The proportion of chlorine introduced is preferably restricted to somewhat less than one molecular equivalent when it is desired to prepare the mono-chlor-derivatives, owing to the readiness with which

the dichlor-derivatives are produced. It has been observed, also, that, when the mono-chlor-derivatives are converted to the dichlor-derivatives with continued chlorination, there is a distinct tendency for para-chlor-diphenyl to be further chlorinated before there is any substantial further chlorination of ortho-chlor-diphenyl.

The relative proportions of diphenyl and solvent may be varied between rather wide limits without materially affecting the result. Conveniently, diphenyl may be dissolved in from one to four times its weight of solvent, but either more or less of the solvent may be used, if desired. Such solvent may be readily recovered from the reaction product by simple distillation. For operation at ordinary temperatures, we have found that benzene gives very satisfactory results and in general is preferred to other solvents mentioned on account of its lower cost. In carrying out chlorinations at temperatures in the neighborhood of 0° C. or lower, however, it is sometimes advisable to employ a solvent which is fluid at such temperatures, such as toluene, chlorbenzene, ortho-dichlor-benzene, etc.

In the following specific examples, various ways of carrying out the invention are illustrated, but it is expressly understood that the invention is not limited thereto.

Example 1.—A quantity of 770 grams (5 moles) diphenyl was dissolved in 1500 cc. benzene. The solution was placed in a suitable flask provided with stirring means, 7.7 grams iron filling and .8 grams iodine added, and then chlorine was introduced while maintaining the temperature between -10° and 0° C. The introduction of chlorine was stopped when 80 per cent of the theoretical amount thereof required for converting all of the diphenyl present to the mono-chlor-derivatives had been added, the time required being 4 hrs. The reaction mixture was filtered and then fractionally distilled under reduced pressure whereby the following yield of materials was obtained:—unchanged diphenyl, 30 per cent; ortho-chlor-diphenyl (B. P. 210–211° C. at 150 mm. pressure), 27 per cent; para-chlor-diphenyl (B. P. 224–226° C. at 150 mm. pressure), 34 per cent; higher chlorinated products, chiefly dichlor-diphenyl derivatives, 17 per cent.

Example 2.—The same quantities of materials were taken as in Example 1 and the temperature of chlorination was maintained between the same limits. The introduction of chlorine, however, was continued for a longer period until 94 per cent of the theoretical amount necessary to convert all of the diphenyl to the mono-chlor-derivative had been introduced, the total time of reaction being 8 hours. The reaction product upon fractionation yielded ortho-chlor-diphenyl, 37 per cent, 4,4'-dichlor-diphenyl (B. P. 327–

329° C. at 750 mm. pressure), 31 per cent; and 30 per cent isomeric dichlor-diphenyl derivatives, (B. P. 240–242° C. at 150 mm. pressure).

Example 3.—In this example the same quantities of materials were employed as in Example 1, but the temperature was maintained between 20 and 25° C. The time of chlorination was 2¾ hours, during which 65 per cent of the theoretical amount of chlorine for the preparation of mono-chlor-diphenyl was introduced. From the reaction product upon fractional distillation were obtained unchanged diphenyl, 27 per cent; ortho-chlor-diphenyl, 30 per cent; para-chlor-diphenyl, 32 per cent; and 9 per cent higher chlorinated derivatives.

Example 4.—A quantity of 752 grams (4 moles) para-chlor-diphenyl was dissolved in 1200 cc. benzene, 6.2 grams iron filings and .6 grams iodine added and the mixture chlorinated at the temperature of 0° C. or lower. The introduction of chlorine was continued for 3½ hours until 90 per cent of the theoretical amount for converting the chlor-diphenyl to the di-chlor-derivatives had been passed in. Fractional distillation of reaction product gave unchanged para-chlor-diphenyl, 20 per cent; 4,4'-dichlor-diphenyl, 43 per cent; and 29 per cent isomeric dichlor-diphenyls and higher chlorinated derivatives.

In all of the foregoing examples, benzene was successfully employed as solvent since the proportion of dissolved materials employed was sufficient to prevent solidification of the solvent at the reaction temperature. Other solvents, however, may be employed with equally good results, such solvents being, generally speaking, included within the group of the aromatic hydrocarbons of lower molecular weight and the liquid chlorinated derivatives thereof.

In similar manner the chlorination of related multinuclear aromatic hydrocarbons may be carried out. In all cases the solvent is substantially unattacked by chlorine under the conditions of the reaction and may be almost completely recovered by distilling from the reaction product. We have found, furthermore, that with suitable modification the herein described method may be applied for the preparation of the corresponding bromine substituted derivatives of diphenyl and related multinuclear aromatic hydrocarbons. The method, accordingly, is adapted, generally, to the preparation of mono- and di-halogen-substituted derivatives of multinuclear hydrocarbons of the class mentioned.

Other modes of applying the principle of our invention may be employed instead of the one explained, change being made as regards the method herein disclosed, provided the step or steps stated by any of the following

claims, or the equivalent of such stated step or steps be employed.

We therefore particularly point out and distinctly claim as our invention:—

5 1. The method of making chlorine and bromine substituted derivatives of diphenyl which comprises subjecting such hydrocarbon to the action of such halogen in a solvent medium included within the group consisting of benzene, toluene, and the liquid mono-
10 and di-halogenated derivatives thereof.

2. The method of making chlorine substituted derivatives of diphenyl which comprises subjecting diphenyl to the action of
15 chlorine in a solvent medium included within the group consisting of benzene, toluene and the liquid chlorinated derivatives thereof.

3. The method of making chlorine substituted derivatives of diphenyl which comprises reacting upon such diphenyl with
20 slightly less than one molecular equivalent of chlorine in a solvent medium included within the group consisting of benzene, toluene and the liquid chlorinated derivatives thereof, whereby a product consisting
25 chiefly of mono-chlorinated diphenyl derivatives, together with a minor proportion of dichlorinated derivatives, is produced.

4. The method of making chlorine substituted derivatives of diphenyl which comprises reacting upon such diphenyl with
30 slightly less than one molecular equivalent of chlorine in the presence of a chlorinating catalyst in a solvent medium included within the group consisting of benzene, toluene and the liquid chlorinated derivatives thereof,
35 whereby a product consisting chiefly of mono-chlorinated diphenyl derivatives, together with a minor proportion of dichlorinated derivatives, is produced.
40

5. The method of making chlorine substituted derivatives of diphenyl which comprises subjecting such diphenyl to the action of chlorine in a solvent medium of benzene.

45 6. The method of making chlorine substituted derivatives of diphenyl which comprises reacting upon such diphenyl with slightly less than one molecular equivalent of chlorine in the presence of a catalyst in a
50 solvent medium of benzene, whereby a product consisting chiefly of mono-chlorinated diphenyl derivatives, together with a minor proportion of dichlorinated derivatives, is produced.

55 Signed by us this 20th day of June, 1929.

EDGAR C. BRITTON.

WESLEY C. STOESEER.

CERTIFICATE OF CORRECTION.

Patent No. 1,835,754.

Granted December 8, 1931, to

EDGAR C. BRITTON ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 2, line 36, for the word "filling" read filings; same page, line 91, for "di-chlor-derivatives" read di-chlor-derivative; page 3, line 53, claim 6, for the misspelled word "dichthorinated" read dichlorinated; and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 1st day of March, A. D. 1932.

(Seal)

M. J. Moore,
Acting Commissioner of Patents.