[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

The Reversibility of the Friedel-Crafts Reaction. Hydrogenation

BY L. L. ALEXANDER AND REYNOLD C. FUSON

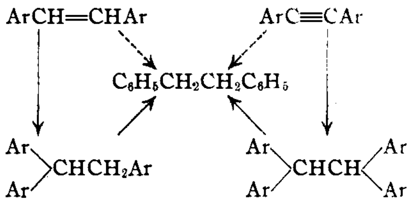
The addition of hydrogen to an ethylenic bond can be accomplished by use of benzene and aluminum chloride at room temperatures.[1] Under these conditions this reaction competes with the addition of benzene to the double bond. However, the latter process is reversible, whereas the former appears to be irreversible. This means that eventually the hydrogenation process will take place to the exclusion of the addition of benzene. Thus, in the case of stilbene the formation of dibenzyl, which is irreversible, must eventually supplant the reaction leading to the production of triphenylethane:[2]

$$(C_6H_5)_2CHCH_2C_6H_5 \overset{C_6H_6}{\rightleftarrows} C_6H_5CH{=}CHC_6H_5 \xrightarrow{H_2} C_6H_5CH_2CH_2C_6H_5$$

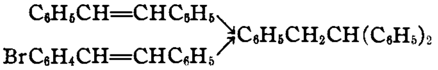
Another way of stating the proposition is to say that in aryl ethanes or ethylenes the aryl groups will be replaced by hydrogen atoms. Experiment has shown that this replacement is subject to certain limitations. The end-product under the conditions mentioned above is dibenzyl rather than ethane. Thus, with dibenzyl (or stilbene), ethylbenzene, styrene, 1,1-diphenylethane or 1,1-diphenylethylene, no replacement of aryl groups is observed.

From these facts emerges the following generalization. *The production of dibenzyl by the action of benzene and aluminum chloride is a general phenomenon for acetylene and ethylene derivatives in which each carbon atom bears at least one aryl group, and for similarly constituted tri- and tetraarylethanes.*

These four classes of compounds may in reality be reduced to two, since the ethylenic and acetylenic types are converted to the triarylethane and tetraarylethane types, respectively, under the conditions used. This is indicated in the following chart



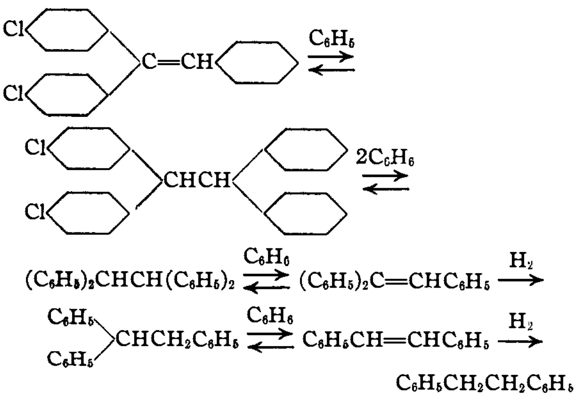
We have found, for example, that stilbene and *p*-bromostilbene give 1,1,2-triphenylethane when treated with benzene in the presence of a limited amount of aluminum chloride.



$$\left.\begin{array}{l} C_6H_5CH{=}CHC_6H_5 \\ BrC_6H_4CH{=}CHC_6H_5 \end{array}\right\rangle C_6H_5CH_2CH(C_6H_5)_2$$

It seems probable, therefore, that the transformation of these compounds into dibenzyl in the presence of large amounts of aluminum chloride involves the triphenylethane as an intermediate.

Similarly, triphenylethylene and 1,1-di-(*p*-chlorophenyl)-2-phenylethylene could be converted either to *sym*-tetraphenylethane or to dibenzyl, depending on the experimental conditions used. Thus, in the case of triphenylethylene the product is *sym*-tetraphenylethane *when 0.3 mole of aluminum chloride is used.* If four moles of aluminum chloride is employed, the chief product is dibenzyl. The same results were obtained with 1,1-di-(*p*-chlorophenyl)-2-phenylethylene. In the latter case, the mechanism must be the following



$$(C_6H_5)_2CHCH(C_6H_5)_2 \overset{C_6H_6}{\rightleftarrows} (C_6H_5)_2C{=}CHC_6H_5 \xrightarrow{H_2}$$

$$\left.\begin{array}{l} C_6H_5 \\ C_6H_5 \end{array}\right\rangle CHCH_2C_6H_5 \overset{C_6H_6}{\rightleftarrows} C_6H_5CH{=}CHC_6H_5 \xrightarrow{H_2} C_6H_5CH_2CH_2C_6H_5$$

These findings make possible a satisfactory interpretation of the fact that dibenzyl results when certain halogen derivatives of ethane, ethylene or acetylene are treated with benzene and aluminum chloride. It will be obvious that dibenzyl may

---

(1) Alexander, Jacoby and Fuson, THIS JOURNAL, **57**, 2208 (1935). It seems probable that a similar explanation might account for the formation of propylbenzene by the action of benzene and aluminum chloride on allyl chloride [Nenitzescu and Isacescu, *Ber.*, **66B**, 1100 (1933)].

(2) Neither the source of the hydrogen nor the mechanism by which it is added have as yet been discovered. It may be, for example, that the process consists of the addition of hydrogen chloride to the ethylenic bond, followed by replacement of the chlorine atom by a hydrogen atom.

be expected from such of these compounds as react to form derivatives in which each of the two carbon atoms bears a phenyl radical. According to the literature, dibenzyl has been obtained in greater or less amounts from a number of such halogen derivatives. The following are illustrative examples: ethylene chloride,[3] ethylene bromide,[3] acetylene dibromide,[4] 1,1,2-trichloroethane,[5] 1,1,2-tribromoethane,[4] 1-phenyl-2-chloroethane,[6] 1-phenyl-1,2-dibromoethane[7] and tolane dibromide.[8]

Experimental Part

***sym*-Tetraphenylethane from Tolane.**—A mixture of 1 g. of tolane, 60 cc. of benzene and 0.5 g. of aluminum chloride was saturated with dry hydrogen chloride, then tightly stoppered and shaken for six hours at room temperature. The color changed from green to brown. The decomposition was carried out in an ice–hydrochloric acid mixture, and the product obtained on removal of the benzene melted, after recrystallization from glacial acetic acid, at 207–208°. There was no depression of a mixed melting point with an authentic sample of *sym*-tetraphenylethane. The yield was 64% of the theoretical amount.

Dibenzyl from Tolane.—A mixture of 1 g. of tolane, 50 cc. of benzene and 4 g. of aluminum chloride was saturated with dry hydrogen chloride. The mixture was placed in a glass-stoppered bottle and shaken at room temperature for twenty hours. The decomposition and the washing of the reaction mixture were effected as described in the other experiments. The brown viscous product was distilled at 4 to 5 mm., and the fraction boiling up to 120° was collected. The distillate crystallized on standing, and melted at 50–51°. It was shown by the method of mixed melting points to be dibenzyl. The yield was 32% of the theoretical amount.

Dibenzyl also has been obtained as a result of the treatment of the following compounds in a manner which was entirely analogous to that described for the production of dibenzyl from tolane.

Starting material	Material, g.	Aluminum chloride, g.	Yield of dibenzyl, %
Triphenylethylene	5	10	28
1,1-Di-(*p*-chlorophenyl)-2-phenylethylene	5	10	27
1,1,2-Triphenylethane	5	10	57
s-Tetraphenylethane	2.5	5	54

1,1,2-Triphenylethane from Stilbene.—A solution of 10 g. of stilbene in 150 cc. of benzene was saturated with hydrogen chloride and shaken for eight hours with 2 g. of aluminum chloride. The decomposition was accomplished with a mixture of ice and hydrochloric acid. The red oil resulting was distilled under reduced pressure. A fraction distilling at 206–210° (12 mm.) was collected, and crystallized on standing. The melting point of the product, as well as the mixed melting point with 1,1,2-triphenylethane (prepared as indicated below), was 51–52.5°. The yield calculated on the basis of triphenylethane was 49% of the theoretical amount.

1,1,2-Triphenylethane from *p*-Bromostilbene.—From 5 g. of *p*-bromostilbene, 100 cc. of benzene, dry hydrogen chloride and 0.5 g. of aluminum chloride, 1,1,2-triphenylethane was prepared in a yield of 37% of the theoretical by a procedure exactly analogous to the conversion of stilbene into 1,1,2-triphenylethane described above.

Synthesis of 1,1,2-Triphenylethane.[9]—A solution of 2 g. of triphenylethylene in 100 cc. of dry ether was freed from oxygen by means of a stream of dry nitrogen gas. Three grams of finely powdered sodium was added, and the mixture was shaken for ten hours at room temperature. The solution was added slowly to 100 cc. of absolute alcohol, and a large part of the ether and alcohol removed. Upon the addition of water and extraction with ether, a liquid residue was obtained which crystallized readily on standing with methyl alcohol. After recrystallization from the same solvent, it melted at 52–53°. The yield was 83% of the theoretical amount.

Synthesis of Di-(*p*-chlorophenyl)-benzylcarbinol.—A Grignard reagent was prepared from 13 g. of magnesium, 63 g. of benzyl chloride and 200 cc. of dry ether. To this solution 85 g. of *p,p'*-dichlorobenzophenone was added, and the solution was stirred for two hours. It was then allowed to stand overnight. After decomposition in an ammonium chloride–ice mixture and separation and concentration of the ether solution, a straw-colored liquid remained. When recrystallized from petroleum ether (high-boiling), the product melted at 116–117°. The yield was 68%.

Anal. Calcd. for $C_{20}H_{16}OCl_2$: C, 69.85; H, 4.66. Found: C, 70.02; H, 4.76.

1,1-Di-(*p*-chlorophenyl)-2-phenylethylene.—Fifty grams of di-(*p*-chlorophenyl)-benzylcarbinol dissolved in 600 cc. of glacial acetic acid was heated to boiling as 50 cc. of concentrated sulfuric acid was slowly added. The mixture was heated under reflux for thirty minutes, and then poured into water. The organic material was extracted with ether and obtained in crystalline form by removal of the ether. After recrystallization from methyl alcohol, it melted at 116.5–117.5°; the mixed melting point with the original carbinol was 90–96°. The yield of the ethylenic compound was practically quantitative.

Anal. Calcd. for $C_{20}H_{14}Cl_2$: Cl, 21.87. Found: Cl, 21.80.

***sym*-Tetraphenylethane from Triphenylethylene.**—A solution of 5 g. of triphenylethylene in 150 cc. of benzene was saturated with dry hydrogen chloride and shaken with 1 g. of aluminum chloride for twenty hours. The resulting red solution was decomposed in ice and hydrochloric acid and, after removal of the benzene, the resulting product was treated with norite and crystallized from an acetic acid solution. The melting point was 206–208°, and a mixed melting point with an authentic sample of *sym*-tetraphenylethane showed no depression. The yield was 70% of the theoretical amount.

***sym*-Tetraphenylethane from 1,1-Di-(*p*-chlorophenyl)-2-phenylethylene.**—A yield of 55% of the calculated quan-

---

(3) Silva, *Compt. rend.*, **89**, 606 (1879).

(4) Anschütz, *Ann.*, **235**, 153 (1886).

(5) Ravitzer, *Bull. soc. chim.*, [3] **17**, 477 (1877).

(6) Nenitzescu, Isasescu and Ionescu, *Ann.*, **491**, 210 (1931).

(7) Anschütz, *ibid.*, **235**, 338 (1886).

(8) Anschütz, *ibid.*, **235**, 209 (1886).

(9) Schlenk and Bergmann, *ibid.*, **463**, 45 (1928).

tity of tetraphenylethylene was obtained from 5 g. of the ethylene, 1 g. of aluminum chloride and 150 cc. of benzene which had been saturated with hydrogen chloride. The procedure was the same as that used for the conversion of triphenylethylene into *sym*-tetraphenylethane.

Dibenzyl from Tetraphenylethylene.—A solution of 7 g. of tetraphenylethylene in 150 cc. of dry benzene was saturated with dry hydrogen chloride and shaken in contact with 20 g. of aluminum chloride for three days. After decomposition and separation had been completed, the benzene was removed and the residue distilled under reduced pressure. A small amount of distillate was collected at 100–200° (8 mm.). This distillate crystallized from dilute alcohol and melted at 52–53°. It was shown by the method of mixed melting points to be dibenzyl. The residue from the distillation was unchanged tetraphenylethylene.

Summary

The production of dibenzyl by the action of benzene and aluminum chloride is a general phenomenon in the case of acetylene and ethylene derivatives in which each carbon atom bears at least one aryl group, and for similarly constituted tri- and tetraarylethanes. These transformations may be explained by assuming that hydrogen adds irreversibly to the ethylenic bond, whereas aromatic hydrocarbons add reversibly.

URBANA, ILLINOIS RECEIVED JUNE 22, 1936

[CONTRIBUTION NO. 163 FROM THE EXPERIMENTAL STATION OF E. I. DU PONT DE NEMOURS & COMPANY]

Acetylene Polymers and their Derivatives. XXVI. The Reaction of Halogen Ethers with Vinylacetylene

BY HARRY B. DYKSTRA

Isochloroprene (I) and chloroprene (II) are obtained by the addition of hydrogen chloride to

$$CH\equiv CCH=CH_2 + HCl \longrightarrow \underset{(I)}{CH_2=C=CHCH_2Cl} \longrightarrow \underset{(II)}{CH_2=CClCH=CH_2}$$

vinylacetylene.[1] The present paper is concerned with analogous compounds obtained by the addition of alpha chloroethers to vinylacetylene.

$$CH\equiv CCH=CH_2 + CH_3OCH_2Cl \longrightarrow \underset{(III)}{CH_3OCH_2CH=C=CHCH_2Cl} \longrightarrow \underset{(IV)}{CH_3OCH_2CH=CClCH=CH_2}$$

Methoxy-5-chloro-1-pentadiene-2,3 (III) and methoxy-5-chloro-3-pentadiene-1,3 (IV) are formed when vinylacetylene and chloromethyl methyl ether have reacted in ether solution containing bismuth chloride. The initial step appears to be 1,4-addition, for III is the principal product of the reaction. On treatment with hydrochloric acid and cuprous chloride, III rapidly rearranges to IV. The presence of IV in the original reaction mixture probably results from isomerization of III induced by the bismuth chloride.

The addition of alpha halogen ethers to vinylacetylene appears to be a general reaction. Compounds obtained in this manner are listed in Table I. The synthesis is a special application of the olefin–halogen ether reaction developed by Norman D. Scott.[2]

Proof of Structure of Methoxy-5-chloro-1-pentadiene-2,3 (III).—This compound is a colorless liquid having an ethereal odor. Other physical properties are recorded in Table I. Failure of III to react with alkaline mercuric iodide reagent indicates the absence of acetylenic hydrogen. It does not polymerize or react with maleic anhydride as it might be expected to do if it contained a 1,3-diene structure. Its chlorine atom is reactive, for on treatment with alcoholic silver nitrate it rapidly yields a copious precipitate of silver chloride. A substantially quantitative yield of silver chloride is obtained in twenty hours at 25°. On oxidation with potassium permanganate, III yields chloroacetic acid. These data are similar to those reported for isochloroprene[1] and indicate that III is methoxy-5-chloro-1-pentadiene-2,3.

Proof of Structure of Methoxy-5-chloro-3-pentadiene-1,3 (IV).—Physical and analytical data for this compound are given in Table I. It is a colorless liquid having weakly lachrymatory properties. It does not yield a derivative with alkaline mercuric iodide reagent, which shows that it is not a true acetylenic compound. Its chlorine atom must be attached to a carbon bearing a

---

[1] Carothers, Berchet and Collins, THIS JOURNAL, **54**, 4066 (1932).

[2] E. I. du Pont de Nemours & Co., U. S. Patent 2,024,749 (1935).