[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF MERCK AND CO., INC.]

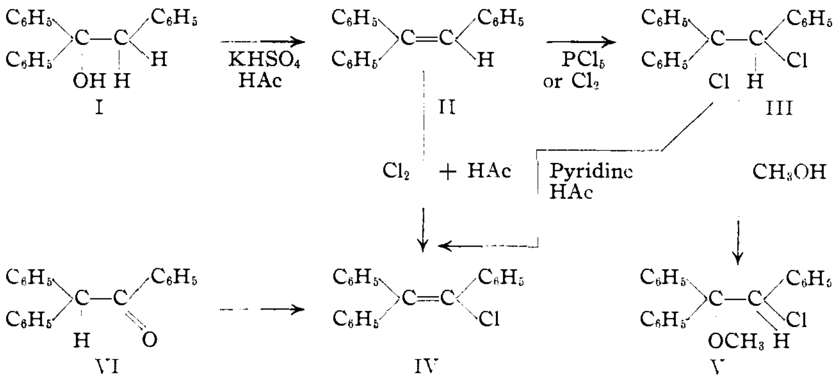
The Preparation of Triphenylchloroethylene

BY JACOB VAN DE KAMP AND MEYER SLETZINGER

This investigation was undertaken in view of the recent interest in the use of triphenylchloroethylene (IV) as a synthetic substance which simulates estrogenic hormones.[1]

The preparation of triphenylchloroethylene has been described in the literature by Gardeur[2] and by Bergmann and Bondi.[3] Gardeur prepared this compound by treating triphenylethanone (ω,ω'-diphenylacetophenone) (VI) with phosphorus pentachloride at 150° in a yield of 58%. The product melted at 117°. Bergmann and Bondi reported a method of preparation whereby triphenylethylene (II), in benzene solution, is treated with phosphorus pentachloride. The reaction product, a viscous oil, soon solidified when allowed to stand with a mixture of glacial acetic acid and methanol. A product melting at 117° was obtained by recrystallization from ligroin. No yield was reported.

When we attempted to repeat Bergmann and Bondi's chlorination of triphenylethylene under the exact conditions described by these authors we were not able to isolate any triphenylchloroethylene. In their description, Bergmann and Bondi use the term "abdampfen," for the evaporation of the benzene from their reaction mixture. We worked up experiments according to their directions, evaporating the benzene at atmospheric pressure, as well as under reduced pressure. Both procedures led to the same result, namely, an oily residue from which no crystalline material could be isolated according to the given instructions. The oily reaction mixture was found to consist largely of triphenyldichloroethane (III) which could be isolated by petroleum ether (b. p. 70–100°) extraction of the oil, followed by recrystallization from the same solvent. The melting point of this dichloro compound was found to be 110.5–111.5°. It could be obtained in higher yield according to this procedure by prolonging the time of reaction. However, when we allowed this oily product to stand with a mixture of glacial acetic acid and methanol, according to Bergmann and Bondi, at room temperature, or at elevated temperatures, we were able to isolate a crystalline material which, when recrystallized from methanol was found to melt at 117°. This product was not triphenylchloroethylene as it gave a depression in melting point when mixed with a sample of triphenylchloroethylene prepared according to Gardeur's method. The product analyzed for $C_{21}H_{19}OCl$. In view of the fact that a considerable amount of triphenyldichloroethane is formed in this chlorination, it was assumed that the latter was partly converted upon standing with glacial acetic acid and methanol to form triphenylchloromethoxyethane (V).



This product was obtained in almost quantitative yield when pure triphenyldichloroethane (III) was refluxed with methanol. It is interesting to note that III, when similarly treated with absolute ethanol, does not give triphenylchloroethoxyethane, but forms triphenylchloroethylene by loss of hydrogen chloride.

In this connection it also may be mentioned that the dichloro compound, when refluxed in benzene, does not change. However, when it is heated just above its melting point (115°) it is converted quantitatively to triphenylchloroethylene, with the loss of hydrogen chloride.

Triphenyldichloroethane (III) could be obtained more easily by the addition of free chlo-

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(1) Robson, Schönberg, and Fahim, *Nature*, **142**, 292 (1938); MacPherson and Robertson, *Lancet*, (2) **237**, 1362 (1939).

(2) Gardeur, *Bull. Acad. Roy. Belgique*, (3) **34**, 67 (1897); *Chem. Zentr.*, **68**, II, 662 (1897).

(3) Bergmann and Bondi, *Ber.*, **64**, 1467 (1931).

rine to triphenylethylene. The triphenylethylene used in these reactions was prepared by an improved procedure. Diphenylbenzylcarbinol (I), when heated with potassium bisulfate at 155–160° for three hours, or when refluxed for a similar length of time in glacial acetic acid gives an excellent yield of the hydrocarbon, a procedure much simpler than that reported by Bergmann and Bondi[3] and by Schlenk and Bergmann.[4]

Finally, we succeeded in obtaining a satisfactory yield of triphenylchloroethylene from triphenylethylene in a simple manner by passing chlorine into a glacial acetic acid solution of the unsaturated hydrocarbon, and removing hydrogen chloride from the triphenyldichloroethane intermediately formed.

This procedure is analogous to that given by Koelsch[5] for the preparation of triphenylbromoethylene.

Experimental Part

Triphenylethylene (II).—(A) Fifty-five grams of diphenylbenzylcarbinol (I) was finely ground with 55 g. of potassium bisulfate, and the mixture heated at 155–160°—preferably with stirring—in an oil-bath for three hours. The reaction mixture was cooled and extracted with 300 cc. of ether. The solid residue was extracted twice more with 50 cc. of ether. The combined ether extracts were evaporated and to the residual oil an equal volume of petroleum ether (b. p. 30–60°) was added. The colorless crystals obtained in the first and second crops weighed 47.2 g. (91.5%); m. p. 67–68°.

Anal. Calcd. for $C_{20}H_{16}$: C, 93.71; H, 6.29. Found: C, 93.41; H, 6.59.

(B) One part of the carbinol I was refluxed in 10 parts of glacial acetic acid for three hours. On cooling and diluting with twice its volume of water the crude triphenylethylene separated and was recrystallized from petroleum ether; m. p. 67–68°; yield, 90%.

Triphenyldichloroethane (III).—(A) A solution of 23.6 g. of triphenylethylene in 78 cc. of dry benzene was added drop by drop, with stirring, to a suspension of 37.6 g. of phosphorus pentachloride in 63 cc. of dry benzene. The mixture was allowed to stand at room temperature for three days. By the end of this time most of the solid (phosphorus pentachloride) had disappeared. The reaction mixture was then carefully poured into twice its volume of cold water with good stirring. The benzene layer was separated and the water layer was extracted with 50 cc. of benzene. The two benzene layers were combined and stirred with an equal volume of water to which sufficient 30% sodium hydroxide solution was added dropwise to make the benzene layer neutral to litmus. The benzene layer was separated, and the water layer extracted twice with benzene. The combined benzene solutions were dried over anhydrous sodium sulfate and the solvent evaporated at atmospheric pressure on a steam-bath. The residual oil, while still warm, was dissolved in 50 cc. of petroleum ether (b. p. 30–60°). Upon cooling and scratching, crystals appeared which melted at 103–106°; recrystallized from petroleum ether, m. p. 110.5–111.5°; yield 3.0 g.

It made no difference whether the benzene was removed at atmospheric or under reduced pressure. In an experiment which was allowed to stand for five days the yield of triphenyldichloroethane was 14.7 g. (49%).

Anal. Calcd. for $C_{20}H_{16}Cl_2$: C, 73.40; H, 4.93; Cl, 21.67. Found: C, 73.52; H, 4.97; Cl, 21.13.

(B) The first chlorinations of triphenylethylene with free chlorine were carried out in chloroform and in ethylene dichloride. The yields in these chlorinations were not very good. Chlorination in glacial acetic acid solution was then carried out. Since triphenylethylene can be prepared in this solvent by dehydration of the carbinol (I) and triphenyldichloroethane will lose hydrogen chloride upon heating in this solvent, the entire process of preparing triphenylchloroethylene from the carbinol can be carried out in this same solvent.

Triphenylchloroethylene (IV).—Sixty-seven grams of diphenylbenzylcarbinol was dissolved in 750 cc. of glacial acetic acid. The solution was refluxed for three hours. At the end of this period the solution was cooled to 30°. Into this solution was then passed 25 g. of chlorine in about fifteen minutes, maintaining the temperature between 30–40° applying outside cooling when necessary. When most of the chlorine had been added, a small portion of the triphenyldichloroethane appeared as white crystals. The mixture was allowed to stand for about one hour until the temperature had dropped of its own accord to room temperature. At the end of this time air was passed through the mixture to remove excess chlorine.

The mixture was heated slowly. When the temperature reached about 80–90° vapors of hydrogen chloride began to escape. Heating was continued until no more hydrogen chloride was given off. By this time the inside temperature of the mixture had reached the boiling point of acetic acid (116–118°). About 100 cc. of acetic acid was removed by distillation so as to be sure that all the triphenyldichloroethane had been decomposed. The reaction mixture was allowed to cool to 90° and 55 cc. of water was added slowly with stirring. It was then slowly cooled and the walls of the flask scratched. At about 40° crystals appeared, and after cooling to 10° these crystals were filtered with suction. (To the filtrate 100 cc. of water was added. This threw out some oily material which crystallized on standing.) The first crop was washed well with cold water and sucked as dry as possible. The crude material was dried at 60° and recrystallized from 12 parts of 95% alcohol using 2 g. of charcoal. This gave 55.5 g. of triphenylchloroethylene, m. p. 117.5–118.5°. From the mother liquors some additional material of the same m. p. was obtained bringing the total yield to 62 g. or an over-all yield of 87.3% based on the carbinol.

Anal. Calcd. for $C_{20}H_{15}Cl$: C, 82.61; H, 5.20. Found: C, 82.68; H, 5.20.

A solution of 14.7 g. of triphenyldichloroethane in 49 cc. of reagent pyridine was refluxed for five hours. During this time the solution darkened. Upon cooling to room

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[4] Schlenk and Bergmann, *Ann.*, **463**, 44 (1928).

[5] Koelsch, This Journal, **54**, 2487 (1932).

temperature and pouring the mixture into 200 cc. of water an oil separated which soon crystallized. Recrystallizing the dried crystals from 50 cc. of ligroin (b. p. 75–115°) with the addition of 1.0 g. of Norit, white triphenylchloroethylene was obtained. The combined first and second crops gave, recrystallized from 12 parts of ethanol, 8.5 g. of m. p. 117.5–118° (65%). This material gave no depression with that obtained above.

Triphenylchloromethoxyethane (V).—One gram of triphenyldichloroethane was refluxed with 15 cc. of methanol for two hours. The mixture was cooled and the crystals which separated were collected. The mother liquors gave some additional material. In all, 0.85 g. of material of m. p. 117.5–118° was obtained. Mixed with triphenylchloroethylene a depression in m. p. was observed.

Anal. Calcd. for $C_{21}H_{19}OCl$: C, 78.13; H, 5.93; Cl, 10.98. Found: C, 77.94; H, 5.96; Cl, 11.21.

Summary

1. A simple method for the preparation of triphenylchloroethylene, giving excellent yields, is described. Bergmann and Bondi's method is discussed.

2. 1,1,2-Triphenyl-1,2-dichloroethane and a triphenylmethoxychloroethane are described.

Rahway, N. J. Received March 5, 1941

[Contribution from the Chemical Laboratory of Iowa State College]

The Action of Organic Nitrogen Bases on Cornstalk Lignin*

By Elton Fisher and R. S. Bower

The commercial availability of monoethanolamine has led to studies of its action on plant tissues. This manuscript reports the action of other commercially available organic nitrogen bases on cornstalk lignin.

Action of Bases on Cornstalk.—Ten-gram samples of air dried ground cornstalks were digested with 110 ml. of anhydrous ethanolamines and N-substituted morpholines for six hours at elevated temperatures. Each sample was then diluted with an equal volume of hot water, filtered and washed with hot water until the filtrate was free of base. The air dried pulp was analyzed for lignin by the cold sulfuric acid method.[1] Table I gives the results obtained.

Table I

Base	Temp., °C.	Weight of pulp, g.	Lignin removed, %
Monoethanolamine	100	4.63	93.9
Diethanolamine	100	4.89	75.6
Triethanolamine	100	6.15	42.6
	130	5.56	53.6
	160	4.80	81.2
Morpholine-ethanol	100	6.61	25.6
N-Phenylmorpholine	100	7.83	23.8

The values given in Fig. 1 except those for Curve H were obtained in a similar manner from 10-g. samples of cornstalks autoclaved with aqueous solutions of the bases for three hours at 20 pounds pressure. Curve H represents the results obtained in a corresponding manner from similar samples digested for six hours at 100° with aqueous solutions of morpholine-ethanol.

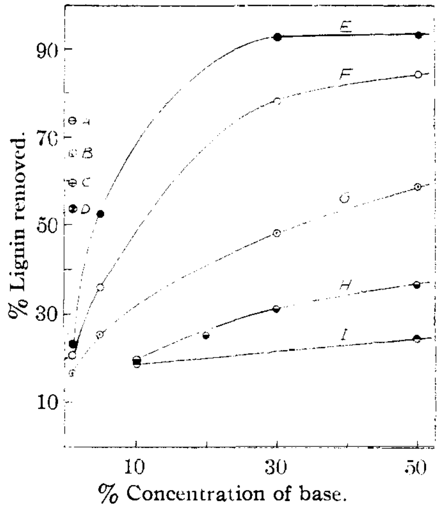

Fig. 1.—A, sodium hydroxide + monoethanolamine; B, sodium hydroxide; C, sodium hydroxide + diethanolamine; D, sodium hydroxide + triethanolamine; E, monoethanolamine; F, diethanolamine; G, triethanolamine; H, morpholine-ethanol at 100°; I, morpholine-ethanol at 20 pounds pressure.

Recovery of Lignins.—The filtrates from the basic extractions were concentrated to 150 ml.; the pentosans were precipitated with 3 volumes of alcohol, filtered and washed with alcohol. After evaporating the alcohol the filtrates were acidified with an excess of dilute sulfuric acid; this caused the lignins to precipitate. The precipitated lignins were filtered, washed and purified by redissolving in the base, precipitating with

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[1] Peterson, Walde and Hixon, *Ind. Eng. Chem., Anal. Ed.*, **4**, 216 (1932).