Anal. Calcd. for $C_{22}H_{26}NO_4$: C, 71.7; H, 7.07; N, 3.80. Found: C, 71.5, 71.6; H, 7.11, 7.17; N, 2.98, 3.03.

Fagarine III Hydrochloride.—Upon dissolving 1.6 g. of fagarine III in 200 ml. of dilute hydrochloric acid and cooling, very fine needle crystals of the hydrochloride separated. These were collected and dried at 130° *in vacuo* over phosphorus pentoxide; m.p. 232–234° dec.

Anal. Calcd. for $C_{22}H_{26}NO_4 \cdot HCl$: C, 65.2; H, 6.68; Cl, 8.77. Found: C, 64.4, 64.6; H, 6.87, 6.93; Cl, 9.15.

Ultraviolet Absorption Spectra.—The ultraviolet absorption spectra were determined using a Beckman model DU quartz spectrophotometer. The solvent was 99% ethanol for the bases, and 0.1 N aqueous hydrochloric acid for the hydrochlorides. Minimum slit widths were used with a 1.00 cm. quartz cell. All measurements were made against a blank of an identical sample of the pure solvent to eliminate its absorption.

Acknowledgment.—The authors wish to express their gratitude to Dr. R. H. F. Manske for supplying us with an authentic sample of α-allocryptopine.

Summary

1. A re-investigation of α-fagarine and its derivatives has shown it to be identical with α-allocryptopine.

2. A second alkaloid, fagarine II, has been isolated and several derivatives have been prepared and analyzed. These data would suggest that fagarine II is isomeric with α-fagarine, differing only in the positions of the substituents.

3. Fagarine III has been isolated in very small amount. The ultraviolet absorption spectra of this alkaloid and its hydrochloride would suggest that it, also, belongs to the cryptopine group of alkaloids.

The Action of Ultraviolet Light on DDT

BY ELMER E. FLECK

The prolonged residual action of DDT (I) is due to its low vapor pressure[1] and to its stability toward oxidation.[2] Recently evidence has been accumulating to show that DDT is not so stable when exposed to direct sunlight in solution as when it is exposed in the solid state.[3]

Attempts have been made to explain this phenomenon by isolating the decomposition products of DDT produced by ultraviolet light. The isolation of 4,4'-dichlorobenzophenone (IV) was accomplished during 1945 in this laboratory by irradiating DDT dissolved in γ-valerolactone in an open Petri dish with ultraviolet light from a 100-watt mercury-vapor lamp. Since that time Wichmann, *et al.*,[4] have confirmed the formation of this compound by isolating the 2,4-dinitrophenylhydrazone of 4,4'-dichlorobenzophenone from the products obtained by irradiation of a benzene solution of DDT in an open Petri dish with ultraviolet light.

The formation of 4,4'-dichlorobenzophenone from DDT has been assumed to proceed first by elimination of hydrogen chloride from the trichloroethane group and then by oxidation of the resulting double bond. This mechanism of reaction was tested by irradiation of solutions of DDT in completely filled quartz cells. A wide variety of solvents were tried, and in every case hydrogen chloride was evolved but dehydrochlorinated DDT could not be isolated.

When a solution of DDT in ethyl alcohol was irradiated with a 360-watt mercury-vapor lamp for sixteen hours, about 1 mole of hydrogen chloride was evolved. A strong odor of acetaldehyde was present, and cooling the solution yielded about 10% of a crystalline compound which melted at 230–231°. This was shown to be 2,3-dichloro-1,1,4,4-tetrakis-(*p*-chlorophenyl)-2-butene (II) by analysis and by mixed melting point determinations with authentic material made by the method of Brand and Bausch.[5] These authors prepared II by hydrogenation of DDT in the presence of Pd–CaCO₃ catalyst. The identity of the two compounds was further substantiated by conversion of the irradiation product into 1,1,4,4-tetrakis-(*p*-chlorophenyl)-1,-2,3-butatriene (III) by refluxing with alcoholic sodium hydroxide. This procedure eliminated 2 moles of hydrogen chloride from II and resulted in a yellow crystalline product which melted with decomposition at 286°. Brand and Bausch give 288° with decomposition for this same compound. Mixed melting points of the two preparations showed no depression.

The butatriene (III), obtained by irradiation and reaction with alkali, was oxidized with chromic anhydride to form IV. This is in accordance with the oxidation of III prepared by the method of Brand and Bausch.[5]

In order to eliminate the possibility of an unknown impurity being present in the *p,p'*-DDT, the irradiation was repeated with a second preparation of *p,p'*-DDT made from DDT produced by a different manufacturer. The same yield of II was obtained.
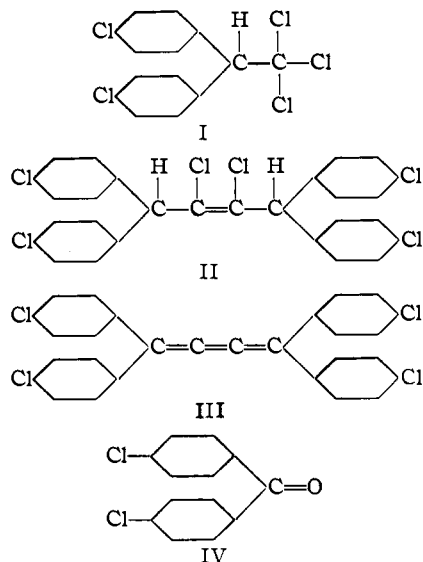
(1) E. E. Fleck, *J. Econ. Entomol.*, **37**, 853 (1944).

(2) O. Zeidler, *Ber.*, **7**, 1181 (1874).

(3) E. E. Fleck, *Ind. Eng. Chem.*, **40**, 707 (1948).

(4) H. J. Wichmann, W. I. Patterson, P. A. Clifford, A. K. Klein and H. V. Claborn, *J. Assoc. Offic. Agr. Chem.*, **29**, 222 (1946).

(5) K. Brand and W. Bausch, *J. prakt. Chem.*, **127**, 219 (1930).

I

II

III

IV

Irradiation of dehydrochlorinated DDT and also of 1,1-dichloro-2,2-bis-(p-chlorophenyl)-ethane (TDE) in alcohol solution in quartz cells, under the same conditions that were used for DDT, resulted in recovery of the unchanged starting material.

The conversion of DDT into II by ultraviolet light provides a second and perhaps more probable mechanism by which sunlight may decompose DDT. The presence of another compound that can serve as a reactor with chlorine would tend to increase the speed of the reaction. In the case where alcohol is used as a solvent the chlorine oxidizes it to form acetaldehyde. When hydrocarbons are present the chlorine may react to form substitution products, or unsaturated groups in the molecule may serve as acceptors of chlorine to form addition compounds. These and other similar reactions may account for the more rapid decomposition of DDT in solution than in the solid state.

Although a large proportion of II would probably not exist at any one time in a DDT spray deposit, its presence can be detected by the yellow color of III formed by heating with alcoholic alkali. By contrast, the dehydrochlorinated DDT is colorless. When II is subjected to the colorimetric test of Schechter and Haller,[6] a wine-red color is produced. This is in contrast to the blue color produced by p,p'-DDT.

Experimental

Description of Apparatus.—The quartz cell used was cylindrical in shape. The diameter was 40 mm. and the height 40 mm. A four × fifty mm. side tube was sealed on halfway up the side of the cylinder. This side tube was connected with a small rubber tube to a glass tube which was drawn down to a capillary. The rubber tube was shielded with a small piece of aluminum foil. The cell and side tubes were completely filled with liquid at the

(6) M. S. Schechter, S. B. Soloway, R. A. Hayes and H. L. Haller, *Ind. Eng. Chem., Anal. Ed.*, 17, 704 (1945).

start of the experiment. As the solution warmed under the ultraviolet light, the excess liquid escaped through the capillary. The capacity of the cell was 42 ml.

In the early experiments a 100-watt Mazda mercury-vapor lamp was used. The light source was 25 cm. above the surface of the irradiated liquid. In the experiments with the quartz cell a 360-watt Uviarc lamp was used. It was fitted with an aluminum reflector and mounted so that the source of light was 25 cm. above the surface of the quartz cell. The cell was placed on a filter paper and was cooled by a strong current of air from an 8-inch fan. The temperature of the solution was between 35 and 40° during the experiments.

Irradiation of DDT in Presence of Air.—A solution of 1 g. of p,p'-DDT (m. p. 108–109°) in 10 ml. of γ-valerolactone was placed in a 100-mm. Petri dish. The irradiation was carried out for forty hours with the 100-watt mercury-vapor lamp. At the end of this period the solution had acquired a yellowish cast, and some of the DDT had crystallized on the side of the Petri dish. The liquid was pipetted out of the dish into water. The oil that separated crystallized when stirred. The mixture was extracted with ether and the ether solution washed with water until the wash was neutral to congo red. The ether was evaporated on the steam-bath, and the residue was taken up in 20 ml. of alcohol. When this solution was held at 0°, crystals separated which proved to be DDT (m. p. 107–108°, yield 0.4 g.).

The mother liquor from this separation was held at −30° for several days. The crystals that separated were recrystallized from alcohol to a constant melting point of 144–145°, yield 0.1 g. No depression of melting point could be observed when the sample was mixed with authentic 4,4'-dichlorobenzophenone.

Irradiation of DDT in Absence of Air.—A solution of 1 g. of p,p'-DDT (m. p. 108–109°) in 30 ml. of boiling alcohol was washed into the quartz cell with alcohol. The cell was cooled to room temperature and completely filled with alcohol. The capillary side tube was filled with alcohol and attached to the cell. The cell was placed with a flat surface up and irradiated for four hours with a 360-watt mercury-vapor lamp. The cell was then reversed and irradiated for four hours through the other window. This was followed by four hours of irradiation on each side of the cell with the side tube as a pivot. This change of surface is necessary, as small amounts of decomposition products deposit on the inside of the window and thereby reduce the yield. Between runs it was necessary to clean the cell with boiling ethyl acetate and also with boiling acetone.

The alcoholic solution irradiated in this manner acquired a yellowish cast. It sometimes contained a small amount of crystalline material. The product of irradiation was removed from the cell and cooled to −30° for several days. Four such runs were combined and filtered. A yield of 0.4 g. of crystalline material of melting point around 200° was obtained. Recrystallization from benzene gave prisms which melted at 230–231°. No yellow color was developed when a carbon tetrachloride solution was treated with tetranitromethane.

Anal. Calcd. for $C_{28}H_{18}Cl_6$: C, 59.29; H, 3.20; Cl, 37.51. Found: C, 59.59, 59.81; H, 3.38, 3.36[7]; Cl, 37.56.

No depression of melting point could be observed when this material was mixed with II prepared by the catalytic reduction of p,p'-DDT.[5]

II is insoluble in water, but very slightly soluble in methanol and ethanol. It is slightly soluble in ethyl acetate and acetic acid, and soluble in hot benzene, toluene, and chloroform.

Hydrogen Chloride Produced by Irradiation of DDT.—Alcoholic solutions of 1 g. of p,p'-DDT were irradiated as above for four-, eight- and sixteen-hour periods. Each alcoholic solution was poured into 200 ml. of water to which 3 ml. of concentrated nitric acid had been added. When precipitation was complete, the mixture was filtered

(7) Analysis by N. Green.

by gravity and the filter paper washed with water. The filtrate was titrated with silver nitrate by means of an electrometric titrimeter.

Anal. Calcd. as moles of hydrochloric acid per mole of DDT: 4-hour irradiation, 0.39; 8-hour irradiation, 0.67; 16-hour irradiation, 0.88.

1,1,4,4-Tetrakis-(*p*-chlorophenyl)-1,2,3-butatriene (III).—A suspension of 100 mg. of II (from irradiated DDT) in 50 ml. of 2 N alcoholic potassium hydroxide was refluxed for two hours. The mixture was poured into 150 ml. of water and filtered by gravity when precipitation was completed. The yellow reaction product was washed with water, and the washings were added to the filtrate. The reaction product was dissolved in 50 ml. of benzene and shaken with water. The aqueous extracts were added to the filtrate.

The benzene solution was concentrated to 5 ml. on the steam-bath, and the yellow-orange needles that separated were recrystallized and dried in vacuum at room temperature. The product melted at 288° with decomposition, and no lowering of melting point could be observed when it was mixed with III prepared in accordance with Brand and Bausch.[5]

The filtrate from the original precipitation together with the washings was neutralized with concentrated nitric acid, and then a 3-ml. excess was added. The solution was titrated with 0.1 N silver nitrate with an electrometric titrimeter.

Anal. Calcd. for $C_{21}H_{18}Cl_6$: 2 moles Cl, 13.40 mg. Cl. Found: 13.65 mg. Cl.

4,4'-Dichlorobenzophenone (IV).—A solution of 45 mg. of III (from irradiated DDT) and 50 mg. of chromic anhydride in 5 ml. of acetic acid was refluxed for two hours. The solution was poured into 50 ml. of water and the reaction product filtered and recrystallized from alcohol. The product weighed 27 mg. and melted at 145–146°. No depression of melting point was observed when the product was mixed with authentic 4,4'-dichlorobenzophenone.

The ketone yielded an oxime of melting point 134–135°. Dittrich[8] gives the melting point as 135°.

Summary

It has been shown that ultraviolet light catalyzes the decomposition of DDT.

One of the decomposition products is 4,4'-dichlorobenzophenone when air is present. In the absence of air 2,3-dichloro-1,1,4,4-tetrakis-(*p*-chlorophenyl)-2-butene is formed. This compound, through loss of hydrogen chloride and subsequent oxidation, may be converted into 4,4'-dichlorobenzophenone.

(8) M. Dittrich, *Ann.*, **264**, 177 (1891).

Catalytic Reduction of Aromatic Ketones

By E. C. Horning and D. B. Reisner[1]

The problem of reducing β-aroylpropionic acids to the corresponding γ-arylbutyric acids in convenient fashion and in good yield has led to continued investigation of classical chemical methods for the reduction of an aryl keto group to a methylene group. This work has led to the development of greatly improved procedures in the form of the Clemmensen–Martin–Sherman procedure[2] and the Wolff–Kishner–Huang method.[3] Modifications of these procedures can be applied to the reduction of aliphatic and alicyclic carbonyl groups as well, and these methods are of particular value because of this degree of generality.

The reduction of a carbonyl group adjacent to an aromatic nucleus does not present a difficult problem in terms of reactivity; the conversion of keto groups of this kind to the corresponding alcohols has been observed under a variety of mild catalytic hydrogenation conditions, and it is known that compounds of the benzyl alcohol type will undergo catalytic hydrogenolysis with ease to yield a fully reduced system. The fact that catalytic methods are not widely used for the reduction of such carbonyl groups to methylene groups is apparently due to the circumstance that appropriate catalytic conditions have not been established in many instances. We have found that certain types of carbonyl compounds can be reduced eas-

ily and in good yield by catalytic means, but that it is not always possible to predict in advance what effect structural changes will have upon the reduction. For example, 6-acetoxycoumaran-3-one can be reduced easily to 6-acetoxycoumaran, but under the same conditions the reduction of 6-hydroxy-coumaran-3-one proceeds very slowly to give a mixture which includes products resulting from reduction of the aromatic ring.[4]

In the case of ketoacids, catalytic reduction with a palladium–carbon catalyst appears to proceed with particular ease in acetic acid at 65°. Two examples of the reduction of β-aroylpropionic acids are described; on a scale of about 0.1 mole the reduction was completed in about thirty or forty minutes, and the product was isolated easily in good yield. There was no apparent change in the rate of reduction during this period, and no attempt was made to isolate an intermediate reduction stage. For acids of this kind, this method may be superior to the procedures now in general use.

The reduction of *o*-benzoylbenzoic acid proceeded smoothly and rapidly to give *o*-benzylbenzoic aid in 95% yield.

The reduction of benzoin, under the same conditions, occurred very much less readily. The rate of reduction was rapid at first, but the time required for completion was much longer (about eight hours) and slightly less than the theoretical

(1) Research Corporation Research Assistant, 1948.

(2) Fieser, *et al.*, This Journal, **70**, 3197 (1948).

(3) Huang. *ibid.*, **68**, 2487 (1946).

(4) Horning and Reisner. *ibid.*, **70**, 3619 (1948).