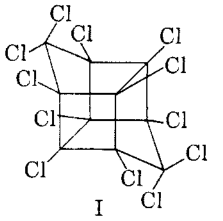
Notes A department for short papers of immediate interest.

Pyrolysis of the Cage Ketone $C_{10}Cl_{10}O$[1]

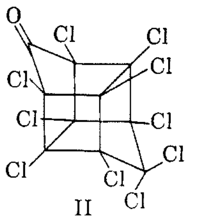
Philip Eaton,[2] Emery Carlson,[3]
Pasquale Lombardo,[3] and Peter Yates[2]

Received December 28, 1959

Hexachlorocyclopentadiene gives on reaction with aluminum chloride a dimeric chlorocarbon, m.p. 485°,[4-6] and with liquid sulfur trioxide a related chloroketone, m.p. 350°.[6] The structures I and II postulated by McBee[7] for these compounds have recently been corroborated by physical methods, comprising dipole moment,[8-10] infrared[8] and x-ray[10] measurements. Their unusual chemical inertness has led us to investigate their thermal stabilities and behavior on pyrolysis.



I



II

It has been reported[7,11] that the chlorocarbon I is remarkably stable to heat, substantial pyrolytic fission occurring only on prolonged heating at or above 500° to produce largely carbonaceous material and chlorine together with a small amount of hexachlorocyclopentadiene.

The thermal stability of the cage system is however markedly reduced by the introduction of the carbonyl group in II. We find that molar equivalents of carbon monoxide and chlorine are readily eliminated at temperatures above 450°. Since the initial organic product was found to be itself thermally labile, a flash pyrolytic technique was developed to permit its isolation. A solution of II in dry carbon tetrachloride was dropped slowly onto the top of a column of ceramic saddles held in a vertical Vycor tube heated by a concentric furnace to 475–500°. The tube was flushed continuously with a rapid stream of dry, oxygen-free, nitrogen. With this apparatus it was possible to effect the pyrolysis and remove the product from the heated zone within approximately ten seconds. The solvent and product were condensed in an ice trap placed immediately below the heated tube. Chromatography of the crude product gave a white crystalline material, C_9Cl_8, m.p. 138–139°, in 80% yield and unchanged II; hexachlorobenzene, arising from pyrolysis of the carbon tetrachloride, was also isolated. Only trace amounts of hexachlorocyclopentadiene were detected, in contradistinction to the observations of Idol[11] who pyrolyzed II under conditions which could lead to the decomposition of the initially formed product. Little or no carbonaceous material was produced; the yield of the C_9Cl_8 product corrected for recovered II was 90–95% in the several pyrolyses carried out. For comparison purposes, I was treated in a similar fashion. At 500° only slight pyrolysis occurred giving trace amounts of hexachlorocyclopentadiene; no carbonaceous material was formed.

The pyrolysis product from II was shown to be octachloroindene, III, by comparison with a sample, m.p. 138–138.5°, prepared by the reaction of phosphorus pentachloride with hexachloroindone (IV), itself prepared by the action of aqueous acetone on octachloro - 3a,4,7,7a - tetrahydro-4,7-methanoindene-1,8-dione (V).[12] The preparation of octachlorindene by this method has been reported previously by Zincke and Gunther,[13] who gave its melting point as 84°; a subsequent report in the patent literature[14] has, however, given a melting point of 132°. Because of this discrepancy it was considered essential to establish the structure of the pyrolysis product independently. Reaction with liquid sulfur trioxide gave the indone IV; chlorination gave a product C_9Cl_{10}, identical with a sample of decachloroindane (VI) prepared by the destructive chlorination of naphthalene in the presence of an iodine/iron catalyst.[14] Treatment of this product with liquid sulfur trioxide gave hexachloroindane-1,3-dione (VII) in

---

[1] Compound II, decachloropentacyclo[$5.3.0.0^{2,6}.0^{4,10}.0^{5,9}$]decan-3-one, alternatively named decachloroöctahydro-1,3,4-metheno-2*H*-cyclobuta[cd]-pentalen-2-one; *cf.* H. E. Ungnade and E. T. McBee, *Chem. Revs.*, **58**, 249 (1958).

[2] Harvard University.

[3] Allied Chemical Corporation.

[4] H. J. Prins, *Rec. trav. chim.*, **65**, 455 (1946).

[5] J. S. Newcomer and E. T. McBee, *J. Am. Chem. Soc.*, **71**, 952 (1949).

[6] E. E. Gilbert and S. L. Giolito, U. S. Reissue Patent 24,435.

[7] E. T. McBee, C. W. Roberts, J. D. Idol, Jr., and R. H. Earle, Jr., *J. Am. Chem. Soc.*, **78**, 1511 (1956).

[8] D. H. Zijp and H. Gerding, *Rec. trav. chim.*, **77**, 682 (1958).

[9] W. H. Mears, General Chemical Research Laboratory, private communication.

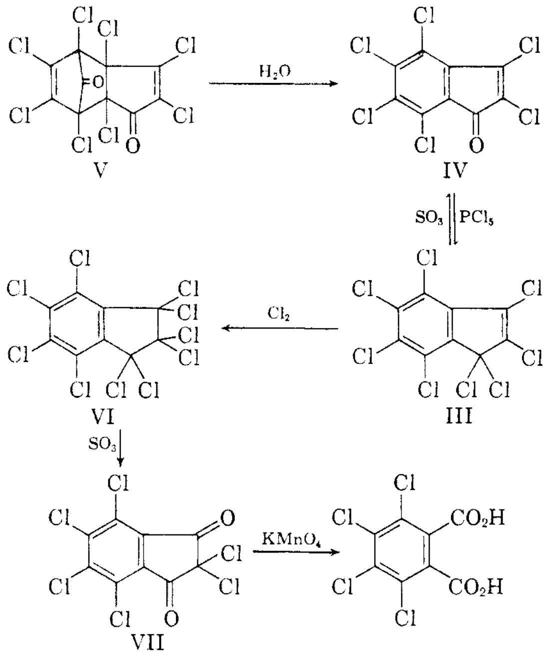
[10] R. Pepinsky and Y. Okaya, Dept. of Physics, Pennsylvania State University, private communication.

[11] J. D. Idol, Jr., Ph.D. Thesis, Purdue, 1954.

[12] T. Zincke and K. H. Meyer, *Ann.*, **367**, 1 (1909).

[13] T. Zincke and H. Gunther, *Ann.*, **272**, 243 (1893).

[14] H. Vollmann, Ger. Patent, **844,143** (1952); *cf. Chem. Abstr.*, **50**, 4227 (1956).



quantitative yield.[15] The diketone was readily oxidized by potassium permanganate to the well known tetrachlorophthalic acid. These reactions provide unambiguous confirmation for the formulation of the pyrolysis product as III.

By analogy with the observed fission of I, it might be considered that octachloroindene is formed from II by cleavage to hexachlorocyclopentadiene and tetrachlorocyclopentadienone, followed by a Diels-Alder recombination with hexachlorocyclopentadiene acting as the dienophile and subsequent decarbonylation and dechlorination. However, hexachlorocyclopentadiene has never been observed to act as a dienophile, while tetrachlorocyclopentadienone is known to undergo very ready dimerization to V[16]; neither V nor its pyrolysis products, octachloroindanone and IV, were detected among the products of the pyrolysis of II under the conditions here described. It seems more likely therefore that the pyrolysis reaction involves the initial loss of the carbonyl group of II as carbon monoxide followed by intramolecular rearrangement and aromatization by loss of chlorine.[17]

EXPERIMENTAL[18]

Dodecachloropentacyclo$[5.3.0.0^{2,6}.0^{4,10}.0^{5,9}]$*decane* (I). The method of Newcomer and McBee[5] was used. Repeated crystallization of the crude product from benzene gave white cubic crystals, m.p. *ca.* 485° (sealed capillary), showing no absorption in the infrared between 2 and 8.6 μ.

Decachloropentacyclo$[5.3.0.0^{2,6}.0^{4,10}.0^{5,9}]$*decan-3-one* (II). Crude material was obtained by the procedure of Gilbert and Giolito.[6] Decolorization was effected by treatment of a methanolic solution with activated charcoal; addition of water to the filtered solution followed by a preliminary air-drying of the precipitated solid gave hydrated II. Anhydrous material was prepared by prolonged refluxing of a xylene solution of the hydrate under a Dean-Stark water trap; on concentration, this solution deposited large white crystals of pure II, m.p. *ca.* 350° (sealed capillary), $\lambda_{max}^{CCl_4}$ 5.58 μ.

Pyrolysis of I *and* II. Pyrolyses were run by permitting solutions in carbon tetrachloride (50 g./l.) to fall dropwise from a pressure-equalizing funnel onto the top of a 30-cm. column of Berl ceramic saddles held vertically within a Vycor tube, 2.8 cm. in diameter, and heated to 500° by a concentric furnace. The tube was flushed continuously with a rapid stream of dry, oxygen-free, nitrogen. Temperatures were measured by iron-constantan thermocouples contained within thin Vycor tubing, one located at the packing-liquid point of contact and the other at the column center. A maximum temperature difference of 100° between these points was maintained by adjusting the rate of addition of solution. Solvent and products were condensed in an ice trap placed immediately below the heated zone. Test runs indicated that hexachlorobenzene was produced by pyrolysis of the solvent (about 0.2% of solvent converted); it was possible to remove it entirely by volatilization on concentrating the condensates on the steam bath.

The infrared spectrum of the condensate from the pyrolysis of I corresponded to that of unchanged starting material contaminated with small amounts of hexachlorocyclopentadiene; no carbonaceous material was formed.

The condensate from the pyrolysis of II was concentrated to one tenth of its original volume (the distillate contained only hexachlorobenzene in addition to carbon tetrachloride) and was chromatographed on neutral alumina. Evaporation of the fraction obtained by elution with carbon tetrachloride gave white crystalline material, m.p. 138–139°, in 80% yield, identical in all respects to octachloroindene; its melting point was undepressed on admixture with authentic material (*vide infra*). Subsequent elution with methanol gave a fraction which contained unchanged II as its methanol adduct. After correction for recovered starting material (about 15%), the yield of octachloroindene ranged from 90–95%. The unpleasant odor of the concentrated condensates indicated the presence of trace amounts of hexachlorocyclopentadiene.

Hexachloroindone (IV). Octachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene-1,8-dione (V; 200 g.), prepared by sulfuric acid hydrolysis of 1,1-dimethoxytetrachlorocyclopentadiene,[12] was dissolved in acetone (500 ml.). Water (*ca.* 350 ml.) was added rapidly to a slight cloudiness. The solution darkened immediately, and yellow crystals of IV separated after 5 min. After standing overnight, the mixture was filtered and the precipitate crystallized from methanol to give 123 g. (82%) of bright yellow crystals, m.p. 149–150°, $\lambda_{max}^{CCl_4}$ 5.77, 6.37 μ.

Anal. Calcd. for C_9Cl_6O: Cl, 63.1. Found: Cl, 63.1.

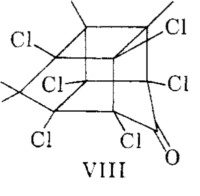
Octachloroindene (V). A heavy-walled glass pressure bottle was charged with 5.6 g. of IV and 10 g. of phosphorus pentachloride. The mixture was heated in an oil bath under autog-

---

(15) *Cf.* J. Bernimolin, *Ber.*, **87**, 640 (1954).

(16) J. S. Newcomer and E. T. McBee, *J. Am. Chem. Soc.*, **71**, 946 (1949).

(17) It may be noted that III is more closely related to the unsymmetrical cage structure VIII; such a structure for the $C_{10}C_{10}O$ ketone, however, appears to be ruled out.[8-10]



VIII

(18) Melting points are uncorrected. Ultraviolet spectra were recorded on a Cary Dual Beam Spectrometer. Infrared spectra were taken on a Perkin-Elmer Model 21 recording spectrometer.

enous pressure at 190–205° for 2 hr. After cooling, water and ether/acetone were added to dissolve all the solids. The ethereal layer was separated, washed with water, dried over sodium sulfate, and diluted with methanol. Partial evaporation of this solution gave white needles (5 g., 79%) of octachloroindene, which were found to be very sensitive to light. The analytical sample, prepared by repeated crystallization from methanol, melted at 138–138.5°, λ_{max}^{KBr} 6.29 μ, $\lambda_{max}^{C_2H_5OH}$ (ϵ), 236 mμ (19,500), 242 mμ (21,000), 250 mμ (29,000), 259 mμ (31,000).

Anal. Calcd. for C_9Cl_8: C, 27.59; Cl, 72.41. Found: C, 27.52; Cl, 72.23.

Chlorination of V; *decachloroindane* (VI). Chlorine gas was bubbled through a solution of 5 g. of V in 75 ml. of carbon tetrachloride held at 50° for 2 hr. Evaporation of the solvent and crystallization of the residue from methanol gave 4.8 g. (81%) of white crystalline material, m.p. 134–135°, identical with a sample of decachloroindane (VI) prepared by the destructive chlorination of naphthalene as described by Vollmann.[14]

Anal. Calcd. for C_9Cl_{10}: Cl, 76.64. Found: Cl, 76.51.

Hydrolysis of V; *hexachloroindone* (IV). Five grams of V were dissolved in 25 ml. of liquid sulfur trioxide. The excess sulfur trioxide was allowed to evaporate overnight from an open beaker. The remaining sulfuric acid–solid mixture was washed with cold water, and the solid crystallized from methanol to give a nearly quantitative yield (4.4 g.) of IV, m.p. 149–150°.

Hexachloroindane-1,3-dione (VII). Five grams of VI were treated with liquid sulfur trioxide in the same manner as above. A quantitative yield (3.8 g.) of VII was obtained as bright yellow crystals, m.p. 155–156°, $\lambda_{max}^{CCl_4}$ 5.65, 5.75 μ.

Anal. Calcd. for $C_9Cl_6O_2$: Cl, 60.30. Found: Cl, 60.28.

This material was identical with a sample prepared by treatment of VI with anhydrous nitric acid as described by Bernimolin.[15]

Oxidation of VII. Three grams of potassium permanganate in 50 ml. of aqueous 5% sodium hydroxide was added with stirring to 1 g. of VII in 10 ml. of warm acetone. After 4 hr., the solution was acidified with concd. hydrochloric acid, bleached with sulfur dioxide, saturated with ammonium sulfate, and extracted with ether. The ethereal extract was washed with water and evaporated to dryness. Sublimation of the residue gave crystals of tetrachlorophthalic anhydride, m.p. 254–256°, identical with an authentic sample.

Acknowledgment. The authors are indebted to Dr. Everett E. Gilbert for his advice and counsel.

DEPARTMENT OF CHEMISTRY
HARVARD UNIVERSITY
CAMBRIDGE, MASS.

GENERAL CHEMICAL DIVISION
ALLIED CHEMICAL CORP.
MORRISTOWN, N. J.

Macrocyclic Compounds. 2-Methyl-2-azacyclohexadecanone

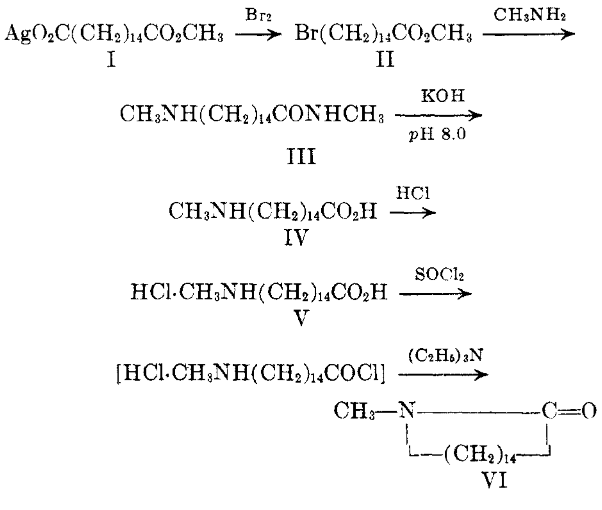
YOSHIO IWAKURA AND KEIKICHI UNO

Received October 1, 1959

Since the structure of natural musk was established as that of a macrocyclic ketone,[1] many macrocyclic compounds have been synthesized. An assumption that cyclic compounds with an approximately 15-membered ring give a musklike odor independent of the type of atoms in the ring skeleton was presented by Ruzicka *et al.*[2] However, in the syntheses of macrocyclic ureas[3] and macrocyclic amides,[4] we found that they gave no odor. Because of the big intermolecular attraction—possibly by H-bonding of the compounds which contain urea- or amide-linkages, it is understood that the melting point becomes high and the volatility becomes low. Assuming that the absence of odor in the macrocyclic ureas and macrocyclic amides was due to their strong intermolecular attraction, we carried out the syntheses of macrocyclic *N*-alkyl amides and *N*,*N'*-dialkyl ureas in which there is no possibility of H-bonding. 2-Methyl-2-azacyclohexadecanone was synthesized from 1,16-hexadecanedioic acid and was found to have a musklike odor.

The sequence of reactions used is shown in Scheme I. In the reaction of the bromoester (II) with methylamine, *N*-methyl-15-methylaminopentadecanamide (III) rather than methyl 15-methylaminopentadecanoate was obtained. 15-Methylaminopentadecanoic acid (IV) was obtained by hydrolysis of III with alcoholic potassium hydroxide, followed by adjusting the *p*H of the solution to 8.0.

Scheme I



When the hydrochloride (V) of the amino acid was treated with thionyl chloride, the amino acid chloride hydrochloride was apparently formed. 2-Methyl-2-azacyclohexadecanone (VI) was prepared by treating the reaction product of amino

---

(1) L. Ruzicka, *Helv. Chim. Acta*, **9**, 715, 1008 (1926).

(2) L. Ruzicka, G. Salomon, and K. E. Meyer, *Helv. Chim. Acta*, **17**, 882 (1934).

(3) Y. Iwakura, K. Uno, and M. Nakada, *J. Chem. Soc. Japan*, **80**, 78 (1959).

(4) Presented at the 12th meeting of the Chemical Society of Japan, Kyoto, April 1959.