[Contribution from the Purdue Research Foundation and Department of Chemistry, Purdue University]

Ring Opening by Chlorinolysis in a Highly Chlorinated Dicyclopentadiene

By E. T. McBee, C. W. Roberts and J. D. Idol, Jr.[1]

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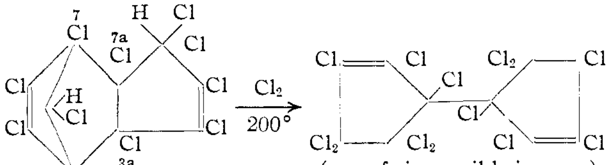
Chlorine reacts at 200° with 1,2,3,3a,4,5,6,7,7a,8-decachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene (I) giving a bis-(perchlorocyclopentenyl) (II) which is identical with the product of exhaustive chlorination of bicyclopentyl. From the evidence cited it is concluded that this transformation involves ring opening in I by chlorinolysis. Compound II is pyrolyzed at 275–300° directly to hexachlorocyclopentadiene and chlorine by a process not involving perchloro-3a,4,7,7a-tetrahydro-4,7-methanoindene as an intermediate.

A recent communication from this Laboratory describes the preparation of 1,2,3,4,5-pentachlorocyclopentadiene[2] and its dimerization to 1,2,3,3a,4,5,6,7,7a,8-decachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene (I). In an attempt to replace the two remaining hydrogen atoms in I by chlorine and so obtain perchloro-3a,4,7,7a-tetrahydro-4,7-methanoindene, compound I was treated with elemental chlorine in a Carius tube at 200°. Not only was replacement of the hydrogen atoms effected, but ring cleavage also occurred. The product was identical with the bis-(perchlorocyclopentenyl) (II), $C_{10}Cl_{14}$, which had been previously prepared by direct, exhaustive chlorination of bicyclopentyl.[3] Identification was achieved by means of analysis, a non-depressed mixed melting point, and superimposable infrared spectra.

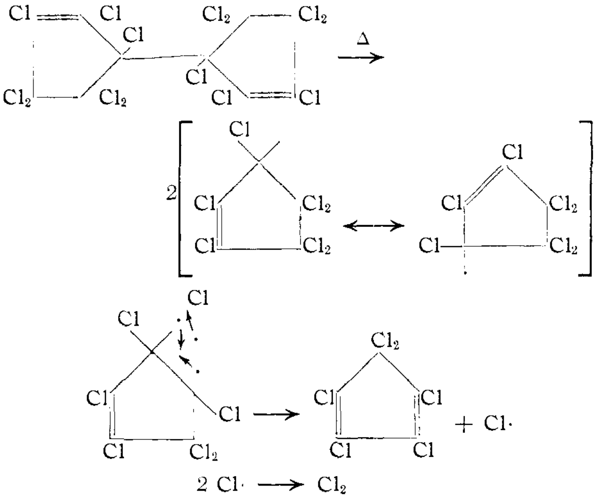
It is not apparent whether ring opening occurs by cleavage of the 3a,4- or the 7,7a-bond, but barring extensive rearrangement of the molecule, one of these processes must occur. The dimer I, m.p. 217°, is known to pyrolyze at temperatures near 350° giving excellent yields of the monomer.[2] Such a thermal degradation followed by chlorination and recombination of the fragments does not seem to be a reasonable reaction course in this case because the chlorination temperature (200°) is less than the melting temperature of the starting material and above the critical temperature of chlorine thus excluding the possibility of reaction in a liquid chlorine medium.



(one of six possible isomers)

I II

Compound II is pyrolyzed at 300° giving 2 molecules of hexachlorocyclopentadiene and one of chlorine. This degradation presumably occurs by the thermally initiated homolytic scission of the exocyclic carbon–carbon bond followed by loss of a chlorine atom from each of the resulting radicals. This follows from the observation made in this Laboratory and elsewhere[4] that at elevated temperatures, hexachlorocyclopentadiene does not add chlorine and may in fact be prepared by pyrolysis of octachlorocyclopentene.



The possibility was considered that II might first rearrange, with loss of a molecule of chlorine, to perchloro-3a,4,7,7a-tetrahydro-4,7-methanoindene (III) and be thence degraded *via* this intermediate to hexachlorocyclopentadiene since III is known to exhibit such behavior.[3] However, when II was partially pyrolyzed at temperatures in the range 250–300° and the reaction mixture subjected to infrared analysis, not even *traces* of III were detected. Pyrolysis of II at higher temperatures, *i.e.* ~400°, resulted in redistribution of the component atoms, hexachlorobenzene being the only product isolated.

Compound II was shown in previous work to contain two isolated ethylenic bonds (λ_{max} 230 mμ, ϵ 16900) by comparison of its ultraviolet spectrum with that of octachlorocyclopentene (λ_{max} 230 mμ, ϵ 10100).[3] Like octachlorocyclopentene,[4] II does not add chlorine. Since the carbon skeleton of II is established by its hydrogenation to bicyclopentyl,[3] the molecule must have one of six possible structures. Presently available data do not permit a choice among these possibilities.

Experimental[5]

Preparation of I.—Compound I, 1,2,3,3a,4,5,6,7,7a,8-decachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene, was prepared from hexachlorocyclopentadiene by reduction with stannous chloride as described by McBee and Smith.[2]

Chlorination of I.—Liquid chlorine (10 g., 0.14 mole) and compound I (10 g., 0.021 mole) were sealed in a Carius tube which was heated for 12 hours at 200° in an electric furnace.

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[1] From a thesis submitted by James D. Idol, Jr., to the Graduate School of Purdue University in Partial Fulfillment of the requirements for the degree of Doctor of Philosophy, August, 1955.

[2] E. T. McBee and D. K. Smith, This Journal, **77**, 389 (1955).

[3] E. T. McBee, J. D. Idol, Jr., and C. W. Roberts, *ibid.*, **77**, 4375 (1955).

[4] J. A. Krynitsky and R. W. Bost, *ibid.*, **69**, 1918 (1947).

[5] Temperatures are uncorrected; melting points in capillary tubes.

The tube was chilled in liquid nitrogen, opened, the excess chlorine allowed to evaporate, and the product extracted with petroleum ether (b.p. 35–37°). The extract, after decolorization with Norite, was concentrated to 75 ml., chilled and filtered; the white tabloids were recrystallized from benzene–methanol to give 8.2 g. (62%) of compound II, m.p. 167–168°; no depression of m.p. was observed on admixture with an authentic sample of II prepared by direct chlorination of bicyclopentyl. The infrared spectra of compound II as prepared by both procedures were identical.

Anal.[6] Calcd. for $C_{10}Cl_{14}$: C, 19.51; Cl, 80.49. Found: C, 19.41; Cl, 79.91.

At lower temperatures, chlorine appeared to have no effect on I. Thus, when chlorine gas was passed into a solution of I in carbon tetrachloride in the presence of actinic light for 48 hr. at 25°, no reaction occurred, the starting material being recovered.

Pyrolysis of II. A. At 250–300°.—Compound II (15 g., 0.024 mole) was placed in a Pyrex tube 1.5 × 10 cm. which was equipped with a side arm leading into a cooled receiver. With the system partially evacuated (25 mm.) the temperature of the tube and contents was raised gradually in a Woods metal-bath to 300° and so maintained for 2 hr. The liquid collected in the receiver was distilled, b.p. 83–86° (2 mm.), giving 6.7 g. (50%) of hexachlorocyclopentadiene, $n^{20}\mathrm{D}$ 1.5657. Chlorine was detected in the exhaust gases from the receiver. The pyrolysis residue was dissolved in 100 ml. of hot benzene; after decolorization with Norite, the solution was diluted with an equal volume of methanol and chilled giving 5.9 g. of II, m.p. and mixed m.p. 165–166°.

When the experiment was repeated at 275°, pyrolysis took place much less readily, and after 3 hr. only the faint odor of hexachlorocyclopentadiene was detected in the product receiver. Of 10 g. of II used, 9.1 g. was recovered. A sample of the recovered crystals, m.p. 161–164°, was dissolved in chloroform and the infrared spectrum of the solution carefully examined for foreign absorption, none being noted.

Using a modified procedure, II (10 g., 0.016 mole) was slowly heated at atmospheric pressure in a cold finger (Dry Ice) sublimator to 250° and the temperature maintained for 3 hr. A white sublimate, 2 g., was shown to be II, m.p. 166–167°. The residue, 7.5 g., crystallized on cooling to nearly pure II, m.p. 163–166°. Infrared analysis of this solid likewise showed no foreign material present.

B. At 425°.—Compound II (10 g., 0.016 mole) was sealed in a carius tube at 1 mm. pressure. The tube was heated rapidly in an electric furnace to 375° and then during the next 4.5 hr., to 425°. After cooling, the tube was opened and the solids extracted with petroleum ether (b.p. 60–70°). Decolorization and chilling of the extracts gave 5.2 g. of hexachlorobenzene, m.p. 222°. On admixture with an authentic sample, m.p. 224–225°,[7] the m.p. was undepressed and the infrared spectra of the two substances (in chloroform) were identical.

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[6] Analysis by Mrs. T. P. Yeh, Purdue University.

[7] E. H. Huntress, "Organic Chlorine Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 477.

[CONTRIBUTION FROM THE INSTITUTE FOR CANCER RESEARCH AND THE LANKENAU HOSPITAL RESEARCH INSTITUTE]

Functional Derivatives of 1,2-Benzanthracene[1]

BY RICHARD M. PECK

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The 6- and 2′-methoxy derivatives of 9,10-dimethyl-1,2-benzanthracene and 7-methoxy-10-methyl-1,2-benzanthracene have been prepared. The 6- and 7-methoxy groups have been converted by hydrolysis, Bucherer reaction, and reaction with phosgene to the corresponding isocyanates.

Since water-soluble derivatives of 9,10-dimethyl-1,2-benzanthracene and other carcinogens have shown interesting biological properties,[2a] it was thought desirable to attach the solubilizing group through a position less vital[2b] to carcinogenic potential than the 3-, 9- or 10-positions. Syntheses were directed toward obtaining the 2′-, 6- and 7-methoxy compounds and thence, through hydrolysis, Bucherer reaction, and reaction with phosgene, the corresponding isocyanates, which permit attachment of the carcinogen to a variety of amino acids and proteins.[3]

Starting materials for the 6- and 7-compounds were the two isomeric keto acids I and II obtained by the reaction of 1,2-naphthalic anhydride either with *p*-methoxyphenylmagnesium bromide or with anisole under Friedel–Crafts conditions. It was found that slow precipitation from a salt solution of a mixture of I and II gave practically pure II until the ratio I:II, as their salts in the mother liquor, was quite high. The remaining acids on crystallization from acetone–benzene gave almost pure I. The ratio of the two compounds produced through one route was approximately the inverse of that from the other reaction. As one would expect from similar syntheses,[4] the predominant product of the Grignard synthesis was the β-keto-α-naphthoic acid (I); the Friedel–Crafts reaction was apparently not influenced by steric effects. During the proof of structure necessary to differentiate between the isomers, it was found that the degradation product III, both derived from II and independently synthesized, has been incorrectly reported in several places in the literature.[5] On examination of the two available references to III it was noted (1) that in either case such strenuous conditions were employed that the possibility existed of methoxyl removal, (2) that a methoxyl analysis was not reported for the compound and (3) that the percentages of carbon and hydrogen in III and its phenolic derivative were too close to allow differentiation. The isomeric *p*-methoxyphenyl

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[1] Supported by an institutional grant from the American Cancer Society.

[2] (a) H. J. Creech, *Cancer Research*, **12**, 557 (1952); E. U. Green, *ibid.*, **14**, 591 (1954); (b) A. Pullman, *Ann. chim.*, **2**, 5 (1947); R. Daudel, *Bull. Cancer*, 110 (1948); H. H. Greenwood, *Brit. J. Cancer*, **5**, 441 (1951).

[3] R. M. Peck, H. J. Creech and G. L. Miller, THIS JOURNAL, **75**, 2364 (1953).

[4] M. S. Newman and P. H. Wise, THIS JOURNAL, **63**, 2109 (1941); M. S. Newman and C. D. McCleary, *ibid.*, **63**, 1542 (1941).

[5] (a) G. Baddeley, *J. Chem. Soc.*, S99 (1949); his reference to Meister, Lucius and Bruning, British Patent 234,173 (1924); (b) F. Unger, *Ann.*, **504**, 285 (1933).