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Diels-Alder Syntheses with Hexachlorocyclopentadiene

BY EDWARD A. PRILL

With respect to the ability of chlorinated dienes to add maleic anhydride or α -naphthoquinone, Norton¹ states that the following generalizations may be drawn: "(a) Dienes of the structure $\text{Cl}-\text{C}=\text{C}-\text{C}=\text{C}$ or $\text{C}=\text{C}(\text{Cl})-\text{C}(\text{Cl})=\text{C}$ do not add dienophiles. (b) Dienes of the structure $\text{C}=\text{C}(\text{Cl})-\text{C}=\text{C}$, in the absence of other chlorine atoms in the molecule, usually add dienophiles as well as do the parent hydrocarbons." These generalizations were drawn from work done, particularly by Carothers and his co-workers, on acyclic, chlorinated dienes. Although cyclopentadiene itself is more reactive than acyclic dienes² it is still rather surprising to find that its fully chlorinated derivative can add certain dienophiles, usually making possible satisfactory yields of the adducts under the conditions used in the following experiments. The new compounds prepared from hexachlorocyclopentadiene^{3,4} are listed in Table I.

a suitable solvent. The sodium and potassium salts of this acid were found to be quite soluble in water but relatively insoluble in ethanol.

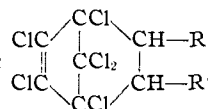
Reaction with Ethyl Maleate.—A mixture of 12 g. of hexachlorocyclopentadiene and 7.6 g. of ethyl maleate (0.044 mole each) was heated at about 100° for twenty-four hours. The remaining reactants were then removed by steam distillation. The adduct was taken up in petroleum ether, dried over sodium sulfate, and freed from the solvent. The adduct was at first a viscous oil and crystallized after a few weeks. It was recrystallized from ethanol. The yield was 2.25 g. or 11.5%.

Reaction with *p*-Benzoquinone.—A mixture of 27.3 g. of hexachlorocyclopentadiene (0.1 mole), 10.8 g. of *p*-benzoquinone (0.1 mole), and 5 ml. of toluene was heated at about 100° for fourteen hours. The dark colored solid reaction product was washed with a small amount of ethanol and then dissolved in 250 ml. of hot ethanol. On cooling 18 g. of yellow crystalline adduct was obtained, and, after concentration of the filtrate, 2 g. more (52.5% of the theoretical).

Reaction with Acrylonitrile.—A mixture of 54.6 g. (0.2 mole) of hexachlorocyclopentadiene and 21.2 g. (0.4 mole) of freshly distilled acrylonitrile plus, as an intended antipolymerization catalyst, 0.25 g. of 4-*t*-butylcatechol

TABLE I

COMPOUND FROM HEXACHLOROCYCLOPENTADIENE OF THE TYPE:



Dienophile used	Product isolated		M. p. (uncor.) °C.	Analyses, % Cl ^a	
	R	R'		Calcd.	Found
Maleic anhydride	CO ₂ H	CO ₂ H	232	54.7	55.0
Ethyl maleate	CO ₂ C ₂ H ₅	CO ₂ C ₂ H ₅	67	47.8	47.9
<i>p</i> -Benzoquinone	CO-CH		188	55.9	56.3
	CO-CH				
Acrylonitrile	CN	H	143	65.3	64.4
Methyl vinyl ketone	COCH ₃	H	70	62.0	62.9
Methyl vinyl ketone	C-CH ₃		130	59.6	59.3
	NOH				

^a The chlorine analyses (Parr bomb) were performed by Victor Cullmann.

Experimental

Reaction with Maleic Anhydride.—A mixture of 27.3 g. (0.1 mole) of hexachlorocyclopentadiene, 9.8 g. (0.1 mole) of maleic anhydride, and 5 ml. of toluene was heated at about 100° for fourteen hours. Unreacted diene and toluene were removed by steam-distillation. The dicarboxylic acid resulting from hydrolysis of the adduct was mostly in the form of a heavy oily layer in the distillation residue (about 1500 ml. of water) and crystallized on cooling to room temperature. (Despite its high melting point this acid liquefies under warm water.) At this stage 27 g. of the acid was obtained, 2 g. more after cooling to 0°, and 3.5 g. more after concentration of the filtrate; the total yield being 83% of the theoretical. From a similar experiment in which the period of heating was three hours, the yield was only 22%. The acid was purified by recrystallization from water. Toluene was also found to be

and 1 ml. of glacial acetic acid, was heated for twenty-four hours at about 100°. The mixture was then subjected to steam distillation, whereupon 32 g. of unreacted diene came over fairly rapidly. The receiver was then changed and the steam distillation continued whereupon the adduct came over very slowly as a waxy solid, about 15 liters of water being condensed in the process. A small amount of non-volatile resin remained. The adduct was recrystallized from methanol-water mixture and was obtained as soft waxy crystals; yield 21 g.

Reaction with Methyl Vinyl Ketone.—A mixture of 27.3 g. (0.1 mole) of hexachlorocyclopentadiene and 14 g. (0.2 mole) of purified methyl vinyl ketone⁵ plus, as an intended antipolymerization catalyst, 0.25 g. of 4-*t*-butylcatechol and 1 ml. of glacial acetic acid, was heated at about 100° for twenty hours. A small amount of unreacted diene was then removed by steam distillation. On continuing the steam distillation a viscous oily product came over so slowly that it appeared advisable to terminate the dis-

(1) J. A. Norton, *Chem. Rev.*, **31**, 379 (1942).

(2) R. Sefton, *J. Soc. Chem. Ind.*, **64**, 104 (1945).

(3) F. Straus, L. Kollek and W. Heyn, *Ber.*, **63B**, 1868 (1930).

(4) Obtained through the courtesy of Hooker Electrochemical Co.

(5) Obtained as an azeotropic mixture through the courtesy of Organic Chemicals Department, Chemical Division, E. I. du Pont de Nemours & Co.

tillation. This oily product was converted into 2 g. of an oxime identical with the oxime later obtained from the main portion of the adduct. The dark viscous oil from the distillation residue was separated from the water and was taken up in methanol, whereupon a considerable amount of methanol-insoluble resin separated out. The methanol solution of adduct was poured into water and the adduct extracted with petroleum ether. After removal of the solvent, 14 g. of the adduct distilled at 154–156° (7 mm.). This finally solidified and was recrystallized from ethanol-water mixture.

A portion of this ketonic adduct was converted into its oxime by warming with hydroxylamine hydrochloride and sodium acetate in ethanol-water solution. The oxime was recrystallized from ethanol-water mixture.

Attempted Reaction with Chloromaleic Anhydride.—A mixture of 27.3 g. (0.1 mole) of hexachlorocyclopentadiene, 26.5 g. (0.2 mole) of chloromaleic anhydride, and 5 ml. of xylene was refluxed for twelve hours. On steam distillation practically all of the diene was recovered unchanged and no adduct could be isolated.

Action of Alkali on the Adducts.—Hexachlorocyclopentadiene itself was very easily decomposed by even weak alkali with the liberation of ionic chlorine. The acid from the maleic anhydride adduct was remarkably stable

toward alkali; boiling its salt with 10% aqueous or alcoholic potassium hydroxide for six hours liberated no significant amount of ionic chlorine. The adducts made with *p*-benzoquinone, acrylonitrile, and methyl vinyl ketone produced ionic chlorine quite easily when warmed with alcoholic potassium hydroxide. The interesting observation was made that the acrylonitrile adduct on heating with alcoholic alkali produced an intense clear red color.

Summary

Hexachlorocyclopentadiene has been found capable of acting as the diene component in the Diels–Alder diene synthesis with certain dienophiles, in which respect it appears to differ from comparably chlorinated, and even some less highly chlorinated, acyclic dienes. Compounds prepared through the additions of maleic anhydride, ethyl maleate, *p*-benzoquinone, acrylonitrile and methyl vinyl ketone to hexachlorocyclopentadiene are described.

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[CONTRIBUTION FROM THE RICHARDSON CHEMISTRY LABORATORY, THE TULANE UNIVERSITY OF LOUISIANA]

Substituted 2-Picolines Derived from 6-Amino-2-picoline¹

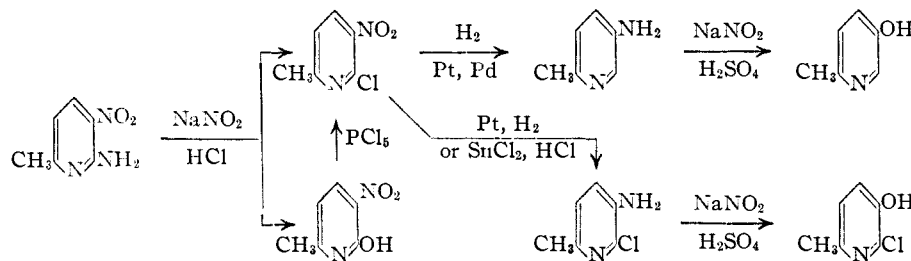
BY EDWIN D. PARKER² AND WILLIAM SHIVE³

In connection with investigations concerning utilization of coal tar bases, a number of substituted 2-picolines derived from 6-amino-2-picoline have been synthesized for various purposes.

One of these products, 5-hydroxy-2-picoline, was prepared for comparison with the “ β -hydroxy- α -picoline”⁴ which Wulff⁵ obtained by alkali fusion of the sulfonation product of 2-picoline. The following equations indicate the methods by which this hydroxy compound and 6-chloro-5-hydroxy-2-picoline were prepared. The 5-hy-

droxy- α -picoline” but did not report the structure of the “nitro- β -hydroxy- α -picoline” which he obtained. Since further investigation in this Laboratory has led to the conversion of this nitrohydroxypicoline to the corresponding chlorohydroxypicoline,⁷ the synthesis of 6-chloro-5-hydroxy-2-picoline as indicated above was carried out in order to compare the product with that obtained from the “nitro- β -hydroxy- α -picoline.” The two compounds were found to be identical.

The 6-amino-5-nitro-2-picoline used in the above syntheses was obtained from 2-picoline by amination and nitration similar to the method of Zeide⁸ except that the nitration of 6-amino-2-picoline and isomerization of the 6-nitroamino-2-picoline were carried out



droxy-2-picoline prepared by this method and the “ β -hydroxy- α -picoline” of Wulff⁵ were found to be identical. Wulff⁶ also nitrated his “ β -hy-

droxy- α -picoline” but did not report the structure of the “nitro- β -hydroxy- α -picoline” which he obtained. Since further investigation in this Laboratory has led to the conversion of this nitrohydroxypicoline to the corresponding chlorohydroxypicoline,⁷ the synthesis of 6-chloro-5-hydroxy-2-picoline as indicated above was carried out in order to compare the product with that obtained from the “nitro- β -hydroxy- α -picoline.” The two compounds were found to be identical.

(1) From a thesis submitted by Edwin D. Parker in partial fulfillment of the requirements for the degree of Master of Science.

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(4) This product has been indexed as 2-picolin-3-ol, *C. A.*, Decennial Index, **21-30** (1927–1936), and has been listed as 3-hydroxy-2-picoline, *C. A.*, **26**, 2471 (1932).

(5) Wulff, U. S. Patent, 1,880,645, Oct. 4, 1932.

(6) Wulff, U. S. Patent 1,889,303, Nov. 29, 1932.

(7) Ballweber and Shive, unpublished work.

(8) Zeide, *J. Russ. Phys.-Chem. Soc.*, **50**, 534 (1920); *C. A.*, **18**, 1497 (1924).