[CONTRIBUTION FROM THE VENABLE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

The Preparation of Hexachlorocyclopentadiene and Certain Derivatives[1]

BY J. A. KRYNITSKY[2] AND R. W. BOST

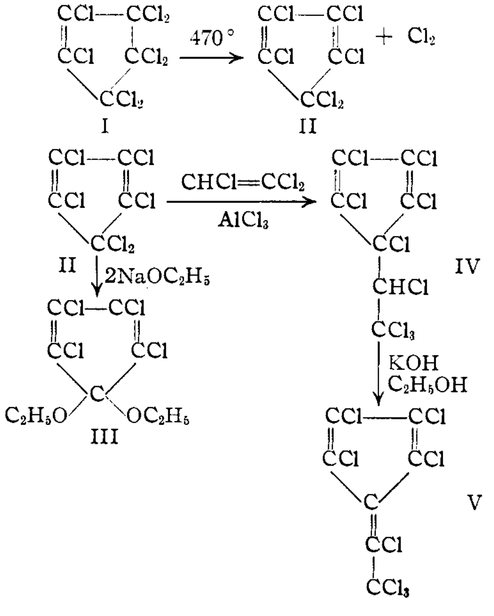
In connection with a study of the stabilities toward hydrolysis of certain highly chlorinated and fluorochlorinated hydrocarbons, it was of interest to prepare some highly chlorinated derivatives of the cyclopentadiene type.

Straus, *et al.*,[3] report the replacement of "positive" hydrogen with chlorine through the action of potassium hypochlorite. In this manner, they first succeeded in obtaining hexachlorocyclopentadiene from the parent hydrocarbon. In the present investigation, such a preparation was tried but soon discarded in favor of the method described below which gave superior yields and could be readily carried out with materials on hand.

During an unsuccessful attempt to prepare decachlorocyclopentane through the vapor phase chlorination of octachlorocyclopentene (I), it was found that at temperatures above 325° the compound does not add chlorine but rather begins to pyrolyze slowly to yield chiefly hexachlorocyclopentadiene (II) and chlorine. Further investigation showed that as the temperature is increased, the rate of pyrolysis is increased and that other products such as hexachlorobenzene are also formed. Thus at 400–430°, 1.05 moles of I yielded in addition to recovered I, 0.47 mole of II and only a trace of hexachlorobenzene. However, at 470–480°, 14.5 moles of I yielded besides the starting material, 10.8 moles of II, and approximately 0.8 mole of hexachlorobenzene. In these pyrolyses, carbon tetrachloride was used as a diluent. To check whether this diluent took part in the reaction, an experiment was carried out using only pure carbon tetrachloride. It was found that at temperatures up to 500°, no appreciable pyrolysis took place and no hexachlorobenzene was found. This is in agreement with data which have been previously reported.[4] A further experiment was run in which (I) was pyrolyzed at 470–480° in the absence of carbon tetrachloride. In this case hexachlorobenzene was obtained in addition to (I) and (II).

It has been shown by several investigators[5,6,7] that halogens attached vicinal to a double bond possess an enhanced activity whereas those attached to a double bond are repressed. Advantage of this difference in reactivities was taken in treating sodium ethoxide with II to produce the diethyl acetal of tetrachlorocyclopentadiene-one (III).

Prins[5,6,8,9,10] found that certain aliphatic chlorinated hydrocarbons could be made to condense, in the presence of aluminum chloride, with chlorinated olefins to yield higher members of the chlorinated aliphatic series. He further showed that many highly chlorinated compounds (containing at least one hydrogen) could be dehydrohalogenated very readily by the action of alcoholic alkali to create a new double bond in the molecule. In the present work, these reactions were extended to include a member of the alicyclic series. Thus, II was condensed with trichloroethylene to give 1-(α,β,β,β-tetrachloroethyl)-pentachlorocyclopentadiene-2,4 (IV). The product thus formed was then dehydrohalogenated by the action of alcoholic potassium hydroxide to produce perchloromethylfulvene (V). The physical properties obtained for these compounds and some of their intermediates are given in Table I.



Experimental

Materials.—Octachlorocyclopentene (I) was prepared in 94% yield by the intramolecular rearrangement of octachloropentadiene-1,3 caused by the action of anhydrous aluminum chloride.[6] The octachloropentadiene-1,3 was in turn prepared in 4 steps with over-all yields of 67–73% from tetrachloroethylene, chloroform and trichloroethylene

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[2] Present address: Naval Research Laboratory, Washington, D. C.

(3) Straus, Kollek and Heyn, *Ber.*, **63B**, 1884 (1930).

(4) C. D. Hurd, "The Pyrolysis of Carbon Compounds," 1st ed. 132 (1929).

(5) H. J. Prins, *J. prakt. Chem.*, **89**, 414–424 (1914).

(6) H. J. Prins, *Rec. trav. chim.*, **51**, 1065–1080 (1932).

(7) Conant, Kirner and Hussey, THIS JOURNAL, **47**, 488 (1925).

(8) H. J. Prins, *ibid.*, **56**, 779 (1937).

(9) H. J. Prins, *ibid.*, **57**, 659–666 (1938).

(10) Böeseken and Prins, *Chem. Zentr.*, **82**, I, 466 (1911).

TABLE I

PHYSICAL PROPERTIES OF SOME HIGHLY CHLORINATED HYDROCARBONS

Compound	Boiling point °C.	Boiling point Mm.	M. p., °C.	t, °C.	n^{t}_{D}	d^{t}_{4}
$CHCl_2CCl_2CCl_3$	112	10	29.5–30	35	1.5401	1.8070
	135	30				
$CCl_2{=}CClCCl_3$	95	15	Visc. liq.	25	1.5471	1.7578
	120.7	48	at − 78			
$CCl_2{=}CClCCl_2CHClCCl_3$	149	5	Glass −78	25	1.5678	1.8107
$CCl_2{=}CClCCl{=}CClCCl_3$	117	3	Glass −78	25	1.5700	1.7664
	143	10.5				
C_5Cl_8 (I)	107	1.6	38–38.2	45	1.5683	1.816
	134	6				
C_5Cl_6 (II)	94	5	−10 to −9	25	1.5629	1.7035
	108	10				
	239	753				
$C_9H_{10}O_2Cl_4$ (III)	114	6.1	−17 to −15	25	1.5088	1.3694
	127	11.7				
	dec.	753				
C_7HCl_9 (IV)	143	1.7	80–80.5			
C_7Cl_8 (V)	121	1.9	53–53.2			
	141	5.5				

through condensation and dehydrohalogenation reactions described by Prins,[4,5,6] involving the intermediates: *unsym*-heptachloropropane, hexachloropropene and 1,1,-2,3,3,4,5,5,5-nonachloropentene-1.

Hexachlorocyclopentadiene (II).—4985 grams (14.5 moles) of I dissolved in 1.5 liter of carbon tetrachloride was passed dropwise over a period of several days through a combustion tube set at a slight incline and electrically heated over a 26 inch zone to 470–480°. Fractionation of the pyrolysis products at reduced pressure yielded 2940 g. (10.8 moles) of II, b. p. 78–84° (1–2 mm.); 618 g. (1.8 moles) of I, b. p. 102–107° (1–2 mm.); and a 236-g. residue which was found to consist almost entirely of hexachlorobenzene. The conversion of I to II was 74.5% and the yield was 85% when compensated for the recovered I. The product had a pale straw color and harsh pungent odor, slightly reminiscent of naphthalene.

Anal. Calcd. for C_5Cl_6: Cl, 78.00; mol. wt., 272.7, *MR*, 51.36. Found: Cl, 78.21, 78.17; mol. wt., 268; *MR*, 52.04.

Tetrachlorocyclopentadiene-one-diethyl Acetal (III).—Freshly shaved sodium (2.04 moles) was dissolved in 800 ml. of absolute ethanol. This was then added dropwise, with efficient stirring, over a period of three hours to a solution of 250 g. (0.92 mole) of II in 200 ml. absolute ethanol. Throughout the addition, the temperature was maintained at 30–35° by means of an external cooling bath. After addition was complete the mixture was stirred overnight at room temperature. Addition of 800 ml. of water caused separation of an organic layer to which 300 ml. of carbon tetrachloride was added. The organic portion was washed several times with water. After removal of solvent and a small amount of forerun, distillation at reduced pressure yielded 198 g. (0.68 mole) of III, b. p. 80.6° at less than 1 mm., and a 26-g. residue. The yield was 74.5% of the theoretical. The product had a pale greenish-yellow color and a fruit-like odor, somewhat like that of green apples.

Anal. Calcd. for $C_9H_{10}O_2Cl_4$: Cl, 48.59; mol. wt., 291.9; *MR*, 63.38. Found: Cl, 49.82, 50.00; mol. wt., 283; *MR*, 63.68.

1-(α,β,β,β-Tetrachloroethyl)-pentachlorocyclopentadiene-2,4 (IV).—Into a flask fitted with a rubber-sealed stirrer, reflux condenser and dropping funnel was placed 1000 g. (3.67 moles) of II. The stirrer was started and 100 g. of anhydrous aluminum chloride was introduced. This mixture was stirred for thirty minutes to allow time for the bright-yellow complex between II and aluminum chloride to form. The mixture was then heated to 40° and 1000 g. (7.62 moles) of trichloroethylene was added dropwise over two and one-half hours. After forty-four hours of stirring at 40°, 500 ml. of ice–water mixture was added. A considerable amount of black solid separated so 1 liter of carbon tetrachloride was added for solvent purposes. The organic layer was washed well with water. After removal of solvent and a 149-g. forerun, distillation yielded 1201 g. (2.97 moles) of IV, b. p. 135–145° (1–2 mm.) and a 160-g. residue. The yield was 81.3% of the theoretical. The product was of a light cherry color when liquid and crystallized to a faint orange solid on standing. Upon several recrystallizations from alcohol, there was obtained a snow-white crystalline solid having a faint camphor-like odor.

Anal. Calcd. for C_7HCl_9: Cl, 78.96; mol. wt., 404.1. Found: Cl, 79.33, 79.02, 79.21; mol. wt., 394.

Experiments carried out at other temperatures (25 and 60°) gave much poorer yields.

Perchloromethylfulvene (V).—Into a flask fitted with a stirrer, thermometer, reflux condenser and a dropping funnel were placed 800 g. (1.98 moles) of IV and 500 ml. of carbon tetrachloride. A solution of 125 g. (2.23 moles) of potassium hydroxide dissolved in a mixture of 300 ml. of methanol and 500 ml. of ethanol was added dropwise with stirring, over four hours. During this addition, the temperature rose to 35–45°. The mixture was then allowed to stir overnight. Addition of 500 ml. of water caused an organic layer to separate. This was washed well with water, and subjected to distillation. After removal of solvent and a 6-g. forerun, there was obtained 650 g. (1.77 moles) of V, b. p. 115–119° (1–2 mm.) and a 62-g. residue. The yield was 89% of theoretical. The product was a clear amber liquid which solidified upon prolonged standing. Two recrystallizations from alcohol gave a snow-white micro-crystalline product having a faint musty camphor-like odor. Unlike the parent hydrocarbon, V showed no tendency to polymerize on standing.

Anal. Calcd. for C_7Cl_8: Cl, 77.15; mol. wt., 367.7; *MR*, 69.86. Found: Cl, 77.48, 77.32; mol. wt., 363; *MR*, 69.21.

Acknowledgment.—The authors wish to express their appreciation to Mr. W. T. Rainey for checking certain experiments in this paper.

Summary

1. A new synthetic method for the preparation of hexachlorocyclopentadiene based on the pyrolysis of octachlorocyclopentene has been described.
2. The Prins reaction has been extended to include a member of the alicyclic series.
3. Three new compounds derived from hexachlorocyclopentadiene were synthesized.
4. Physical properties for the above substances and some of their intermediates are given.

CHAPEL HILL, NORTH CAROLINA
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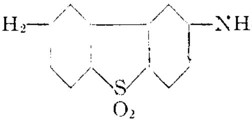
[CONTRIBUTION FROM THE WM. H. CHANDLER CHEMISTRY LABORATORY, LEHIGH UNIVERSITY]

Studies in the Sulfone Series. I. The Preparation of 2,8-Diaminodibenzothiophene-5-dioxide

BY C. R. NEUMOYER[1] AND E. D. AMSTUTZ

During the past few years numerous attempts have been made to improve the therapeutic index of the potent but toxic antibiotic, 4,4'-diaminodiphenyl sulfone. From these investigations have come such materials as diasone,[2,3] promin, the formaldehyde-bisulfite derivative,[3] certain carboxylic acid derivatives,[4] and the unsymmetrical diacyl compounds.[5] The work reported in this present paper was likewise designed to yield materials of more favorable therapeutic index but was directed along different lines.

2,8-Diamino-dibenzothiophene-5-dioxide (I) may be considered to be derived from 4,4'-diaminodiphenyl sulfone (II) by direct union of the 2,2'-positions.



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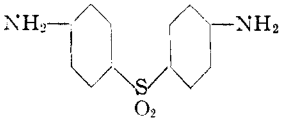
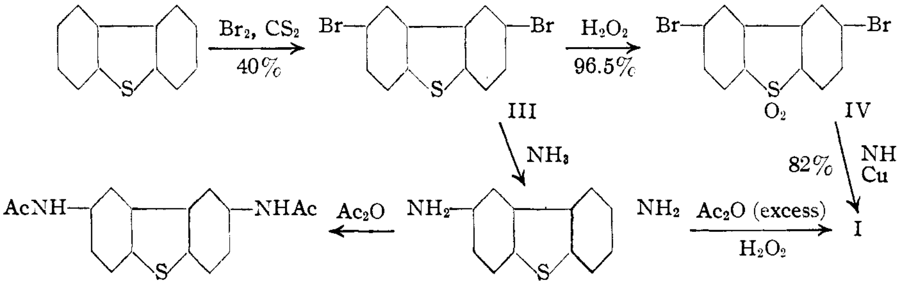


II

An investigation of the preparation of the compound and some of its derivatives has been made.

In most of its mono- and di-substitution reactions dibenzothiophene is attacked at the 2- and the 2,8-positions. Thus it has been shown that the product of mono-bromination is the 2-bromo derivative,[6] and in dibromination the 2,8 compound. Gilman has reported[7] the successful substitution of the halogen of 2-bromodibenzothiophene by the amino group. The following reaction sequence[8] was adapted to obtain (I).



The 2,8-dibromo derivative (III) was obtained in 40% yield by long refluxing of a carbon bisulfide[9] solution of bromine and dibenzothiophene. The conversion to the dioxide (IV) was accomplished in almost quantitative yield by refluxing the sulfide with hydrogen peroxide in glacial acetic acid. Amination of the dibromo sulfone with concentrated aqueous ammonia and a trace of copper powder at 175–220° afforded the corresponding diamine.

We also carried out the diamination of 2,8-dibromodibenzothiophene and obtained in this way the corresponding diamino compound which melted at 199.5–201.5°. Burger and his coworkers reported a melting point of 193–194° for the same compound while Courtot and Pomonis[10] found the compound to melt at 178°. Our diamine also yielded a diacetyl derivative which melted at 304–305.5° as compared to 253–255° for Burger's sample of the same material, and 237–239° (dec.) for Courtot's substance.

All attempts to oxidize the 2,8-diacetamidodibenzothiophene to the dioxide were fruitless, only colored materials of indefinite melting ranges being obtained. After the diamine had been refluxed

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[1] The Wm S. Merrell Co. Post-doctorate Fellow in Organic Chemistry, 1944–1946. Present address: Heyden Chemical Corp., Garfield, N. J.

[2] Raiziss, Clemence and Freifelder, *J. Am. Pharm. Assocn.*, **33**, 43 (1944).

[3] Bauer, THIS JOURNAL, **61**, 617 (1939).

[4] Gray and Platt, *J. Chem. Soc.*, 42 (1942).

[5] Shonle and Van Arendonk, THIS JOURNAL, **65**, 2375 (1943).

[6] Cullinane, Davies and Davies, *J. Chem. Soc.*, 1435 (1935).

[7] Gilman and Jacoby, *J. Org. Chem.*, **3**, 108 (1938).

[8] A second synthetic approach *via* the Beckmann rearrangement of the dioxime of 2,8-diacetyldibenzothiophene (Burger, Wartman and Lutz, THIS JOURNAL, **60**, 2628 (1938)) was discarded after preliminary experiments indicated that the method was not applicable to the preparation of reasonable quantities of material.

[9] The use of acetic acid as a solvent served to shorten the time required for the reaction, but the product was difficult to purify.

[10] Courtot and Pomonis, *Compt. rend.*, **182**, 893, 931 (1926).