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

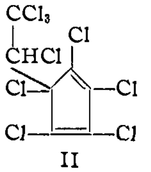
The Chemical Behavior of Hexachlorocyclopentadiene. II. Condensation with Trichloroethylene[1]

By J. S. Newcomer[2] and E. T. McBee

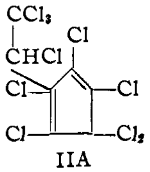
The exceptional reactivity of hexachlorocyclopentadiene (I) in the presence of aluminum chloride may be attributed to the pentachlorocyclopentadienyl cation, $C_5Cl_5^+$. The resonance forms of this ion provide a theoretical basis for the susceptibility of I toward addition reactions, either as an addend or augend. The former is illustrated by the addition of chloroform to I to produce a nonachloromethylcyclopentene[3] and by the addition of chlorine in the presence of aluminum chloride to form octachlorocyclopentene.[4] The latter is illustrated by the addition of I to trichloroethylene to form 5-(1,2,2,2-tetrachloroethyl)-pentachlorocyclopentadiene (II). Both processes are illustrated by the dimerization of I to form a compound $C_{10}Cl_{12}$ (XVI). A summary of the reactions reported in this paper is shown diagrammatically in Fig. 1.

Since the presentation of this paper,[4,5] Krynitsky and Bost[6] reported the preparation of a compound C_7HCl_9 by the condensation of I with trichloroethylene in the presence of aluminum chloride. These investigators also reported the preparation of a chlorocarbon C_7Cl_8 by the dehydrochlorination of C_7HCl_9 with alcoholic alkali. No proof of the structure of these materials was presented. Investigations in this Laboratory have shown that the condensation of I with trichloroethylene may be controlled to produce high yields of either C_7HCl_9 (II) or C_7Cl_8(l), octachloro-1 or 2-vinylcyclopentadiene (IV), with a small quantity of a dimer of I as a by-product. Although I readily dimerizes in the presence of aluminum chloride, the rate of dimerization at 80° is not as rapid as the rate of condensation with trichloroethylene. By performing the condensation at 80°, and then increasing the temperature to 110–115°, the aluminum chloride effects rearrangement and dehydrochlorination of II to form IV. On the other hand, the dehydrochlorination of II with alcoholic alkali occurs without rearrangement to form an isomeric solid chlorocarbon C_7Cl_8(s), octachloro-5-ethylidenecyclopentadiene (III).

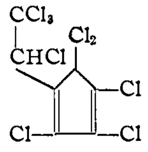
It is highly improbable that dehydrochlorination of C_7HCl_9 with alcoholic alkali involves a rearrangement. Consequently, the corresponding chlorocarbon C_7Cl_8(s) may be represented by structure III or IIIA, IVA, IVB, or IVC, depending upon whether it was derived from the structure II, IIA, IIB, or the bicyclic compound.



II



IIA



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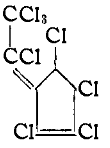
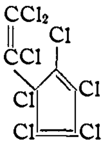
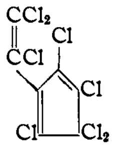


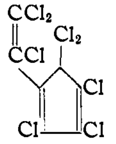
III



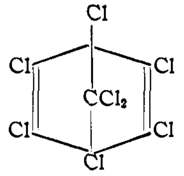
IIIA



IVA



IVB



IVC

The isomeric chlorocarbons, C_7Cl_8(l) and C_7Cl_8(s) display entirely different chemical properties. The former undergoes reactions analogous to those of hexachlorocyclopentadiene, corresponding to structures IVA and IVB. The latter undergoes reactions typical of polychlorinated compounds which contain a trichloromethyl group attached to a carbon atom of an ethylenic bond, thus corresponding to structure III.

The bicyclic structure IVC can account in no apparent manner for either of these two types of reactions. In addition, IVC is not in accord with molecular refraction data, nor with the observed reactivity of both chlorocarbons toward alcoholic silver nitrate as well as toward alcoholic alkali. Furthermore, the liquid chlorocarbon, which was produced by the more drastic conditions, was converted to the unsaturated derivatives of ethylcyclopentane (XIII and XIV) by treatment with antimony pentafluoride. Fluorination of XIII with silver difluoride formed a chlorotridecafluoroethylcyclopentane. If the liquid chlorocarbon is assumed to have structure IVC, then cleavage must have occurred during the formation of the unsaturated compounds XIII and XIV. It is improbable that cleavage of the bicyclic compound would produce unsaturated derivatives of ethylcyclopentane, but more plausible to expect the cleavage

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[1] Abstracted from the doctoral thesis of J. S. Newcomer.

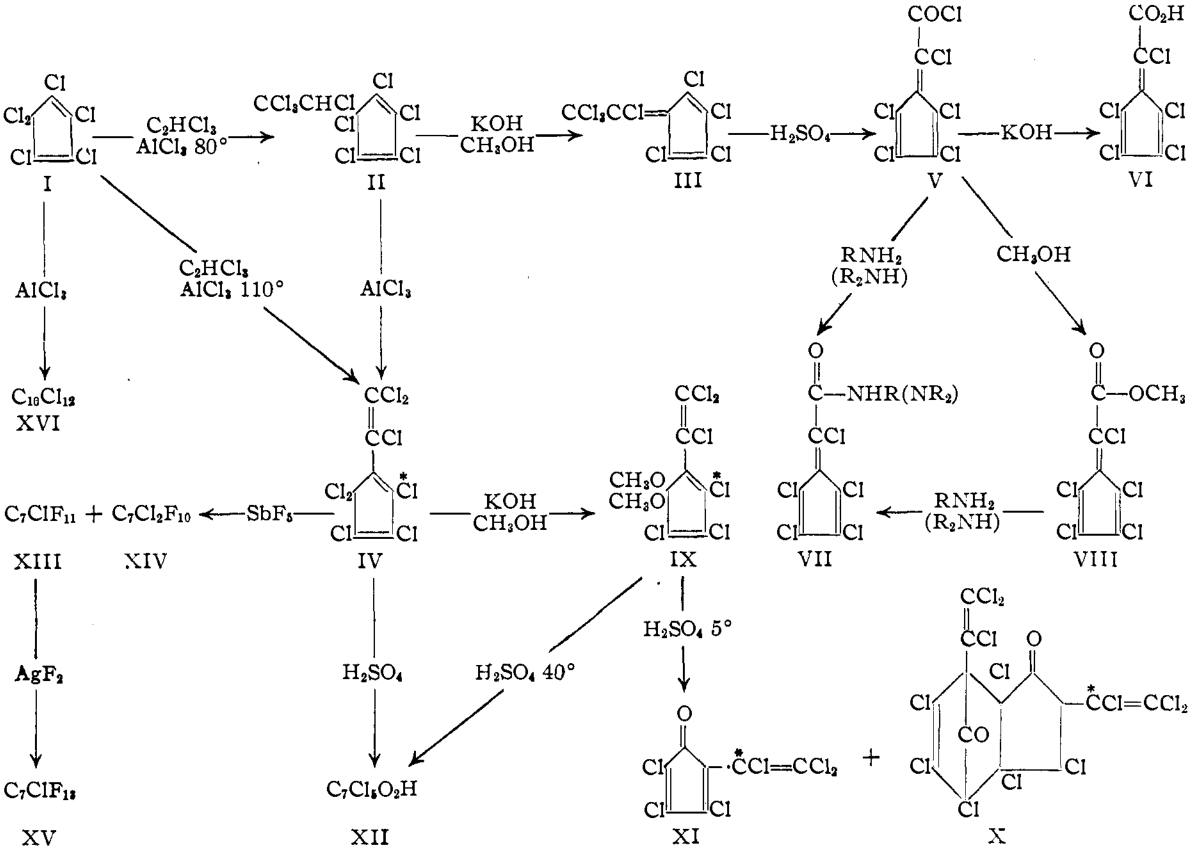
[2] Present address: Sharples Chemicals, Inc., Wyandotte, Michigan.

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

[4] J. S. Newcomer and E. T. McBee, This Journal, **71**, 946 (1949).

[5] J. S. Newcomer and E. T. McBee, presented before the 111th Meeting of the Am. Chem. Soc., April 14–18, 1947.

[6] J. A. Krynitsky and R. W. Bost, This Journal, **69**, 1918 (1947).



Chlorotridecafluoroethylcyclopentane. (*Position of trichlorovinyl group uncertain.)

to occur at a position allylic to the two ethylenic linkages to form unsaturated derivatives of methylcyclohexane, which might undergo further cleavage to form cyclohexene derivatives. However, no compound of these types of structures was obtained.

The fluorination of C_7Cl_8(l) (IV) with antimony pentafluoride to give high yields of the seven carbon atom compounds XIII and XIV may be contrasted with our previous investigations[7] in which it was shown that the fluorination of (tetrachlorophenyl)-pentachloroethane, (pentachlorophenyl)-dichlorotrifluoroethane, mixtures of polychloropolyfluoroethylbenzenes, pentachlorobenzotrifluoride, and hexachlorobenzene, under similar conditions, produced predominantly a six carbon atom compound, $C_6Cl_2F_8$.

The liquid chlorocarbon reacts rapidly with methanolic alkali to form an acetal, $C_7Cl_6(OCH_3)_2$ (IX), whereas the solid chlorocarbon reacts sluggishly to form a mixture of products. Structure III could form an acetal only by the elimination of a chloride ion to form an organic cation in which the charge could resonate from the terminal carbon atom of the side chain to one of the carbon atoms of the ring containing a chlorine atom. If this type of resonance were significant in the cation derived from structure III, then it should also be significant in the cations derived from structures IIIA, IVA, and IVB, since common resonance hybrids would be produced. Therefore, if III formed an acetal, IIIA, IVA, and IVB would also be expected to form acetals. The chlorocarbons C_7Cl_8(l) and C_7Cl_8(s) represent two of these four possible structures, but only the former forms an acetal. Hence, structure III cannot form an acetal and the structure of C_7Cl_8(l) is limited to IIIA, IVA, or IVB. Structure IIIA could form an acetal only by rearrangement, whereas IVA and IVB could form acetals with or without rearrangement. It seems highly improbable that IIIA would be converted to a completely conjugated system upon treatment with alcoholic alkali, but not in the presence of aluminum chloride for eleven hours at 110°, which are the conditions employed for the preparation of C_7Cl_8(l). The structure of this material is limited to octachloro-1 or 2-vinylcyclopentadiene (IVA or IVB). Further evidence supporting this contention is afforded by hydrolysis of the acetal with sulfuric acid at 5° to form a blood-red ketone, hexachloro-2 or 3-vinylcyclopentadienone (X) and its colorless Diels–Alder dimer (XI). In addition, reduction of C_7Cl_8(l) with zinc and acid resulted in the replacement of two chlorine atoms, and treatment with sulfuric acid formed a diketone $C_7HCl_5O_2$-(XII). This same diketone was obtained by hy-

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(7) E. T. McBee, *et al.*, *Ind. Eng. Chem.*, **39**, 384 (1947).

drolysis of the acetal (IX) with sulfuric acid at 40°, thus illustrating the expected reaction of hexachloro-2 or 3-vinylcyclopentadienone (X) with sulfuric acid. These results are in accord with those expected of a simple derivative of hexachlorocyclopentadiene.[4]

There is no reason to expect structures IVA and IVB to behave differently toward alcoholic alkali. Therefore, the structure of C_7Cl_8(s) is limited to III or IIIA. Both of these compounds could have been derived only from structure II, thus establishing the compound C_7HCl_9 as 5-(1,2,2,2-tetrachloroethyl)-pentachlorocyclopentadiene. The dehydrochlorination of II with alcoholic alkali to form IIIA would involve the removal of a primary chlorine atom which is not in an allylic position. Furthermore, the product of this type of dehydrochlorination results in the formation of an isolated double bond. On the other hand, it is more plausible to expect the dehydrochlorination of II to involve the removal of a tertiary chlorine atom which is also allylic to two double bonds. Furthermore, the product III contains a completely conjugated system of double bonds. In addition, III would be expected to react sluggishly with alcoholic alkali, as is the case, whereas IIIA should be exceedingly reactive. Contributing evidence that C_7Cl_8(s) has the structure III was obtained by its conversion to a white solid, pentachloro-2,4-cyclopentadienylideneacetyl chloride (V) by reaction with sulfuric acid. Although this material is an isomer of hexachloro-2 or 3-vinylcyclopentadienone (X), it has entirely different chemical and physical properties. It does not undergo Diels–Alder reactions, and can be distilled at atmospheric pressure with only slight decomposition. Also, it does not react with concentrated sulfuric acid at 100°, whereas X reacts readily at 40°. The acid chloride (V) is converted to methyl pentachloro-2,4-cyclopentadienylideneacetate (VIII) by refluxing with methanol or more rapidly by potassium hydroxide and methanol. Treatment of V with aqueous alkali forms the acid (VI). The amides (VII) were obtained by the action of the appropriate amines on both V and VIII.

Prill[8] has demonstrated the use of hexachlorocyclopentadiene in the diene synthesis. Derivatives of hexachlorocyclopentadiene in which the allylic chlorine atoms are replaced by methoxy and ethoxy groups have been found to react similarly.[4] The ease with which these highly chlorinated compounds undergo the diene synthesis may be attributed partially to the required *cis*-butadienoid configuration of the ring system. It is interesting to note, however, that III does not react with maleic anhydride under ordinary conditions. Another contrast is afforded by the dimerization of X at or below room temperature, as compared with the failure of IV to form an adduct with maleic anhydride in twenty hours at 135°.

Experimental

Materials.—Hexachlorocyclopentadiene was obtained through the courtesy of the Hooker Electrochemical Company. Other reagents were obtained from the usual chemical supply concerns.

Dimer of Hexachlorocyclopentadiene (XVI).—A mixture of I (397 g.) and anhydrous aluminum chloride (40 g.) was stirred for one hour at 90–95°. In order to decrease the viscosity, carbon tetrachloride (300 ml.) was added and the mixture was heated for an additional three hours at 75–80°. The cooled reaction mixture was poured onto cracked ice, washed by decantation, and steam-distilled to remove the solvent. The resulting tan solid was recrystallized from benzene to give XVI (268 g.), a white solid which sublimes without melting at temperatures above 240°.

Anal. Calcd. for $C_{10}Cl_{12}$: Cl, 77.9, mol. wt., 544. Found: Cl, 77.9, mol. wt. (cryoscopic in benzene), 508, 529, 543.

The dimer was also prepared using tetrachloroethylene as the solvent. Although an 88% conversion to the dimer was obtained in the absence of a solvent, this method is not preferred because of the difficulty in controlling the highly exothermic dimerization.

5-(1,2,2,2-Tetrachloroethyl)-pentachlorocyclopentadiene (II).—One-fifth of 2.0 moles of trichloroethylene was added to a mixture of I (1.97 moles) and aluminum chloride (0.3 mole) during a period of twenty minutes as the temperature was increased to 80°. The remainder of the trichloroethylene was added during a period of forty minutes at 80°. After allowing the reaction to continue for an additional 1.5 hours, the purple mixture was cooled and poured onto ice. Recrystallization of the resulting tan solid from methanol gave II (1.80 moles), a white solid having a melting point of 80–81°.

Anal. Calcd. for C_7HCl_9: Cl, 78.9. Found: Cl, 78.6.

Octachloro-5-ethylidenecyclopentadiene (III).—A solution of potassium hydroxide (1.5 moles) in methanol (1 l.) was added to a stirred suspension of II (1.5 moles) in methanol (1.5 l.) during a period of twenty-five minutes at 42–45°. After dilution of the cooled reaction mixture with water, the resulting liquid was crystallized from pentane to obtain III (1.38 moles), a white solid of m. p. 53°, b. p. 146° at 7 mm.

Anal. Calcd. for C_7Cl_8: Cl, 77.2; mol. wt., 368. Found: Cl, 77.4; mol. wt. (cryoscopic in benzene), 370, 372.

It is important to avoid the use of an excess of alkali in the dehydrochlorination, for when 180% excess alkali was used, the yield of desired product was decreased to 27%.

Octachloro-1- or 2-vinylcyclopentadiene (IV).—During a period of thirty-five minutes, commercial trichloroethylene (17.0 moles) was added to a stirred mixture of I (16.3 moles) and aluminum chloride (60 g.) as the temperature was increased from 30 to 84°. External cooling was necessary for one hour to maintain the temperature at 75–87°. Heat was then applied to keep the temperature at 80–85° for three hours, 102–104° for fifteen hours, and 111–114° for eight hours. The cooled reaction mixture was poured onto ice, diluted with carbon tetrachloride, washed, dried, and subjected to distillation in a Claisen flask to obtain 5000 g. of liquid of boiling range 110–175° at 6–8 mm. Rectification of the distillate gave 38 g. of unreacted I and 3853 g. (10.46 moles) of IV; yellow liquid, b. p. 148–149° (13 mm.), 138° (5 mm.), d^{20}_4 1.736, n^{20}_D 1.5852, M_D 70.9.

Anal. Calcd. for C_7Cl_8: Cl, 77.2. Found: Cl, 77.6.

A by-product from this reaction is a viscous yellow liquid; b. p. 168–171° at 3 mm., 79.2% Cl, d^{20}_4 1.8129, n^{20}_D 1.6011.

Pentachlorocyclopentadienylideneacetyl Chloride (V).—A mixture of III (100 g.) and concd. sulfuric acid (800 g.) was heated with vigorous stirring for two hours at 90–95°. White needles sublimed to cooler portions of

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[8] E. A. Prill, This Journal, **69**, 62 (1947).

the reactor during the reaction period. Upon cooling, light yellow solid separated from the reaction mixture. The slurry was poured onto ice, and the resulting solid was washed with water and recrystallized rapidly from methanol to give V (65 g.); white needles of m. p. 85.0–85.5°, b. p. 266–267° at 750 mm.

Anal. Calcd. for C_7Cl_6O: Cl, 68.1. Found: Cl, 68.0.

N,N-Diethylpentachloro-(cyclopentadienylideneacetamide) (VII).—During a period of five minutes, diethylamine (6.3 g.) was added at room temperature to a solution of V (17 g.) in *n*-pentane (100 ml.). The yellow precipitate was washed thoroughly with water and recrystallized from a mixture of carbon tetrachloride and *n*-pentane to give VII (10 g.); yellow crystals m. p. 107°.

Anal. Calcd. for $C_{11}H_{10}Cl_5NO$: Cl, 50.7; N, 4.1; mol. wt., 349. Found: Cl, 50.7, 50.9; N, 4.0; mol. wt. (Rast), 343.

By employing a similar procedure, the diethylamide was also prepared by the action of diethylamine on the methyl (pentachlorocyclopentadienylidene)-acetate (VIII).

N-Phenylpentachloro-(cyclopentadienylideneacetamide) was prepared by the action of aniline on V in pentane solution. This amide is a white solid, m. p. 220°.

Anal. Calcd. for $C_{13}H_6Cl_5NO$: Cl, 47.9. Found: Cl, 47.9.

Methyl Pentachlorocyclopentadienylidene)-acetate (VIII). Method A.—A solution of potassium hydroxide (0.18 mole) in methanol (100 ml.) was added to a solution of V (0.17 mole) in methanol (200 ml.) during a period of twenty minutes at 45–47°. The reaction mixture was allowed to cool, diluted with water and filtered to obtain a white solid (39 g., m. p. 80–88°). The clear filtrate was acidified with dilute hydrochloric acid to obtain an additional quantity of white solid (11 g., m. p. 116°). Recrystallization of the former material from a mixture of hexane and carbon tetrachloride produced white crystals (25 g., m. p. 116°), which did not depress the melting point of that obtained upon acidification of the filtrate.

Anal. Calcd. for $C_8H_3Cl_5O_2$: Cl, 57.5. Found: Cl, 57.1.

Method B.—A solution of V (30 g.) in methanol (400 ml.) was refluxed for three hours. The solution was cooled, diluted with water, and the resulting solid was filtered. After two recrystallizations from a mixture of pentane and carbon tetrachloride, the solid melted at 84–97°; after three recrystallizations, 108–113°; and after four recrystallizations, pure VIII (7 g., m. p. 116°) was obtained. The product did not depress the melting point of that obtained by the action of alcoholic alkali on V.

Dimer of Hexachlorovinylcyclopentadienone (XI). Step 1.—A solution of potassium hydroxide (280 g.) in methanol (1000 ml.) was added to a stirred solution of IV (100 g.) in methanol (500 ml.) during a period of forty-five minutes at 40–45°. The cooled reaction mixture was diluted with water to dissolve potassium chloride and the resulting organic layer was washed with water to obtain a tan liquid (84 g.) having a sweet odor characteristic of the acetals of tetrachlorocyclopentadienone. Four recrystallizations of the product gave a pale yellow or white solid (60 g.), hexachloro-5,5-dimethoxy-1- or 2-vinylcyclopentadiene; m. p. 39°.

Step 2.—During a period of forty minutes, the acetal, prepared in step 1, (132 g.) was added to vigorously stirred concentrated sulfuric acid (800 ml.) at 0–5°. The blood-red solution was dropped onto cracked ice and the resulting red oil was washed with water. The addition of ethyl alcohol (90 ml.) at room temperature resulted in the crystallization of long red needles, which were recrystallized twice from acetone to give XI (2.8 g.); long white needles, m. p. 207°. The dimer evolves carbon monoxide at temperatures above 250°.

Anal. Calcd. for $C_{14}Cl_{12}O_2$: Cl, 68.0; mol. wt., 626. Found: Cl, 68.0, 68.1, 67.8; mol. wt. (ebullioscopic in benzene), 633, 639.

A blood red oil was obtained by evaporation of the alcohol from the filtrate. The oil is probably hexachloro-2 or 3-vinylcyclopentadienone (X).

Hexachlorovinylcyclopentenedione (XII): Method A.—A mixture of IV (1000 g.) and concentrated sulfuric acid (4000 g.) was stirred vigorously for seven hours at 120–125°. The reaction mixture gradually becomes black and resolves into a one-phase system. The cooled solution was extracted five times with a total of five liters of carbon tetrachloride. Evaporation of the solvent gave orange needles, which after two recrystallizations from carbon tetrachloride gave the diketone $C_7HCl_5O_2$ (XII) (315 g.); yellow needles, m. p. 96°.

Anal. Calcd. for $C_7HCl_5O_2$: Cl, 60.2. Found: Cl, 60.1, 60.1.

The diketone is decomposed by 5% aqueous potassium carbonate at room temperature.

Method B.—During a period of five minutes, hexachloro-5,5-dimethoxy-1 or 2-vinylcyclopentadiene (50 g.) was added to concentrated sulfuric acid (300 g.) at 40°. The blood-red mixture was dropped onto cracked ice and the red organic layer was washed with water and crystallized from petroleum ether (35–37°) to give an orange-red solid. Three additional recrystallizations produced the diketone XII (1.5 g.); yellow needles, m. p. 96°.

Fluorination of Octachloro-1 or 2-vinylcyclopentadiene.—A three-necked flask containing liquid C_7Cl_8 (440 g., 1.19 moles) was equipped with a thermometer, stirrer, distilling arm, and a dropping funnel containing antimony pentafluoride (2650 g., 12 moles). The distillation arm was connected to a water condenser, receiver, a second condenser, and finally a receiver cooled by ice water. The chlorocarbon was heated to 130° before the addition of antimony pentafluoride was begun. The heat was then discontinued and the temperature was regulated at 120–135° by the rate of addition of antimony pentafluoride. It was necessary to supply heat to maintain this temperature range after 1200 g. of the antimony fluoride had been added. At the conclusion of the addition, the temperature was increased gradually up to 170° to continue the gentle distillation of organic product. All of the product was collected in the first receiver. The colorless liquid distillate was washed with concd. hydrochloric acid, water, and dried to obtain 268 g. of clear, colorless, fluorinated product. Rectification of the crude product from a 52 in. column packed with small glass helices gave two clear-cut fractions; C_7ClF_{11}, 153.5 g., b. p. 90–92°, d^{20}_4 1.7009, n^{20}_D 1.3210, and $C_7Cl_2F_{10}$, 62.5 g., b. p. 116°, d^{20}_4 1.7174, n^{20}_D 1.3482.

Anal. Calcd. for C_7ClF_{11}: Cl, 10.7; F, 63.7; mol. wt., 328. Found: Cl, 10.9, 10.7; F, 63.8, 62.7; mol. wt. (vapor density), 328, 330.

Anal. Calcd. for $C_7Cl_2F_{10}$: Cl, 20.6; F, 55.1; mol. wt., 345. Found: Cl, 21.0; F, 55.6, 55.7; mol. wt. (vapor density), 346, 349.

Both fractions gave positive tests with permanganate indicating the presence of unsaturated linkages, as well as positive tests with alcoholic alkali establishing the presence of active halogen.

Chlorotridecafluoroethylcyclopentane.—The unsaturated derivative of ethylcyclopentane, C_7ClF_{11} (118 g., 0.36 mole), was passed over silver difluoride (20 moles) during a period of two and one-half hours at 295–300°. At the conclusion of the addition, the reactor was swept out with nitrogen for three hours. The product was collected in an ice-water trap followed by a dry ice trap. The crude product (115 g.) was washed twice with water and dried over Drierite. Rectification gave only one fraction, chlorotridecafluoroethylcyclopentane, C_7ClF_{13}; 67 g., b. p. 102°, d^{20}_4 1.7999, n^{20}_D 1.3073.

Anal. Calcd. for C_7ClF_{13}: Cl, 9.6; F, 67.5; mol. wt., 366. Found: Cl, 9.8, 10.2; F, 67.8, 68.3; mol. wt. (vapor density), 369, 370.

The physical constants of the product are in close agreement with those of a compound C_7ClF_{13} obtained by Perkin[9] and believed to be a chlorotridecafluoroethyl-

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[9] Private communication, M. Perkin, E. I. du Pont de Nemours and Co., Wilmington, Delaware.

cyclopentane, and differ appreciably from those of the four known chloroperfluoromethylcyclohexanes.[10]

Acknowledgment.—The authors express their indebtedness to the Hooker Electrochemical Company for defraying the expenses of this investigation and for supplying the hexachlorocyclopentadiene.

Summary

The condensation of hexachlorocyclopentadiene with trichloroethylene in the presence of aluminum chloride produces 5-(1,2,2,2-tetrachloroethyl)-pentachlorocyclopentadiene, which undergoes dehydrohalogenation with aluminum chloride and alkali to form two isomeric chlorocarbons, C_7Cl_8, octachloro-1 or 2-vinylcyclopentadiene and octachloro-5-ethylidenecyclopentadiene, respectively. The former chlorocarbon was identified by its conversion to the unsaturated derivatives of ethylcyclopentane, C_7ClF_{11} and $C_7Cl_2F_{10}$, chlorotridecafluoroethylcyclopentane, hexachloro-5,5-dimethoxy-1 or 2-vinylcyclopentadiene, hexachloro-2 or 3-vinylcyclopentadiene, hexachloro-2 or 3-vinylcyclopentadienone and its Diels–Alder dimer, and hexachlorovinylcyclopentenedione. The latter chlorocarbon was identified by its conversion to pentachlorocyclopentadienylideneacetyl chloride and functional derivatives thereof.

Whereas hexachlorocyclopentadiene readily undergoes the Diels–Alder reaction and also forms a dimer in the presence of aluminum chloride, the isomeric chlorocarbons C_7Cl_8 do not react with maleic anhydride under ordinary conditions. On the other hand, hexachloro-2 or 3-vinylcyclopentadienone dimerizes spontaneously via Diels–Alder.

RECEIVED[11] OCTOBER 29, 1948

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[10] B. W. Hotten, Ph.D. Dissertation, Purdue University, 1945; J. Davis, Ph.D. Dissertation, 1947.

[11] Original manuscript received May 17, 1948.

[CONTRIBUTION FROM THE NORTHERN REGIONAL RESEARCH LABORATORY, PEORIA, ILLINOIS[1]]

Interpretation of Lignin. III. The Synthesis and Polymerization of Stable Monomers[2]

BY ALFRED RUSSELL,[3] JOHN H. BAITY[4] AND HERBERT E. SMITH

There have already been described syntheses of three polymeric materials; one of these had many of the properties of spruce lignin[5] and the others were methoxyl-free analogs.[6] The polymers resulted by chain-like intermolecular aldolization of certain aryl methylketoaldehydes. The monomeric units were prepared by the Fries rearrangement of the monoacetates of monohydroxyarylaldehydes and could not be isolated due to their reactivity under the anhydrous conditions of the rearrangement reaction—polymerization proceeding at once to give polydihydrobenzopyrones.

It would be of interest to demonstrate the existence of similar stable monomeric units and their separate polymerization. Such methylketoaldehydes should be available by two general methods, either nuclear acylation of *suitably chosen* hydroxyarylaldehydes or nuclear formylation of *suitably chosen* hydroxyaryl ketones. Inactivation of the carbonyl group in the initial material by any conventional method would most likely be ineffective because the acylated or formylated reaction product would likely polymerize as soon as the inactivated carbonyl group was liberated if it did not do so even before liberation of the protected group.

A much more elegant procedure is to prepare a monomer which, because of its configuration, cannot polymerize easily. This may be accomplished by selecting the starting material so that the carbonyl group already present is chelated with an hydroxyl group and the second carbonyl group enters ortho to another hydroxyl group. A second chelate ring will form at once and, at least in some cases, the monomer should be stable.

Six such schemes may be tried rather easily since the starting materials are accessible: the nuclear acylation of β-resorcylaldehyde or of pyrogallic aldehyde; the nuclear formylation of resacetophenone, 2,6-dihydroxyacetophenone, gallacetophenone and 2,4,6-trihydroxyacetophenone (phloracetophenone).

No success was had in acylation attempts and the application of the Gattermann procedure to gallacetophenone was equally futile. However, the formylation of the other three hydroxy ketones by the Gattermann procedure, modified in one instance, was entirely successful and satisfactory yields were obtained of the three methylketoaldehydes — 2,4 - dihydroxy - 3 - formylacetophenone, 2,6-dihydroxy-3-formylacetophenone and 2,4,6-trihydroxy-3-formylacetophenone. All three monomers are stable, easily crystalline with sharp melting points. All three are unchanged by 40% aqueous alkali and by 50% sodium methoxide in methanol, but may be polymerized to red or brown amorphous materials by

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[1] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

[2] Article not copyrighted.

[3] Deceased.

[4] Former Employee, Industrial Chemical Section, Agricultural Residues Division.

[5] A. Russell, THIS JOURNAL, **70**, 1060 (1948).

[6] A. Russell, *ibid.*, **70**, 2864 (1948).