$CCl_3CCl_2CF_3$.[6] To prove the structure of (I), it was stirred at room temperature with excess sulfuric acid for six hours and poured in water. During the acid treatment hydrogen fluoride was evolved. An irritating oil was obtained which reacted with phenylhydrazine to give a hydrazone identical with that from (II), melting at 97–98°. The fluorinated material boiling at 97° is without doubt (IV) since its boiling point is 43° higher than that of (III). This is in agreement with the general change in boiling point caused by replacing a chlorine atom by an atom of fluorine in such groups.

Experimental

Fluorination of $CCl_2{=}CClCHCl_2$ (II) with Catalyst.—Ground antimony trifluoride, 537 g. (3 moles), was placed in a two-liter round-bottom flask surmounted by a 550-mm. air condenser. The top of this tube contained a thermometer and a bent tube connected to a water cooled downward condenser for distillation. A filter flask, containing about 200 ml. of concentrated hydrochloric acid and attached to the condenser with an adapter, served as a receiver. Fifteen milliliters of antimony pentachloride was added as catalyst. Then (II), 500 g. (2.35 moles), was added gradually from a dropping funnel, heat being applied at the same time. The reaction soon started and product distilled smoothly at 54°. Fresh olefin was added at the same rate at which product was removed. The distillate was washed three times with concentrated hydrochloric acid, once with dilute sodium hydroxide solution, dried and distilled to give 357 g., 92%, of (III), b. p. 53.7°.

Fluorination of (II) without Catalyst.—The apparatus was the same in this case as before. Ground antimony trifluoride, 970 g. (5.4 moles), was placed in the reaction flask, addition of 852 g. (4 moles) of (II) started and heat applied. The reaction was slow to start, rather strong heat being required. The distillate temperature at the start was 140° but it gradually went down, staying for awhile around 110°. During the addition of the last 300 g. of (II) the temperature was in the vicinity of 54°. The product was purified as before and distilled with the following results: 175 g., 26%, of (III), b. p. 53.7°; 157 g., 21%, (IV), b. p. 97°, $n^{20}{}_D$ 1.4253; 179 g., 24%, (I), b. p. 114.4°, $n^{20}{}_D$ 1.4452; 44 g. of material boiling from 115 to 180°.

Fluorination of $CHCl{=}CClCHCl_2$ (VII).—Two-hundred forty-eight grams (1.33 moles) of (VII) and 230 g. of ground antimony trifluoride (1.3 moles) reacted without catalyst as described above. The temperature of the distillate during the reaction was 100–110°. Purification gave 160 g., 82%, of (VIII), b. p. 89°, $n^{20}{}_D$ 1.4150. The use of a small amount of antimony pentachloride as catalyst was found to hasten the reaction. However, when more than about 5 ml. of catalyst was used, the yield was decreased considerably.

Summary

The fluorination of two allylic polychlorides, $CCl_2{=}CClCHCl_2$ and $CHCl{=}CClCHCl_2$, has been studied. In the case of the first one, an isomerization leading to the formation of a $—CF_3$ group was observed. Two new compounds, $CHCl{=}CClCF_2Cl$ and $CCl_2{=}CClCHF_2$, are reported.

COLUMBIA, S. C. RECEIVED OCTOBER 8, 1947

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[6] Henne and Whaley, THIS JOURNAL, **64**, 1158 (1942).

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

Reactions of Some Highly Chlorinated Unsaturated C_5 Hydrocarbons with Chlorine and Copper[1]

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

In connection with a study of some highly chlorinated hydrocarbons, it was of interest to investigate some chlorination and coupling reactions of some polychlorinated unsaturated C_5 hydrocarbons which were used as intermediates in the preparation of hexachlorocyclopentadiene.[3]

Early work by Prins[4] showed that hexachloropropene can be made to add chlorine, in the presence of sunlight, to give almost quantitative yields of the octachloro compound. Later, McBee and co-workers[5,6] reported that the action of chlorine at high temperatures and pressures on polychloropentanes and heptanes results in a chlorinolysis with the formation of carbon tetrachloride, hexachloroethane, and a substance which was later shown to be octachlorocyclopentene. Recently, Prins[7] has reported that hexachlorocyclopentadiene reacts readily with chlorine to form octachlorocyclopentene yet octachloro-1,3-pentadiene (I) does not add the halogen but does give a small amount of hexachloroethane on continual exposure.

In this work, chlorinations of both octachloro-1,3-pentadiene (I) and 1,1,2,3,3,4,5,5,5-nonachloro-1-pentene (II) were carried out in the presence of direct sunlight. It was found that at temperatures of 100–130°, (I) undergoes a chlorinolysis reaction to form considerable amounts of hexachloroethane and carbon tetrachloride. However, at lower temperatures (36–52°), the extent of reaction was found to be much reduced and only small amounts of the chlorinolysis products were obtained. Experiments with (II) showed that this compound, like (I), is also cleaved through the action of chlorine to form hexachloroethane and *s*-heptachloropropane. With (II), however, reaction was found to proceed more rapidly than

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[1] From a thesis presented by John A. Krynitsky to the Graduate School of the University of North Carolina, June, 1943, in partial fulfillment of the requirements for the degree of Doctor of Philosophy. This work was done under a contract between the Naval Research Laboratory, Washington, D. C., and the University of North Carolina. Publication was delayed for security reasons.

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

[3] Krynitsky and Bost, THIS JOURNAL, **69**, 1918 (1947).

[4] H. J. Prins, *J. prakt. Chem.*, **89**, 414–429 (1914).

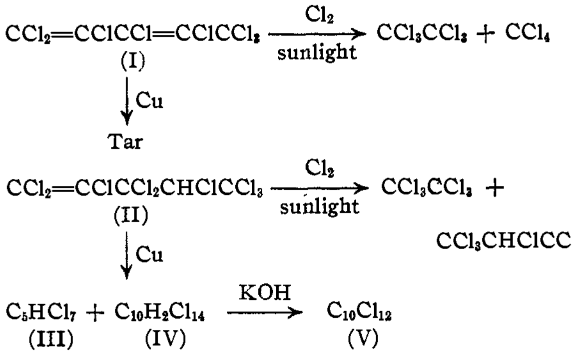
[5] McBee, Hass and Pierson, *Ind. Eng. Chem.*, **33**, 181–185 (1941).

[6] McBee, Hass and Bordenca, *ibid.*, **35**, 317–320 (1943).

[7] H. J. Prins, *Rec. trav. chim.*, **65**, 455–467 (1946).

with (I) and considerable amounts of hexachloroethane were obtained even at the lower temperatures (35–47°). In neither case was there any evidence of chlorine having been added to form the higher chlorinated pentanes.

Prins[4] found that certain compounds having chlorine atoms activated by a double bond undergo a coupling reaction when treated with an agent such as copper–bronze. Thus hexachloropropene yielded a compound C_6Cl_8 which is probably a perchloromethylenecyclopentene.[8] In the present work, this coupling reaction was extended to the compounds (I) and (II). When (I) was treated with equimolar quantities of freshly precipitated copper, a reaction took place with the evolution of heat. From this reaction mixture, no recognizable products were obtained except for a small amount of the starting (I). With (II), however, two definite compounds were obtained having the empirical formulas C_5HCl_7 (III) and $C_{10}H_2Cl_{14}$ (IV). (III) was found to react quantitatively with one mole of alcoholic potassium hydroxide while (IV) reacted with two moles. In the latter case, a compound $C_{10}Cl_{12}$ (V) was isolated. From their methods of formation and the quantitative reaction of (IV) with potassium hydroxide, (IV) is believed to be 3,4-bis-(α,β,β,β-tetrachloroethyl)-hexachloro-1,3,5-hexatriene and (V), 3,4-bis-(trichlorovinyl)-hexachloro-1,3,5-hexatriene.



$$\begin{tikzcd} \underset{(I)}{CCl_2{=}CClCCl{=}CClCCl_3} \arrow[r, "Cl_2", "\text{sunlight}"'] \arrow[d, "Cu"] & CCl_3CCl_3 + CCl_4 \\ \text{Tar} & \end{tikzcd}$$

$$\begin{tikzcd} \underset{(II)}{CCl_2{=}CClCCl_2CHClCCl_3} \arrow[r, "Cl_2", "\text{sunlight}"'] \arrow[d, "Cu"] & CCl_3CCl_3 + CCl_3CHClCCl_3 \\ \underset{(III)}{C_5HCl_7} + \underset{(IV)}{C_{10}H_2Cl_{14}} \arrow[r, "KOH"] & \underset{(V)}{C_{10}Cl_{12}} \end{tikzcd}$$

Experimental

Action of Chlorine on Octachloro-1,3-pentadiene (I).—Into a 500-ml. quartz flask fitted with a gas inlet tube was placed 90 g. of (I). A slow stream of chlorine was admitted in the presence of direct sunlight for a total of thirty-two hours. During this period, the contents of the flask was maintained at 100–130° by means of an electric heater. Upon cooling, the reaction mixture turned to a semi-solid mass. This was found to be soluble in hot alcohol and was accordingly recrystallized three times from this solvent. There resulted 30 g. of a white crystalline material having a strong camphor odor, which was identified as being hexachloroethane by means of melting point, sublimation point and molecular weight determinations.

A later experiment was performed under similar conditions but employing ice-cooled traps to condense volatile products. Upon treatment of 90 g. of (I) with chlorine for seven hours, the traps were found to contain 17 g. of carbon tetrachloride which was identified by its boiling point, refractive index and density.

Action of Chlorine on 1,1,2,3,3,4,5,5,5-Nonachloro-1-pentene (II).—Into a flask, as above, was placed 90 g. of (II). Chlorine was admitted slowly in the presence of direct sunlight over a period of twenty-seven hours. During this addition, the temperature varied between 35 and 47°. The reaction mixture was transferred to a Claisen flask and distilled. A white, crystalline solid was noted to sublime and a total of 14 g. of this solid was collected at 30 mm. pressure in an ice-cooled receiver along with a small amount of a colorless liquid. No definite temperature could be obtained for the collection of this material. After removal of all solid, further distillation yielded fraction (a) 22 g., b. p. (4 mm.) 94–105° and fraction (b) 30 g., b. p. (3 mm.) 123–30°. Fraction (b) was identified as being recovered (II). Three recrystallizations of the solid material from alcohol gave a white crystalline compound which was identified as being hexachloroethane.

Inasmuch as fraction (a) was collected over a rather wide range, it was fractionated through a 50 cm. column of the Whitmore–Lux type packed with glass helices. There was obtained 10 g. of a colorless liquid b. p. (3–4 mm.) 93.2–93.5°. This was found to react quantitatively with 1 mole of alcoholic potassium hydroxide, proving it to contain one hydrogen. This together with molecular weight determinations showed it to have the molecular formula C_3HCl_7. Comparison with known unsymmetrical heptachloropropane showed the two compounds to be dissimilar. Since only one other structure is possible for a compound having this formula, the compound was concluded to be *s*-heptachloropropane: calcd. for C_3HCl_7: mol. wt. 285.2. Found: mol. wt. 290, 294 (titration with potassium hydroxide).

Reaction of (II) with Copper.—Into a flask fitted with a stirrer, thermometer and reflux condenser were placed 170 g. (0.45 mole) of (II) and 250 ml. of methanol. The temperature was raised to 60° and 29 g. (0.46 mole) of freshly precipitated copper was added in small portions, with stirring, over a period of two and one-half hours so as to maintain the temperature at 60–64°. The mixture was then refluxed overnight. After cooling, the material was washed three times with water. The organic layer contained a precipitate which was removed by filtration. Fractionation of the clear, dark amber, viscous filtrate through the Whitmore–Lux column yielded 34 g. of light golden (III) b. p. (1–2 mm.) 95–100° and a deep red resinous residue. (III) was found to react quantitatively with one mole of alcoholic potassium hydroxide showing it to contain one hydrogen. This and molecular weight determinations established its formula as being C_5HCl_7. Calcd. for C_5HCl_7: mol. wt., 309.2. Found: mol. wt., 285 (ebullioscopic), 303, 293 (titration with potassium hydroxide).

Two recrystallizations of the precipitate from carbon tetrachloride yielded 7 g. of white crystalline (needles) (IV) having a strong biphenyl-like odor and melting at 205–206°. (IV) was found to react quantitatively with two moles of alcoholic potassium hydroxide indicating the presence of two hydrogens. This together with the molecular weight determinations and analyses established its formula as being $C_{10}H_2Cl_{14}$. *Anal.* Calcd. for $C_{10}H_2Cl_{14}$: Cl, 80.27; mol. wt., 618.4. Found: Cl, 80.31, 80.57; mol. wt., 584 (ebullioscopic), 610, 622 (titration with potassium hydroxide).

Reaction of (I) with Copper.—When 91 g. (0.26 mole) of (I) was treated with 17 g. (0.27 mole) of copper under the conditions described above, a tarry reaction mixture was obtained. From this, no identifiable materials except for 23 g. of recovered (I) were obtained.

Reaction of (IV) with Potassium Hydroxide.—Five grams of (IV) dissolved in 30 ml. of hot carbon tetrachloride was treated with an excess of an alcoholic potassium hydroxide solution (approx. 0.35 *N*) to a strong permanent pink of phenolphthalein. The mixture was boiled on a steam-bath for five minutes and the excess base was neutralized carefully with dilute hydrochloric acid. Upon evaporation to one-half volume and cooling in an ice-bath, a white crystalline solid separated. Two

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(8) Brederode, Gerding and Prins, *Rec. trav. chim.*, **65**, 184 (1946).

recrystallizations from carbon tetrachloride yielded 3 g. of white crystalline (V). (V) had practically no odor and melted at 113–113.5°. From analyses and molecular weight determinations, the formula of (V) was established as being $C_{10}Cl_{12}$.

Anal. Calcd. for $C_{10}Cl_{12}$: Cl, 78.00; mol. wt., 545.5. Found: Cl, 77.94; mol. wt., 537.

Summary

1. Octachloro-1,3-pentadiene (I) when treated with chlorine in the presence of direct sunlight at elevated temperatures undergoes chlorinolysis to yield hexachloroethane and carbon tetrachloride.

2. 1,1,2,3,3,4,5,5,5-Nonachloro-1-pentene (II) reacts as above but at lower temperatures to give hexachloroethane and *s*-heptachloropropane.

3. (II) reacts with copper to yield chiefly a dehalogenated product, C_5HCl_7 (III), and a smaller amount of a coupled product, $C_{10}H_2Cl_{14}$ (IV).

4. No definite products were obtained through the reaction of (I) with copper.

5. (IV) is dehydrohalogenated by potassium hydroxide to give $C_{10}Cl_{12}$ (V).

6. Structural formulas are suggested for compounds (IV) and (V).

CHAPEL HILL, NORTH CAROLINA

RECEIVED AUGUST 2, 1947

[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE COLLEGE, AND THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

The Electric Moments of Some *p*-Substituted Phenyl Selenocyanates and Thiocyanates

BY TOD W. CAMPBELL AND MAX T. ROGERS

The electric moments of a series of *para* substituted phenyl thiocyanates and phenyl selenocyanates have been studied to obtain information concerning the nature of resonance in these compounds. None of the substances whose dipole moments are reported here have been measured previously, but values have been reported for phenyl thiocyanate,[1] *p*-chlorophenyl thiocyanate,[1] *p*-tolyl selenocyanate[2] and *p*-chlorophenyl selenocyanate[2] so that group moments may be calculated for the thiocyano- and selenocyano- groups in aromatic compounds.

Experimental Part

Materials

Benzene.—Baker C. P. benzene was dried over sodium and filtered before use, $d^{25}{}_4$ 0.87344, $n^{25}{}_D$ 1.4978.

***p*-Dimethylaminophenyl Thiocyanate and *p*-Aminophenyl Thiocyanate.**—These were prepared by the method of Brewster and Schroeder[3]: *p*-dimethylaminophenylthiocyanate, white needles, m. p. 75°; *p*-aminophenyl thiocyanate,[3a] m. p. 57°.

***p*-Dimethylaminophenyl Selenocyanate and *p*-Aminophenyl Selenocyanate.**[4]—These were prepared from cyanogen triselenide[5] and, respectively, dimethylaniline (m. p. product 105°) and aniline (m. p. of product 91–92°).

***p*-Nitrophenyl Thiocyanate and *p*-Nitrophenyl Selenocyanate.**—These were prepared from diazotized *p*-nitroaniline and, respectively, ferric thiocyanate (m. p. of product 133°) and potassium selenocyanate (m. p. of product 137–138°).[6]

***p*-Selenocyanophenyl Thiocyanate** was prepared from diazotized *p*-aminophenyl thiocyanate and potassium selenocyanate in a buffered solution.[7] The product melted at 111.5–112° after repeated recrystallization from a ligroin–benzene mixture.

***p*-Methoxyphenyl selenocyanate** was synthesized from diazotized anisidine and potassium selenocyanate. The product[8] melted at 65°.

Apparatus and Method

Electric moments were measured in benzene solution at 25° using a heterodyne-beat apparatus and technique previously described.[9] The experimental data and molar polarizations are shown in Table I; the derived values of the molar polarization at infinite dilution (P^{∞}), the molecular refraction, MR_D, and the dipole moment, are shown in Table II. The molecular refraction of each compound was obtained from the refractive indices of the solutions[2] (Table I) or, in the cases of *p*-aminophenyl selenocyanate and *p*-methoxyphenyl selenocyanate, from empirical atomic and group refractions.[10]

Discussion of Results

The observed dipole moments are compared in Table III with the vector sums of the moments of the substituents, assuming free rotation about single bonds. The group moments and angles used are: C_{aromatic}–H, 0.4 (assumed), 180°; C_{ar}–NO_2, 3.55, 0°; C_{ar}–NH_2,[11] 1.86, 143°; C_{ar}–$N(CH_3)_2$,[11] 1.98, 180°; C_{ar}–OCH_3,[11] 1.37, 119°; C_{ar}–SCN,[2] 3.36, 58°30′; C_{ar}–SeCN,[2] 3.83, 53°30′. (The angle is 0° when the negative end of the dipole is directed away from the ring.)

There is an increase in dipole moment when an electron donating group is *para* to the selenocyano or thiocyano group and this increment may be attributed to enhancement of resonance. The effect is greater with the dimethylamino group

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[2] M. T. Rogers and T. W. Campbell, THIS JOURNAL, **69**, 2039 (1947).

[3] R. Q. Brewster and W. Schroeder, "Organic Syntheses," Vol. II, John Wiley and Sons, 1943, p. 574.

[3a] E. Söderbäck, *Ann.*, **419**, 217 (1919).

[4] F. Challenger, A. T. Peters and J. Halevy, *J. Chem. Soc.*, 1648 (1926).

[5] A. Verneuil, *Ann. chim. phys.*, [6] **9**, 328 (1886).

[6] H. Bauer, *Ber.*, **46**, 92 (1913).

[7] F. Challenger and A. T. Peters, *J. Chem. Soc.*, 1364 (1928).

[8] O. Behagel and M. Rollmann, *J. prakt. Chem.*, **123**, 336 (1929).

[9] M. T. Rogers and J. D. Roberts, THIS JOURNAL, **68**, 843 (1946).

[10] The group refractions of the —SCN and —SeCN groups were taken to be 13.4 and 18.0.

[11] Estimated from values of various *para* disubstituted benzene derivatives in the literature using principally the *p*-chloro-, *p*-fluoro- and *p*-methyl- compounds.