[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE SPRAGUE ELECTRIC CO.]

Pentachlorophenyl Derivatives. II. The Bromination of Ethylpentachlorobenzene

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In a previous report from these laboratories[1] it was shown that the major product isolated from the chlorination of ethylpentachlorobenzene is 1-pentachlorophenyl-2-chloroethane. It is our present purpose to show that in contrast to the chlorination, the bromination of ethylpentachlorobenzene results in a single product and that, furthermore, the product obtained is the α-substituted product, 1-pentachlorophenyl-1-bromoethane.

When ethylpentachlorobenzene and an equivalent of bromine in carbon tetrachloride solution are illuminated at room temperature with a 500-watt unfrosted bulb hydrogen bromide is slowly evolved and the bromine color gradually disappears. Removal of the solvent gives an almost quantitative yield of a white solid, I, which after crystallization from acetone melts at 123–124°. The same product can be obtained by dropwise addition of bromine with mechanical stirring to ethylpentachlorobenzene illuminated and maintaind at 100°. That I is not the β-bromide which would be expected by analogy with the results obtained on chlorination is readily shown by ring chlorination of 1-phenyl-2-bromoethane by the method of Silberrad.[2] The product obtained, II, melts at 98–99° and a mixed melting point with I shows a strong depression. Analysis indicates that II has the empirical formula $C_8H_4Cl_5Br$, and it seems reasonable to assume that II is 1-pentachlorophenyl-2-bromoethane and that I is 1-pentachlorophenyl-1-bromoethane.

That I is, indeed, the α-bromide can be shown in two other ways. 1-Pentachlorophenyl-1-bromoethane, I, can be obtained, albeit in poor yield, by refluxing the known methylpentachlorophenylcarbinol[3] with 48% hydrobromic acid. Also, when the α-bromide is refluxed in acetic acid containing an excess of potassium acetate an 89% yield of an acetate, III, is obtained. Hydrolysis of III with potassium hydroxide in aqueous acetone gives a quantitive yield of methylpentachlorophenylcarbinol.[4] Therefore, III must be 1-pentachlorophenyl-1-acetoxyethane and I is the α-bromide.

When the crude product, obtained by refluxing 1-pentachlorophenyl-1-bromoethane, I, with alcoholic potassium hydroxide, was crystallized from absolute ethanol, pentachlorostyrene[1] was obtained in the first crop of crystals. Concentration of the mother liquors gave a crude product which after extensive crystallization melted at 88–89° and analyzed correctly for 1-pentachlorophenyl-1-ethoxyethane.

As has already been pointed out[1] the finding that ethylpentachlorobenzene chlorinates predominantly in the β-position but brominates cleanly in the α-position is unexpected. The fact that the α-bromination goes cleanly casts considerable doubt on any ortho-effect type of explanation for the β-chlorination and focuses attention on the mechanisms of the two reactions involved. Qualitatively both the bromination and chlorination show the same characteristics. The chlorination is strongly catalyzed by light and does not proceed in the dark. The reaction with sulfuryl chloride is catalyzed by benzoyl peroxide and has an induction period which may be shortened either by purification of the starting materials or adding fresh benzoyl peroxide. The bromination, too, is strongly photocatalyzed. Whereas it required eight hours for one mole of bromine to react with freshly distilled ethylpentachlorobenzene with illumination at 100–125°, the time required in diffuse daylight was sixty-four hours. It is possible to accelerate the reaction under the latter conditions by raising the temperature and at 180° one mole of bromine reacts in six hours. Under these conditions, however, the reaction does not give only the α-bromide, I. I can be separated easily by crystallization from acetone and from the mother liquors, it is possible to isolate a white solid, IV, which after repeated crystallizations from both alcohol and acetic acid melts from 94–96°. IV may also be obtained in good yield by adding bromine to pentachlorostyrene in carbon tetrachloride solution. Analysis indicates that IV has the empirical formula $C_8H_3Cl_5Br_2$ and on the basis of its synthesis from pentachlorostyrene it must be 1-pentachlorophenyl-1,2-dibromoethane.[5] Furthermore, the bromination seems to show the same sort of inhibition that was observed in the chlorination. The rate of bromination is noticeably accelerated by the use of distilled ethylpentachlorobenzene. Both reactions thus appear to be of the radical rather than ionic type, and it

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[1] Ross, Markarian and Nazzewski, THIS JOURNAL, **67**, 1914 (1947).

[2] Silberrad, *J. Chem. Soc.*, **127**, 1267 (1925).

[3] Lock, *Ber.*, **66**, 1527 (1933).

[4] Using this series of reactions it is possible to obtain methylpentachlorphenyl carbinol in an over-all yield of 80% starting with the readily available ethylpentachlorobenzene. This is a far more convenient route to the carbinol than the Lock procedure[3] which involves reaction of pentachlorobenzaldehyde with a methyl Grignard. Moreover, it has the very important advantage that all of the products obtained are very easily purified.

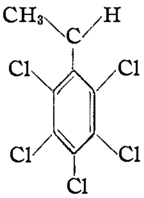
[5] The dibromide, IV, probably does not arise by substitution of the monobromide, for ethylpentachlorobenzene when treated with two equivalents of bromine in carbon tetrachloride at room temperature with illumination gives no dibromide even after one hundred and sixty-eight hours. The evolution of hydrogen bromide stopped after fifty hours and the only product isolated was the α-bromide. It is probable that IV is formed by addition of bromine to pentachlorostyrene which may be formed from the α-bromide by dehydrohalogenation at 180°.

seems unlikely that the difference in products is ascribable to a difference in mechanism.

Another possibility is that the results which we have observed are due to a difference in reactivity of the chlorine and bromine free radicals. Schumacher[6] has compared the reactivities of the chlorine, bromine, and iodine atoms in the general reaction

$$\text{RH} + \text{Halogen}\cdot \longrightarrow \text{R}\cdot + \text{H}\cdot\text{Halogen}$$

He reports that whereas the reaction with a chlorine atom is exothermic, the reaction with a bromine atom is slightly endothermic and with an iodine atom it is strongly endothermic. Also the activation energy is, in general, 5–10 kcal. higher for the bromine atom and about 20 kcal. higher still for an iodine atom. In accord with this we have observed that, whereas the chlorination is strongly exothermic, the bromination is at best only slightly exothermic and may even be endothermic. This may account for the observed β-chlorination of ethylpentachlorobenzene. If the barrier to reaction with a chlorine atom is small, reaction will occur at the most accessible point. With ethylpentachlorobenzene this is the β-position which is favored both sterically and statistically. When the barrier becomes higher the attacking free radical shows selectivity and attacks at the position which is favored energetically. In the bromination which probably has a much higher activation energy the contribution which the resonating structures V–VIII make in reducing the energy of activation becomes important and reaction occurs in the α-position.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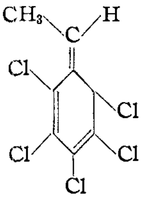
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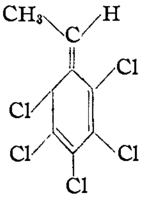
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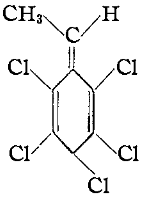
VIII

Experimental[7]

1-Pentachlorophenyl-1-bromoethane, I.—Bromine (25 cc., 0.5 mole) in 500 cc. of carbon tetrachloride was added to ethylpentachlorobenzene (139 g., 0.5 mole) in 500 cc. of carbon tetrachloride. The mixture was illuminated at room temperature with a 500-watt unfrosted bulb until the bromine color disappeared (ninety-six hours). Removal of the solvent at the water pump yielded 163 g. (91%) of the α-bromide of melting point 117–120°. Recrystallization from acetone gave 140 g. (71%) of m. p. 123–124°.

Anal. Calcd. for $C_8H_4Cl_5Br$: C, 26.88; H, 1.13. Found: C, 27.01, 26.94; H, 1.06, 1.20.

I was also prepared by adding bromine (84 cc., 1.66 moles) at the rate at which it reacted to redistilled ethylpentachlorobenzene (557 g., 2 moles) heated to 100° in a 3-necked flask fitted with a reflux condenser, a mechanical stirrer, and a dropping funnel extending below the level of the liquid and illuminated with a Hanovia ultraviolet lamp (Type 16103) with filter removed.[8] When 70% of the bromine had been added the temperature was raised gradually to 125° to keep the reaction mixture liquid. The total time of addition was eight hours. The crude product was evacuated overnight over potassium hydroxide. After this treatment the crude product weighed 679.5 g. and melted from 95–110°. Crystallization from acetone gave 530 g. (89.5%) of the α-bromide having m. p. 118–121°. Another crystallization raised the melting point to 123–124°.

When the bromination was run as above but in diffuse daylight at 180–190° it was possible to treat two moles of bromine with 2 moles of ethylpentachlorobenzene in six hours. This gave 690 g. of an oily product from which we isolated 220 g. of the α-bromide by crystallization from acetone. Removal of the solvent from the mother liquors gave a slush which after three crystallizations from absolute ethanol followed by four crystallizations from glacial acetic acid yielded 75 g. of 1-pentachlorophenyl-1,2-dibromoethane melting from 94–96°.

Anal. Calcd. for $C_8H_3Cl_5Br_2$: C, 22.00; H, 0.69. Found: C, 22.00, 21.81; H, 0.98, 0.92.

In preparing the α-bromide, I, from methylpentachlorophenylcarbinol, the carbinol (2 g.) was refluxed for two hours with 10 g. of 48% hydrobromic acid. The reaction mixture was poured into water and the solid obtained was filtered off and crystallized from methanol to yield 0.35 g. of I, having m. p. 120–122°. Recrystallization from acetone raised the melting point to 123–124° and a mixed melting point with an authentic sample of I showed no depression.

1-Pentachlorophenyl-2-bromoethane, II.—β-Phenethyl bromide (92.5 g., 0.5 mole) and aluminum chloride (2.5 g.) were placed in a 500 cc., 3-necked flask equipped with a reflux condenser, thermometer and dropping funnel. A mixture of sulfur monochloride (4.1 g.) and sulfuryl chloride (404 g.) was added dropwise at room temperature. After a short period of time the aluminum chloride went into solution and the evolution of hydrogen chloride began. The temperature was maintained below 60° by means of an ice-bath until approximately one-half of the chlorinating mixture had been added. The temperature was then maintained at 60–65° with a Glass-Col heater for the remainder of the addition and for seventy-five minutes thereafter. The mixture was left standing overnight. The following morning hydrogen chloride was still being evolved. The reaction mixture was heated at 70° for an additional hour. The excess chlorinating mixture was removed with the water pump to yield a yellowish green solid. This was taken up in benzene and washed with dilute hydrochloric acid, water, dilute sodium hydroxide and water again. The benzene layer was separated and dried over anhydrous magnesium sulfate. Filtration and removal of the benzene gave 158 g. of a light brown product melting from 88–95°. Crystallization from 95% ethanol gave 125 g. (70%) of product melting from 96–98°. A sample recrystallized three times for analysis melted at 98–99°.

Anal. Calcd. for $C_8H_4Cl_5Br$: C, 26.88; H, 1.13. Found: C, 26.52, 26.71; H, 1.11, 1.20.

1-Pentachlorophenyl-1-acetoxyethane, III.—1-Pentachlorophenyl-1-bromoethane, I (17.9 g., 0.05 mole), was refluxed for twenty hours with potassium acetate (19.6 g. 0.20 mole) in 275 cc. of acetic acid. Most of the acetic acid was then removed with the water pump and the crude product was taken up in a mixture of benzene and water. The benzene layer was separated and dried over drierite. The crude product obtained by removal of the benzene was crystallized from acetone–water to yield 15 g. (85%) of III melting from 90–95°. Three crystallizations from methanol raised the melting point to 101–102°.

Anal. Calcd. for $C_{10}H_7Cl_5O_2$: C, 35.68; H, 2.16. Found: C, 35.28, 35.42; H, 2.27, 2.14.

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(6) Schumacher, *Angew. Chem.*, **53**, 501 (1940).

(7) The microanalyses were performed by Dr. Carl Tiedcke.

(8) It is not our contention that illumination of this type is essential to the reaction. This particular lamp was used only because it happened to be most convenient.

Methylpentachlorophenylcarbinol.—1-Pentachlorophenyl-1-acetoxyethane was refluxed for four hours in 150 cc. of acetone and 25 cc. of water containing 1 g. of potassium hydroxide. Most of the acetone was removed with a water pump and water wast hen added. The crude product was filtered off and crystallized from methanol–water to yield 1.5 g. of the carbinol melting at 124–125°. A mixed melting point with an authentic sample of the carbinol showed no depression.

Dehydrohalogenation of 1-Pentachlorophenyl-1-bromoethane, I.—The α-bromide (35.8 g., 0.1 mole) was refluxed for four hours with 300 cc. of absolute ethanol containing potassium hydroxide (11.2 g., 0.2 mole). The mixture was stirred mechanically during the refluxing. The reaction mixture was poured into 2 liters of water. The crude product was filtered off and crystallized from ethanol to give two crops of crystals. The first weighed 12.5 g. and melted at 109–112°. Recrystallization raised the melting point to 113–114.5° and a mixed melting point with pentachlorostyrene showed no depression. The second crop weighing 7 g. and melting from 63–70° was purified by crystallizing successively from acetone, methanol, ethanol and three times from glacial acetic acid. After this treatment the compound melted at 88–89° and analysis indicates that it is 1-pentachlorophenyl-1-ethoxyethane.

Anal. Calcd. for $C_{10}H_9Cl_5O$: C, 37.24; H, 2.79. Found: C, 37.30, 37.48; H, 2.80, 2.72.

1-Pentachlorophenyl-1,2-dibromoethane, IV.—Pentachlorostyrene (5 g., 0.018 mole) and bromine (2.9 g., 0.018 mole) in 150 cc. of carbon tetrachloride were left standing for seven days at room temperature. Removal of the solvent gave a white crystalline solid melting from 88–90° with some previous softening. Crystallization from acetic acid gave 4.5 g. (57%) of IV melting at 95–96°. A mixed melting point with the dibromide isolated from the bromination of pentachlorophenylethane showed no depression.

Summary

Methods of preparation and structural proofs for 1-pentachlorophenyl-1-bromoethane, 1-pentachlorophenyl-2-bromoethane and 1-pentachlorophenyl-1,2-dibromoethane are described.

It is suggested that the difference in the direction of substitution on chlorination and bromination of ethylpentachlorobenzene is ascribable to a difference in the reactivities of chlorine and bromine atoms.

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p-Triphenylmethylphenyl and 2-Fluorenyl Isocyanates as Reagents for Alcohols

BY BENJAMIN WITTEN AND E. EMMET REID

Phenyl (I)[1] and α-naphthyl (II)[2] isocyanates are useful for the identification of alcohols, but most of their derivatives have rather low melting points. *p*-Xenyl (III)[3] and 4-iodobiphenyl (IV)[4] iso-

TABLE I

MELTING POINTS OF CARBAMATES

Alcohol	Carbamate							
	p-Triphenylmethylphenyl (V) M. p., °C. (cor.)	2-Fluorenyl (VI) M. p., °C. (cor.)	*p*-Xenyl (3) (III) M. p., °C.	Phenyl (1) (I) M. p., °C.[a]	α-Naphthyl (2) (II) M. p., °C.	*p*-Nitrophenyl (5,6) M. p., °C.	3,5-Dinitrophenyl (6) M. p., °C.	4-Iodobiphenyl (4) IV M. p., °C.
Methyl	214	120	126	47	124	178	127	191.1
Ethyl	216	120	121	52	79	130	83	200.5
n-Propyl	177	114	130	57	80	110	97	188.7
n-Butyl	140	112	109	61	71	96	70	174
n-Amyl	85	93	95	46	68	91	58	165.5
n-Hexyl	81	98	93	42	59	104	75	156.3
n-Heptyl	55	97	105	65	62	105	61	150.9
n-Octyl	61	119	109	74	66	111	69	149.2
n-Nonyl	62	110	115	60	65.5	104	66	149.2
n-Decyl	64	100	112	59.5	72	117	70	147
n-Undecyl	68	109	112	52	73[b]	99.5	62	146.5
n-Dodecyl	70	112	113	74	80	117	81	145.7
n-Tridecyl	74	107	114[b]	70[b]	80[b]			144.5
n-Tetradecyl	76	106	113[b]	71	81[b]			143
n-Pentadecyl	77	108	113[b]	72	85			141.5
Cetyl	79	108	113[b]	73	82.3	118	86	138.5
n-Heptadecyl	79	108	113[b]	79[b]	88.5			138.5
n-Octadecyl	79	107	114[b]	79	89[b]	115	88	137.2

[a] Melting points reported by van Gelderen, *Rec. trav. chim.*, **52**, 969–975 (1933), methyl 124°, ethyl 119°, *n*-propyl 130°, *n*-butyl 109°, *n*-amyl 102°, *n*-hexyl 98°, *n*-heptyl 105°, *n*-octyl 110°, *n*-nonyl 115°, *n*-decyl 111°, *n*-undecyl 106°, *n*-dodecyl 113°. Melting points reported by Morgan and Pettet, *J. Chem. Soc.* 1124–1126 (1931); methyl 127°, ethyl 119°, *n*-propyl 129°, *n*-butyl 109°, *n*-amyl 99°. [b] New compound (m. p. cor.).

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(1) Huntress and Mulliken, "Identification of Pure Organic Compounds, Tables of Data on Selected Compounds of Order I," John Wiley and Sons, Inc., New York, N. Y., 1941.

(2) Huntress and Mulliken, ref. 1; Tischer, *Ber.*, **72B**, 291–297 (1939).

(3) Morgan and Pettet, *J. Chem. Soc.*, 1124–1126 (1931); M. J. van Gelderen, *Rec. trav. chim.*, **52**, 969–975 (1933).

(4) Siniti Kawai and Kunisaburo Tamura, *C. A.*, **24**, 4256; *Proc. Imp. Acad.* (*Japan*), **6**, 198–200 (1930).