

micro analyses on the nitrate salt, and acknowledges the technical assistance of Mr. C. E. Fisher of The Lyndon Institute, Lyndon Center, Vermont. The author also thanks the American Cyanamid Company for the thiourea used in this work.

Summary

1. The preparation of the nitrate, hydrochloride and sulfate salts of *p*-aminophenylguanidine has been described.

2. Some experimental evidence has been presented which indicates that the free base, *p*-aminophenylguanidine, has been obtained as a dihydrate.

BURLINGTON, VERMONT

[CONTRIBUTION NO. 84 FROM THE EXPERIMENTAL STATION OF E. I. DU PONT DE NEMOURS AND COMPANY]

POLYMERS FROM BENZYL CHLORIDE AND RELATED COMPOUNDS

BY RALPH A. JACOBSON

RECEIVED OCTOBER 27, 1931

PUBLISHED APRIL 6, 1932

The formation of an insoluble hydrocarbon by the action of aluminum chloride on benzyl chloride was observed many years ago by Friedel and Crafts.¹ In the same year Gladstone and Tribe² obtained related materials from benzyl chloride by the action of a copper-zinc couple, and previous to these observations a similar product had been obtained by means of copper.³ Although the formation of polymeric substances from benzyl chloride has since been referred to in a number of instances,⁴ little information is available concerning the nature or properties of the polymers. Insoluble amorphous products have sometimes been obtained while in other instances the polymers have been soluble resins, yet the experimental conditions pertinent to the formation of one or the other have not been defined. In view of this situation and as part of a general study of polymeric substances, the earlier work has been repeated and extended. The study has also included the polymerization of *p*-bromobenzyl chloride

¹ Friedel and Crafts, *Bull. soc. chim.*, **43**, 53 (1885).

² Gladstone and Tribe, *J. Chem. Soc.*, **47**, 448 (1885).

³ Zincke, *Ber.*, **2**, 739 (1869).

⁴ Schramm, *ibid.*, **26**, 1706 (1893); Radziewanowski, *ibid.*, **27**, 3237 (1894); Auger, *Bull. soc. chim.*, [3] **21**, 562 (1899); Mailhe, *Chem. Z.*, **29**, 464 (1905); Lavaux and Lombard, *Bull. soc. chim.*, [4] **7**, 541 (1910); Lavaux, *Ann. chim.*, [8] **20**, 488 (1910); von Braun and Deutsch, *Ber.*, **45**, 1267 (1912); Badische Anilin und Soda-Fabrik, German Patent 280,595, Issued November 21, 1914, *Chem. Zentr.*, **86**, 71 (1915); Korczynski, Reinholz and Schmidt, *Roczniki Chem.*, **9**, 731 (1929); *Chem. Abstracts*, **24**, 1858 (1930); Ushakov and Kon, *Zhur. Prikladnoĭ Khim.* **3**, 69 (1930); *Chem. Abstracts*, **24**, 3796 (1930).

under similar conditions, and the formation of polymers from *p*-dibromobenzene and *p*-xylylene bromide by means of the Wurtz reaction.

When benzyl chloride was polymerized by aluminum chloride, two products were obtained in varying amounts depending upon the experimental conditions. One of these was an infusible, insoluble, amorphous solid and the other a soluble, brown resin which softened and melted at 70–85°. The latter was soluble in all proportions in chloroform, carbon disulfide, and aromatic hydrocarbons, but insoluble in alcohols, ketones, and aliphatic hydrocarbons. Although the soluble polymer exhibited typical resin characteristics, it was not compatible with pyroxylin, cellulose acetate, polyvinyl acetate, polyvinyl chloride, drying oils, or with glyptal resins. Molecular weight determinations in benzene by the ebullioscopic method gave for different lots of resin, values varying from 1260 to 2250. It is of interest that an amount of aluminum chloride as small as 0.005 mole per mole of benzyl chloride was sufficient to effect polymerization within a few minutes. Under these conditions the insoluble amorphous polymer and the resin were obtained in a ratio of about 2.5 to 1. When the quantity of aluminum chloride was increased tenfold, polymerization occurred more vigorously to yield the insoluble polymer as the main product and only a small amount of the resin. With 0.004 mole of ferric chloride the polymerization proceeded slowly and the fusible soluble resin was the main product. The polymerization proceeded still more slowly with stannic chloride to yield as the only product, a soluble resin having a molecular weight of about 1300 to 1500.

Chemically, both the soluble and the insoluble polymers were hydrocarbons having the empirical formula C_7H_8 . The only exception was the resin obtained by means of stannic chloride, which contained a small amount of chlorine. In view of the experimental conditions employed, it is surprising that the reaction should yield exclusively materials of high molecular weight.^{4a} The formation of considerable quantities of 9,10-dihydroanthracene by the intercondensation of two benzyl chloride molecules might reasonably be expected especially since such a condensation would involve the formation of a six-membered ring. The properties of the soluble polymers can be accounted for by assuming that they are hydrocarbon chains containing the group $-\text{C}_6\text{H}_4-\text{CH}_2-$ as the structural unit. It is likely that coupling occurs mainly in the position para to the methylene group, since the para isomer is usually obtained in larger amounts than the ortho or meta isomers when the Friedel-Crafts reaction is applied to toluene, diphenyl and related compounds.⁵ Undoubtedly


^{4a} Since this paper was submitted, an article by Wertyporoch and Farnik has appeared [*Ann.*, **491**, 265 (1931)] in which the isolation of small amounts of tolyl benzyl chloride is reported.

⁵ Gattermann and Koch, *Ber.*, **30**, 1622 (1897); Limpricht, *Ann.*, **312**, 92 (1900);

occasional ortho and perhaps meta linkages may occur to render the chains unsymmetrical. The properties of the insoluble and infusible polymers can be explained by assuming a three-dimensional structure as in the case of Bakelite C.⁶

While no information concerning the number of structural units in the hydrocarbon chain of the insoluble polymer could be obtained, the average number of C₇H₆ groups in the chains of the soluble resins varied from 14 to 29, as indicated by molecular weight determinations. Reliable information concerning the arrangement of the units in the chain could not be secured on account of the resistance of the polymers to reagents. Attempts to oxidize the products revealed a high degree of stability, such oxidizing agents as potassium permanganate and potassium dichromate being without effect. By the action of nitric acid on the soluble polymer, an infusible resin containing nitrogen was obtained, but the presence of nitro groups could not be established. Chromium trioxide in boiling acetic acid gave products corresponding approximately to the structure (—C₆H₄—COC₆H₄CO—)_x. However, the presence of ketone groups could not be demonstrated by the usual methods. The action of bromine upon the soluble polymer yielded a product containing one bromine atom for two C₇H₆ groups.

The main product from the reaction of aluminum chloride and *p*-bromobenzyl chloride in carbon disulfide was an insoluble and infusible polymer. This was accompanied by a small amount of resin similar in solubility characteristics to the benzyl resins. When ferric chloride was used as the catalyst, the entire product was a soluble resin. Both the soluble and insoluble polymers were halogenated hydrocarbons having the empirical formula (C₇H₅Br)_x, for which the structural unit would be the group

Br  CH₂—. Molecular weight determinations gave values from 2000 to 2600, indicating that the chains of the soluble resins averaged from 12 to 15 units. A similar soluble halogenated hydrocarbon, (C₇H₅Br)_x, was obtained by Boeseken⁷ although the molecular weight was not determined. As in the case of the benzyl chloride polymers, the chains would be unsymmetrical, since linkage through the position meta to the methylene group is also possible. The polymers were not readily attacked by oxidizing agents but bromination of the soluble resin yielded a product containing one bromine atom per C₇H₅Br group.

Liebermann and Zsuffa, *Ber.*, **44**, 857 (1911); Lawrence, *THIS JOURNAL*, **43**, 2577 (1921); Blanc, *Am. Perfumer*, **17**, 541 (1923); *Perfumery Essent. Oil Record*, **14**, 40 (1923); Stephen, Short and Gladding, *J. Chem. Soc.*, **117**, 510 (1920); Huston, *THIS JOURNAL*, **46**, 2775 (1924).

⁶ Carothers, *Chem. Reviews*, **8**, 353 (1931).

⁷ Boeseken, *Rec. trav. chim.*, **23**, 100 (1904).

By the action of sodium upon *p*-dibromobenzene and upon *p*-xylylene bromide, polymeric substances were also obtained. The polymer obtained from *p*-dibromobenzene and sodium in ether was readily soluble in aromatic hydrocarbon solvents and contained about 19.5% halogen. A polymer of similar properties but containing only 12.7% halogen was formed when the reaction was conducted in toluene. The chains in each case probably consist of phenylene groups and terminate at both ends in bromine atoms. The formulas $C_{48}H_{32}Br_2$ and $C_{84}H_{56}Br_2$ are indicated by the analytical data and molecular weights, and compare favorably with the formulas, $C_{48}H_{32}Br_2$ and $C_{78}H_{52}Br_2$, assigned by Goldschmidt⁸ to two polymers obtained by the reaction of *p*-dibromobenzene with sodium in ether⁹ for three and five days, respectively. From *p*-xylylene bromide, an infusible and insoluble polymer having the empirical formula $(C_8H_8)_x$ was obtained. From the method of preparation and the properties of this polymer, it is certain that structurally it consists of long chains of $-CH_2-\langle \text{hexagon} \rangle-CH_2-$ groups. The absence of accompanying soluble polymers of lower molecular weight is unexpected since in an analogous reaction between decamethylene bromide and sodium,¹⁰ an entire series of hydrocarbons was obtained. An infusible polymer of similar appearance and properties was obtained from *p*-xylylene bromide and magnesium, though this product contained 4.72% bromine. Assuming that bromine is present at both ends of the chain, the chains of this polymer would consist of 31 C_8H_8 groups and the polymer would have a molecular weight of about 3200.

Experimental

Polymerization Experiments.—A mixture of 51 g. (0.4 *M*) of benzyl chloride and 0.267 g. (0.002 *M*) of powdered aluminum chloride reacted at room temperature. Evolution of hydrogen chloride began at once and within twenty minutes the mass had become solid. The yellow product was placed in boiling dilute hydrochloric acid for fifteen minutes, washed with hot water, and finally extracted several times each with alcohol, ether and acetone. The pale yellow granular solid was infusible, and practically insoluble in the common organic solvents; yield, 16.5 g.

Anal. Calcd. for $(C_7H_8)_x$: C, 93.33; H, 6.67. Found: C, 92.83, 93.09, 93.32; H, 6.97, 7.15, 6.86; Cl, none.

The solvents used in the extraction of the above polymer were combined and distilled. Following the recovery of 10.5 g. of benzyl chloride, there remained in the distilling flask 6.5 g. of a transparent brittle light brown resin (m. p. 70–80°), which was soluble in aromatic hydrocarbons in all proportions, but insoluble in aliphatic hydrocarbons.

⁸ Goldschmidt, *Monatsh.*, **7**, 42 (1886).

⁹ Riese [*Ann.*, **164**, 161 (1872)], also obtained a polymer by the interaction of *p*-dibromobenzene and sodium. Kraus and White [*THIS JOURNAL*, **45**, 768 (1923)], obtained a tar from *o*-dichlorobenzene and sodium in liquid ammonia.

¹⁰ Carothers, Hill, Kirby and Jacobson, *ibid.*, **51**, 5279 (1930).

Anal. Calcd. for $(C_7H_6)_n$: C, 93.33; H, 6.67; mol. wt. 1260. Found: C, 93.16, 92.16; H, 6.94, 7.01; mol. wt. 11.91, 1241 (cryoscopic in benzene).

When the amount of aluminum chloride was increased tenfold, the reaction proceeded more vigorously and yielded a larger quantity of the insoluble polymer. Other factors such as the presence of solvents and the nature of the catalyst also influenced the reaction. The results of a number of experiments with benzyl chloride and *p*-bromobenzyl chloride under varying conditions are shown in the accompanying table. The products obtained by treating *p*-dibromobenzene and *p*-xylylene bromide with sodium are also indicated.

TABLE I
PREPARATIONAL AND ANALYTICAL DATA

Compound	Condensing agent		Solvent	Mole	Insoluble polymer, g.	Soluble polymer, g.	M. p., °C.	
	Mole	Mole						
A Benzyl chloride	0.4	AlCl ₃	0.02	33.5	2.0	70-80
B Benzyl chloride	.4	AlCl ₃	.002	CS ₂	0.83	12.0	6.5	80-85
C Benzyl chloride	.4	FeCl ₃	.0041	CS ₂	.83	1.5	22.0	84-88
D Benzyl chloride	.4	SnCl ₄	.0019	None	28	68-75
E <i>p</i> -Bromobenzyl chloride	.1	AlCl ₃	.01	CS ₂	.42	8.0	2.0	120-135
F <i>p</i> -Bromobenzyl chloride	.1	FeCl ₃	.004	CS ₂	.83	None	15.5	125-135
G <i>p</i> -Dibromobenzene	.1	Na	.22	Ether	.5	None	4.8	Infusible
H <i>p</i> -Dibromobenzene	.1	Na	.22	Toluene	.47	None	6.0	Infusible
I <i>p</i> -Xylylene bromide	.f	Na	.44	Toluene	1.6	20 (in-fusible)	None	

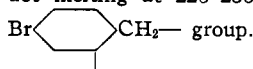
	Analyses						Mol. wt. b. p. in benzene
	C		H		Halogen		
A Ins. sol.	92.70	93.05	7.08	6.30		
A Sol. pol.	92.89	92.85	6.62	6.52		2277 2304
B Ins. sol.	93.13	93.35	6.79	7.07		
B Sol. pol.	93.18	93.39	6.72	6.87		1680 1727
C Ins. sol.	92.92	92.89	7.06	7.08		
C Sol. pol.	92.94	92.81	6.87	6.68		1764 1789
D Sol. pol.	92.02	92.18	6.58	6.47	Cl, 1.39, 1.40		1514 1529
E Ins. sol.	54.83	54.81	3.56	3.64	Br, 47.66, 47.84		
E Sol. pol.	56.70	56.38	3.73	3.52	Br, 45.39, 45.44		1977 2158
F Sol. pol.	54.37	54.41	3.24	3.38	Br, 52.35, 52.35		2420 2600
G	74.09	74.12	4.19	4.45	Br, 19.21, 19.58		
H	81.36	81.53	4.37	4.62	Br, 12.58, 12.88		
I	91.94	91.95	8.46	7.96			

Oxidation and Bromination Experiments.—The benzyl resin was recovered unchanged when treated with potassium permanganate or with potassium dichromate. Strong nitric acid at 100° converted the resin into a hard infusible mass containing nitrogen but the presence of nitro groups could not be confirmed by qualitative tests. Reaction of the resin with chromium trioxide in boiling acetic acid yielded a resin (m. p. 175-185°) whose analysis indicated the presence of ketone groups. However, the presence of these could not be established by the usual tests. Bromination of the benzyl resin in sunlight yielded a product containing one bromine atom per two C_7H_6 groups.

Anal. Calcd. for $(C_6H_4CO)_z$: C, 80.77; H, 3.85. Found: C, 79.11, 79.23; H, 4.08, 4.29.

Anal. Calcd. for $(-C_6H_4CHBrC_6H_4CH_2-)_z$: C, 64.87; H, 4.24; Br, 30.89. Found: C, 65.81, 65.97; H, 4.38, 4.58; Br, 30.98, 31.04.

Attempts to oxidize the *p*-bromobenzyl resin with chromium trioxide, permanganate and with sodium dichromate were unsuccessful. Bromination in sunlight gave a product melting at 225–235° the analysis of which indicated one bromine atom per



Anal. Calcd. for $(-C_7H_4Br_2-)_x$: Br, 64.40. Found: Br, 63.20, 62.82.

Summary

1. Polymerization of benzyl chloride has been effected by small amounts of aluminum chloride, ferric chloride, and stannic chloride. Aluminum chloride yielded mainly an insoluble hydrocarbon $(C_7H_6)_x$ and a small amount of soluble resin having the same empirical formula. The proportions of these were reversed when ferric chloride was employed, while stannic chloride yielded entirely the soluble polymer. The molecular weights of the soluble resin varied from 1260 to 2250. The hydrocarbon chains were not readily attacked by oxidizing agents.

2. Polymerization of *p*-bromobenzyl chloride has been effected under similar conditions and with comparable results. The structural unit of both the insoluble and soluble polymers was C_7H_5Br and the molecular weights of the resin varied from 1300 to 1500.

3. Polymers have been obtained from *p*-dibromobenzene and *p*-xylylene bromide by means of the Wurtz reaction. The former yielded a soluble polymer whereas the latter gave an infusible insoluble polymeric hydrocarbon having the empirical formula $(C_8H_8)_x$.

WILMINGTON, DELAWARE

[201ST CONTRIBUTION FROM THE COLOR AND FARM WASTE DIVISION, BUREAU OF CHEMISTRY AND SOILS, U. S. DEPARTMENT OF AGRICULTURE]

THE CHEMISTRY OF LIGNIN. VI. THE DISTILLATION OF ALKALI LIGNIN WITH ZINC DUST IN AN ATMOSPHERE OF HYDROGEN

BY MAX PHILLIPS AND M. J. GOSS

RECEIVED OCTOBER 29, 1931

PUBLISHED APRIL 6, 1932

In a previous communication by one of us¹ the results of some experiments on the distillation of lignin with zinc dust in an atmosphere of hydrogen were given. Among the products of distillation obtained were catechol, guaiacol, and a phenolic methyl ether which gave a 3,5-dinitrobenzoyl derivative melting at 110°.

The present paper gives the results of a further study of the same reaction. In addition to the degradation products mentioned above, we have succeeded in isolating a phenolic compound which has been identified as 1-*n*-propyl-3-methoxy-4-hydroxybenzene (I). When oxidized with

¹ Phillips, THIS JOURNAL, 53, 768 (1931).