

After distillation of solvent, 27.0 g. of residue remained which was fractionated giving cyclopentamethylenediphenylgermane, b.p. 125–128° (0.08 mm.),  $n_D^{20}$  1.5873.

*Anal.* Calcd. for  $C_{17}H_{20}Ge$ ; C, 68.75; H, 6.80, Ge, 24.45. Found: C, 68.99, H, 6.75, Ge, 24.15.

*Cyclopentamethylenediphenylstannane.* To 72.5 g. (0.211 mole) of diphenyltin dichloride dissolved in 200 cc. of anhydrous ether, was added, dropwise, 1,5-dilithiopentane. The lithium compound was prepared from 9.5 g. of lithium in accordance with the method of West and Rochow.<sup>12</sup> The reaction vessel was equipped in the usual manner and an atmosphere of pure nitrogen was used throughout this preparation. The rate of addition was such that a constant ether reflux was maintained. After the addition of the lithium compound had been completed, the reaction mixture was allowed to stand overnight.

Hydrolysis was accomplished by slowly adding 200 cc. of cold water and stirring. The two-phase system was transferred to a large separatory funnel and the aqueous layer separated. The ether layer was gravity filtered. The filtrate was washed with 50 cc. of *N* sodium hydroxide solution and the ether layer again separated and filtered. This filtrate was dried over calcium chloride. Distillation of the ether left 41.6 g. of a crude milky oil. On distillation the oil yielded 9 g. of a clear colorless liquid, cyclopentamethylene-diphenylstannane, b.p. 138°–140° (0.10 mm.),  $n_D^{20}$  1.6007.

(12) R. West and E. G. Rochow, *J. Org. Chem.*, **18**, 1739 (1953).

*Anal.* Calcd. for  $C_{17}H_{20}Sn$ : C, 59.51, H, 5.89, Sn, 34.60. Found: C, 60.03, H, 6.15, Sn, 34.85.

*Cyclopentamethylenediphenylplumbane.* This compound was prepared in the same manner as was the analogous tin compound described above. Infrared analysis of the product indicated the formation of cyclopentamethylenediphenylplumbane but on standing and exposure to light and air, the product rapidly colored and after several days a resinous solid was observed forming. No physical properties are therefore reported.

*Cyclopentamethylenebromostannane* was prepared by the action of a standardized potassium bromide-potassium bromate solution on cyclopentamethylenediphenylstannane in carbon tetrachloride, b.p. 166° (wax bath temperature) (0.40 mm.–0.45 mm.). Quantitative data on the bromination and infrared data supported the structure. The action of anhydrous hydrogen bromide gave rise to the same product. The by-product in this reaction was benzene.

*Cyclopentamethylenephenyltin iodide* was prepared by the treatment of the cyclopentamethylenediphenylstannane with iodine in carbon tetrachloride solution. Iodination data and infrared figures confirmed the structure, b.p. 219°<sup>13</sup> (0.45 mm.–0.85 mm.).

BUFFALO, N. Y.

(13) Wax bath temperature.

[CONTRIBUTION FROM E. I. DU PONT DE NEMOURS & CO. EXPLOSIVES DEPARTMENT, EXPERIMENTAL STATION LABORATORY]

## Polymeric Ligands. I. Some Salicylic Acid Derivatives

R. C. DEGEISO, L. G. DONARUMA, AND E. A. TOMIC

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The preparation and properties of a salicylic acid-formaldehyde copolymer are described. The preparation of the zinc(II), nickel(II), uranyl, iron(III), and aluminum(III) chelates is described. The thermal and spectral properties of the chelates are discussed.

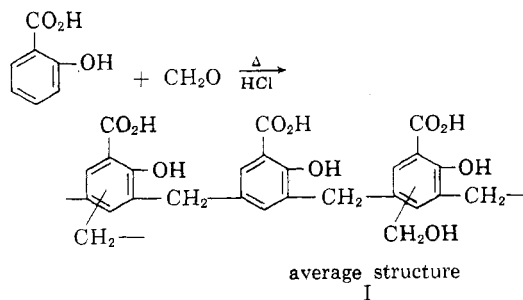
Salicylic acid chelates have been known for many years.<sup>1</sup> However, a number of these materials are water-soluble, and therefore, salicylic acid often cannot be used as a metal precipitant. If a polymer could be fashioned from salicylic acid, a highly water-insoluble ligand should be produced, which would be useful as a metal precipitant. We also wished to find out if the polymeric metal chelates were more stable, thermally, in air, than the parent polymer.

Salicylic acid polymers have been prepared before.<sup>2</sup> However, none of these systems have been

fully characterized and no polymeric chelates have ever been prepared from such systems.

We have prepared a fully characterized polymeric salicylic acid and prepared several different metal chelates from the polymeric ligand.

When salicylic acid was condensed with formaldehyde, a water-insoluble polymer was obtained which had an average molecular weight of  $6700 \pm 15\%$ . The analyses and neutral equivalents



(1) F. J. Welcher, "Organic Analytical Reagents," D. VanNostrand Co., Inc., New York, 1947, Vol. II, p. 118.

(2) W. H. Butler (to Bakelite Corp.), U. S. Patent 2,144,101 (1939); M. VanLoon (to Bataafische Petroleum Moatschappij), Dutch Patent 65,636 (1950); E. C. Yokel (to Eastman Kodak Co.), U. S. Patent 2,565,418 (1951); G. Baumhardt, *Eng. e quim* (Rio de Janeiro), **4**, No. 25 (1932). *Chem. Abstr.*, **48**, 2012a (1954). K. Ashida, "Chem. High Polymers," *Japan*, **9**, 397 (1952); *Chem. Abstr.*, **48**, 7817h (1954). H. Kawabe and M. Yanagita, *Rept. Sci. Res. Inst.* (Japan), **28**, 264 (1952); M. Sugihara, *Sci. Ind. Japan*, **27**, 236 (1953); S. Umezawa and U. Ohtsuka, *Japan* 1598/1953. *Chem. Abstr.*, **48**, 2290 (1954). S. Matsumura and T. Komiya, *Japan* 1693/1953. *Chem. Abstr.*, **48**, 3596 (1954).

compare favorably with the structure (I) shown above. The polymer was soluble in ethanol, acetone, dimethylformamide, and dimethyl sulf-

oxide. It was also soluble in aqueous bicarbonate, carbonate, and alkali solutions. Upon heating in air at a rate of 5° per minute the polymer started to decompose at 190°. The decomposition was complete at 520°. The polymer reacted with ferric ion to give a blue coloration typical of salicylic acid when contacted with iron(III). When ethanol solutions of the polymer were treated with aqueous solutions of various metal ions, polymeric chelates were precipitated. Table I shows the analyses of some of the polymeric metal chelates prepared.

TABLE I

ANALYSES OF METAL CHELATES OF A SALICYLIC ACID-FORMALDEHYDE POLYMER

Chelate	Calcd. Values, %			Obs. Values, %		
	C	H	Metal	C	H	Metal
Zn(II)	52.96	3.25	16.63	52.1	3.6	17.1
				52.3	4.0	17.3
Ni(II)	53.86	3.30	15.19	50.6	4.7	
				50.3	4.9	15.6
Al(III)	60.23	3.69	5.20	52.37	4.9	7.07
Fe(III)	57.04	3.50	10.20	54.25	4.17	13.47
UO <sub>2</sub> <sup>+2</sup>	41.01	2.51	35.46	41.7	2.8	
				41.6	2.9	34.2

The analyses show that in most cases, close to theoretical uptake of metal was observed. The aluminum(III) and iron(III) chelates gave somewhat anomalous analyses, but these values could be repeatedly obtained from several different preparative procedures. Moreover, chelation of trivalent cations, like Fe(III) and Al(III), which both form d<sup>2</sup>sp<sup>3</sup> hybrids, by a polymeric ligand might be expected to be unusual since it would be difficult for a polymeric structure to surround the metal atom in the proper fashion to complete the coordination shells. These cations can therefore be expected to retain at least one of their original ligands when chelated by such a polymer.

The infrared spectra of the polymeric chelates (in potassium bromide pellets) were consistent with the expected structures. In all cases, disappearance of the phenolic hydroxyl bonds occurred due to donation of one unshared electron pair of the phenolic hydroxyl group to the metal ion.

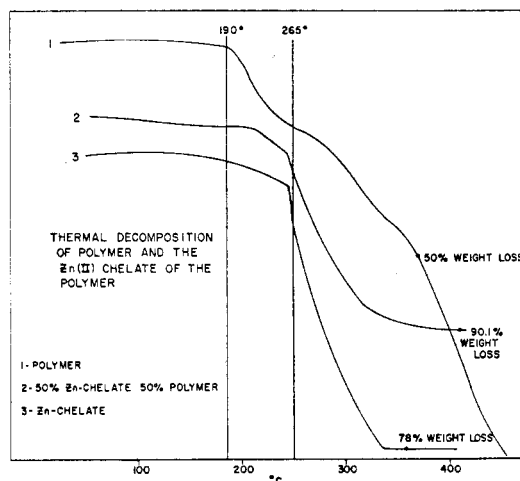
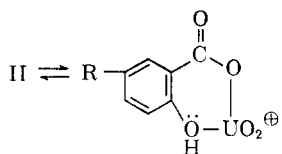
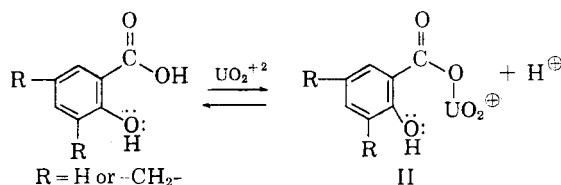


Figure 1

The change in the vibration of the carboxyl group became apparent in a shift of the peak at 11.25  $\mu$  in salicylic acid to 10.6  $\mu$  in uranyl salicylate. This change in vibration of the carboxyl group also was observed in sodium salicylate and therefore is not indicative of chelation exclusively. The chelate formation is obviously characterized by the change in vibration of the phenolic hydroxyl group in the region between 3 and 4  $\mu$ .

When the chelate of the polymer was destroyed by elution of uranyl ion with 1 *N* nitric acid, the ligand did not show any changes in its infrared spectrum, and the ability of the ligand to reform the same uranyl chelate was not impaired.

All of the polymeric metal chelates can be decomposed with dilute acid. The original polymeric ligand and the appropriate metal salt were easily recovered.

The polymeric metal chelates started to decompose between 190 and 220°. The rate of decomposition became very rapid at approximately 260°. The unchelated material starts to decarboxylate at 190° (Fig. 1, graph 1). Figure 1, graph 3 shows the decomposition pattern of the zinc chelate. This decomposition, typical of all chelates of the polymer, is not preceded by decarboxylation as in the case of the unchelated polymer (Fig. 1, graph 1). In a mixture of unchelated and chelated material the pattern of graph 2, Fig. 1, suggests the decarboxylation of the unchelated material between 190 and 260°, which is followed by complete decomposition of the organic matter in a manner comparable to the decomposition of the chelated polymer.

## EXPERIMENTAL

*Preparation and characterization of the salicylic acid-formaldehyde copolymer.* Salicylic acid (190 g.), 13 ml. of water, 114 g. of 37% formaldehyde solution, and 1 g. of oxalic acid were heated to reflux in a resin kettle with good stirring. After 1 hr., a solution of 50 ml. of 37% hydrochloric acid and 50 ml. of water was added to the reaction mixture.

This mixture was refluxed, with good stirring until solid polymer formed. Stirring and heating were continued until the polymer formed rather fine particles. The polymer was removed by filtration, washed with boiling water, and dried. The polymer was reprecipitated twice from ethanol with 20% aqueous sodium chloride solution. The product was then extracted with water in a Soxhlet extractor until the extract gave a negative test for chloride ion. The polymer was then dried at about 20 mm. vacuum and 60°.

Titration of the polymer with 0.1 *N* sodium hydroxide gave a neutral equivalent of 160.49. Found: C, 63.37 and 63.08; H, 4.82 and 4.69.

*Anal.* Calcd. for a neut. equiv. of 164.8: C, 63.15; H, 4.99.

These data agree with formula I. The infrared spectrum of the polymer was consistent with formula I.

Determination of the molecular weight of the polymer by light scattering on a Brice-Phoenix Instrument in either alcohol or acetone gave values of  $6700 \pm 15\%$ .

*Preparation of metal chelates. Zinc(II).* A 0.015-mole sample (2.04 g.) of zinc(II) chloride was dissolved in 100 ml. of water, and 1 ml. of hydrochloric acid (concd.) was added to effect complete dissolution. A 0.02-mole sample of salicylic acid formaldehyde polymer (3.6 g.) was added to 18.5 ml. of 1 *N* sodium hydroxide and 100 ml. of ethanol. The resulting solution had an apparent pH of 5.5. The polymer solution was added dropwise to the zinc solution under rapid stirring with magnetic stirrer. Sodium hydroxide, 1 *N*, was added to maintain an apparent pH of 5.2. A white precipitate formed which was filtered through a Büchner funnel 24 hr. after precipitation was complete, washed with

100 ml. of water followed by 100 ml. of alcohol, air dried, then placed into a Soxhlet extractor and extracted with ethanol for 24 hr. The resulting product was placed into an Abderhalden apparatus and dried *in vacuo* for 24 hr. over phosphorus pentoxide at the temperature of refluxing ethanol and then analyzed for carbon, hydrogen, and zinc in a conventional manner. The results of these analyses are given in Table I.

The preparations of the other chelates were carried out in the same manner. The amounts used were:

Nickel(II): 0.015 mole of nickel(II) chloride, hexahydrate (3.57 g.) and 0.02 mole of polymer (3.6 g.).

Aluminum(III): 0.01 mole of aluminum(III) chloride, hexahydrate (2.4 g.) dissolved in 100 ml. of water, and 0.03 mole of polymer (5.4 g.) dissolved in 250 ml. of ethanol under addition of 10 ml. of 1 *N* sodium hydroxide. Apparent pH was 2.5.

Iron(III): 0.01 mole of iron(II) chloride hexahydrate (2.7 g.) and 0.03 mole of polymer (5.4 g.) dissolved in 250 ml. ethanol upon addition of 10 ml. of 1 *N* sodium hydroxide. Apparent pH was 1.3.

UO<sub>2</sub><sup>++</sup>: 0.015 mole of uranium(VI) nitrate hexahydrate (7.53 g.) and 0.02 mole of polymer.

*Thermal stability of chelates.* Samples of metal chelates prepared and dried as described before were heated from room temperature to constant weight at a rate of 5°/min. on a thermobalance (system of P. Chevenard) which measures and registers weight continually as the temperature of the material is raised.

WILMINGTON, DEL.

[CONTRIBUTION FROM THE ISRAEL INSTITUTE FOR BIOLOGICAL RESEARCH]

## Homologs of Diphenylmethane. I. Homologs with an Even Number of Rings

ARJEH B. GALUN, ASHER KALUSZYNER, AND ERNST D. BERGMANN

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The condensation of chloral or 1-aryl-2,2,2-trichloroethanols with substituted benzenes to give 1,1-diaryl-2,2,2-trichloroethanes is described. The trichloroethanes were converted to the corresponding diphenylmethane derivatives by heating them with potassium hydroxide solution in boiling diethylene glycol.

Higher homologs of diphenylmethane, containing alternating phenylene and methylene groups  $C_6H_5-CH_2(C_6H_4CH_2)_n C_6H_5$ , are practically unknown, and many simple derivatives of diphenylmethane, especially those containing different substituents in the two benzene rings, were hitherto prepared by complicated routes and in low yields.

We found that derivatives and higher homologs of diphenylmethane are easily prepared by condensing aromatic compounds with either chloral or 1-aryl-2,2,2-trichloroethanols (I, VIII),<sup>1</sup> followed by degradation of the trichloromethyl groups and decarboxylation of the carboxylic acids so obtained. The last two steps were carried out without isolation of the intermediate products (see chart).

These "D.D.T.-type" condensations gave in most cases good yields of pure materials. For optimal yields the conditions of the initial condensation reaction had to be slightly modified from compound

to compound, but using about 700 ml. of concentrated sulfuric acid per mole of reactants reasonable yields may be expected. Some sulfonation is usually encountered; it is therefore advisable to avoid the use of oleum unless the aromatic components are at least slightly deactivated—(e.g., in bromobenzene. The sulfonation products, if formed, are easily separated from the trichloroethanes by water extraction. The trichloroethanes were smoothly converted into the corresponding diphenylmethanes by potassium hydroxide in refluxing diethylene glycol (five hours at 185°). Shorter reaction times and lower temperatures effect only dehydrohalogenation, yielding 1,1-diaryl-2,2-dichloroethylenes. Analogously, the condensations of 2,2,2-trichloro-1-phenylethanol (I) with *m*-bromotoluene and of 1-(*p*-bromophenyl)-2,2,2-trichloroethanol (VIII) with chlorobenzene were studied; the products (IX and X) were converted into 4-bromo-2-methyldiphenylmethane (XI) (see below) and 4-bromo-4'-chlorodiphenylmethane (XII), respectively. Also from 1,1-di(*p*-

(1) F. D. Chattaway and R. J. K. Muir, *J. Chem. Soc.*, 701 (1934).