ture overnight, then vacuum distilled to give 214.5 g. (92.0%) of adduct boiling at 87-89°/0.25 mm.

The *diamide*, prepared from the above diacid chloride and excess concentrated ammonium hydroxide, was recrystallized from ethanol for analysis. It melted at 261-262°.

Anal. Calcd. for $C_{10}H_{14}N_2O_2$: C, 61.84; H, 7.27; N, 14.43. Found: C, 61.6, 61.4; H, 7.07, 7.17; N, 14.3, 14.3.

Bicyclo[2.2.2]octene-5-trans-2,3-dicarboxylic acid (Ib). A mixture of 176.3 g. (0.75 mole) of bicyclo[2.2.2]octene-5-*trans*-2,3-dicarbonyl chloride and 1 l. of water was allowed to stand at room temperature overnight. The resulting white solid, after filtering, washing well with water, and drying, weighed 141.4 g. (96.2%) and melted at 213-215°. For analysis it was recrystallized from water and it then melted at 214-215°. Alder and Stein[5] reported a melting point of 211°.

Anal. Calcd. for $C_{10}H_{12}O_4$: C, 61.21; H, 6.17. Found: C, 61.4, 61.4; H, 6.17, 6.07.

Bicyclo[2.2.2]octane-trans-2,3-dicarboxylic acid (II). A solution of 78.4 g. (0.40 mole) of bicyclo[2.2.2]octene-5-*trans*-2,3-dicarboxylic acid and 650 ml. of 10% sodium carbonate was hydrogenated using 0.78 g. of 10% palladium-on-charcoal. After the theoretical amount of hydrogen was consumed, the catalyst was filtered and the product precipitated with concentrated hydrochloric acid. The white solid, after filtering and drying, weighed 76.8 g. (92.2%) and melted at 234-235.5°. After recrystallizing from 1:1 methanol-water the melting point was 234-235°. A mixture with authentic bicyclo[2.2.2]octane-*trans*-2,3-dicarboxylic acid[2] melted at 233-234.5°. The authentic diacid and the present acid have identical infrared spectra (Nujol mull).

Anal. Calcd. for $C_{10}H_{14}O_4$: C, 60.60; H, 7.12. Found: C, 60.3, 60.5; H, 7.28, 7.31.

SUMMIT RESEARCH LABORATORIES
CELANESE CORPORATION OF AMERICA
SUMMIT, N. J.

Dialkylaminoalkyl Pentachlorophenyl Sulfides

JAMES H. SHORT

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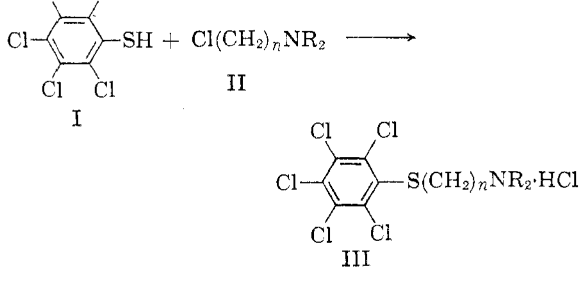
The availability of pentachlorothiophenol (I) prompted the synthesis of a few dialkylaminoalkyl pentachlorophenyl sulfides (III). The desired compounds were prepared by the condensation of I with dialkylaminoalkyl chlorides (II).



One compound, 3-dimethylaminopropyl pentachlorophenyl sulfide (III. $n = 3$, R = CH_3), was quaternized with methyl iodide and *o*-bromobenzyl bromide.

The six compounds were tested for various pharmacological and chemotherapeutic activities including effect on blood pressure, anti-serotonin activity, monamine oxidase inhibition, psychopharmacological activity, and anticancer activity. They were tested for ability to inhibit growth of various gram-negative bacteria such as *E. coli*, and for their effect on parasites such as *S. obvelata*, *E. tenella*, *S. mansoni*, *T. cruzi* and *H. nana*. No particularly outstanding activity was observed.

EXPERIMENTAL[1]

3-Dimethylaminopropyl pentachlorophenyl sulfide hydrochloride. To a mixture of 14 g. (0.05 mole) of pentachlorobenzenethiol and 8 g. (0.05 mole) of dimethylaminopropyl chloride hydrochloride in 350 ml. of 2-propanol was added a solution of 6.6 g. (0.1 mole) of 85% potassium hydroxide in 10 ml. of water. The resulting solution was refluxed overnight. The reaction mixture was poured into 1.0 l. of water, extracted with ether, and dried. Alcoholic hydrogen chloride was added to give 12.6 g. (63%) o fine, white leaflets, m.p. 229-230.5°. Recrystallization twice from dry ethanol raised the melting point to 230.5-231°.

Anal. Calcd. for $C_{11}H_{12}Cl_5NS{\cdot}HCl$: C, 32.70; H, 3.24; Cl, 52.66; N, 3.47; S, 7.93. Found: C, 32.95; H, 3.35; Cl, 52.73; N, 3.54; S, 8.08.

2-Dimethylaminoisopropyl pentachlorophenyl sulfide hydrochloride. Pentachlorobenzenethiol, 14 g. (0.05 mole), and 8.0 g. (0.05 mole) of dimethylaminoisopropyl chloride hydrochloride were allowed to react and the reaction worked up as described above, to yield 9.1 g. (45%) of material melting at 184-190°. Three recrystallizations from ethanol-acetone raised the melting point to 198-200°.

Anal. Calcd. for $C_{11}H_{12}Cl_5NS{\cdot}HCl$: C, 32.70; H, 3.24; Cl, 52.66; N, 3.47; S, 7.93. Found: C, 32.87; H, 3.24; Cl, 52.89; N, 3.58; S, 8.03.

2-Dimethylaminoethyl pentachlorophenyl sulfide hydrochloride. A mixture of 14 g. (0.05 mole) of pentachlorobenzenethiol, 5.4 g. (0.05 mole) of 2-dimethylaminoethyl chloride in an equal weight of xylene, and 2.7 g. (0.05 mole) of sodium methoxide in 400 ml. of dry ethanol was heated under reflux overnight. After working up as described above, 13.6 g. (70%) of product was obtained, m.p. 228-231°. One recrystallization from dry ethanol, with the aid of charcoal, raised the melting point to 232-234°.

Anal. Calcd. for $C_{10}H_{10}Cl_5NS{\cdot}HCl$: C, 30.80; H, 2.84; Cl, 54.55; N, 3.59; S, 8.22. Found: C, 30.86; H, 3.00; Cl, 54.26; N, 3.50; S, 8.26.

2-Di-n-butylaminoethyl pentachlorophenyl sulfide hydrochloride. Pentachlorobenzenethiol, 14 g. (0.05 mole), and 9.6 g. (0.05 mole) of di-*n*-butylaminoethyl chloride in an equal weight of xylene were allowed to react, and then worked up as described above. It was necessary to add ether to the alcoholic solution in order to induce the product to precipitate. The yield was 20.5 g. (86.5%), m.p. 121-124°. Recrystallization from ethanol-ether with the aid of charcoal gave white needles, and did not raise the melting point.

Anal. Calcd. for $C_{16}H_{22}Cl_5NS{\cdot}HCl$: C, 40.53; H, 4.89; Cl, 44.87; N, 2.95; S, 6.76. Found: C, 40.52; Y, 5.08; Cl, 44.79; N, 3.29; S, 6.87.

[3-(Pentachlorophenylthio)propyl]trimethylammonium iodide. 3-Dimethylaminopropyl pentachlorophenyl sulfide was prepared as described above on a 0.05 mole scale. The ether solution was taken to dryness, and the residual oil dissolved in 100 ml. of acetone. Methyl iodide, 42 g. (0.3 mole), was added and the solution was allowed to stand at room temperature for 6 hr., during which time a cream-colored solid precipitated. The solid weighed 25 g. (98%)

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[1] Microanalyses are due to Mr. Elmer Shelberg and staff of the Abbott Microanalytical Laboratory.

and melted at 199–201°. One recrystallization from methanol raised the melting point to 207–208°.

Anal. Calcd. for $C_{12}H_{15}Cl_5INS$: C, 28.28; H, 2.96; N, 2.75. Found: C, 28.58; H, 2.97; N, 2.55.

(o-Bromobenzyl)dimethyl[3-(pentachlorophenylthio)propyl]-ammonium bromide. To 0.05 mole of 3-dimethylaminopropyl pentachlorophenyl sulfide in 100 ml. of acetone was added 12.5 g. (0.05 mole) of *o*-bromobenzyl bromide.[2] On standing 4 hr. at room temperature, an oil precipitated and solidified. The product was cream-colored and weighed 20 g. (65%), m.p. 181–182°. Two recrystallizations from a mixture of ethanol and 2-propanol did not raise the melting point.

Anal. Calcd. for $C_{18}H_{18}Br_2Cl_5NS$: C, 35.01; H, 2.94; N, 2.27. Found: C, 35.31; H, 3.19; N, 2.23.

ORGANIC CHEMISTRY DEPARTMENT
ABBOTT LABORATORIES
NORTH CHICAGO, ILL.

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[2] D. F. DeTar and L. A. Carpino, *J. Am. Chem. Soc.*, **78**, 477 (1956).

Synthesis of Benzyl Vinylcarbamate and 3-*O*-Vinylcarbamoyl-D-mannitol Pentanitrate[1]

M. L. WOLFROM, G. H. MC.FADDEN, AND ALAN CHANEY

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After completion of the investigation concerned with the preparation of poly(vinylamine),[2] further amounts of this polymer were desired for study. In the interim, Hart had described a new synthetic route for this material.[3,4] This report is concerned with the preparation of a monomer having potential use in this synthesis and certain anomalous reactions encountered.

In essence, the synthesis involves the application of the Curtius reaction to acryloyl chloride followed by conversion of the vinyl isocyanate (II) obtained to benzyl vinylcarbamate (III). Hart[3,4] has described a three-step process which involves the

$$CH_2{=}CHCOCl \xrightarrow{NaN_3} \underset{\text{I}}{CH_2{=}CHCON_3} \tag{1}$$

$$CH_2{=}CHCON_3 \xrightarrow{\text{Heat}} \underset{\text{II}}{CH_2{=}CHNCO} \tag{2}$$

$$CH_2{=}CHNCO \xrightarrow{C_6H_5CH_2OH} \underset{\text{III}}{CH_2{=}CHNHCO_2CH_2C_6H_5} \tag{3}$$

isolation of the intermediate materials. It has been found that this process can be considerably simplified and the isolation of the intermediates eliminated. Thus, acryloyl chloride[5] was converted to the azide by treatment in toluene solution with aqueous sodium azide solution.[3] The acryloyl azide (I) was then heated in the presence of benzyl alcohol to produce the benzyl vinylcarbamate (m.p. 43–44°) in 60% over-all yield from the acryloyl chloride. Lower yields were experienced if attempts were made to isolate the intermediate vinyl isocyanate. Furthermore, if the acryloyl azide solution in toluene was not carefully purified to remove all traces of acid contamination, the expected product was not obtained. In the best method, pyridine was added to the azide decomposition mixture to ensure the absence of acid conditions.

The product obtained in the above process, if the system was contaminated with acid, was dibenzyl ethylidenedicarbamate (IV).

$$RCH(NHCO_2CH_2C_6H_5)_2$$
$$\text{IV. } R = CH_3$$
$$\text{V. } R = CH_3CH_2$$

The structure of this new compound was established by direct synthesis from acetaldehyde and benzyl carbamate and by hydrolysis and isolation of derivatives in addition to elemental analysis and molecular weight determination. Dibenzyl ethylidenedicarbamate (IV) also resulted from the acid-catalyzed reaction of benzyl alcohol and vinyl isocyanate (II), from the treatment of benzyl vinylcarbamate (III) with various acids, and from the acid-catalyzed reaction of benzyl carbamate and benzyl vinylcarbamate (III). In this last instance, the yield was higher than could have been due to the benzyl vinylcarbamate alone.

The acid-catalyzed conversion of benzyl vinylcarbamate (III) to dibenzyl ethylidenedicarbamate (IV) probably proceeds by initial cleavage of the reactant to benzyl carbamate and an unidentified fragment. The benzyl carbamate subsequently condenses with the unchanged benzyl vinylcarbamate to afford the product. Martell and Herbst[6] have made similar suggestions about the course of the reaction between benzyl carbamate and aldehydes.

Martell and co-workers,[6,7] in their studies of the condensation of benzyl carbamate with aldehydes, investigated only a single aliphatic aldehyde, isovaleraldehyde. Thus, an attempt was made to explore the generality of the reaction; following the method developed for acetaldehyde, propanal afforded dibenzyl propylidenedicarbamate (V). However, the corresponding derivatives could not be obtained with methanal, butanal, 2-propanone,

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[1] This work was carried out under contract between the Ordnance Corps (DA-33-019-ORD-2025) and The Ohio State University Research Foundation (Project 675). The support of the supervising agency, the Ballistic Research Laboratories of Aberdeen Proving Ground, Md., is gratefully acknowledged.

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