trisiloxane,[5] simultaneously appeared in the water-cooled condenser. However, no other cyclopolysiloxanes were noted in the course of these distillations.

**Acknowledgment.**—The author is greatly indebted to Dr. Earl W. Balis of this Laboratory for the carbon, hydrogen and silicon analyses reported here.

## Summary

The following *n*-butoxy silicon compounds have been prepared: dimethyl-*n*-butoxychlorosilane, dimethyldi-*n*-butoxysilane, methyltri-*n*-butoxysilane, tetramethyl-1,3-di-*n*-butoxydisiloxane and hexamethyl-1,5-di-*n*-butoxytrisiloxane.

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(5) Hyde and DeLong, THIS JOURNAL, 63, 1194 (1941).

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# NOTES

## Preparation of Salts of 2-Phenylethene-1-sulfonic Acid[1]

BY F. G. BORDWELL, C. M. SUTER,[2] J. M. HOLBERT AND C. S. RONDESTVEDT

In connection with some other work it became necessary to prepare salts of 2-phenylethene-1-sulfonic acid in appreciable quantity. Salts of this acid have previously been obtained by the reaction of ammonium sulfamate with styrene[3] and by the reaction of sodium bisulfite with styrene in the presence of oxygen.[4] The yields are not good by either of these procedures. It has now been found that the reaction of dioxane sulfotrioxide[5] with styrene can be used to obtain good yields of 2-phenylethene-1-sulfonic acid.

The sodium, calcium and barium salts of the acid were isolated on addition of water and the appropriate metallic carbonate or hydroxide to the original sulfonation mixture. The salts were identified by conversion to 2-phenylethene-1-sulfonyl chloride,[3,4] 2-phenylethene-1-sulfonamide[3,4] and to the *p*-chlorobenzylthiouronium salt.[6] In addition the anilide, S-benzylthiouronium salt and *p*-toluidine salt were prepared.

A water-insoluble compound, $C_{16}H_{16}O_3S$, was obtained as a by-product in this sulfonation. Preliminary observations indicate that this material is a sultone.

### Experimental

**Sodium 2-Phenylethene-1-sulfonate.**—To a stirred suspension of dioxane sulfotrioxide[5] prepared by distillation of 160 g. (2 moles) of sulfur trioxide into a cooled mixture of 175 ml. of dry dioxane and 175 ml. of dry ethylene chloride, was added dropwise 257 ml. (2.2 moles) of styrene. The addition required two hours, the flask being cooled by an ice-bath during that time. The mixture was allowed to stand overnight, heated on the steam-bath for thirty minutes, and then poured into 700 ml. of water. After standing, the layers were separated. Evaporation of the ethylene chloride layer yielded 52 g. of colorless water-insoluble material, m. p. 142–145°. After several crystallizations from acetone–water and from alcohol the substance melted at 152–153°. The yield of crude material was 9% based on sulfur trioxide. A qualitative analysis for the elements showed the presence of sulfur.

*Anal.* Calcd. for $C_{16}H_{16}O_3S$: C, 66.66; H, 5.55; mol. wt., 288. Found: C, 66.52, 66.47; H, 5.70, 5.70; mol. wt., 278 (Rast method[7]).

The aqueous layer was neutralized with sodium hydroxide, and the following crops of crystals collected: (1) from 1350 ml., 40 g.; (2) from 500 ml., 158 g.; (3) from 350 ml., 46 g.; (4) residue, 125 g. The calcium and barium salts are much less soluble. Crops 1, 2 and 3 were practically pure sodium 2-phenylethene-1-sulfonate since they gave S-benzylthiouronium 2-phenylethene-1-sulfonate in yields and purity comparable to that from an authentic sample of this compound. The yield from these crops was 244 g. (60% based on sulfur trioxide). The residue contained sodium 2-phenylethene-1-sulfonate, sodium sulfate and probably sodium 2-hydroxy-2-phenylethane-1-sulfonate.

The *p*-chlorobenzylthiouronium salt of 2-phenylethene-1-sulfonic acid after several crystallizations from dilute alcohol melted at 203–204° (Suter and Milne[6] report 199°).

*Anal.* Calcd. for $C_{16}H_{17}O_3N_2ClS_2$: N, 7.28. Found: N, 6.94.

The S-benzylthiouronium salt was crystallized from dilute alcohol to a constant m. p., 166–167°.

*Anal.* Calcd. for $C_{16}H_{17}O_3N_2S_2$: N, 8.00. Found: N, 7.50.

The *p*-toluidine salt was crystallized from water containing a drop of acetic acid to a constant m. p., 208–209°.

*Anal.* Calcd. for $C_{15}H_{17}O_3NS$: neut. equiv., 291. Found: neut. equiv., 289.

2-Phenylethene-1-sulfonanilide was prepared and crystallized to a constant m. p., 114–114.5°.

*Anal.* Calcd. for $C_{14}H_{13}O_2SN$: N, 5.40. Found: N, 5.22.

2-Phenylethene-1-sulfonyl chloride[4] was readily prepared from crops 1, 2 and 3 (but not from the residue) by heating the dried salt on the steam-bath with an equimolar quantity of phosphorus pentachloride for six hours, and after removal of the phosphorus oxychloride under vacuum, pulverizing the resultant mass under ice-water. The yield of crude material, m. p. 86–89°, was practically

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[1] This investigation was supported by a grant from the Abbott Fund of Northwestern University.

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[3] Qinlico and Fleischner, *Atti accad. Lincei*, 1, 1050 (1938).

[4] Kharasch, May and Mayo, *J. Org. Chem.*, 3, 175 (1938); Kharasch, Schenk and Mayo, THIS JOURNAL, 61, 3092 (1939).

[5] Bordwell, Suter and Webber, *ibid.*, 67, 827 (1945), and ref. cited therein.

[6] Suter and Milne, *ibid.*, 65, 582 (1943).

[7] Fuson and Shriner, "Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1940, pp. 122.

quantitative. Crystallization of the material from carbon disulfide or hexane gave a purer product, m. p. 89–89.5°, but considerable loss was entailed.

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## The Preparation of *t*-Butylamine by the Low-Pressure Hydrogenation of 2,2-Dimethylethylenimine[1]

By Kenneth N. Campbell, Armiger H. Sommers and Barbara K. Campbell

We recently needed large amounts of *t*-butylamine, and developed a method for preparing it by the hydrogenation of 2,2-dimethylethylenimine. While our paper was being cleared by O. S. R. D., a Note by Karabinos and Serijan[2] appeared, in which the high-pressure hydrogenation of the imine to *t*-butylamine is described. We should like to point out that the hydrogenation can be carried out satisfactorily at low pressures, by the following procedure:

A citrate of magnesia bottle, wound for electrical heating, was charged with 100 ml. of pure dioxane, 35.5 g. of freshly-distilled 2,2-dimethylethylenimine and 9 g. of Raney nickel. The bottle was attached to a Parr low-pressure hydrogenation apparatus and flushed several times with hydrogen to remove air. Hydrogenation was carried out at 60° and an initial pressure of 60 lb./sq. in.; absorption was quantitative and complete in two hours. The solutions from two such runs were combined and distilled through a 10–15 plate Fenske–Whitmore column to give 58 g. of *t*-butylamine, b. p. 44.0–44.5°, $n^{20}\text{D}$ 1.3770. The amine yielded an α-naphthylthiourea, m. p. 153–154°, and a benzoyl derivative, m. p. 134–135°.

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[1] The work described in this paper was done under a contract, recommended by the Committee on Medical Research, between the Office of Scientific Research and Development and the University of Notre Dame.

[2] Karabinos and Serijan, This Journal, **67**, 1856 (1945).

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## Bromine Analogs of DDT[1]

By Stanley J. Cristol and H. L. Haller

In connection with entomological and pharmacological work on the insecticide DDT [1-trichloro-2,2-bis-(*p*-chlorophenyl)-ethane], it was necessary to prepare certain bromine-containing analogs of DDT. Of the three relatively simple analogs, that from chloral and bromobenzene and those from bromal with chlorobenzene or bromobenzene, the first, 1-trichloro-2,2-bis-(*p*-bromophenyl)-ethane, has already been described.[2] The preparation of the other two, 1-tribromo-2,2-bis-(*p*-chlorophenyl)-ethane (I) and 1-tribromo-2,2-bis-(*p*-bromophenyl)-ethane (II), has now been effected, although in poor yield, by the sulfuric acid-catalyzed condensation of bromal with the appropriate halobenzene.

Compound I is fairly stable, can be recrystallized from 95% ethanol, and when pure melts at 146–147°. On the other hand, II is very unstable. Recrystallization of the pure compound, m. p. 173–174°, from ethanol or from benzene–ligroin gave a mixture which melted at about 140° with decomposition. Purification of II was effected by tedious recrystallization from Skellysolve B (petroleum ether, b. p. 60–70°). I and II both eliminate the elements of hydrogen bromide in ethanolic alkali to produce the corresponding olefins. The position of the ring halogen atoms was shown by oxidation of the olefins to the *p,p'*-dihalobenzophenones. Dinitro derivatives of I and II were also prepared.

**1-Tribromo-2,2-bis-(*p*-chlorophenyl)-ethane (I).**—To a well-stirred mixture of 100 g. (0.36 mole) of bromal and 320 g. (5.7 moles) of chlorobenzene cooled in an ice-bath, 560 g. of 100% sulfuric acid was added dropwise over a period of one hour. The temperature of the mixture was kept below 6° during the addition, and the resulting mixture was stirred in an ice-bath for twenty-four hours. The product mixture was poured onto ice and water, and the organic fraction was extracted with ether. The ethereal solution was washed with water and dilute sodium bicarbonate solution, and then dried over anhydrous sodium sulfate. The ether and excess chlorobenzene (about 60% was recovered) were removed under reduced pressure. The residual oil was crystallized from Skellysolve B, giving 42 g. (24%) of crude I. The product was recrystallized from 95% ethanol, and when pure melted at 146–147° (cor.). About 70% recovery was obtained in the recrystallization.

*Anal.* Calcd. for $C_{14}H_9Cl_2Br_3$: C, 34.46; H, 1.86. Found: C, 34.68; H, 1.85.

Use of stronger or weaker acid, increase in temperature and modifications in reaction time for the condensation resulted either in poorer or unaffected yields of product. Use of acetic acid as solvent for the condensation resulted in the formation of an almost quantitative yield of the diacetate of bromal hydrate,[3] m. p. 77–77.8°, rather than the desired product I.

*Anal.* Calcd. for $C_6H_7O_4Br_3$: Br, 62.6; mol. wt., 383. Found: Br, 61.8; mol. wt. (in benzene), 360.

**1,1-Dibromo-2,2-bis-(*p*-chlorophenyl)-ethylene** was obtained by heating at reflux for one hour a solution of 1.0 g. of I and 0.6 g. of potassium hydroxide in 40 ml. of 95% ethanol. The reaction mixture was poured into ice water; the product oiled out, but rapidly crystallized. The solid was separated by filtration and was recrystallized from 95% ethanol. It melted at 104–105° (cor.). The yield was not determined as a portion of the preparation was lost.

*Anal.* Calcd. for $C_{14}H_8Cl_2Br_2$: C, 41.32; H, 1.98. Found: C, 41.23; H, 1.90.

A solution of 125 mg. of the olefin in 5 ml. of glacial acetic acid was heated to reflux and 125 mg. of chromic anhydride was added through the condenser. Refluxing was continued for one hour. Bromine vapors were evolved during the first fifteen minutes. The product mixture was cooled and then poured into water; the oil which precipitated solidified rapidly and was filtered and dried. The yield of almost pure *p,p'*-dichlorobenzophenone was 68 mg. (88%), and the product, after recrystallization, melted at 146–147° (cor.). The melting point was not depressed upon admixture with known *p,p'*-dichlorobenzophenone.

**Dinitro Derivative of I.**—A mixture of 500 mg. of I and 5 ml. of fuming nitric acid was warmed in a water-bath at

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[1] The work described in this paper was carried out under a transfer of funds, recommended by the Committee on Medical Research, from the Office of Scientific Research and Development to the Bureau of Entomology and Plant Quarantine.

[2] Zeidler, *Ber.*, **7**, 1180 (1874).

[3] Gabutti, *Gazz. chim. ital.*, **30**, II, 191 (1900).