

*Diphenylsilane and benzophenone.* Nine and two-tenths grams (0.05 mole) of diphenylsilane and 9.1 g. (0.05 mole) of benzophenone were heated in a distillation flask for 2 hr. at 220–230°. Distillation gave 0.3 g. (3%) of crude diphenylsilane, b.p. 113–125°/3 mm., and 1.05 g. (11%) of crude benzophenone, b.p. 130–135°/3 mm. The colorless, solid distillation residue was recrystallized from petroleum ether (b.p. 60–70°) to give 12.5 g. (68.5%) of benzohydroxydiphenylsilane (III), m.p. 79–81°. Recrystallization of a sample from ethanol raised the melting point to 81.5–82.5°.

*Anal.* Calcd. for  $C_{25}H_{22}OSi$ : Si, 7.65. Found: Si, 7.59, 7.59.

Supporting evidence for the structure was obtained by the infrared spectrum, which was almost identical with the spectrum of compound II except for a band at 4.7  $\mu$  attributable to the Si—H group.

Additional evidence conforming the structure of this compound was obtained by acid hydrolysis, which yielded an oil, from which some benzohydril ether, m.p. 108–109° was isolated. This benzohydril ether was shown to be identical with an authentic sample by mixed melting point and infrared spectra.

*Phenylsilane and benzophenone.* Five and four-tenths grams (0.05 mole) of phenylsilane and 9.1 g. (0.05 mole) of benzophenone were placed under nitrogen in a Schlenk tube. The sealed tube was immersed in an oil bath, which was heated slowly up to 250° and maintained at this temperature for 4 hr.<sup>10</sup> The run was worked up by distillation. There were recovered 0.35 g. (6.5%) of phenylsilane, b.p. 115–120°/750 mm., and 0.55 g. (6%) of crude benzophenone, boiling over the range 130–145°/3 mm. In addition, 2.9 g. (20%) of benzohydroxyphenylsilane (IV), b.p. 145–148°/0.07 mm.,  $n_D^{20}$  1.5863,  $d_4^{20}$  1.076, and 7.6 g. (64.6%) of bis(benzohydroxy)phenylsilane (V), b.p. 238–243°/0.07 mm.,  $n_D^{20}$  1.6032, were obtained. After standing for 5 days in the refrigerator, V crystallized, melting over the range 53–60°. Recrystallization from methanol raised the melting point to 63–63.5°.

*Anal.* Calcd. for  $C_{19}H_{15}OSi$  (IV): Si, 9.66; MR, 90.44. Found: Si, 9.49, 9.56; MR, 90.62. Calcd. for  $C_{22}H_{20}O_2Si$  (V): Si, 5.94. Found: Si, 5.98, 6.07.

Supporting evidence for the structure of both compounds IV and V was obtained by the infrared spectra, which were almost identical with that of compound III except some difference in the absorption intensity at 4.6–4.7  $\mu$  where the Si—H band is located.

*Triphenylsilane and benzalacetophenone.* Thirteen grams (0.05 mole) of triphenylsilane and 10.4 g. (0.05 mole) of benzalacetophenone were heated in a distillation flask for 16 hr. at 150°. Distillation under reduced pressure thereafter gave back 85% of the starting materials. No crystalline material was isolated from the dark brown distillation residue.

In a second run 13 g. (0.05 mole) of triphenylsilane and 10.4 g. (0.05 mole) of benzalacetophenone were heated for 2 hr. at 250°. The dark brown reaction mixture was worked up by distillation. Fraction 1, 1.7 g., boiling at 145–160°/3 mm., gave after crystallization from petroleum ether (b.p. 60–70°) 0.70 g. (15.5%) of stilbene, m.p. 120–122°. Fraction 2, 3.1 g., boiling at 175–200°/3 mm., gave after crystallization from petroleum ether (b.p. 60–70°) 0.80 g. (5.8%) of triphenylsilanol. The dark brown distillation residue was dissolved in petroleum ether and chromatographed on alumina. Besides yellow oils, which could not be crystallized or further purified, there were obtained 0.60 g. (5.5%) of benzylacetophenone, m.p. 71–72°, and 1.25 g. (9.4%) of hexaphenyldisiloxane, m.p. 223–226°.

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(10) As a precautionary measure, this sealed tube reaction was carried out behind appropriate shields.

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### Preparation of 3,4-Dichlorotetrahydrothiophene-1,1-dioxide-Cl<sup>36</sup>

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After the discovery of the nematocidal activity of 3,4-dichlorotetrahydrothiophene-1,1-dioxide,<sup>1</sup> it became necessary to prepare this compound in a radioactive form for tracer studies. The incorporation of carbon-14, sulfur-35, and chlorine-36 in the compound was considered. Chlorine-36 was selected because it involved the minimum handling of radioactive material and would provide desired information on the fate of the chlorine in the molecule.

Although the steps in the synthesis are not new, modification was necessary for the use of radioactive chlorine. The need for preparing the compound with an adequate specific activity made it necessary to avoid an excessive dilution of the chlorine-36 with stable chlorine, and to perform the reaction at elevated temperatures to ensure the maximum yield of product. (The reaction of chlorine with 2,5-dihydrothiophene-1,1-dioxide does not proceed readily at room temperatures.) The availability of chlorine-36 labeled hydrochloric acid<sup>2</sup> fixed the starting point, and the known chloride-chlorine exchange reaction<sup>3</sup> was selected to provide the labeled chlorine gas. The reaction between equivalent quantities of the labeled chlorine and 2,5-dihydrothiophene-1,1-dioxide at 60–70°C for four hours gave an 80% yield (crude) of the 3,4-dichlorotetrahydrothiophene-1,1-dioxide -Cl<sup>36</sup>, consisting predominantly of the *trans* isomer.

#### EXPERIMENTAL

The radiochlorination method of Craig, Tryon, and Brown<sup>4</sup> was used with some modifications. A gas train was arranged in the following sequence: a cylinder of chlorine gas, a concentrated sulfuric acid bubbler, a bleed-off valve, a fritted

(1) Diamond Alkali Company, trade name, "PRD."

(2) Oak Ridge National Laboratory, Oak Ridge, Tenn.

(3) R. S. Halford, *J. Am. Chem. Soc.*, **62**, 3233 (1940).

(4) J. T. Craig, P. F. Tryon, and W. G. Brown, *Anal. Chem.*, **25**, 1661 (1953).

glass tube immersed in 3 ml. of radioactive hydrochloric acid solution (containing 10 microcuries of chlorine-36), a concentrated sulfuric acid bubbler, a fritted glass tube immersed in 6 ml. of chloroform in a heavy walled glass tube containing 1.6 g. (0.014M) of 2,5-dihydrothiophene-1,1-dioxide (m.p. 64–66°) chilled to  $-58 \pm 3^\circ\text{C}$ , and a calcium chloride drying tube.

Chlorine gas from the cylinder was slowly bubbled through the gas train. An immediate exchange occurred between the chlorine gas and the radioactive hydrochloric acid solution.<sup>5,6</sup> One gram (0.014M) of radioactive chlorine gas was collected and the glass tube was then sealed.

The sealed tube was heated to 60–70° for about 4 hr. The tube was chilled, opened, and the contents poured into an evaporating dish. After evaporating to dryness, the yield of crude 3,4-dichlorotetrahydrothiophene-1,1-dioxide was 2.4 g., or about 80%.

The dry crystals were dissolved in 20 ml. of hot water and filtered hot. The filtrate was then chilled in ice water for 3 hr. and the crystals filtered on a Büchner funnel. The recrystallization was repeated; the final purified material weighed 1.6 g., representing 65% of the theoretical yield.

Infrared analysis<sup>6</sup> showed that the final product contained 58% of the *trans* 3,4-dichlorotetrahydrothiophene-1,1-dioxide, 37% of the *cis* isomer, and 5% of 3-chloro-2,3-dihydrothiophene-1,1-dioxide. These values were obtained by comparing the infrared curves of the product with standards made from solutions of the pure *cis* and *trans* isomers in acetonitrile and a solution of pure 3-chloro-2,3-dihydrothiophene-1,1-dioxide in nitromethane. The *trans* isomer shows an absorption peak at 8.25  $\mu$ , the *cis* isomer at 8.33  $\mu$ , and 3-chloro-2,3-dihydrothiophene-1,1-dioxide at 13.03  $\mu$ .

The purified product was dissolved in acetone and aliquots were pipetted into stainless steel cup planchets. The acetone was evaporated and the radioactivity of the product was determined.

The measured activity in a windowless counter was 6.4 counts per minute per microgram.

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(5) F. A. Long and A. R. Olson, *J. Am. Chem. Soc.*, **58**, 2214 (1936).

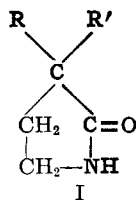
(6) I. E. Smiley and J. J. Mannion, unpublished results.

### Some 3,3-Disubstituted-2-Pyrrolidinones

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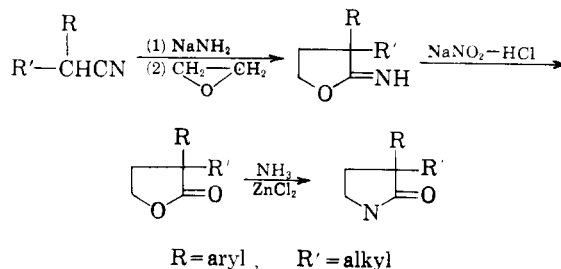
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Certain barbituric acid derivatives have long been standard as hypnotics and for use as anti-convulsants. They offer a natural starting point for studies seeking other compounds possessing similar activities. 3,3-Disubstituted-2-pyrrolidinones (I)



maintain part of the configuration of the barbiturates and seemed to offer a promising field for investigation.

Because of its relationship to phenobarbital (5-ethyl-5-phenylbarbituric acid), 3-ethyl-3-phenyl-2-pyrrolidinone was the first compound prepared. The synthetic scheme for this and related pyrrolidinones was as follows:



The method of preparation of the lactones was a modification of the procedure used by Anker and Cook<sup>1</sup> for some related compounds.

Variations of the aryl-alkyl derivatives include 3-*n*-butyl-3-phenyl-, 3-ethyl-3-*p*-chlorophenyl-, and 3,3-diphenyl-2-pyrrolidinone. An *N*-methyl derivative was prepared by alkylation of 3-ethyl-3-phenyl-2-pyrrolidinone employing sodium hydride.

Attempts at preparation of dialkyl derivatives by the same methods failed when the aliphatic nitriles could not be alkylated in the presence of sodamide. No further investigation of other methods was made. Related compounds of this type, with *N*-alkyl substitution, have been prepared by Clarke, Mooradian, Lucas, and Slauson<sup>2</sup> using a different approach.

When tested orally in rats the best compound was 3-ethyl-3-phenyl-2-pyrrolidinone. The average protective dose against both electro- and metrazol shock was shown to be about 60 mg./kg. This was considerably below the average hypnotic dose of about 188 mg./kg. A limited clinical trial has shown that the anticonvulsant activity carries over to human use.

### EXPERIMENTAL<sup>3</sup>

*α*-Ethyl-*α*-phenyl- $\gamma$ -butyrolactone. To the sodamide prepared from 4.2 g. (0.187 g.-atom) of sodium in 200 ml. of liquid ammonia was added, at a dropwise rate, 27.38 g. (0.187 mole) of *α*-phenylbutyronitrile.<sup>4</sup> Stirring was continued for one hour and then there was added 8.25 g. (0.187 mole) of ethylene oxide in 50 ml. of dry ether. After stirring for 44 hr., 15 g. of ammonium chloride was added and then, cautiously, 5 ml. of water. The solids were separated by filtration, were washed with ether, and the ether was re-

(1) R. M. Anker and A. H. Cook, *J. Chem. Soc.*, 806 (1948).

(2) R. L. Clarke, A. Mooradian, P. Lucas, and T. J. Slauson, *J. Am. Chem. Soc.*, **71**, 2821 (1949).

(3) The Skelly B referred to throughout the Experimental is petroleum ether (b.p. 60–71°).

(4) F. Bodroux and F. Taboury, *Bull. soc. chim. France*, [4] **7**, 666 (1910).