purity in 10 ml. ether was added dropwise to a stirring solution of 2.29 g. (10 millimoles) of 6-furoylaminopurine in 25 ml. pyridine. The reaction was highly exothermic and the mixture became dark and eventually too thick to stir. The reaction mixture was maintained at 70° for 1 hr. and allowed to cool. The mixture was transferred to a larger flask with a little methanol. The solvents were distilled off under reduced pressure (water aspirator) and the residue extracted with 0.1*N* sodium hydroxide. Neutralization of the alkaline extract precipitated the product. The yield was 0.47 g. (2.18 millimoles, 21.8%), m.p. 263–265°. Recrystallization from methyl Cellosolve gave pure kinetin, m.p. 267–268° (sealed capillary) (1, 2, 3). A mixed melting point with an authentic sample showed no depression.

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Structure of "3-Phenylthiazetidine"

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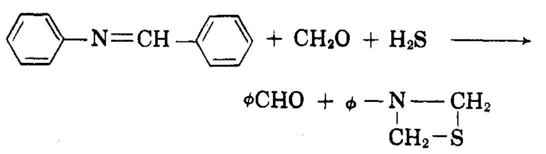
A recent article[1] described the reaction of formaldehyde, hydrogen sulfide, and *N*-benzylidene aniline, and reported that the structure of the product is that of "3-phenylthiazetidine." This preparation was repeated.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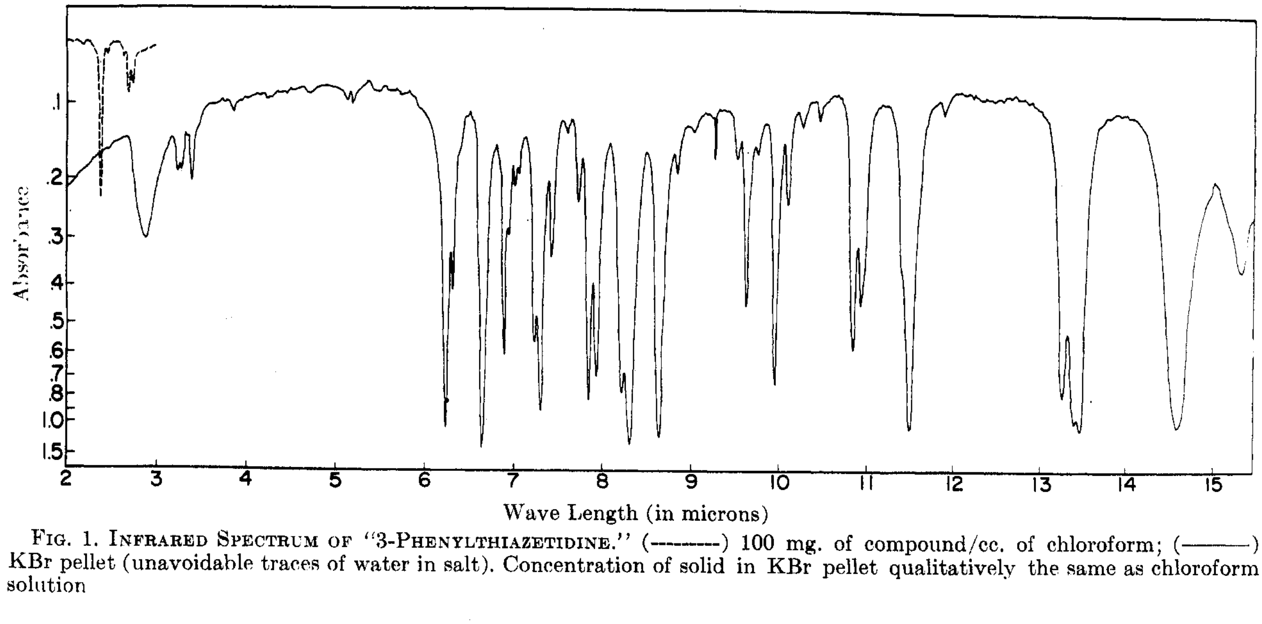
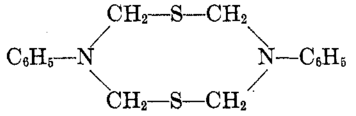


FIG. 1. INFRARED SPECTRUM OF "3-PHENYLTHIAZETIDINE." (---------) 100 mg. of compound/cc. of chloroform; (———) KBr pellet (unavoidable traces of water in salt). Concentration of solid in KBr pellet qualitatively the same as chloroform solution

A product was isolated which appeared to be the one described earlier[1] although the melting point was somewhat higher. The infrared spectrum (Fig 1) showed clearly that —NH—, —SH, —OH and C=O were absent, and that C=S, C=C, and C=N were probably absent. A nuclear magnetic resonance spectrum showed only two types of hydrogen, one of which was obviously phenyl hydrogen. Combustion analysis agreed quite closely with the formula C_8H_9NS, (mol. wt. 151). However, ebullioscopic molecular weight determinations showed an average value of 308 in ethanol, indicating that the actual empirical formula should be $C_{16}H_{18}N_2S_2$.

On the basis of the above information, we suggest that the product originally formulated as 3-phenylthiazetidine (I) is, in fact, the highly symmetrical 3,7-diphenyl-1,5-dithia-3,7-diazacyclooctane (II).


II

EXPERIMENTAL

"3-Phenylthiazetidine." Hydrogen sulfide was bubbled into 250 g. of 38% aqueous formaldehyde solution until 20 g. was absorbed. A solution of 100 g. of benzylidene aniline in 850 ml. of absolute alcohol was prepared and mixed with the hydrogen sulfide–formaldehyde solution. As the two solutions were mixed, a strong blue-green color developed which gradually faded. The mixture was maintained at room temperature for 24 hr. During the course of this time a crystalline solid precipitated from the solution. This was filtered and refluxed with 1 l. of absolute methyl alcohol. After cooling, the solution was filtered and the solid product was dried. It weighed 75 g. and melted in the range 173–178° on a Kofler hot stage between crossed Polaroids. This substance was recrystallized from chloroform to give crystals melting sharply at 186°. Melting was preceded by a phase transformation from plates to needles beginning at about 170°.

Anal. Calcd. for C_8H_9NS: C, 63.55; H, 6.00; mol. wt.

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[1] Collins and Graymore, *J. Chem. Soc.*, 4089 (1953).

151. Found: C, 63.60, 63.59; H, 6.04, 6.06; mol. wt.: (ebull.) 308 (ethanol).

The product was further characterized by a study of its infrared spectrum (Fig. 1), which showed clearly the absence of —NH, —SH, —OH, or C=O. Indications were strong that there was no C=S, C=C, or C=N.

A study of the nuclear magnetic resonance spectrum[2] showed hydrogen peaks indicative of only two types of C—H bonds. One occurred at +69 cycles per second (rel. to H_2O) quite characteristic of phenyl hydrogens. The second at +2 cycles was consistent with the shift to be expected for the eight equivalent hydrogen atoms on the 8-membered ring.

The above data indicate that the compound alleged to be 3-phenylthiazetidine is actually a dimer of this compound, probably with an 8-membered ring structure.

Acknowledgments. The author is indebted to Dr. Rudolf Zbinden, who measured and interpreted the infrared spectrum, and to Dr. Catherine Looney, who measured and interpreted the nuclear magnetic resonance spectrum.

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(2) L. H. Meyer, A. Saika, and H. S. Gutowsky, *J. Am. Chem. Soc.*, **75**, 4567 (1953).

Addition of Propargyl Acetal to Cyclohexanone in the Presence of Sodamide[1]

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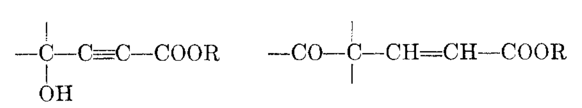
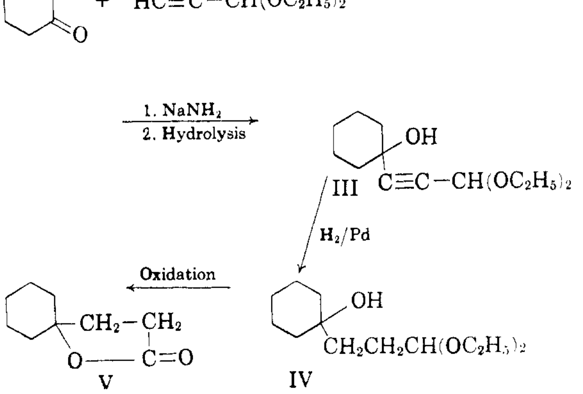
The addition of the sodio derivative of propiolic esters, NaC≡C—COOR, to the carbonyl group of certain ketones (cyclohexanone, 2-methyl-cyclohexanone, and 2-methyl-2-carbomethoxycyclohexanone) was reported several years ago.[3] In each case the reaction produced an acetylenic carbinol (I). A Michael type addition of certain aromatic ketones to the triple bond of propiolic ester in the presence of sodamide was also reported in the same series of papers.[4] In this case the products were β-substituted acrylic esters (II). The versatility of this reaction could be extended if it were possible to carry out a condensation of this type with aromatic ketones to produce acetylenic carbinols rather than the β-substituted acrylic esters. Since propargyl diethylacetal, $HC\equiv C-CH(OC_2H_5)_2$, does not have the conjugated structure necessary for a Michael type reaction, it should in all cases react with ketones to produce acetylenic carbinols.



$$-\overset{|}{\underset{OH}{C}}-C\equiv C-COOR \qquad -CO-\overset{|}{\underset{|}{C}}-CH=CH-COOR$$

I II

In the present paper we are reporting the successful addition of the sodio derivative of propargyl diethylacetal to cyclohexanone. The reaction with cyclohexanone was carried out by adding cyclohexanone to an ether suspension of the sodium derivative of propargyl diethylacetal. Acid hydrolysis liberated the acetylenic carbinol(III). Since attempted isolation of this acetylenic carbinol by distillation in a vacuum resulted in its polymerization, it was reduced catalytically and the reduction product, β-(1-hydroxycyclohexyl)propionaldehyde diethylacetal (IV) was isolated by vacuum distillation.



The structure of (IV) was established by oxidation to the known lactone of β-(1-hydroxycyclohexyl)-propionic acid (V).

The addition of the sodio derivative of propargyl acetal to the aromatic ketone 6-methoxy-1-tetralone was attempted using the conditions which were successful in the case of cyclohexanone as well as by a variety of other procedures. In no case was it possible to isolate anything other than unreacted 6-methoxy-1-tetralone from the reaction mixture.

EXPERIMENTAL

Reaction with cyclohexanone. A solution of 12.8 g. (0.1 mole) of propargyl acetal[5] in 10 ml. of absolute ether was added to a suspension of sodamide[6] [prepared from 2.3 g. (0.1 mole) of sodium] in approximately 150 ml. of liquid ammonia. A pale yellow precipitate of the sodio salt formed immediately. Cyclohexanone (9.8 g., 0.1 mole) in 10 ml. of absolute ether was added slowly and with continuous shaking. The ammonia was allowed to evaporate from the resulting red solution and the residue was shaken with 500 ml. of a cold saturated solution of ammonium sulfate containing 9.8 g. (0.1 mole) of concentrated sulfuric acid. The mixture was extracted with three 40-ml. portions of ether, the combined ether extract was washed twice with 15-ml. portions of water and the ether was removed by evaporation in a

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(1) This work was supported in part by a Frederick Gardner Cottrell grant from the Research Corporation.

(2) Taken from the Master's Degree thesis of Herbert A. Schroeder, June 1955.

(3) W. E. Bachmann and E. K. Raunio, *J. Am. Chem. Soc.*, **72**, 2530 (1950).

(4) W. E. Bachmann, G. I. Fujimoto, and E. K. Raunio, *J. Am. Chem. Soc.*, **72**, 2533 (1950).

(5) J. C. Sheehan and C. A. Robinson, *J. Am. Chem. Soc.*, **71**, 1436 (1949).

(6) J. A. Nieuwland, T. H. Vaughn, and R. R. Vogt, *J. Am. Chem. Soc.*, **56**, 2120 (1934).