

urea solutions. In turn, Nogami *et al.* (6) analyzed the adsorption of tryptophan from urea solutions in much the same manner, using the Feldman and Gibaldi paper as a reference. There are implications of direct interaction in each of the results of the present investigation. Perhaps the most striking evidence of this interaction is that the introduction of methyl *o*-methoxybenzoate, a liquid, into a 5 *M* urea solution results immediately in the formation of a flocculent white precipitate, the composition of which is currently unknown.

These findings demonstrate the need for caution in interpreting solubility phenomena involving cosolvent systems, in general, and urea-water mixtures, in particular. At present, few, if any, simplifying assumptions appear to be valid for this purpose.

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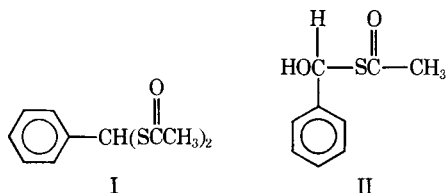
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## Preparation of Bis(acetylthiobenzyl)sulfide

**Keyphrases** □ Bis(acetylthiobenzyl)sulfide—synthesis □ NMR spectroscopy—structure □ Mass spectroscopy—structure

Sir:

Bongartz (1), in 1886, obtained a product from the reaction of benzaldehyde and thioacetic acid, m.p. 147–148°, which he believed to be phenylmethanedithiol diacetate (I). In 1952, Cairns *et al.* (2) synthesized this compound from phenylmethanedithiol and found the melting point to be 37–38°.

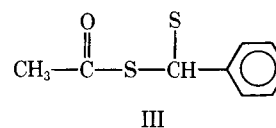


By utilizing the procedure of Böhme *et al.* (3) in the reaction of benzaldehyde and thioacetic acid to obtain the hydroxymethyl thioester (II), a small amount of a compound, m.p. 150–151°, which displayed the same

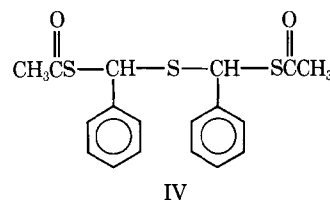
properties as the material isolated by Bongartz (1), was obtained. The NMR spectrum showed absorption at 7.32 $\delta$ , a singlet at 5.85 $\delta$ , and a singlet at 2.29 $\delta$ , having an integration ratio of 5:1:3. Mass spectral analysis indicated that the compound contained the following groups:

<i>m/e</i>	<i>m/e</i>
15 CH <sub>3</sub>	77 C <sub>6</sub> H <sub>5</sub>
28 CO	78 C <sub>6</sub> H <sub>6</sub>
32 S	90 C <sub>6</sub> H <sub>5</sub> CH
43 CH <sub>3</sub> CO	105 OC <sub>6</sub> SHS
58 CH <sub>2</sub> CS	121 C <sub>6</sub> H <sub>5</sub> CHS
60 COS	154 SCH(C <sub>6</sub> H <sub>5</sub> )S
75 CH <sub>3</sub> COS	165 CH <sub>3</sub> COSCH(C <sub>6</sub> H <sub>5</sub> )

From the NMR and mass spectral data, the following partial structure was assigned:



The elemental analysis and molecular weight indicate the compound to be C<sub>18</sub>H<sub>18</sub>O<sub>2</sub>S<sub>3</sub>. Thus, we propose the structure of the compound reported by Bongartz (1) as phenylmethanedithiol diacetate to be bis(acetylthiobenzyl)sulfide (IV).



The reaction of benzaldehyde with thioacetic acid was conducted as follows. Benzaldehyde, 21.2 g. (0.2 mole), and thioacetic acid, 15.2 g. (0.2 mole), were mixed together and heated at 100° for 18 hr. After cooling, 1.6 g. of a white crystalline solid was obtained. The solid was recrystallized from methanol and then from petroleum ether (63–68°), and it was identified as bis(acetylthiobenzyl)sulfide (IV), m.p. 150–151°. The NMR and IR are in agreement with the assigned structure.

*Anal.*—Calcd. for C<sub>18</sub>H<sub>18</sub>O<sub>2</sub>S<sub>3</sub>: C, 59.63; H, 5.00; S, 26.54; mol. wt., 362. Found: C, 59.43; H, 5.02; S, 27.10; mol. wt., 361 (osmometer).

Mass spectral data were obtained from a Nuclide mass spectrometer.

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