When working with the alternate chromatographic column (SP-2250 DA), we have found it is advantageous to use acid-treated glass wool as column plugs. In addition, for both columns, small amounts of glass wool were placed in the glass inlet to retain nonvolatiles which would otherwise contaminate the top of the column. This insert was changed daily.

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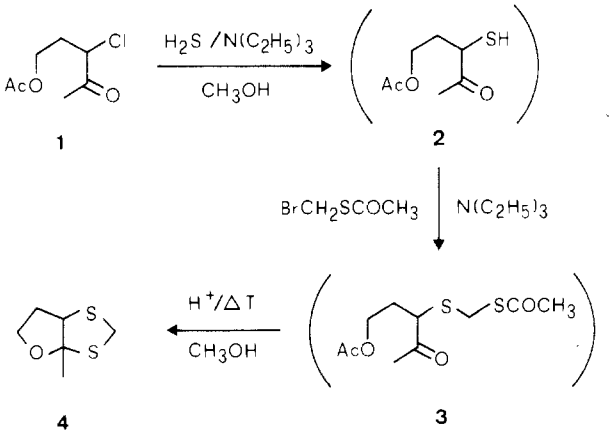
Synthesis of 1-Methylbicyclo[3.3.0]-2,4-dithia-8-oxaoctane, a Degradation Product of Thiamin

Peter Gygax

5-Acetoxy-3-chloro-2-pentanone (1), when treated with hydrogen sulfide/base, gave 5-acetoxy-3-mercapto-2-pentanone (2) which was heated with bromomethyl acetyl sulfide/base to give 5-acetoxy-3-acetyl-2-thiapentane-1-thioacetate (3). Heating 3 with methanol in an acidic medium gave the title compound 4 with a 35–40% overall yield.

Although pure thiamin is odorless, commercial samples possess a characteristic odor, probably arising from decomposition products. As thiamin is used in the flavor industry and is widely spread in foodstuffs, a great number of papers dealing with the decomposition of thiamin (Dwivedi and Arnold, 1973) exist.

Seifert et al. (1978) reported the effect of UV irradiation on thiamin. Among the volatiles, they isolated an oil which seems to be responsible for the characteristic odor. The structure elucidation by means of physical methods showed it to be 1-methylbicyclo[3.3.0]-2,4-dithia-8-oxaoctane (4). Synthetic efforts were unsuccessful, probably due to the instability of the intermediate products. As the structure is only based on physical data, we decided to synthesize this compound. The retrosynthetic consideration shows that the readily available 5-acetoxy-3-chloro-2-pentanone (1) possesses the elements for building up the correctly



substituted tetrahydrofuran ring system. 1 was therefore converted into 5-acetoxy-3-mercapto-2-pentanone (2) by reaction with hydrogen sulfide in the presence of an organic base. This substance was not purified due to the well-known instability of α-mercaptoketones (Mueller et al., 1977), and therefore it was directly converted into the mixed acetal 3 by reaction with bromomethyl acetyl sulfide in the presence of triethylamine. Refluxing the crude acetal 3 in methanol with traces of hydrobromic acid resulted in the formation of the "thiamine odor compound" 4 with a 35–40% overall yield.

EXPERIMENTAL SECTION

Infrared spectra of thin liquid films were obtained on a Perkin-Elmer Model 257 infrared spectrometer.

^1H NMR spectra (360 MHz) were determined with a Bruker WH-360 spectrometer by using $CDCl_3$ as solvent and Me_4Si as an internal standard.

^{13}C NMR spectra were recorded under the same conditions by using a Varian XL-100 spectrometer.

MS spectra were performed on a CEC 21-110 double-focusing spectrometer with an indirect inlet system.

Packed-Column GLC. A 0.3 cm i.d. × 3 m long glass column packed with 80–100 mesh Chromosorb G AWDMCS coated with 2% Carbowax 20 M was used at 180 °C. The injector, the thermal conductivity detector, and the outlet were kept at 220 °C.

Capillary GLC. A 0.2 mm i.d. × 45 m long UCON 50 HB 5100 glass column was used at 140 °C. The injector, collector, and the thermal conductivity system were kept at 220 °C.

1-Methylbicyclo[3.3.0]-2,4-dithia-8-oxaoctane (4). A total of 250 mL of methanol and 15.18 g (0.15 mol) of triethylamine were saturated with hydrogen sulfide at 0 °C. 5-Acetoxy-3-chloro-2-pentanone (26.8 g, 0.15 mol) was added dropwise to this solution while bubbling H_2S through the reaction mixture at the same time. The temperature was kept between 0 and 10 °C by means of an ice bath. After the addition which took 30 min, the stream of H_2S was interrupted and the reaction mixture was stirred for another 3 h without cooling. The reaction flask was then carefully evacuated (foaming) on a water aspirator and stirred under vacuum for 2 h.

After being flushed with nitrogen, 25.4 g (0.15 mol) of the freshly prepared bromomethyl acetyl sulfide (Boehme et al., 1959) was added instantaneously to the solution of crude mercaptoketone 2, followed by the dropwise addition

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of 15.18 g (0.15 mol) of triethylamine in 15 mL of methanol. During the addition period which was 10 min, the temperature was kept at 5 °C by means of an ice–salt bath. After being stirred for 1 h without being cooled, the reaction mixture was poured into 500 mL of ether and 400 mL of ice-cold 0.25 N hydrochloric acid. The aqueous layer was extracted with 150 mL of ether. The combined etheral extracts were washed 3 times with 150 mL of cold water, dried over magnesium sulfate, and evaporated at 50 °C/20 torr, giving 36.8 g of crude **3** as a yellow oil which could not be distilled without decomposition. This oil was dissolved in 350 mL of methanol and 2 mL of 48% hydrobromic acid and refluxed for 19 h. The cold reaction mixture was then stirred with 1.5 g of finely powdered anhydrous potassium carbonate for 2 h and afterward freed from the solvent (50 °C/20 torr). The residue was dissolved in methylene chloride and filtered. After evaporation of the solvent, the residue was distilled through a Vigreux column, giving 8.94 g (37.8%) of pure 1-methylbicyclo[3.3.0]-2,4-dithia-8-oxaoctane (**4**), bp 69–73 °C/0.2 torr.

The IR, MS, ^{13}C NMR, and ^{1}H NMR (100 MHz) spectra are identical with those of an authentic sample derived from thiamin by UV degradation. In addition, a 360-MHz ^{1}H NMR spectrum was recorded: δ 1.85 (s, 3 H, CH_3), 2.08 (dddd, $J_{C_6H'}$ = 13 Hz, J_{C_7H} = 7 Hz, $J_{C_7H'}$ = 3 Hz, J_{C_6H} = 3 Hz, C_6H), 2.45 (dddd, J_{C_6H} = 13 Hz, J_{C_7H} = 8.5 Hz, $J_{C_7H'}$ = 8.5 Hz, J_{C_6H} = 8 Hz, C_6H'), 3.74 (dd, J_{C_6H} = 3 Hz, $J_{C_6H'}$ = 8 Hz, C_5H), 3.80 (d, $J_{C_3H'}$ = 11 Hz, C_3H), 4.02 (ddd, J_{C_7H} = 8.5 Hz, $J_{C_6H'}$ = 8.5 Hz, J_{C_6H} = 3 Hz, C_7H'); 4.17 (ddd, $J_{C_7H'}$ = 8.5 Hz, $J_{C_6H'}$ = 8.5 Hz, J_{C_6H} = 7 Hz, C_7H), 4.24 (d, J_{C_3H} = 11 Hz, C_3H').

DISCUSSION

The synthetic substance **4** is identical with the material resulting from the UV degradation of thiamin (^{1}H NMR, ^{13}C NMR, IR, MS, packed-column GLC, and capillary GLC). With respect to the ring linkage, two isomers of **4** are possible. The 360-MHz ^{1}H NMR spectrum which is of first order clearly shows the presence of only one isomer.

The second isomer which would be helpful for spectral comparison could not be found. Although all coupling constants can be determined, it is difficult to decide whether the two rings are cis or trans fused because of the fact that the Karplus equation may not be applied to five-membered rings containing two heteroatoms (Wilson and Bazzone, 1974).

Odor Description of 4. Synthetic material: sulfurous, onionlike, fried onionlike, leeklike, meaty, and slightly metallic. Material resulting from thiamin degradation: onionlike, cerallike, leeklike, and meaty.

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Preferential Retention of Benzo[*a*]pyrene in Tobacco Smoke by β-Lactoglobulin in the Cigarette Filter Structure

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Preferential retention of benzo[*a*]pyrene in tobacco smoke by β-lactoglobulin, added to the cigarette filter structure, was studied. The retention rate of benzo[*a*]pyrene in tobacco smoke by the cigarette filter varied, dependent upon the dose of β-lactoglobulin which was introduced to the filter, while those of smoke condensate and nicotine in tobacco smoke remained at the constant level throughout the doses of β-lactoglobulin in the present study. Twenty milligrams of β-lactoglobulin in a cigarette filter tip was estimated to be capable of reducing the benzo[*a*]pyrene concentration in the dry total particulate matter to a level of half that in intact tobacco smoke.

Cigarette commodities, which were assembled with the filter structure by acetylcellulose fiber tow, have been extensively merchandized. The recent trend for sophistication of the cigarette filter led to an introduction of charcoal granule into the multilayered filter structure successfully. Hygienic criteria for competency of the cigarette filter have been focused on removal of the smoke condensate and nicotine from cigarette smoke.

Wynder and Hoffmann (1964) evaluated a relative importance of tobacco smoke constituents in experimental tobacco carcinogenesis. Benzo[*a*]pyrene (B[*a*]p) and polyaromatic hydrocarbons were proposed to be indicators for tumor initiator while volatile phenol and long-chain fatty acids were to be those for tumor promotors. Recent progress on the studies of experimental tobacco carcinogenesis detected a tobacco-specific carcinogen, *N'*-nitrosonornicotine (U.S. Department of Health, Education

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