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### A CONVENIENT ONE-POT SYNTHESIS OF 2-METHYL-2-BENZYLTHIOPROPANAL

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## A CONVENIENT ONE-POT SYNTHESIS OF 2-METHYL-2-BENZYLTHIOPROPANAL

Submitted by Gerald S. Jones, Jr.\*† and David R. Elmaleh  
(06/13/89)

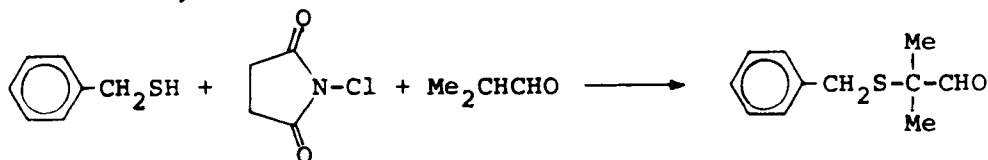
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During a synthetic effort aimed at the development of novel chelating bis(aminoethanethiol) ligands, it became necessary to prepare 2-methyl-2-(benzylthio)propanal. The most recent of the four literature references,<sup>1-4</sup> a Russian patent,<sup>1</sup> describes the controlled addition of sulfuryl chloride to a mixture of benzyl mercaptan and isobutyraldehyde at two time points during the reaction. In a Japanese patent, the synthesis of the title compound was reported in roughly 75% yield *via* hydrolysis of the corresponding dimethyl acetal.<sup>2</sup> Retrosynthetically, 2-methyl-2-benzylthiopropional dimethyl acetal could have been prepared from the corresponding  $\alpha$ -halo analog which was obtained from isobutyraldehyde dimethyl acetal. A similar route has been described which afforded 2-methyl-2-bromopropanal diethyl acetal in an overall yield of about 25% from isobutyraldehyde.<sup>5</sup> There are two essentially identical reports of the synthesis of the title compound in virtually quantitative yield by the reaction of 2-methyl-2-bromopropanal (derived from the diethyl acetal) with sodium benzylthiolate.<sup>3,4</sup> However, the overall yield of the  $\alpha$ -sulfenylated aldehyde by this method was probably closer to 25% when the preparation of the requisite precursor is taken into account. Improved methods for the preparation of 2-methyl-2-bromopropanal have been reported;<sup>6,7</sup> however, each method requires two or more steps or the purchase of rather expensive brominating agents.

We now report an efficient, one-step synthesis of 2-methyl-2-benzylthiopropional from equimolar amounts of benzyl mercaptan, isobutyraldehyde and N-chlorosuccinimide. This route obviates the controlled addition and multi-step methods employed previously and affords the product in 40-50% yield.



## EXPERIMENTAL SECTION

2-Methyl-2-benzylthiopropional.- Benzyl mercaptan (11.7 mL, d 1.058, 0.1 mol) in 75 mL

benzene was added dropwise to a suspension of N-chlorosuccinimide (13.35 g, 0.1 mol)<sup>8</sup> in 300 mL benzene containing isobutyraldehyde (7.21 g, 0.1 mol) stirred at 40°. After 12 hrs, the reaction mixture was filtered and the filtrate was concentrated to about 50 mL, then refiltered. In this manner, a nearly quantitative yield of succinimide was obtained. Concentration of the filtrate afforded a golden liquid which was distilled in vacuo to give 9.27 g (48%) of a colorless liquid, bp. 115-130°/2 mm, lit.<sup>2</sup> bp. 90-115°/7 mm, lit.<sup>3,4</sup> bp. 144-147°/14 mm;  $n_D^{20}$  1.5460, lit.<sup>3,4</sup>  $n_D^{21}$  1.5450; mp. of 2,4-dinitrophenylhydrazone 120-121° (EtOH), lit.<sup>4</sup> mp. 122°; <sup>1</sup>H NMR (60 MHz; CCl<sub>4</sub>): δ 1.34 (s, 6H, CH<sub>3</sub>), 3.49 (s, 2H, CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>), 7.23 (s, 5H, C<sub>6</sub>H<sub>5</sub>), 9.24 (s, 1H, CHO).

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## IMPROVED SYNTHESIS OF NITRO DERIVATIVES OF N-PHENYLGLYCINE

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Nitro derivatives of N-phenylglycine which are structurally similar to stable explosives TNT (2,4,6-trinitrotoluene) and tetryl (N-methyl-N,2,4,6-tetranitroaniline) are used in different explosive formulations. Methods of synthesis and properties of three nitro derivatives of