Conversion of Thioamides and N^2-Acyl-N^1-methyl-N^1-thioacylhydrazines into Amides and N^1N^2-Diacyl-N^1-methylhydrazines by Trimethyloxonium Fluoroborate

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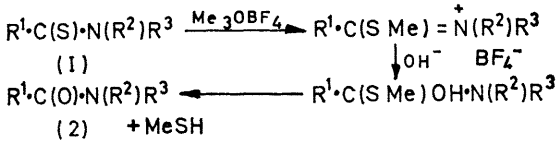
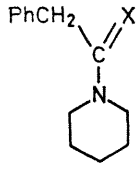
Summary Thioamides and N^2-acyl-N^1-methyl-N^1-thioacylhydrazines, with or without benzylic protons α to both the thiocarbonyl and carbonyl carbons, have been converted into the corresponding amides and N^1N^2-diacyl-N^1-methylhydrazines in high yield by treating with trimethyloxonium fluoroborate.

THERE has been no report of the use of trialkyloxonium fluoroborate[1] for converting thioamides into amides in spite of the extensive application[2–5] of this reagent in organic synthesis.

We have found that *NN*-disubstituted thioamides, either with or without benzylic protons α to the thiocarbonyl carbon, undergo conversion into the corresponding amides on treatment with Meerwein's reagent.[2] Thus, *NN*-di-isopropyl thioacetamide† (1a; R^1 = Me, R^2 = R^3 = $CHMe_2$), m.p. 84°, on treatment with trimethyloxonium fluoroborate overnight at room temperature in dry benzene followed by decomposition with 50% aqueous sodium carbonate gives *NN*-di-isopropylacetamide (2a; 65%, b.p. 58°/0·3 mm). Similarly, *NN*-dimethylthiobenzamide (1b; R^1 = Ph, R^2 = R^3 = Me), m. p. 38° (lit[6a] m.p. 39°),*NN*-diethylthiobenzamide (1c; R^1 = Ph, R^2 = R^3 = Et), m.p. 41° (lit.[6b] m.p. 41°), *NN*-di-isopropylthiobenzamide (1d; R^1 = Ph, R^2 = R^3 = $CHMe_2$), m.p. 100°, and *NN*-di-isobutylthiobenzamide (1e; R^1 = Ph, R^2 = R^3 = $CH_2{\cdot}CHMe_2$), m.p. 77°, give the corresponding amides [(2b, 65%, b.p. 160°/3 mm),[7] (2c, 60%, b.p. 155°/3·5 mm),[7] (2d, 95%, m.p. 70°; lit.[8] 69—71°), and (2e, 60%, m.p. 61°)].

Thioamides with benzylic protons α to the thiocarbonyl carbon, such as *NN*-dimethylphenylthioacetamide (1f; R^1 = $PhCH_2$, R^2 = R^3 = Me), m.p. 79° (lit[6c] 79—80°), *NN*-diethylphenylthioacetamide (1h; R^1 = $PhCH_2$, R^2 = R^3 = Et), m.p. 56—57°; (lit.[6d] m.p. 56—57°), *NN*-di-isopropyl-phenylthioacetamide (1h; R^1 = $PhCH_2$, R^2 = R^3 = $CHMe_2$), m.p. 104°, and *NN*-di-isobutylphenylthioacetamide (1i; R^1 = $PhCH_2$, R^2 = R^3 = $CH_2{\cdot}CHMe_2$), m.p. 43°, upon treatment with trimethyloxonium fluoroborate under the same conditions as before yielded the corresponding amides





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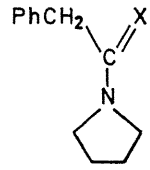

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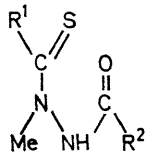

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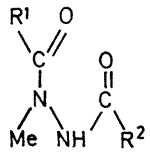

(6)

a; R^1 = Ph, R^2 = CH_2Ph
b; R^1 = R^2 = Ph
c; R^1 = R^2 = CH_2Ph
d; R^1 = CH_2Ph, R^2 = Ph

[(2f, 70%, b.p. 95°/0·3 mm), (2g, 70%, b.p. 120—122°/0·3 mm), (2h, 92%, m.p. 51°) and (2i, 70%, b.p. 143°/0·3 mm)]. Both phenylthioacetylpiperidide (3; X = S), m.p. 80° (lit.[9]

† Satisfactory elemental analyses were obtained for all new compounds reported.

m.p. 79—80°), and phenylthioacetylpyrrolidide (4; X = S), m.p. 69°, could also be converted into the amides [(3; X = O, b.p. 122—125°/0·3 mm; lit. 138—139°/0·4 mm,[10a] 200—203°/12 mm[10b]) and (4; X = O, m.p. 48°)] in 84% yield.

Extension of this procedure with N^1-methyl-N^2-phenylacetyl-N^1-thiobenzoylhydrazine (5a; M^+ 284, m.p. 178°), N^2-benzoyl-N^1-methyl-N^1-thiobenzoylhydrazine (5b; M^+ 270, m.p. 167°), N^1-methyl-N^2-phenylacetyl-N^1-phenylthioacetylhydrazine (5c; M^+ 298, m.p. 107°), and N^2-benzoyl-N^1-methyl-N^1-phenylthioacetylhydrazine (5d; M^+ 284, m.p. 116°) was equally successful and the N^1N^2-diacyl-N^1-methylhydrazines [(6a, 70%, M^+ 268, m.p. 115°); (6b, 80%, M^+ 254, m.p. 145°); (6c, 75%, M^+ 282, m.p. 91°), and (6d, 70%, M^+ 268, m.p. 88°)] were obtained in satisfactory yields.

The mechanism of formation of the amides and the N^1N^2-diacyl-N^1-methylhydrazines under the above conditions can easily be explained, as shown in the diagram.

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