

HYDROGEN SULPHIDE ELIMINATION FROM THIOAMIDES AND THE  
SYNTHESIS OF YNAMINES. PHENYLETHYNYLAMINES FROM  
PHENYLTHIOACETAMIDES

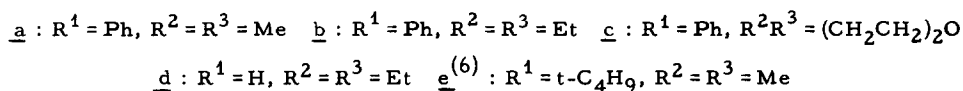
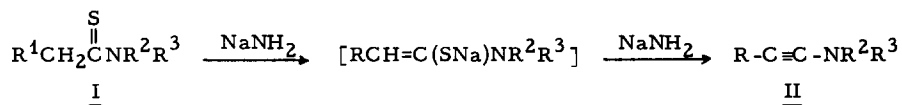
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We recently described the synthesis of ynamines from ketene-S,N-acetals by thiol elimination with base <sup>(1)</sup>. Yields were fair in the case of the preparation of a typical phenylethynylamine but not outstanding compared to those obtained by other methods <sup>(2)</sup>.

It has now been discovered that, more simply, thioacetamides under certain circumstances lose hydrogen sulphide to form ynamines. This reaction has so far remained unreported, while desulphurization of N-monosubstituted thioacetamides to ketenimines <sup>(3)</sup> and of substituted ureas to carbodiimides <sup>(4)</sup> is well known. Incidentally, a similar situation exists for the likewise unknown dehydration of N,N-disubstituted amides compared to the known reaction of N-monosubstituted amides to ketenimines <sup>(5)</sup>.



Phenylthioacetamides Ia-c when dissolved in xylene and added dropwise with efficient stirring and under nitrogen to a fivefold excess of sodamide in boiling xylene react to form bulky precipitates of intermediate thiolate salts which redissolve in the course of a few hours to generate ynamines Iia-c <sup>(9)</sup>. Iia and Iib are formed in sixty and ninety percent yield, respectively. Iic, on the other hand, is only formed in ten percent yield, for reasons which are not at present apparent : formation of the intermediate thiolate seems to proceed normally but is followed

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by an extremely sluggish desulphurization reaction. Thioacetamides Id-e also form thiolate salts which under these conditions cannot be induced to eliminate sodium sulphide. Here, yields are nil and failure has been attributed to the weak acidity of the hydrogen atom to be eliminated in the formation of the acetylenic bond, when R<sup>1</sup> is H or t-butyl instead of phenyl.

Attempts at desulphurization of Ia-e by heavy metal salts such as yellow mercuric oxide or lead oxide were unsuccessful.

Elimination of the elements of hydrogen sulphide from suitably substituted thioacetamides is a straightforward method for the preparation of ynamines which it is felt could be extended to other examples in the aromatic series and which has already shown definite advantages for the synthesis of IIa and IIb.

#### References

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- (9) Compounds described in this communication gave satisfactory elemental analytical data, infrared and nmr spectra.