New Reactions between Enamines and Mercapto-Compounds[1]

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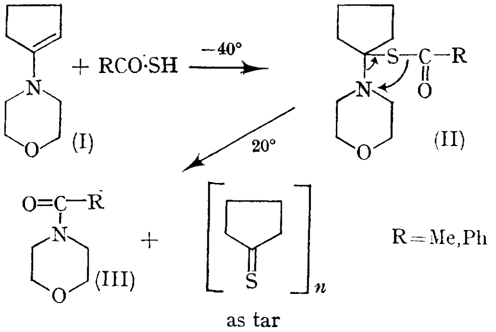
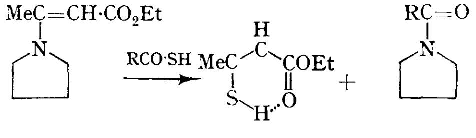
It is known that thiols add to enamines to give α-amino-sulphides.[2,3] Only solid derivatives could be isolated and characterized as they decompose at elevated temperature and regenerate the enamine and thiol in quantitative yields.[3] Now we have studied the reaction of thio-acids and α-mercapto-acids with enamines.

(A) 1-Morpholinocyclopent-1-ene reacts violently with thioacetic acid (or thiobenzoic acid) at room temperature to give quantitative yields of *N*-acetylmorpholine (or *N*-benzoylmorpholine) and sulphur-containing tarry products. By running the reaction at −40° in ether, the addition product could be isolated; its n.m.r. spectrum at −40° in $CDCl_3$ was devoid of signals attributable to olefinic protons and it is thus concluded that the addition product has the structure (II).

By an *S*→*N*-acyl migration, occurring at somewhat elevated temperature, the *N*-acylamine (III) is formed quantitatively. Similar enamines, derived from cyclic ketones and aldehydes, react in the same way producing the corresponding *N*-acylamine. However, with less reactive enamines, the reaction requires some hours in benzene at reflux temperature.

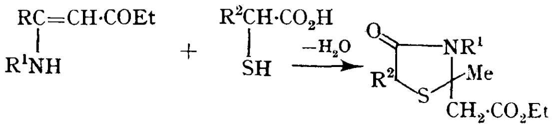


(B) Enamines derived from β-dicarbonyl compounds and secondary amines react in the same way as above and give the corresponding *N*-acylamines. In these cases, the thiocarbonyl compounds formed (existing mainly as the enethiol stabilized by hydrogen bonding to the carbonyl group) can be isolated. Ethyl 3-mercaptocrotonate, (IV), is thus formed in good yields (>50%) as follows:



This method is superior to previous methods[4] as it is quite general, and gives, directly, pure products without admixture of the corresponding β-dicarbonyl compound and *gem*-dithiol (separation *via* Pb-salt is unnecessary).

(c) Enamines derived from β-keto-esters and ammonia or methylamine produce thiazolones (V)† in good yields (~50%) when reacted with α-mercapto-acids (or the corresponding esters).



This method is being extended to other systems.

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† All elemental analyses were consistent with the molecular formulae.

[1] Considered as part of the series "Enamine Chemistry", for part XI, see P. Jakobsen and S.-O. Lawesson, *Tetrahedron*, in the press.

[2] N. J. Leonard and A. S. Hay, *J. Amer. Chem. Soc.*, 1956, **78**, 1984.

[3] S.-O. Lawesson, E. H. Larsen, and H. J. Jakobsen, *Rec. Trav. chim.*, 1964, **83**, 461.

[4] F. Duus and S.-O. Lawesson, *Arkiv Kemi*, in the press, and references therein.