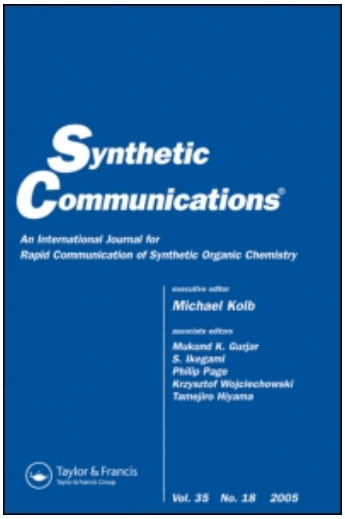

Synthetic Communications
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597304

A Conventent Synthesis of Functonalised Heterocuclic Enamines from Alpha-Thioiminium Salts and Active Methylene Compounds Under Solid-Liquid PTC Conditions

Paramjit Singh[a]; Manohar. S. Batra[a]; Harjit Singh[a]
[a] Department of Chemistry, Guru Nanak Dev University, Amritsar, India

To cite this Article Singh, Paramjit , Batra, Manohar. S. and Singh, Harjit(1984) 'A Conventent Synthesis of Functonalised Heterocuclic Enamines from Alpha-Thioiminium Salts and Active Methylene Compounds Under Solid-Liquid PTC Conditions', Synthetic Communications, 14: 6, 533 — 536
To link to this Article: DOI: 10.1080/00397918408059575
URL: http://dx.doi.org/10.1080/00397918408059575

SYNTHETIC COMMUNICATIONS, 14(6), 533-536 (1984)

A CONVENIENT SYNTHESIS OF FUNCTIONALISED HETEROCYCLIC ENAMINES FROM ALPHA-THIOIMINIUM SALTS AND ACTIVE METHYLENE COMPOUNDS UNDER SOLID-LIQUID PTC CONDITIONS

Paramjit Singh, Manohar S. Batra and Harjit Singh*
Department of Chemistry, Guru Nanak Dev University,
Amritsar - 143 005, India

Functionalised enamines constitute a category of synthetic intermediates useful in carbon, carbon bond formation reactions and have been procured through a variety of condensation and extrusion reactions.[1] In one approach active methylene compounds have been condensed with lactim thioethers in the presence of a base at relatively higher temperature.[2,3] In view of our interest in the synthesis of functionalised enamines through sulphur extrusion reactions,[4] we have studied the title reaction under non-hydrolytic solid-liquid PTC using solid KF(base)/TEBA(catalyst). A recent report[5] on the sulphur extrusion of α-thioiminium salts and their reactions with active methylene compounds prompts us to report our results.

3,4-Dihydro-1-methyl-2(methylthio)5H-pyrrolium iodide (1,R=CH_3),[6] a nonprotic cyclic thioiminium salt, with malononitrile in dichloromethane furnishes $\Delta^{2,\alpha}$-pyrrolidinemalononitrile (2,R=CH_3) in 90% yield. The results of similar reactions of ethyl cyanoacetate, ethyl acetoacetate, nitromethane, acetophenone and

 0039-7911/84/1406-0533$3.50/0

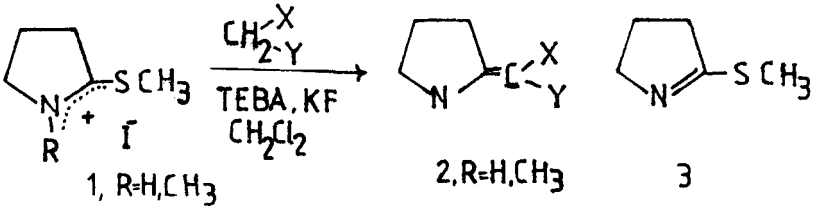

Table 1

Sr. No.	X	Y	Time(h.)[e] R=H	Time(h.)[e] R=CH_3	%yield of 2[a] R=H	%yield of 2[a] R=CH_3
1.	CN	CN	6	6	65[b](30)[c]	90[b](65)[c]
2.	CN	COOEt	6	6	75(30)	87(65)
3.	$COCH_3$	COOEt	8	8	60	60(50)
4.	COOEt	COOEt	12	9	10[d]	55(50)
5.	H	NO_2	12	8	10[d]	28[d](15)
6.	H	COC_6H_5	-	9	-	30(25)

a) All the compounds gave satisfactory i.r., ^{1}H nmr and mass spectral data, (b) procedure A (c) procedure B (d) the yields did not improve even after prolonged periods.

diethyl malonate are given in table-1. 3,4-Dihydro-2-(methylthio)-5H-pyrrolium iodide(1,R=H), a cyclic monoprotic thioiminium salt, with active methylene compounds under similar reaction conditions also gives the corresponding functionalised enamines (Table-1).

The higher yields of the products in the case of the non-protic thioiminium salt than the protic salt may be attributed to a competitive deprotonation of the latter to the lactim thioether. It has been

found that under these conditions lactim thioether(3) with ethyl cyanoacetate gives ethyl α-cyano $\Delta^{2,\alpha}$ pyrrolidineacetate (Table-1, entry 2, R=CH_3) in 15% yield and N-methylpyrrolidine-2-thione and pyrrolidine -2-thione fail to react. It may also be observed that weakly acidic active methylene compounds also give the title reaction but the yields are poor. The mode of performing these reactions also influences the yields of the products, as (A) by adding a solution of (1,R=CH_3) to a stirred mixture of active methylene compound, KF and TEBA, the products are obtained in higher yields, than (B) by stirring a mixture of all the constituents.

This method of synthesising heterocyclic functionalised enamines is advantageous over the previous sulphur extrusion method[4] where relatively unstable and lachrymatic halogeno derivatives of active methylene compounds are used. Further, the reactions have been performed at room temperature in the presence of a mild base and the work up is convenient due to the use of a low boiling solvent.

Experimental

Reaction of Alpha-thioiminium salt(1) with active methylene compounds.

General Procedure :

To a stirred solution of the active methylene compound (3 m.mole), in dichloromethane containing suspension of KF(15 m.mole) and TEBA (catalyst) was added dropwise a solution of alpha-thioiminium salt in dichloromethane. The reaction mixture was stirred at room temperature and after completion of reaction (tlc), organic layer was separated, washed with

water, dried ($Na_2 SO_4$) and solvent was distilled off. The residue was crystallised from dichloromethane to give the functionalised heterocyclic enamine(2).

Acknowledgement : We thank CSIR, New Delhi for financial assistance.

References :

1. a. H.Singh, C.S.Gandhi and M.S.Bal, Synthesis, 1020 (1980) and references therein.
   b. K.Shiosaki, G.Fels and H.Rapoport, J.Org.Chem. 46, 3230(1981) and references therein.
2. K.Bhandari, V.Virmani, V.A.Murti, P.C.Jain and N.Anand, Indian J.Chem., 17B, 104(1979).
3. G.Lhommet, M.G.Richaud and P.Maitte, J.Heterocyclic Chem., 19, 431(1982).
4. H.Singh, A.S.Ahuja and C.S.Gandhi, J.Chem.Res., (M), 2935 (1979); (S), 364(1979).
5. C.Jolivean and C.G.Wermuth, Tetrahedron, 39, 2295 (1983).
6. R.Gompper and W.Elser, Organic synthesis Coll. Vol. 5, p 780.