

# SYNLETT Spotlight 305

## Ethyl 2-Cyano-3,3-bis(methylthio)acrylate

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This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

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Dedicated to my father late B. M. Kalyankar and dedicated to my supervisor Dr. S. V. Bhosale (Reader) on the occasion of his 37<sup>th</sup> birthday.

### Introduction

Ethyl 2-cyano-3,3-bis(methylthio)acrylate (Figure 1) was prepared by the reaction of ethyl cyanoacetate, carbon disulfide and dimethyl sulfate in the presence of a base.<sup>1</sup> Gommer and co-workers studied this reaction thoroughly. The electron-attracting groups on C<sub>2</sub> makes it a very useful reagent for the preparation of heterocyclic com-

pounds.<sup>2</sup> Moreover, Ethyl 2-cyano-3,3-bis(methylthio)acrylate can also be prepared efficiently using sodium ethoxide as a base.<sup>3</sup> In the literature numerous reports appeared highlighting its chemistry and use.

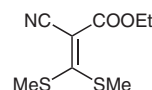
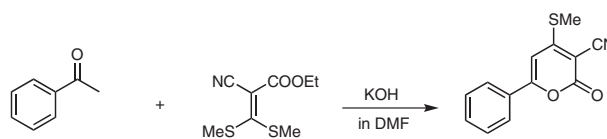


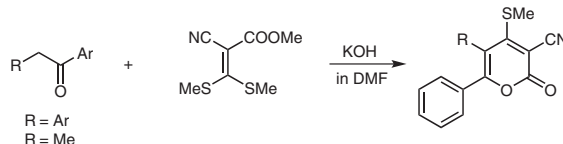
Figure 1 Ethyl 2-Cyano-3,3-bis(methylthio)acrylate

### Abstracts

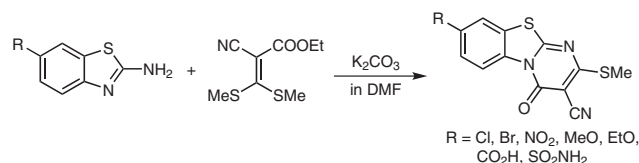
(A) Tominaga et al. reported the synthesis of 2*H*-pyran-2-one starting from acetophenones and ethyl 2-cyano-3,3-bis(methylthio)acrylate in the presence of KOH in DMF.<sup>4</sup>



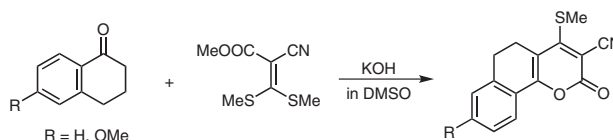
(B) The 2*H*-pyran-2-one derivatives have been prepared by reacting an aryl methyl ketone and 1,2-diarylethanone with methyl 2-cyano-3,3-bis(methylthio)acrylate in the presence of KOH in DMF.<sup>5</sup>



(C) Baheti et al. described the synthesis of 4*H*-pyrimido[2,1-*b*]benzothiazole-8-substituted 2-thiomethyl-3-cyano-4-ones by the reaction of 2-amino-6-substituted benzothiazole with ethyl 2-cyano-3,3-bis(methylthio)acrylate in the presence of anhydrous potassium carbonate in DMF.<sup>6</sup> The synthesized compounds were further investigated for analgesic and CNS-depressant activity.



(D) Recently, the group of V. J. Ram described the synthesis of 4-methylsulfanyl-2-oxo-5,6-dihydro-2*H*-benzo[*h*]chromene-3-carbonitriles by the reaction between 1-tetralone and methyl 2-cyano-3,3-dimethylthioacrylate in the presence of KOH/DMSO in catalytic amounts.<sup>7</sup>



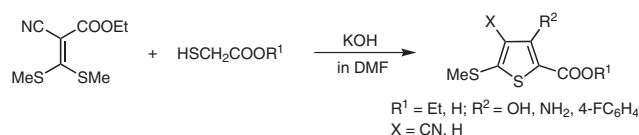
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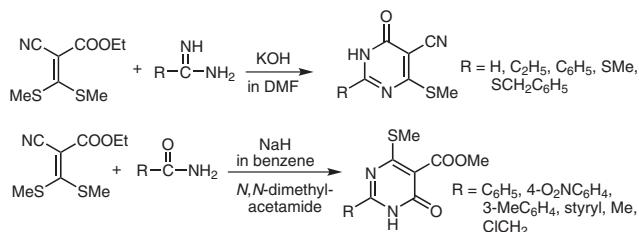
DOI: 10.1055/s-0029-1219338; Art ID: V31109ST

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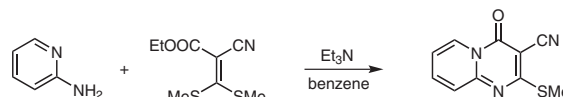
(E) The condensation reaction between ethyl 2-cyano-3,3-bis(methylthio)acrylate and alkyl 2-mercaptoacetate leading to highly functionalized thiophenes was reported by V. J. Ram and co-workers.<sup>8</sup>



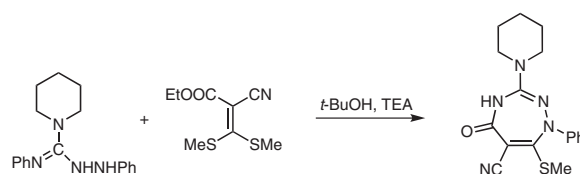
(F) Suitably functionalized pyrimidine derivatives were synthesized by condensation of ethyl 2-cyano-3,3-dimethylthioacrylate with amidine.<sup>9</sup> Kohara and co-workers also synthesized pyrimidine derivatives starting from ketene dithioacetal and amides in the presence of sodium hydride in DMA.<sup>9</sup>



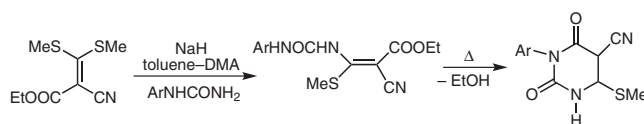
(G) Mukharjee et al. reported the synthesis of pyridopyrimidine starting from cyanoketene dithioacetal and 2-aminopyridine in the presence of triethylamine in benzene.<sup>10</sup>



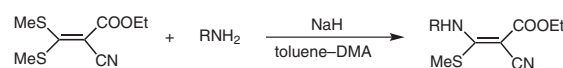
(H) The synthesis of triazepines was described by Omran et al. by condensation of *N,N'*-diphenylpiperidine-1-carbohydrazonamide with ethyl 2-cyano-3,3-dimethylthioacrylate in the presence of *t*-BuOH and TEA.<sup>11</sup>



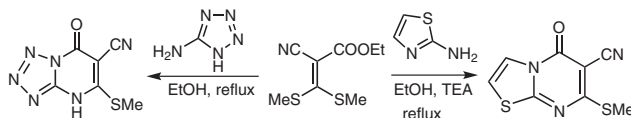
(I) Yang and co-workers describe the synthesis of 3-aryl-5-cyano-6-methylthio pyrimidine-2,4-diones from ethyl 2-cyano-3,3-dimethylthioacrylate with arylureas in toluene and DMA under mild condition.<sup>12</sup>



(J) Novel ketene *N,S*-acetals were prepared by the reaction of ethyl 2-cyano-3,3-bis(methylthio)acrylate with low nucleophilic aromatic amines using sodium hydride in toluene.<sup>13</sup>



(K) Metwally and co-workers described the reaction of ethyl 2-cyano-3,3-bis(methylthio)acrylate with aminoazoles (5-aminotetrazole monohydrate and 2-aminothiazole) in the presence or absence of triethylamine leading to the corresponding pyrimidines.<sup>14</sup>



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