Pergamon

Tetrahedron Letters, Vol. 38, No. 18, pp. 3289-3290, 1997
© 1997 Published by Elsevier Science Ltd
All rights reserved. Printed in Great Britain
0040-4039/97 $17.00 + 0.00

PII: S0040-4039(97)00587-X

Reaction of Heterocyclic Allyl Sulphides with Ethyl Diazoacetate: a Simple Method for the Synthesis of Conjugated Dienoic Esters

Vincenzo Calò,*Angelo Nacci, Vito Fiandanese and Angela Volpe

CNR Centro di Studio sulle Metodologie Innovative di Sintesi Organiche, Dipartimento di Chimica, Università di Bari,
via Orabona 4-70126 Bari, (Italy)

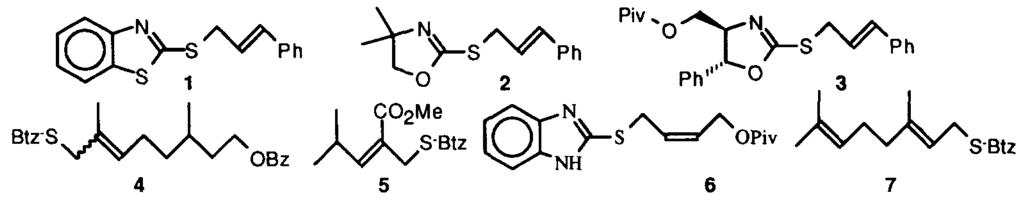
Abstract: Heterocyclic allyl sulphides **1-6** react with an excess of ethyl diazoacetate in the presence of copper(I)exafluorophosphate acetonitrile complex in dichloromethane under mild conditions to give, through the formation of homoallylic sulphides intermediates, conjugated dienoic esters in high yields.

The synthesis of conjugated dienoates can be accomplished through the Ireland ester enolate rearrangement of allylic α-(phenylthio) acetates,[1] ammonium ylides fragmentation[2] or orthoester Claisen rearrangement,though the latter method requires a subsequent introduction of a α,β-unsaturation into the γ,δ-unsaturated intermediate.[3-5]

We report that conjugated dienoates can be simply prepared by treatment of heterocyclic allyl sulphides with an excess of ethyl diazoacetate at r.t. in dichloromethane in the presence of a copper(I) complex (scheme 1).

Scheme 1

The allylic substrates chosen are oxazolin- and benzothiazol-2-yl thioethers[6] **1-7** reported in figure 1.

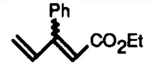
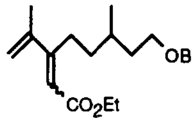
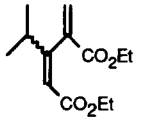
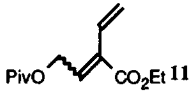
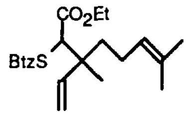


Btz= Benzothiazole-2-yl; Bz= Benzyl; Piv= Pivaloyl

Figure 1

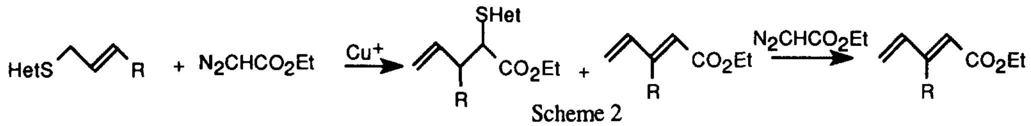
Thus, treatment of sulphides **1-3** (1 equivalent) with 3-4 equivalents of ethyl diazoacetate in dichloromethane in the presence of 0.05 equivalents of copper(I)hexafluorophosphate acetonitrile complex at r.t. affords ethyl 3-phenyl-2,4-pentadienoate **8** in a 76-94% yields as a mixture of geometrical isomers together with BtzS-CH_2CO_2Et. Sulphides **4-6** give the corresponding dienoates **9-11** whereas compound **7** affords the homoallylic sulphide **12** as a 4:1 mixture of diastereoisomers (Table 1).

Table 1. Reaction of sulphides **1-7** with ethyl diazoacetate catalysed by $[Cu(CH_3CN)_4]PF_6$

Sulphide	Product (Yield%)	Sulphide	Product (Yield%)
1 - 3	 8 (76-94)	4	 9(85)
5	 10(68)		
6	 11(76)	7	 12 (71)

The reaction was performed by dropwise slow addition of ethyl diazoacetate (3-4 equiv) at r.t. to the substrate (1 equiv) and the copper complex (0.05 equiv) dissolved in dichloromethane. The progress of the reaction was monitored by T.L.C. (petroleum ether: ethyl acetate 20:1) and the reaction products were separated by chromatography by means of the same eluent. NMR, IR and MS data are consistent with these structures.

In these reactions homoallylic sulphides, as proved by the isolation of compound **12**, are intermediates[7-12] which, by further reaction with the diazo compound, are converted into dienoates by a β-elimination process. In fact, for example, reaction of **1-6** with only one equivalent of ethyl diazoacetate gives a mixture of the dienoic ester and the homoallylic sulphide (Scheme 2).



Scheme 2

In conclusion, since allylic sulphides arise from allylic alcohols,[6] this procedure allows a simple two-steps conversion of an allyl alcohol into a α,β,γ,δ-unsaturated ester.

Acknowledgement: Work supported by the Ministry of the University, (MURST) 40 and 60%

REFERENCES

1. Ireland, R. E.; Mueller, R. H. *J. Am. Chem. Soc.*, **1972**, *94*, 5897-5898.
2. Vedejs, E.; Engler, D. A. *Tetrahedron Lett.*, **1977**, 1241-1244.
3. Ziegler, F. E. *Chem. Rev.* **1988**, *88*, 1423-1452.
4. Posner, G. H.; Kinter, C. M. J. *J. Org. Chem.*, **1990**, *55*, 3967-3969.
5. Posner, G. H.; Crouch, R. D.; Kinter, C. M. J.; Carry, J-C. J. *Org. Chem.*, **1991**, *56*, 6981-6987.
6. Caló, V; Nacci, A; Fiandanese, V. *Tetrahedron*, **1996**, *52*, 10799-10810.
7. Ando, W. *Acc. Chem. Res.*, **1977**, *10*, 179-185.
8. Doyle, M.P. *Chem. Rev.*, **1986**, *86*, 919-939.
9. Adams, J; Spero, D. M. *Tetrahedron*, **1991**, *47*, 1765-1808.
10. Padwa, A; Hornbuckle, S.F. *Chem. Rev.*, **1991**, *91*, 263-309.
11. Padwa, A; Austin, D.J. *Angew. Chem. Int. Ed. Eng.*, **1994**, *33*, 1797-1815.
12. Ye, T; McKervey M. A. *Chem. Rev.*, **1994**, *94*, 1091-1160.

(*Received in UK* 11 *December* 1996; *revised* 25 *March* 1997; *accepted* 26 *March* 1997)