Tetrahedron Letters,Vol.30,No.41,pp 5653-5654,1989
Printed in Great Britain

0040-4039/89 $3.00 + .00
Pergamon Press plc

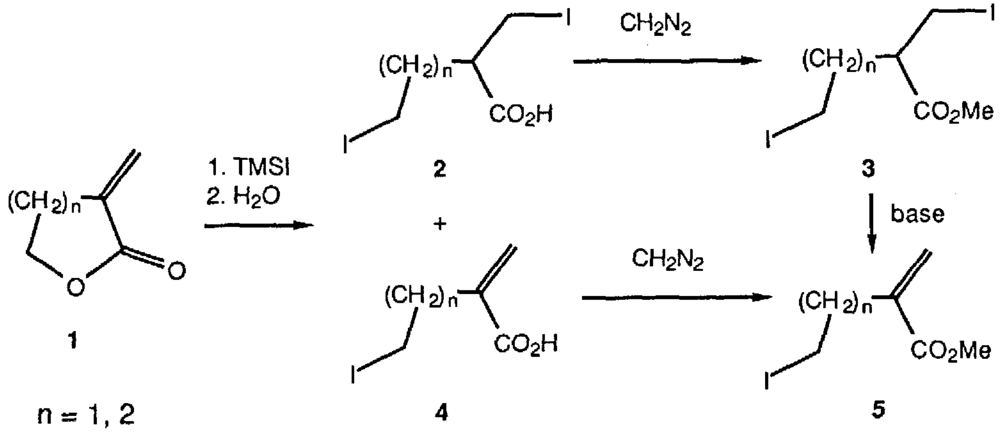
PREPARATION OF METHYL-2-(ω-IODOALKYL)PROPENOATES AND A FACILE ROUTE TO 2-CARBOMETHOXY-1,3-BUTADIENE

Alex I. D. Alanine[a], Colin W.G. Fishwick*[a], Andrew D. Jones[a], and Michael B. Mitchell[b].
[a] School of Chemistry, The University of Leeds, Leeds LS2 9JT.
[b] Smith Kline & French Research Ltd, Old Powder Mills, Tonbridge, Kent TN11 9AN.

Summary : α-Methylene-γ-and-δ-lactones undergo facile ring opening with trimethylsilyl iodide to yield 2-(iodoethyl)propenoic acid and 2-(iodopropyl)propenoic acid respectively, which are methylated to afford the corresponding esters. Treatment of methyl-2-(iodoethyl)propenoate with base generates 2-carbomethoxy-1,3-butadiene which undergoes dimerisation or can be trapped in-situ.

In connection with our interests in concerted cycloaddition chemistry, we required access to methyl-2-(ω-iodoalkyl)propenoates **5**. Inspection of the literature however, revealed the absence of satisfactory routes to these compounds.

We were aware of the use of trimethylsilyl iodide (TMSI)[1] for the cleavage of saturated lactones directly to iodo-acids[2]. Thus, despite the reported facile 1,4-addition of TMSI to α,β-unsaturated acids[3], we hoped that treatment of the α-methylene lactones **1** with TMSI would give rapid access to the desired iodides **5** after methylation. We report here that with suitable modification, this procedure affords the required ω-iodo esters **5** in good yields (scheme 1).

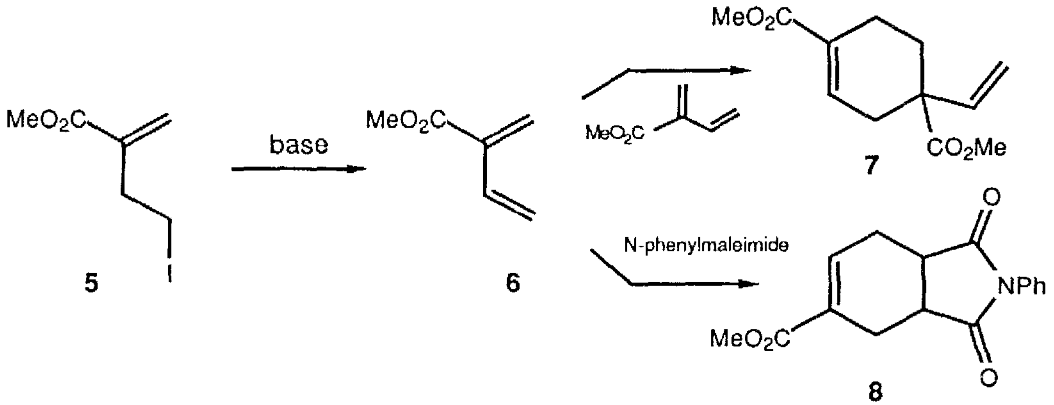


scheme 1

In a typical experiment, a mixture of α-methylene-γ-butyrolactone **1**, (n=1) (392mg, 4mmol), TMSCl (868mg, 8mmol) and NaI (1.2g, 8mmol) in anhydrous acetonitrile (10ml) was heated at reflux for 16 hrs. After aqueous work-up, NMR examination revealed the presence of a 3:2 ratio of unsaturated acid **4**, (n=1) and bis-iodide **2**, (n=1). This latter product presumably results from 1,4-addition of a second mole of TMSI to acid **4**, (n=1). Treatment of this mixture with a slight excess of ethereal diazomethane produced the corresponding esters **3** and **5**, (n=1). It was found that by treating this mixture with an equivalent of diisopropylethylamine at room temperature the bis-iodide **3**, (n=1) could be readily converted into the desired ester **5**, (n=1) 656mg, (68% from **1**, n=1) after Kugelrhor distillation. The homologous ester **5**, (n=2) was similarly prepared in 74% overall yield from lactone **1**, (n=2).

In addition, it was found that treatment of iodo-ester **5**, (n=1) with 1.2 equivalents of diisopropylethylamine in acetonitrile at reflux afforded ester **7** in 92% yield. This presumably results from Diels-Alder dimerisation of the reactive 2-carbomethoxy-1,3-butadiene **6**[4], generated via dehydrohalogenation of **5**, (n=1). Futhermore, this diene could also be trapped *in-situ* with N-phenyl maleimide to yield cycloadduct **8** in 87% isolated yield (scheme 2).

The methods described above are thus simple and convenient routes to these useful synthetic intermediates.



scheme 2

Acknowledgment

We thank the SERC for a studentship to AIDA and Smith Kline & French Research Ltd and the SERC for a CASE studentship to ADJ.

References.

1. G.A. Olah, S.C. Narang, *Tetrahedron*, 1982, 38, 2225.
2. G.A. Olah, S.C. Narang, B.G.B. Gupta and R. Malhotra, *J. Org. Chem.*, 1979, 44, 1247.
3. T. Azuhata and Y. Okamoto, *Synthesis*, 1983, 461.
4. A number of reports concerning the generation of this reactive diene have appeared, see O. Goldberg and A. S. Dreiding, *Helv. Chim. Acta.*, 1976, 59, 1904. ; J.M. McIntosh and R.A. Sieler, *J. Org. Chem.*, 1978, 43, 4431.

(Received in UK 29 August 1989)