Tetrahedron Letters,Vol.23,No.33,pp 3407-3410,1982 0040-4039/82/333407-04$03.00/0
Printed in Great Britain

NEW SYNTHESIS OF KETENE THIOACETALS, VINYLSULFIDES AND THEIR SELENO ANALOGUES

J.N. Denis and A. Krief*
Facultés Universitaires Notre-Dame de la Paix
Department of Chemistry
61, rue de Bruxelles, B-5000 - Namur (Belgium)

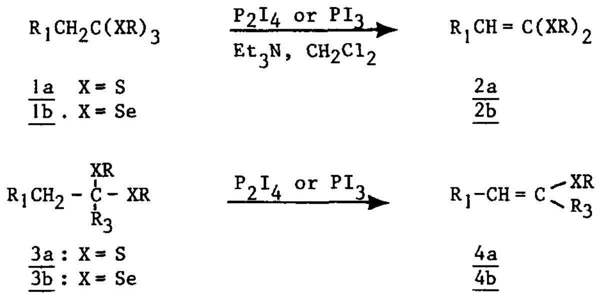
Title compounds have been prepared on reaction of thioacetals, orthothioesters and their seleno analogues with diphosphorus tetraiodide (P_2I_4) or phosphorus triiodide (PI_3).

Ketene thioacetals [1] 2a and vinylsulfides [1] 4a, valuable synthetic building blocks, have been often [3] prepared by β elimination reactions of two heteroatomic moieties on suitable derivatives [1,2].

We have recently described [2] such kind of transformation using readily available β-hydroxythioacetals, β-hydroxyorthothioesters and their seleno analogues as starting materials and P_2I_4 [4] and PI_3 [5] as the reagents.

We now disclose that the same reagents are able to produce, in an unprecedented reaction, ketene thioacetals 2a, vinylsulfides 4a and their seleno analogues 2b and 4b simply from orthothioesters 1a, thioacetals 3a and their seleno analogues [7] 1b and 3b (Scheme).

SCHEME



$$R_1CH_2C(XR)_3 \xrightarrow[Et_3N,\ CH_2Cl_2]{P_2I_4 \text{ or } PI_3} R_1CH=C(XR)_2$$

1a X = S
1b . X = Se

2a
2b

$$R_1CH_2-\overset{XR}{\underset{R_3}{C}}-XR \xrightarrow{P_2I_4 \text{ or } PI_3} R_1-CH=C\begin{matrix}XR\\R_3\end{matrix}$$

3a : X = S
3b : X = Se

4a
4b

The reactions which occur by formal removal of a thiol or a selenol are usually conducted at room temperature in methylene chloride and triethylamine (∿4eq) in the presence of P_2I_4 (0.55eq - Method A) or PI_3(1.1eq - Method B) (See Table, typical experiment). The desired products are usually obtained free from any sulfur, selenium or phosphorus containing by-products which are in fact water soluble.

Although working particularly well with all the orthothio-and orthoselenoesters as well as with methylselenoacetals derived from ketones, the reaction does not take place with methylselenoacetals derived from aldehydes, with phenylselenoacetals and with methylthio, and phenylthioacetals wether derived from aldehydes or ketones. In the three first cases however, successful conversion can be observed by heating them in dimethylformamide (DMF) with P_2I_4 (Method C) (See Table).

It has been recently argued [7] that one must avoid such combination since dimethyliodomethylene ammonium iodide is immediately formed when P_2I_4 and DMF are mixed. We have ourselves observed ,sometime ago ,the formation of such compound [8] . We however found [4b] that valuable transformations can be performed in that medium and that is also the case in the just reported reactions.

These reactions are not regio-and stereoselective (See Table, entries 8,9 and 11) in the case of vinylsulfides and vinylselenides. They are however particularly useful for the connective synthesis of ketene methylthio- and methylseleno acetals since the starting orthoesters can be prepared in high yield from thio (seleno) orthoformiate[6,7] and alkylhalides and since no regio and stereochemical problems are involved.

Finally, P_2I_4 (1eq) in CH_2Cl_2 reacts quite instantaneously (25°, 0.1h) with triethyl orthoproprionate but the reaction takes a completely different course from the one we report for thio- and selenoanalogues ethyl propionate is formed in 78% yield along with ethyliodide. This kind of reactivity has already been reported with oxygenated acetals [9].

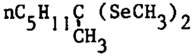
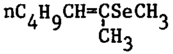
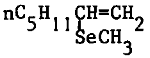
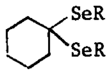
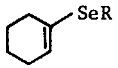
Typical experiment *(Method A).*

SYNTHESIS OF 1,1-BIS (METHYLSELENO)-1-DODECENE 1,1,1 tris(methylseleno) dodecane (0.225g, 0.5 mmol) and triethylamine (0.125g, 1.25 mmol) are added at 20° to a stirred suspension of P_2I_4 (0.160g, 0.28 mmol) in CH_2Cl_2 (2 ml). The resulting mixture is stirred for 1 more hour hydrolysed with a saturated solution of bicarbonate and extracted with ether, the ether is then removed in vacuo The crude product (0.196 g) which is analytically pure has however been purified by Preparative Layer Chromatography (PLC) (SiO_2, pentane, rf 0.47) leading to the pure ketene selenoacetal (0.160 g, 90% yield).

The authors thank Prof. L. Hevesi (FUNDP) and Dr. W. Dumont for providing them with the starting materials 1 (entries 1, 3, 5 and 6 for L.H.) and 3 (entries 8-11 for W.D.).

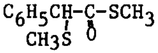
The authors are grateful to Roussel-Uclaf (France) and to F.U.N.D.P. (Namur, Belgium) for financial support.

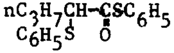
TABLE

Entry	Starting material 1 or 3	(Method used)[a] Yield %	Reaction products 2 or 4	(Method, temperature °C, time)[b] Yield %
1	$CH_3CH_2C(SeCH_3)_3$	(a) 70	$CH_3CH{=}C(SeCH_3)_2$	(A,20,1)88 , (B,20,1)90
2	$nC_{11}H_{23}C(SeCH_3)_3$	(a) 67	$nC_{10}H_{21}CH{=}C(SeCH_3)_2$	(A,20,1)90 , (C,20,0.75)87
3	$C_6H_5CH_2C(SeCH_3)_3$	(a) 85	$C_6H_5{-}CH{=}C(SeCH_3)_2$	(A,20,1)86
4	$nC_4H_9C(SeC_6H_5)_3$	(a) 35	$nC_3H_7CH{=}C(SeC_6H_5)_2$	(A,20,4)76
5	$CH_3CH_2C(SCH_3)_3$	(a) 70	$CH_3CH{=}C(SCH_3)_2$	(A,20,5)67
6	$C_6H_5CH_2C(SCH_3)_3$	(a) 80	$C_6H_5CH{=}C(SCH_3)_2$	(A,20,24)[c]84 , (B,20,24)[c]79
7	$nC_4H_9C(SC_6H_5)_3$	(a) 32(mp:75 - 76.5°)	$nC_3H_7CH{=}C(SC_6H_5)_2$	(A,20,24)[d]80
8	 $nC_5H_{11}\underset{CH_3}{C}(SeCH_3)_2$	(b) 81	 $nC_4H_9CH{=}\underset{CH_3}{C}SeCH_3$  $nC_5H_{11}\underset{SeCH_3}{C}H{=}CH_2$	(A,20,3)71 $\left.\begin{matrix}42\\58\end{matrix}\right]$ ratio ; (B,20,3)73 $\left.\begin{matrix}72\\28\end{matrix}\right]$ ratio
9	$C_{10}H_{21}CH(SeCH_3)_2$	(b) 97	$nC_9H_{19}CH{=}CHSeCH_3$	(A,20,24)0 ; (C,80,1)85 , (Z E = 1 1)
10	 R=CH_3	(b) 80	 R=CH_3	(A,20,1.5)80
	R=C_6H_5	(b) 75	R=C_6H_5	(A,20,70) traces , (C,80,1.5)88
11	$C_{10}H_{21}CH(SCH_3)_2$	(b) 85	$nC_9H_{19}CH{=}CHSCH_3$	(C,80,20)[e]35 , (C,50,24)57[f] , (Z.E = 1.1)

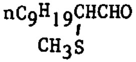
a. Method a from $LiC(XR)_3$[6] and the corresponding alkylbromide in THF at -78°.
Method b from the corresponding carbonyl compound [10] and RXH in the presence of $ZnCl_2$.

b. Method A P_2I_4 (0.55eq)/NEt_3(4.4eq) , Method B . PI_3 (1.1eq)/NEt_3 (3.3eq) , Method C : P_2I_4/DMF.

c.  $C_6H_5\underset{CH_3S}{CH}-\underset{O}{C}-SCH_3$ was also isolated in 12% yield (mp.63-63.5°)

d.  $nC_3H_7\underset{C_6H_5S}{CH}-\underset{O}{C}SC_6H_5$ was also isolated in 7% yield.

e. We were unable to cleanly purify such reaction mixture.

f.  $nC_9H_{19}\underset{CH_3S}{CH}CHO$ was also isolated in 9% yield.

REFERENCES AND NOTES

1. "Umpolung of the Reactivity of Carbonyl Compounds through Sulfur containing Reagents", B.T. Grobel and D. Seebach, Synthesis, 357 (1977).

2 J.N Denis, S Desauvage, L. Hevesi and A. Krief, Tet. Lett., 4009 (1981) and references cited.

3. For synthesis of such compounds by elimination of an hydrogen and an heteroatom, see for example .

   a. L.C. Rinzema, J. Stoffelsma and J.F. Arens, Rec. Trav. Chim. Pays-Bas, 78, 354 (1959).
   b. A. Froling and J.F. Arens, Rec. Trav. Chim. Pays-Bas, 81, 1009 (1962).
   c. D. Seebach, K.-H. Geiss, A.K. Beck, B. Graf and H. Daum, Chem. Ber., 105, 3280 (1972).
   d. M. Sevrin, W. Dumont and A. Krief, Tet Lett., 3835 (1977).

4 a M. Lauwers, B. Regnier, M. Van Eenoo, J.N Denis and A. Krief, Tet. Lett , 1801 (1979).
   b. Aldrich Technical Information 191.
   c. Available from Aldrich Company, Product n°21865-0

5 a. J.N. Denis and A. Krief, J.C.S. Chem Comm., 544 (1980).
   b. Available from Merck Darmstadt, Product n°821025.

6 a. D Seebach, Chem. Ber., 105, 487 (1972).
   b D. Seebach, Angew. Chem. Int. Ed., 6, 442 (1967).
   c. D. Seebach and M. Braun, Angew. Chem. Int. Ed , 11, 49 (1972).
   d. D. Seebach and N. Peleties, Chem. Ber., 105, 511 (1972)
   e D. Van Ende, A. Cravador and A. Krief, J. Organometal. Chem., 177, 1, (1979)

7 A.B Shortt and H.S Mosher, Synthetic Communications, 11, 733 (1981)

8 Other N,N-dialkyl amides do not seem to produce a similar species when reacted with P_2I_4 and we assume the formation of a charge transfer complex. J.N. Denis unpublished results.

9 J N. Denis and A. Krief, Angew. Chem. Int. Ed., 19, 1006 (1980)

10. a. W Dumont and A. Krief, Angew. Chem Int. Ed , 16, 540 (1977).
   b. A. Burton, L. Hevesi, W Dumont, A. Cravador and A. Krief, Synthesis 877 (1979).

(Received in UK 24 May 1982)