Tetrahedron Letters,Vol.24,No.15,pp 1657-1660,1983 0040-4039/83/151657-04$03.00/0
Printed in Great Britain

REDUCTION OF THIIRANES TO ALKENES AND ALKANES

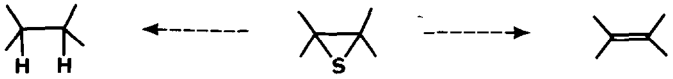
J.R. Schauder, J.N. Denis and A. Krief[*]

Facultés Universitaires Notre-Dame de la Paix
Department of Chemistry
61, rue de Bruxelles, B-5000 - Namur (Belgium)

Various reagents were tested in order to reduce thiiranes to alkanes or olefins. The results of this investigation is presented in this letter.

Thiiranes are valuable synthetic intermediates which are easily prepared from epoxides [1] and bromohydrins [2] and which also can be synthesized with the concomitant formation of a new carbon-carbon bond [3,4,5].
They are precursors of olefins [2,4,5,6] and, since the pioneering work of Barton [4] and Kellogg [5], they have been used as intermediates in the synthesis of the more strained ones.

Recently, we became interested in this functional group not only for its afore-mentioned application but also for its potential for direct reduction to alkanes.



3 1 2

We hoped to find reactions which could allow the last transformation (1 3) under conditions which would avoid the concomitant reduction of a carbon-carbon double bond, so that this group, if present even at the same level of substitution, would remain intact during the process. As a consequence, 2 must not be an intermediate during the 1 to 3 transformation.
We were aware when we started the work of the high propensity of any of the intermediates (radical or anion) arising from the cleavage of the first C-S bond to produce the olefin by β elimination reaction. Thus, successful conditions would require an immediate "hydrogen" uptake from the first intermediate.
Raney nickel in ethanol (-40°, 7h or 90°C,0.5h - Method A) [1,7], lithium in ethylamine (-15°, 0.5 h >- Method B), zinc in acetic acid (130°, 4h - Method C) [8] and tributyltin hydride/AIBN (1 mol.eq./110°, 1h - Method D) were chosen for such purpose.
Raney nickel in ethanol (Method A, -40°C) and lithium in ethylamine (Method B, -15°C) were among the reagents used, those who showed the higher aptitude to produce alkanes from thiiranes. This reaction only occurs with monosubstituted thiiranes in the first case and with terminal and α,β disubstituted ones in the second one.

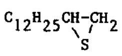
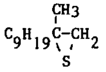
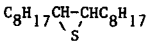
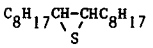
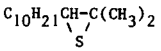
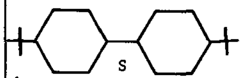
However only the reaction involving Raney nickel satisfies our selectivity requirement : 1-tetradecene is not reduced to tetradecane under conditions (-40°, 4h or 10h) which allows the reduction of 1-tetradecene episulfide to tetradecane. In the case of lithium in ethylamine for example (entries a, b, c), the corresponding olefins were reduced to alkanes in identical yield [9]. Under the reported conditions (A and B) the reduction of tri- and tetrasubstituted [10] thiiranes almost exclusively stopped at the alkene stage and no further reduction to alkane was observed. This is also the case of α,di- or α,β-disubstituted thiiranes when reacted with Raney nickel at -40°C and of all the thiiranes tested when reacted with this reagent at higher temperature (+90° instead of -40°) or with zinc in acetic acid (Method C) or tributyltin hydride (Method D).

Methods A, B, D proved to be valuable for the desulfurization of thiiranes into olefins, the reactions are highly regioselective and even occur on hindered derivatives (entry e). However, they are not completely stereoselective (Table).

Since the synthesis of olefins from thiiranes is a useful process, we have tried, in the course of this study, other reagents able to perform such transformation. P_2I_4 already successfully used for the deoxygenation of epoxides to olefins[11] proved to be valuable for the desulfurization of their thio analogues 1 although more drastic conditions (DMF, 80°, Method E) are required in the last case.

Thus terminal α,β-disubstituted and trisubstituted thiiranes produce the corresponding olefins in good yield. However, in the case of the tetrasubstituted thiirane 1e, a mixture of products is formed which includes the expected olefin and olefins resulting from the migration of the carbon-carbon double bond in 2e.
Finally, in the case of α,β-disubstituted thiiranes, we have looked at the stereochemical course of their P_2I_4 monitored desulfurization and found that the reaction is highly stereoselective and leads to an olefin possessing a stereochemistry identical to that of the starting thiirane.

TABLE

Entry	Reagents / Thiiranes [f]	Raney Nickel/Ethanol (A) -40°,7h	Raney Nickel/Ethanol (A) 90°	Li/EtNH$_2$/-15° (B)	Zn/CH$_3$COOH/130° (C)	Bu$_3$SnH/110°,1h (D)	P$_2$I$_4$/DMF/80°,1h (E)
		Yield (olefin/alkane ratio,2/3) [cis/trans olefinic ratio]					
a	1a  $C_{12}H_{25}\underset{S}{CH{-}CH_2}$	90[a](16/74)[b]	90(74/16)[b]	73(0/100)	62(100/0)	81(100/0)	97(100/0)
b	1b  $C_9H_{19}\underset{S}{\overset{CH_3}{C}{-}CH_2}$	-	90(92/8)	69(0/100)	80(100/0) [d]	83(100/0)	-
c	1c  $C_8H_{17}\underset{S}{CH{-}CHC_8H_{17}}$ Z	-	90(88/12)[30/70]	-	-	-	85(100/0) [93/7]
c'	1c'  $C_8H_{17}\underset{S}{CH{-}CHC_8H_{17}}$ E	62(92/8)[c]	90(92/8) [0/100]	70(13/87)	90(100/0) [0/100]	86(100/0) [22/78]	91(100/0) [0/100]
d	1d  $C_{10}H_{21}\underset{S}{CH{-}C(CH_3)_2}$	59(99/1)[c]	91(100/0)	80(98/2)	70(100/0) [e]	86(100/0)	67(100/0)
e	 1e	-	91(100/0) [100/0]	81(100/0) [24/76]	84(100/0) [87/13]	90(100/0) [79/21]	-

a) This reaction is over after 4h ; b) 10% 2-tetradecene is also formed ; c) The reaction is slow and requires 22h to produce the reported yield ; d) 20% 2-methyl-2-tridecene is also formed ; e) 4% 2-methyl-1-tridecene is also formed ; f) Thiiranes 1a-1d have been prepared from the corresponding epoxides according to ref.1b, for 1e see ref. 10.

REFERENCES

1. a) "Thiiranes", M. Sander, Chem. Rev. 66, 297 (1966).
   b) T.H. Chan, J.R. Finkenbine, J. Am. Chem. Soc. 94, 2880 (1972) and references cited.

2. D. Van Ende, A. Krief, Tetrahedron Lett. 2709 (1975).

3. a) A.I. Meyers, M.E. Ford, Tetrahedron Lett. 2861 (1975) ; J. Org. Chem. 41, 1736 (1976)
   b) C.R. Johnson, A. Nakanishi, N. Nakanishi, K. Tanaka, Tetrahedron Lett. 2865 (1975).

4. a) D.H.R. Barton, B.J. Willis, J. Chem. Soc., Chem. Commun. 1225 (1970) ; J. Chem. Soc., Perkin Trans I, 305 (1972).
   b) D.H.R. Barton, F.S. Guziec, I. Shahak, J. Chem. Soc., Perkin Trans.I, 1794 (1974).

5. a) R.M. Kellogg, S. Wassenaar, Tetrahedron Lett. 1987 (1970).
   b) R.M. Kellogg, M. Noteboom, J.K. Kaiser, Tetrahedron, 32, 1641 (1976).
   c) R.M. Kellogg, Tetrahedron, 32, 2165 (1976).

6. a) "Cyclic Sulfides in Organic Synthesis", E. Vedejs and G.A. Krafft, Tetrahedron, 38, 2857 (1982) and references cited.
   b) B.M. Trost, S.D. Ziman, J. Org. Chem. 38, 932 (1973).

7. A.M. Creighton, L.N. Owen, J. Chem. Soc. 1024 (1960).
   J.M. Stewart, J. Org. Chem. 29, 1655 (1964).

8. D.J. Humphreys, C.E. Newall, G.H. Phillipps, G.A. Smith, J. Chem. Soc., Perkin Trans I, 45 (1978).

9. "Modern Synthetic Reactions", H.O. House (1972), Ed. W. Benjamin Inc., see ed., p. 205. Although, non conjugated non terminal olefins are normally stable to solution of alkali metals in low molecular-weight amines , we found that 9-octadecene is reduced (> 70%) under the described conditions.

10. The authors thank Professor Kellogg for providing them with a sample of the thiirane 1e (virtually pure sym-thiirane) ^{5b}.

11. a) R. Magnane, mémoire de licence, Facultés Universitaires Notre-Dame de la Paix, Namur, June 1976.
    b) J.N. Denis, R. Magnane, M. Van Eenoo, A. Krief, Nouv. J. Chim. 3, 705 (1979).
    c) H. Suzuki, T. Fuchita, A. Iwasa, T. Mishina, Synthesis, 905 (1978).

The authors are grateful to I.R.S.I.A. (Belgium) for financial support.

(Received in UK 13 January 1983)