Tetrahedron Letters No. 48, pp 4223 - 4226, 1977. Pergamon Press. Printed in Great Britain.

A NEW 1,2-ELIMINATION REACTION WITH A RADICAL MECHANISM

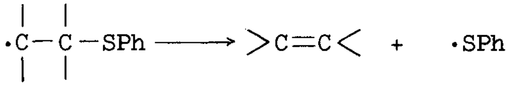
Basil Lythgoe* and Ian Waterhouse

Department of Organic Chemistry, The University, Leeds LS2 9JT

(Received in UK 23 September 1977; accepted for publication 6 October 1977)

We here report a new 1,2-elimination reaction, which proceeds by a radical mechanism, has interesting stereochemical characteristics, and promises to have useful applications in synthetic work.

The reaction was first observed during an attempt[1] to prepare the sulphide (3) from the hydroxy sulphide (1) by reaction[2] of the S-methyldithiocarbonate (2) with tri-n-butyltin hydride. The desired compound was not formed; instead, both substituent groups were smoothly eliminated giving (ca. 65%) the olefin (4). The same kind of reaction also took place between tributyltin hydride and the chloro-sulphide (8), giving (87%) cholest-2-ene (9). It was clear that both eliminations were initiated by the hydride with the removal either of a chlorine atom[3] or of the S-methyldithiocarbonate radical,[2] so generating an intermediate radical which then lost ·SPh radical to give the olefin:

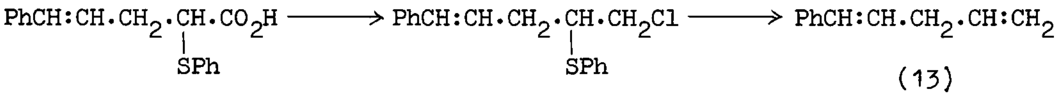


$$\cdot\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-SPh \longrightarrow \rangle C{=}C\langle \; + \; \cdot SPh$$

The postulated intermediate, the detailed structure and length of life of which remains as a problem for further study, is identical with, or closely related to, that formed in the first step of the radical addition of thiophenol to an olefin, a step known[4] to be reversible.

Since ketones can frequently be regioselectively phenylsulphenylated,[5] and then reduced to give 1-hydroxy-2-sulphides, the new reaction affords a regioselective method of converting a ketone to an olefin. For example, cholestan-3-one (5) was converted *via* the sulphide (7) into a mixture (*ca*. 1:2) of the alcohols (6) and (10). Conversion into the corresponding mixture of *S*-methyldithiocarbonates and treatment with tributyltin hydride gave (82%) the olefin (9). Its formation in this way, as well as from the diaxial chloro-sulphide (8), shows that the new reaction is sterically undemanding, a feature which is frequently advantageous in work with cyclic compounds.

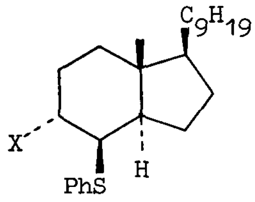
A second application depends on the fact that various synthetic routes, e.g. the reaction[6] of phenylthiomethyl-lithium with carbonyl compounds, and the reduction of 2-phenylthioesters and 2-phenylthioketones, lead to 1-hydroxy-2-sulphides, from which by reaction with e.g. thionyl chloride, 1-chloro-2-sulphides can often be easily obtained. A new way of building up olefins from smaller fragments is thus opened; for example, the α-phenylthioacid (11), made[7] from cinnamyl chloride and α-phenylthioacetic acid, was converted into the chloro-sulphide (12) and thence into phenylpenta-1,4-diene (13):



$$\mathrm{PhCH{:}CH.CH_2.\underset{\substack{|\\ SPh}}{C}H.CO_2H} \longrightarrow \mathrm{PhCH{:}CH.CH_2.\underset{\substack{|\\ SPh}}{C}H.CH_2Cl} \longrightarrow \mathrm{PhCH{:}CH.CH_2.CH{:}CH_2}$$

(11) (12) (13)

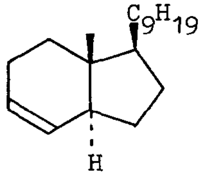
We have further found that β-hydroxy sulphones will undergo the new elimination as effectively as β-hydroxy sulphides, so that internal olefins can be obtained by synthesis. Thus metallation of n-octyl phenyl sulphone with ethyl magnesium bromide, and reaction[8] with n-heptaldehyde gave the diastereoisomeric β-hydroxy sulphones (14), which were treated with butyl-lithium and then with thiobenzoyl chloride[9] to obtain the thiobenzoates (15). Reaction with tributyltin hydride gave *trans*-pentadec-7-ene (16), essentially free (g.l.c.; n.m.r.) from the *cis*-isomer, in *ca*. 61% yield from the starting



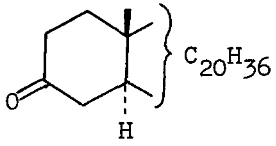
(1) X = HO

(2) X = $\mathrm{MeS{\cdot}\underset{\overset{\|}{S}}{C}{\cdot}O}$

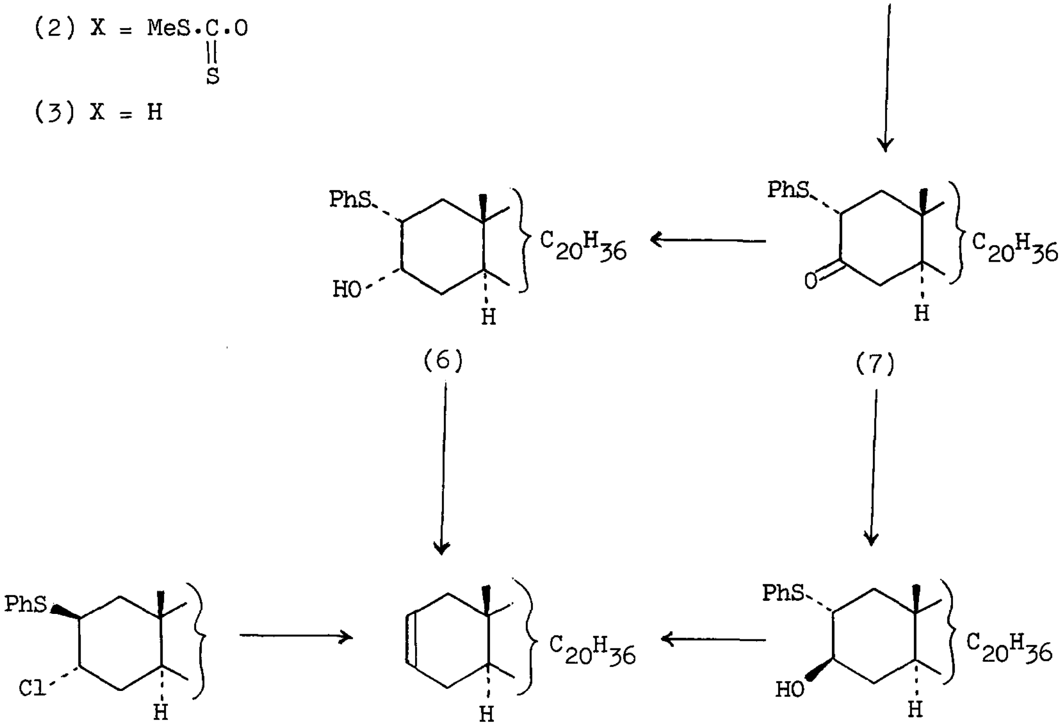
(3) X = H



(4)



(5)



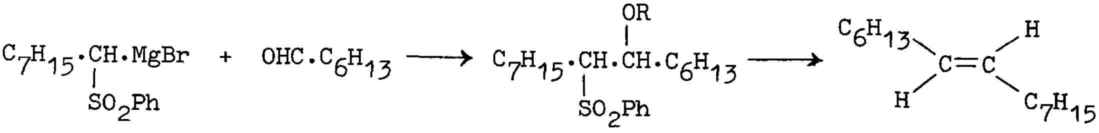
(6)

(7)

(8)

(9)

(10)



(14) R = H

(15) R = CPh=S

(16)

components. Although other methods[10] of achieving a similar result are available, the simplicity of the present method may lead to its adoption for some *trans*-disubstituted olefins.[11]

References

1. Experiment by Mr. S. Ruston.
2. D. H. R. Barton and S. W. McCombie, *J.C.S. Perkin I*, 1975, 1574.
3. L. W. Menapace and H. G. Kuivila, *J.Amer.Chem.Soc.*, 1964, *86*, 3047.
4. C. Walling, Free Radicals in Solution, Wiley, New York, 1957, Chapter 7.
5. D. Seebach and M. Teschner, *Chem.Ber.*, 1976, *109*, 1601; B. M. Trost, T. M. Salzmann, and M. Kuroi, *J.Amer.Chem.Soc.*, 1976, *98*, 4887.
6. (a) E. J. Corey and D. Seebach, *J.Org.Chem.*, 1966, *31*, 4097.
   (b) R. L. Sowerby and R. M. Coates, *J.Amer.Chem.Soc.*, 1972, *94*, 4758.
7. Method of K. Iwai, M. Kawai, H. Kosugi, and H. Uda, *Chem.Letters*, 1974, 385.
8. Method of L. Field, *J.Amer.Chem.Soc.*, 1952, *74*, 3919.
9. H. Staudinger and J. Siegwart, *Helv.Chim.Acta*, 1920, *3*, 824.
10. e.g. M. Schlosser and K. F. Christman, *Annalen*, 1967, *708*, 1.
11. Methods for the formation of olefins from β-hydroxy sulphides have been reported by I. Kuwajuma, S. Sato, and Y. Kurata, *Tetrahedron Letters*, 1972, 737; by Y. Watanabe, M. Shiono, and T. Mukaiyama, *Chem.Letters*, 1975, 871; and in ref. 6b. Methods for the formation of olefins from β-hydroxy sulphones have been reported by M. Julia and J-M. Paris, *Tetrahedron Letters*, 1973, 4833. The stereochemical outcome of these various methods has not yet been disclosed.