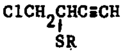
**Tetrahedron Letters No.19, pp. 2179-2182, 1966. Pergamon Press Ltd.
Printed in Great Britain.**

THE STRUCTURE OF SULFENYL CHLORIDE-VINYLACETYLENE ADDUCTS

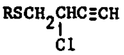
P. E. Butler and W. H. Mueller
Analytical Research Division and Central Basic Research Laboratory
Esso Research and Engineering Company
Linden, New Jersey, U.S.A.

(Received 3 February 1966; in revised form 16 March 1966)

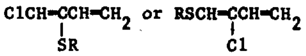
The addition of sulfenyl chlorides to vinylacetylene has been reported(1) to give exclusive anti-Markownikov products of structure I. Based on our work with the addition of sulfenyl chlorides to unsaturated


$\mathrm{ClCH_2\underset{\underset{\displaystyle SR}{|}}{C}HC{\equiv}CH}$

I


$\mathrm{RSCH_2\underset{\underset{\displaystyle Cl}{|}}{C}HC{\equiv}CH}$

II


$\mathrm{ClCH{=}\underset{\underset{\displaystyle SR}{|}}{C}CH{=}CH_2}$ or $\mathrm{RSCH{=}\underset{\underset{\displaystyle Cl}{|}}{C}CH{=}CH_2}$

III

R = ethyl, propyl, phenyl

systems(2) we believed these assignments to be anomalous. On the basis of further work in this laboratory, we wish to propose the reverse orientation, structure II, for these adducts. This assignment is consistent with the previously reported(3) Markownikov addition of sulfenyl chlorides to terminal olefins and is now part of a consistent picture in the literature.

The addition of methanesulfenyl chloride to vinylacetylene in methylene chloride at -20°C gave a product containing 8% I, 81% II, and 8% III as determined by NMR and IR analysis(4).

The high resolution IR spectrum of the mixture was similar to that reported(1) and contained intense bands at 3298 cm^{-1} ($-C\equiv C\underline{H}$) and 2120 cm^{-1} (terminal $C\equiv C$) characteristic of both the major isomer (II) and the reverse addition product (I). The NMR spectrum of the major isomer, II, displays a sharp, 3-proton singlet at 2.23 ppm (relative to internal TMS) for the S-methyl; a double triplet at 4.66 ppm for the methine proton adjacent to chlorine ($RS\overset{a}{C}H_2\overset{b}{C}HCl\overset{c}{C\equiv CH}$), $J_{ab} = 7.1$ cps, $J_{bc} = 2.3$ cps; a 2-proton doublet at 3.02 ppm for the SCH_2 group; and a 1-proton doublet at 2.75 ppm for the acetylenic proton which is solvent dependent and can be shifted downfield by admixture with pyridine.

The NMR spectrum of I, the isomer derived from reverse addition to the olefinic double bond, had resonance signals at 2.23 ppm for the SCH_3 group; a 3-proton multiplet (A_2B) centered at 3.73 ppm for the coincident methylene ($ClCH_2-$) and methine ($\supset CHS$) groups; and a doublet at 2.70 ppm ($J = 2.23$ cps) for the acetylenic proton.

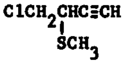
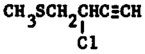
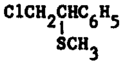
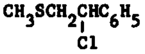
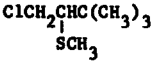
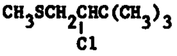
The IR spectrum of the mixture also contained bands characteristic of the conjugated product such as III which was not previously identified(1). These were at 3095 and 3020 cm^{-1} ($=CH$ str.); 1615 cm^{-1} (conj. $C=C$); 995, 922 and 805 cm^{-1} (CH and CH_2 o.o.p. def.). No evidence for the presence of an allenic structure, due to 1,4 addition, was found. NMR peaks in the olefin region characteristic of III were found at 5.5-7.2 ppm.

Considerable amounts of spectral data on similar compounds(2) support strongly our assignment of the methylene and methine groups which allows the assignment of II as the major product.

Table I is a summary of the chemical shifts of these protons in several representative compounds studied in this laboratory.

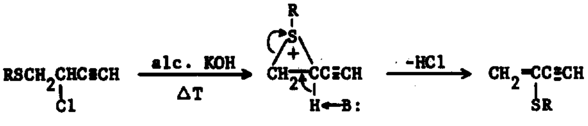
TABLE I

Chemical Shifts Of Protons Alpha To Chlorine And Sulfur(a)

RSCl Adduct	$>$CHCl	$-CH_2Cl$	$>$CHS-	$-CH_2S-$
 $ClCH_2CH(SCH_3)C\equiv CH$		----- 3.73(b) -----		
 $CH_3SCH_2CH(Cl)C\equiv CH$	4.66			3.02
 $ClCH_2CH(SCH_3)C_6H_5$		------ 3.83(b)-----		
 $CH_3SCH_2CH(Cl)C_6H_5$	4.91			2.93(c) 3.19
 $ClCH_2CH(SCH_3)C(CH_3)_3$		3.54(c) 3.94	2.43	
 $CH_3SCH_2CH(Cl)C(CH_3)_3$	3.82			2.61(c) 3.01

(a) Chemical shifts in ppm from internal TMS. (b) These protons are nearly coincident and form an ABC system approximating a singlet. (c) These protons form the AB part of an ABX system; the chemical shifts are approximated from a first order analysis of the pair of overlapping quartets.

These NMR assignments appear to have been reversed by the Russian workers(1) in an attempt to explain the results of their dehydrochlorination experiments in which IV was obtained as the major product. Although the NMR spectrum reported for the elimination product is consistent with IV, we believe its formation may be explained by the following mechanism:



II IV

Thus the abstraction of the labile propargylic proton rather than the methylenic proton in the episulfonium ion intermediate leads to IV.

REFERENCES

1. S. I. Radchenko and A. A. Petrov, Zhurnal Organicheskoi Khimii 1, 47 (1965). English Trans; J. Org. Chem. of USSR 1, 45 (1965).
2. To be published, P. E. Butler and W. H. Mueller.
3. R. A. Turner and R. Connor, J. Am. Chem. Soc. 69, 1009 (1947); N. Kharasch and C. M. Buess, ibid. 71, 2724 (1949). R. C. Fuson, C. C. Price, and D. M. Burness, J. Org. Chem. 11, 475 (1946); G. Yu. Épshtein, I. A. Usov, and S. Z. Ivin, J. Gen. Chem. USSR 34, 2362 (1964).
4. The distilled material (bp 85°/9 mm) gave the correct elemental composition for a monoadduct mixture.