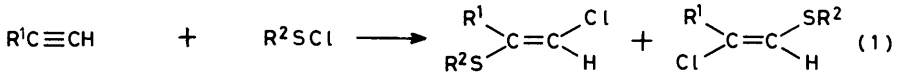
Control of Regioselectivity in the Addition of Sulphenyl Chlorides to 3,3-Dimethylbutyne (t-Butylacetylene) as a Method for Differential Functionalization of Triple Bonds

By **Giuseppe Capozzi** * and **Corrado Caristi**, Istituto di Chimica Organica, Università di Messina, 98100 Messina, Italy
Vittorio Lucchini * and **Giorgio Modena**, Centro Meccanismi di Reazioni Organiche del CNR, Istituto di Chimica Organica, Università di Padova, 35100 Padova, Italy

Methanesulphenyl chloride and toluene-*p*-sulphenyl chloride react with 3,3-dimethylbutyne to give regio- and stereo-specifically (*E*)-1-chloro-3,3-dimethyl-2-methylthiobut-1-ene (3a) and (*E*)-1-chloro-3,3-dimethyl-2-*p*-tolylthiobut-1-ene (3b). *trans–cis*-Acid-catalysed isomerization of (3a) and (3b) may occur. Sulphenyl chlorides catalyse the conversion of (3a) and (3b) into (*Z*)-2-chloro-3,3-dimethyl-1-methylthiobutene (4a) and (*Z*)-2-chloro-3,3-dimethyl-1-*p*-tolylthiobutene (4b) respectively. The hydrolysis of compounds (3) and (4) affords 1-chloro-3,3-dimethylbutan-2-one (5) and 2-chloro-3,3-dimethylbutanal (6).

THE addition of sulphenyl chlorides to terminal alkynes gives 1 : 1 adducts, exclusively with the *trans*-configuration and with a marked preference for *anti*-Markownikov orientation [equation (1)].[1-3] However the regio- and stereo-selectivity may be masked by acid-catalysed or light-induced isomerization processes.[4,5]



(2) R^1 = Bu^t (1) a; R^2 = Me (*E*)-AM (*E*)-M
b; R^2 = *p*-MeC_6H_4
AM = *anti*-Markownikov
M = Markownikov

We report here a reinvestigation of the addition of methanesulphenyl chloride (1a) and toluene-*p*-sulphenyl chloride (1b) to 3,3-dimethylbutyne (2) (t-butylacetylene).[5,6] A new type of conversion of the AM adducts into the M isomers, catalysed by the sulphenyl chloride itself, was observed. The hydrolysis of the AM and M vinyl chlorides was also studied; they afford in fair yields 1-chloro-3,3-dimethylbutan-2-one and 2-chloro-3,3-dimethylbutanal respectively.

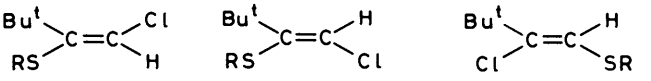
RESULTS

Addition of Methanesulphenyl Chloride (1a) *and Toluene-p-sulphenyl Chloride* (1b) *to t-Butylacetylene* (2).—The additions of the sulphenyl chlorides (1) to the alkyne (2) were carried out in chloroform or carbon tetrachloride at room temperature and were monitored by ^1H n.m.r. spectroscopy.

When methanesulphenyl chloride (1a) was added in chloroform to an excess of t-butylacetylene, the (*E*)-AM adduct (*E*)-(3a) was initially observed together with the (*Z*)-AM adduct (*Z*)-(3a) in a 9 : 1 molar ratio; (*E*)-(3a) isomerizes completely to (*Z*)-(3a) in about 30 min. It seems plausible therefore that the *E*-isomer is the primary product; the conversion into the more stable *Z*-isomer is probably due to the presence of trace amounts of acid in the reaction mixture.[4]

Under the same conditions, toluene-*p*-sulphenyl chloride (1b) behaves analogously; in this case, however, it is possible to observe initially the AM adduct (*E*)-(3b) as the sole product. The conversion into the (*Z*)-(3b) isomer is much slower: 10% conversion after 12 h and complete conversion in about 5 days.

Different behaviour was observed when even a slight excess of the sulphenyl chlorides (1a) or (1b) was added in chloroform to t-butylacetylene. Three systems of resonances could be recognized, which may be attributed to the (*E*)- and (*Z*)-AM adducts and to the (*Z*)-M adduct. With a slight (≤5%) excess of toluene-*p*-sulphenyl chloride (1b) it was still possible to observe the primary adduct (*E*)-(3b) as the sole product; however after 12 h all three isomers were detectable in various amounts. Complete conversion of compounds (*E*)- and (*Z*)-(3b) into the M isomer (*Z*)-(4b) was observed in about 3 days, with the (*E*)-(3b) isomer disappearing more rapidly. The isomerization process was accelerated with a greater excess of the sulphenyl chloride (1b), to the point that even in the early stages all isomers were observed; complete conversion into the *Z*-(4b) isomer took about 1 day.

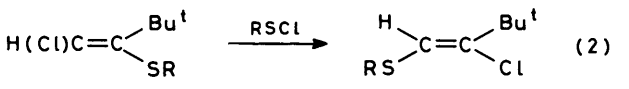


(*E*)-(3) (*Z*)-(3) (*Z*)-(4)
a; R = Me
b; R = *p*-MeC_6H_4

With methanesulphenyl chloride (1a) a similar but much faster isomerization was observed, and, regardless of the excess of the chloride, all isomers (*E*)-(3a), (*Z*)-(3a), and (*Z*)-(4a) were initially detected. Complete isomerization to the M isomer (*Z*)-(4a) took about 1 day.

When the additions were carried out in carbon tetrachloride, only the resonances of the (*E*)-AM adducts (*E*)-(3a) and (*E*)-(3b) were observed, irrespective of the molar proportions of the reagents; these species remain unaltered for a long time.

Reaction of the AM *Adducts in Chloroform with Sulphenyl Chlorides.*—When the AM adducts (3a) or (3b), either conformationally pure or as (*E*)-(*Z*) mixtures, were treated in chloroform with < 1 mol equiv. of the sulphenyl chlorides (1a) or (1b), quantitative conversion into the (*Z*)-M adducts (4a) or (4b), respectively, was observed [equation (2)]. Characteristic features of the isomerization process are: (i)

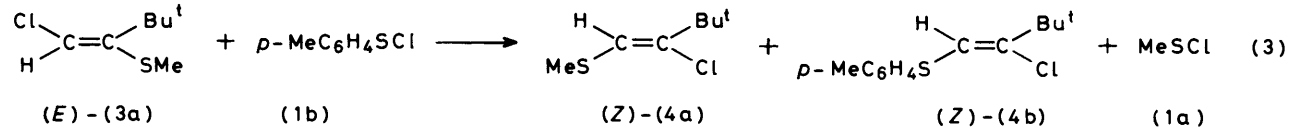


(3) (*Z*)-(4) (2)

a; R = Me
b; R = *p*-MeC$_6$H$_4$

5% of the sulphenyl chloride is sufficient for complete transformation, although larger quantities cause a faster reaction; (ii) in the reaction of pure (*E*)-(3) the intermediate formation of (*Z*)-(3) was detected.

A better insight into the mechanism of the isomerizations (2) was gained from examination of the products of the reaction between the methylthiovinyl chloride (*E*)-(3a) and an equimolar amount of toluene-*p*-sulphenyl chloride (1b) [equation (3)]. Compound (*Z*)-(4b) was the major product



(*E*)-(3a) (1b) (*Z*)-(4a) (*Z*)-(4b) (1a) (3)

(*ca.* 80%), with (*Z*)-(4a) as the minor component (*ca.* 10%); methanesulphenyl chloride (1a) was also formed. Complete transformation to the (*Z*)-(4b) isomer may be achieved by removing (1a) and the solvent under reduced pressure and dissolving the residue in pure solvent.

Hydrolysis of the Adducts (3) *and* (4) *with Trifluoroacetic Acid.*—The AM adducts (3), in either conformation, when dissolved in trifluoroacetic acid, reacted exothermally in a few minutes to give 1-chloro-3,3-dimethylbutan-2-one (5)

TABLE 1

^{1}H N.m.r. data for the AM H(Cl)C=C(XR)Bu^t and M H(RX)C=C(Cl)Bu^t vinyl sulphides and sulphones

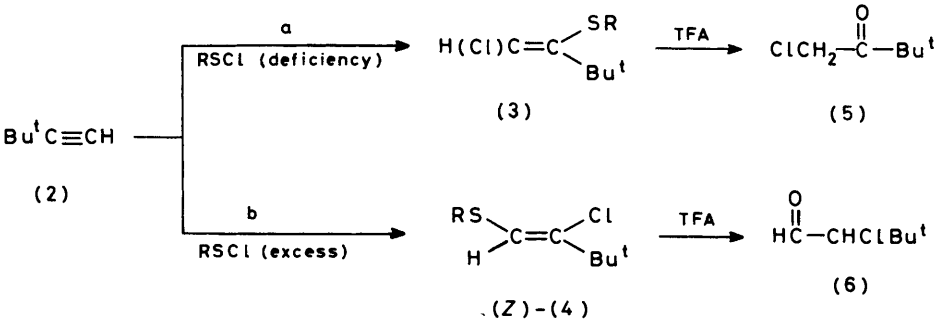
R = Me	X	Solvent	H	Me	Bu^t
(*E*)-(3a)	S	$CDCl_3$	5.51	2.21 [a]	1.36
		CCl_4	5.43	2.20 [a]	1.34
(*Z*)-(3a)	S	$CDCl_3$	6.43	2.31	1.19
(*Z*)-(4a)	S	$CDCl_3$	5.96	2.33	1.18
(*E*)-(7a)	SO_2	$CDCl_3$	7.58	3.06	1.51
(*Z*)-(7a)	SO_2	$CDCl_3$	6.84	3.12	1.37
(*Z*)-(8a)	SO_2	$CDCl_3$	6.57	3.13	1.27

R = *p*-MeC$_6$H$_4$	X	Solvent	ArH	H	Me	Bu^t
(*E*)-(3b)	S	$CDCl_3$	7.20—7.16	6.15	2.32	1.33
		CCl_4	7.14—7.10	6.12	2.33	1.32
(*Z*)-(3b)	S	$CDCl_3$	7.11—7.07	6.69	2.29	1.23
(*Z*)-(4b)	S	$CDCl_3$	7.47—7.02	6.24	2.32	1.21
(*E*)-(7b)	SO_2	$CDCl_3$	7.80—7.23	7.76	2.44	1.31
(*Z*)-(7b)	SO_2	$CDCl_3$	7.97—7.26	6.68	2.44	1.18
(*Z*)-(8b)	SO_2	$CDCl_3$	8.00—7.28	6.69	2.45	1.18

[a] ^5J(HCSC=CH) 0.45 Hz.

(8b) with *m*-chloroperbenzoic acid and reduction to the alkyl sulphones (9b) and (10b) (Scheme 2).[6] We have applied the same procedure to the methylthio-adducts (3a) and (4a). N.m.r. parameters for the vinyl sulphones (*E*)-(7), (*Z*)-(7), and (*Z*)-(8) are also given in Table 1. The alkyl sulphones (9) and (10) may be distinguished unambiguously on the basis of the alkyl n.m.r. signals, thus allowing the assignment of the correct regiochemistry to the primary adducts (n.m.r. data are in the Experimental section).

The stereochemistry of the methylthio-adducts (3a) and (4a) was determined by measuring the nuclear Overhauser effect (n.O.e.) enhancements [7] of the vinyl hydrogen resonance upon irradiation of the methyl or t-butyl peaks.



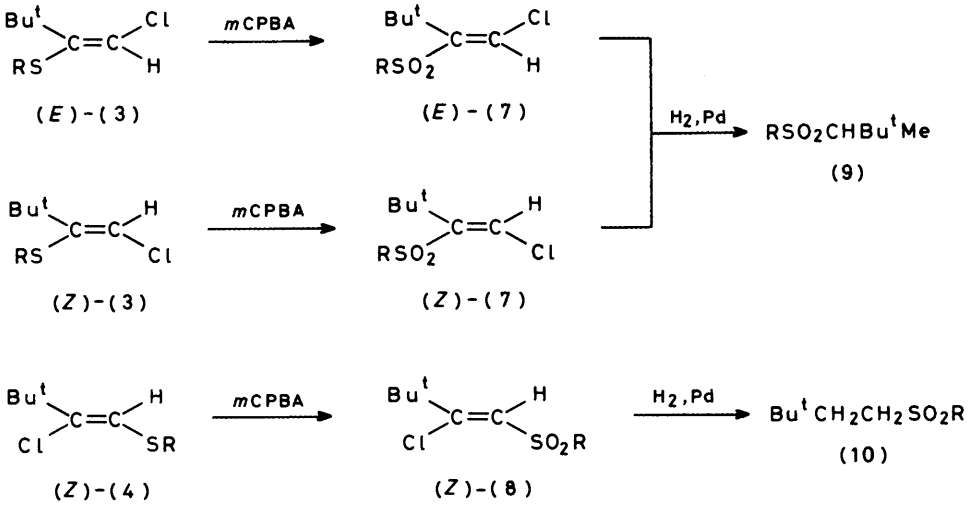
SCHEME 1 TFA = CF_3CO_2H

(Scheme 1). The reaction of the *M* adducts (*Z*)-(4) was much slower; only after 7 h was the vinyl chloride absent, and 2-chloro-3,3-dimethylbutanal (6) was obtained in high yield.

Determination of the Configuration of the β-*Thiovinyl Chlorides* (E)-(3), (Z)-(3), *and* (Z)-(4).—The ^{1}H n.m.r. parameters of the title compounds (3) and (4) are reported in Table 1. The AM or M regiochemistry of the *p*-tolylthio-adducts (3b) and (4b) has been determined previously by oxidation to the corresponding vinyl sulphones (7b) and

Average results of three determinations are in Table 2. In addition, n.O.e. measurements can confirm the regio-orientation determined by the chemical procedure of Scheme 2.

The assignment of stereochemistry to *p*-tolylthio AM adducts (*E*)-(3b) and (*Z*)-(3b) is based on literature data.[6] With regard to the M adduct (*Z*)-(4b), irradiation of the t-butyl resonance causes an n.O.e. enhancement of the vinyl hydrogen resonances; the compound must be attributed the *Z*-configuration, in contrast with the literature assignment.[6]



SCHEME 2 a; R = Me b; R = *p*-MeC_6H_4 *m*CPBA = *m*-$ClC_6H_4CO_3H$

The configuration of the (*Z*)-AM adducts (*Z*)-(3a) and (*Z*)-(3b) was confirmed by crystal structure determinations of the corresponding sulphones (*Z*)-(7a) and (*Z*)-(7b).[8]

TABLE 2

N.O.e. enhancements of the vinyl hydrogen resonances in the vinyl chlorides (*E*)-(3a), (*Z*)-(3a), (*Z*)-(4a), and (*Z*)-(4b) upon irradiation of selected resonances. Average of three measurements; standard deviations in parentheses

		Nuclei irradiated	
	Solvent	Me	Bu^t
(*E*)-(3a)	CCl_4	1.21(4)	1.01(3)
(*Z*)-(3a)	$CDCl_3$	0.98(3)	1.24(4)
(*Z*)-(4a)	$CDCl_3$	1.12(2)	1.28(4)
(*Z*)-(4b)	$CDCl_3$	—	1.38(1)

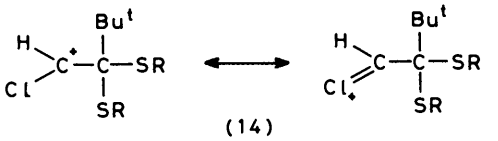
DISCUSSION

The results just reported indicate that the additions of methanesulphenyl chloride (1a) and toluene-*p*-sulphenyl chloride (1b) to t-butylacetylene (2) give, both in chloroform and carbon tetrachloride, the stereospecific *anti* and regiospecific *anti*-Markownikov adducts as the sole primary products. Our results parallel those reported for the addition of other sulphenyl chlorides in different solvents.[5,6]

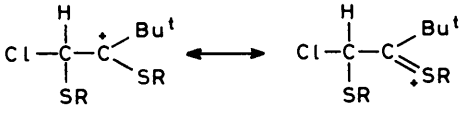
The *anti*-mode of addition may be rationalized in terms of a mechanism involving in-plane attack of chloride ion on the ring carbon atoms of intermediate thiirenium ions.[5,9,10] The intermediacy of thiirenium ions in these addition reactions has been amply proved.[1] The in-plane attack implies also, for steric and inductive reasons, a preference for AM orientation.[10] In the case of the addition to t-butylacetylene this orientation is exclusive; in fact the other observed isomers, the (*Z*)-AM and the (*Z*)-M adducts (*Z*)-(3) and (*Z*)-(4), are secondary products derived from the (*E*)-AM adduct (*E*)-(3).

trans–cis-Isomerization is possible, with the acetylene present in excess, only in chloroform, and the process is markedly faster for the methylthio-compound. The process may be attributed to the presence of traces of hydrogen chloride formed from the decomposition of the sulphenyl chloride [11] (which is more likely in the case of methanesulphenyl chloride). The greater stability of the *cis*- over the *trans*-configuration of vinyl sulphides with an electronegative substituent in the β-position and, more generally, in vinyl compounds with electronegative substituents in vicinal positions, has been reported [12] and has been given a theoretical justification.[13]

The AM to M isomerization is induced by the sulphenyl chloride, when in excess or when added to the AM adducts in either configuration. This fact, and the scrambling reaction (3), suggest that the isomerization proceeds through addition of sulphenyl chloride across the double bond of (*E*)-(3), with formation of the double-addition saturated compounds (11) and (12), followed by elimination, as outlined in Scheme 3. The intermediate may be either the thiiranium ion (13) or the AM α-chloro and the M β-chloro open cations (14) and (15), stabilized by resonance.



(14)



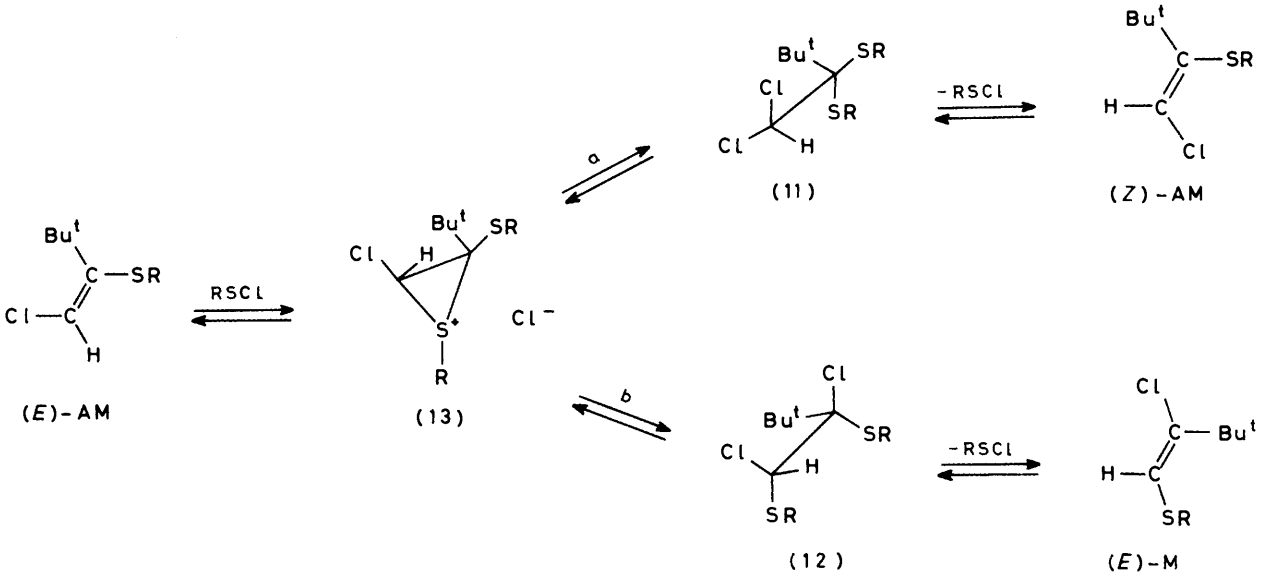
(15)

Scheme 3 shows that only the M addition brings about the conversion into the M alkene, irrespective of the nature of the intermediate. The AM addition can cause only the isomerization to the (*Z*)-AM adduct. (This mechanism can also be proposed, as an alternative to the acid catalysis, for the *trans–cis*-isomerization.)

Similar considerations hold for the addition–elimination mechanisms for the other isomers, and the general

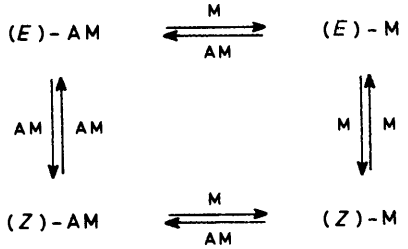
Scheme 4 can be proposed (diagonal crossings are possible with open intermediates).

Of the four possible isomers, the (*E*)-M isomer has been neither detected nor isolated. Eventually, total conversion into the (*Z*)-M isomer is observed. We shall not try to offer here a rationale for the greater thermodynamic stability of the (*Z*)-M isomer compared with the (*Z*)-AM isomer.



SCHEME 3 a, *anti*-Markownikov addition b, Markownikov addition

The controllable isomerization to the M adducts offers an easy method for differential functionalization of t-butylacetylene. Depending on the relative proportions of the alkyne and the sulphenyl chlorides, the AM (either *E* or *Z*) or the M vinyl sulphides can be obtained exclusively as final products.



SCHEME 4

From the AM adducts the α-chloromethyl ketone (5) is obtained with trifluoroacetic acid (route a in Scheme 1). This route corresponds to the usual M functionalization of terminal alkynes. When applied to terminal alkynes with primary or secondary alkyl substituents, our procedure might present, in comparison with the classical halogenation of ketones,[14] the distinct advantage of total regioselectivity.

Of greater synthetic interest is the AM functionalization of the alkyne (2), by treatment of the M adduct with trifluoroacetic acid (route b in Scheme 1), which leads to the α-chloroaldehyde (6). The AM functionalization of terminal alkynes is not usually accomplished easily.[15]

EXPERIMENTAL

3,3-Dimethylbutyne (2) (t-butylacetylene) and 3-chloroperbenzoic acid are commercial products. Methanesulphenyl chloride (1a) [16] and toluene-*p*-sulphenyl chloride (1b) [17] were prepared by literature methods. ^{1}H N.m.r. spectra were recorded on a Bruker WP-60 instrument. Samples for n.O.e. measurements were prepared according to suggested procedures.[7]

Reaction of the Sulphenyl Chlorides (1a) *and* (1b) *with t-Butylacetylene* (2).—(a) *With excess of t-butylacetylene.* The reactions were carried out in carbon tetrachloride or chloroform following the published procedure.[6] In carbon tetrachloride only the (*E*)-AM adducts (E)-1-chloro-3,3-dimethyl-2-methylthiobutene-1-ene (*E*)-(3a), and (*E*)-1-chloro-3,3-dimethyl-2-*p*-tolylthiobutene-1-ene, (*E*)-(3b), were isolated, in >90% yields. When the addition was carried out in chloroform, a mixture of *E*- and Z-isomers (*E*)-(3a) and (*Z*)-(3a), or (*E*)-(3b) and (*Z*)-(3b), was obtained, in different ratios depending on reaction time. Overall yields were >90%.

(b) *With excess of sulphenyl chloride.* When t-butylacetylene was treated in chloroform with a 25% excess of the sulphenyl chlorides (1a) or (1b) for 1 day at room temperature, (*Z*)-2-chloro-3,3-dimethyl-1-methylthiobut-1-ene, (*Z*)-(4a) and (*Z*)-2-chloro-3,3-dimethyl-1-*p*-tolylthio-but-1-ene (*Z*)-(4b) products were isolated in >80% yields.

All these adducts were purified (but not separated) by vacuum distillation (1 mmHg) and characterized by n.m.r. spectroscopy. The *Z*- and *E*-isomers were separated as their sulphonyl derivatives.

Hydrolysis of the Adducts (3) and (4) *with Trifluoroacetic Acid.*—The AM adducts (3a) or (3b) (10 mmol) (either configuration) were dissolved in trifluoroacetic acid (30 ml) at 0 °C. After 1 h methylene dichloride (60 ml) was added and the solution washed with water and sodium carbonate in water to neutrality, and dried ($CaCl_2$). The solvent was

removed under reduced pressure at room temperature and the residue distilled *in vacuo*. 1-Chloro-3,3-dimethylbutan-2-one (b.p. 50—52 °C at 15 mmHg) was obtained in 60% yield and was identified by comparison with an authentic sample.[18,19]

The M adduct (*Z*)-(4a) or (*Z*)-(4b) (3.5 mmol) was dissolved in trifluoroacetic acid (10 ml) at 0 °C and the solution kept at room temperature for 1 day. The solution was then poured into diethyl ether (100 ml), potassium carbonate (20 g) added, and the mixture stirred for 3 h, filtered, and dried ($CaCl_2$). Evaporation followed by distillation of the residue *in vacuo* gave 2-chloro-3,3-dimethylbutanal (6) (b.p. 40—42 °C at 15 mmHg) in 75% yield, the n.m.r. parameters for which were identical with those reported for a sample prepared by a different route.[19]

Oxidation of the Vinyl Sulphides (E)-(3), (Z)-(3), *and* (Z)-(4) *to the Sulphones* (E)-(7), (Z)-(7), *and* (Z)-(8).—Following the reported procedure,[6] the title sulphides (3) and (4), either conformationally pure or as a stereoisomeric mixture, were oxidized with 3-chloroperbenzoic acid in dichloromethane to give the corresponding sulphones. The *p*-tolyl sulphones (*E*)-(7b), (*Z*)-(7b), and (*Z*)-(8b), recrystallized from light petroleum, showed characteristics identical to those reported.[6] The methyl sulphones were separated and purified by chromatography on silica gel (eluant: ether–light petroleum, 1 : 1). (E)-1-*Chloro*-3,3-*dimethyl*-2-*methylsulphonylbut*-1-*ene* (*E*)-(7a) was purified by bulb-to-bulb distillation (1 mmHg, oil bath at 180 °C); its *Z-isomer* (*Z*)-(7a) had m.p. 85—86 °C (from light petroleum); (Z)-2-*chloro*-3,3-*dimethyl*-1-*methylsulphonylbut*-1-*ene* (*Z*)-(8a) had m.p. 43—44 °C (from light petroleum); elemental analyses: (*E*)-(7a) (Found: C, 42.7; H, 6.45; Cl, 18.2; S, 16.2%); (*Z*)-(7a) (Found: C, 42.55; H, 6.6; Cl, 18.2; S, 16.5%); (*Z*)-(8a) (Found: C, 42.5; H, 6.7; Cl, 17.9; S, 16.2%); $C_7H_{13}ClO_2S$ requires C, 42.75; H, 6.6; Cl, 18.1; S, 16.3%.

Reduction of the Vinyl Sulphones (E)-(7), (Z)-(7), *and* (Z)-(8).—Hydrogenation of the AM vinyl sulphones (*E*)-(7a) and (*Z*)-(7a) over 5% palladium on charcoal in ethanol (3.5 atm H_2 for 4 h at room temperature) yielded the same *methyl* 1,2,2-*trimethylpropyl sulphone* (9a), 88% yield, bulb-to-bulb distillation (1 mmHg, oil bath at 130 °C); ^{1}H n.m.r., δ($CDCl_3$): 1.20 (Bu^t), 2.88 ($MeSO_2$), 2.88 (q), and 1.43 (d) (C*HMe*, ^3J 7.3 Hz) (Found: C, 49.7; H, 9.5; S, 18.8; $C_7H_{16}O_2S$ requires C, 51.2; H, 9.8; S, 19.5%). Under the same conditions hydrogenation of the M vinyl sulphone (*Z*)-(8a) gave 3,3-*dimethylbutyl methyl sulphone* (10a), 90% yield, m.p. 64—65 °C (from light petroleum); ^{1}H n.m.r., δ($CDCl_3$): 0.96 (Bu^t), 2.90 ($MeSO_2$), and 3.00 and 1.72 (complex m, AA'BB', CH_2CH_2) (Found: C, 50.6; H, 9.5; S, 20.0%).

Hydrogenation of the *p*-tolyl sulphones (*E*)-(7b), (*Z*)-(7b), and (*Z*)-(8b) gave the alkyl sulphones (9b), m.p. 67—68 °C (from MeOH), and (10b), m.p. 97—98 °C (from MeOH),[6] which were characterized on the basis of their ^{1}H n.m.r. data: ^{1}H n.m.r., δ($CDCl_3$): (9b) 1.21 (Bu^t), 1.15 (d) and 2.94 (q) (C*HMe*, ^3J 7.1 Hz), 2.44 (Ar*Me*), and 7.25—7.84 (ArH); (10b) 0.86 (Bu^t), 1.58 and 3.05 (complex m, AA'BB', CH_2CH_2), 2.46 (Ar*Me*), and 7.27—7.87 (ArH).

This work has been carried out with financial assistance from ' Progetto Finalizzato del CNR per la Chimica Fine e Secondaria '.

[2/219 *Received*, 8*th February*, 1982]

REFERENCES

[1] G. Capozzi, V. Lucchini, and G. Modena, *Rev. Chem. Interm.*, 1979, **2**, 437.
[2] G. Modena and G. Scorrano, *Mechanism React. Sulfur Comp.*, 1968, **3**, 115.
[3] G. H. Schmid, ' The Chemistry of the Carbon–carbon Triple Bond,' Part 1, ed. S. Patai, Wiley, Chichester, 1978, p. 275.
[4] V. Caló, G. Modena, and G. Scorrano, *J. Chem. Soc. C*, 1968, 1344.
[5] G. H. Schmid, A. Modro, F. Lenz, D. G. Garratt, and K. Yates, *J. Org. Chem.*, 1976, **41**, 2331.
[6] V. Caló, G. Scorrano, and G. Modena, *J. Org. Chem.*, 1969, **34**, 2020.
[7] J. H. Noggle and R. G. Schirmer, ' The Nuclear Overhauser Effect. Chemical Applications,' Academic Press, New York, 1971.
[8] G. Capozzi, G. Valle, and A. Pasquetto, *Cryst. Struct. Commun.*, 1981, **10**, 477.
[9] Z. Rappoport, *Acc. Chem. Res.*, 1981, **14**, 7.
[10] V. Lucchini, G. Modena, G. Valle, and G. Capozzi, *J. Org. Chem.*, 1981, **46**, 4720.
[11] I. B. Douglass, R. V. Norton, R. G. Weichman, and R. B. Clarkson, *J. Org. Chem.*, 1969, **34**, 1803.
[12] W. A. Sheppard and C. M. Sharts, ' Organic Fluorine Chemistry,' Benjamin, New York, 1969; M. Oki and K. Kobayashi, *Bull. Chem. Soc. Jpn.*, 1970, **43**, 1234; G. Capozzi, L. Da Col, V. Lucchini, and G. Modena, *J. Chem. Soc., Perkin Trans. 2*, 1980, 68.
[13] N. D. Epiotis, *J. Am. Chem. Soc.*, 1973, **95**, 3087; M. H. Whangbo, D. J. Mitchell, and S. Wolfe, *ibid.*, 1978, **100** 3698; F. Bernardi, A. Bottoni, N. D. Epiotis, and M. Guerra, *ibid.*, p. 6018.
[14] H. O. House, ' Modern Synthetic Reactions,' Benjamin–Cummings, Menlo Park, California, 1972, p. 459.
[15] G. Zweifel and H. Arzoumanian, *J. Am. Chem. Soc.*, 1967, **89**, 291.
[16] I. B. Douglass, *J. Org. Chem.*, 1959, **24**, 2004.
[17] H. Lecher, F. Holschneider, K. Koeberle, W. Speer, and P. Stoecklin, *Ber.*, 1925, **58**, 409.
[18] F. Iimura, *Nippon Kagaku Zasshi*, 1957, **78**, 48 (*Chem. Abstr.*, 1959, **53**, 5187).
[19] P. Duhamel, L. Duhamel, and J. Gralak, *Bull. Soc. Chim. Fr.*, 1970, **10**, 3641.