Tetrahedron. Vol 27. pp. 6101–6108 Pergamon Press 1971. Printed in Great Britain

THE STEREOCHEMISTRY OF Ei REACTION OF N-*p*-TOLUENESULPHONYL SULPHILIMINES[1]

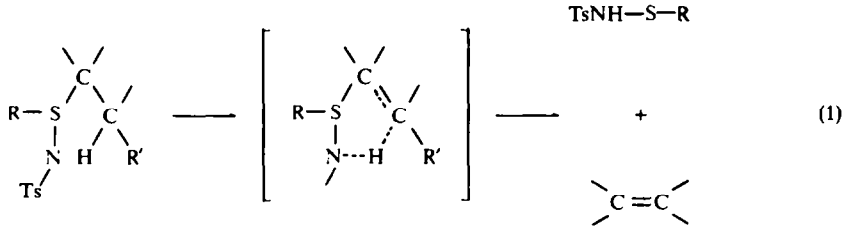
K. TSUJIHARA, K. HARADA, N. FURUKAWA and S. OAE

Department of Applied Chemistry, Faculty of Engineering, Osaka City University, Sugimotocho, Osaka, Japan

(*Received in Japan* 31 *July* 1971; *Received in the UK for publication* 24 *August* 1971)

Abstract—The stereochemistry of the pyrolysis of S-alkyl-N-*p*-tosylsulphilimines was investigated with both the *erythro* and *threo* isomers of S-phenyl-S-1-phenyl-2, 2-phenylmethoxy-1-ethyl-N-benzenesulphonylsulphilimine I_E and I_T. Pyrolyses revealed that I_E gives only *trans*-1-methoxystilbene V_T in nearly quantitative yield while a mixture of 5·5% *trans*-V_T and 94·5% *cis*-V_C are formed from I_T. The kinetics of the reactions of both I_E and I_T obey a good 1st order rate equation. Pyrolysis is considered to proceed *via* a concerted *cis* elimination involving a five membered cyclic transition state.

RECENTLY WE FOUND that S-alkyl-N-*p*-toluenesulphonylsulphilimines having β-hydrogen atoms afford the corresponding olefins and N-*p*-toluenesulphonylsulpheneamide in relatively high yield upon pyrolysis at 100°. Kinetic studies of the pyrolysis indicate the reaction is 1st order, in both benzene and DMSO solutions, of unimolecular dependence on the sulphilimine.[2] Based on the kinetic results, substituent effects, and β-hydrogen-deuterium kinetic isotope effect (k_H/k_D value), the mechanism involving an intramolecular concerted five membered cyclic transition state shown below was suggested.[3]



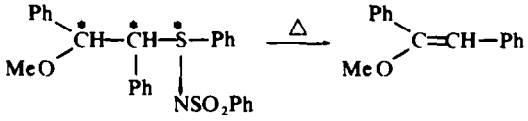
(1)

Both the mechanism and product distribution suggest that the sulphilimine is of a similar nature to those of t-amine-oxides[4] or sulphoxides[5] bearing β-hydrogen atoms. The pyrolysis of sulphilimines is substantially faster than that of the corresponding sulphoxides although somewhat slower than that of the analogous t-amineoxides. However, since S-alkyl N-sulphonyl sulphilimines can be prepared easily by treating sulphides with chloramine-T,[6] this pyrolytic reaction is anticipated to be a new convenient synthetic method for various olefins. Therefore, a detailed study on the stereochemistry of the reaction has been desired. In order to investigate the stereochemistry of the pyrolysis, the two diastereoisomers of the following S-phenyl S-1-phenyl-2,2-phenylmethoxy-1-ethyl-N-benzenesulphonyl sulphilimine (I) were pre-

pared and subjected to pyrolysis. We present the results of the pyrolyses and the implications of the mechanism of the Ei reaction together with the possible synthetic utilization.

RESULTS AND DISCUSSION

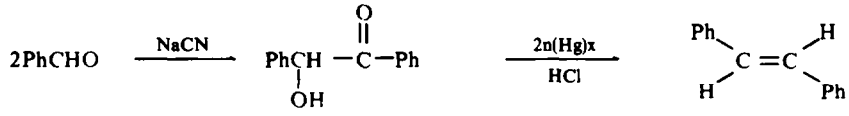
S-phenyl-S-1-phenyl-2,2-phenylmethoxy-1-ethyl-N-benzenesulphonyl sulphilimine (I) was actually obtained as a racemate of two diastereomers, namely *erythro* and *threo*, although the compound has three asymmetric centers and hence can exist as four diastereomeric isomers.



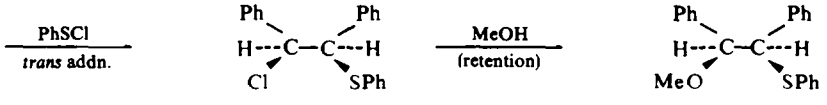
(I)

* asymmetric center

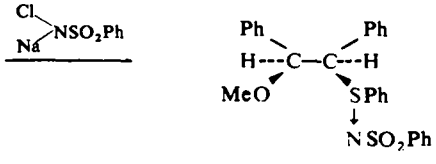
The *erythro*-I_E was prepared through the following sequence of reactions.



trans-stilbene

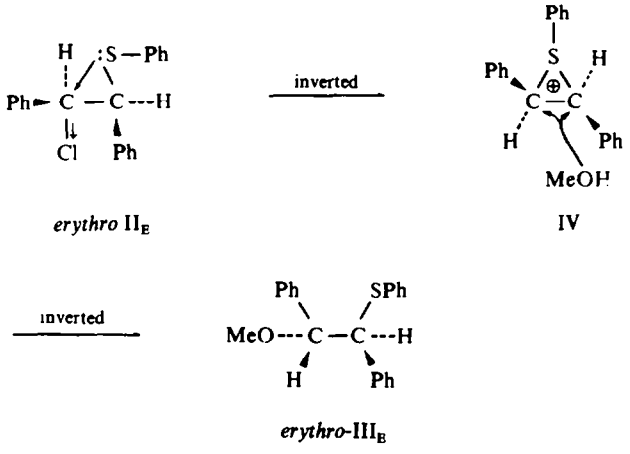


erythro-II_E *erythro* III_E



erythro-I_E

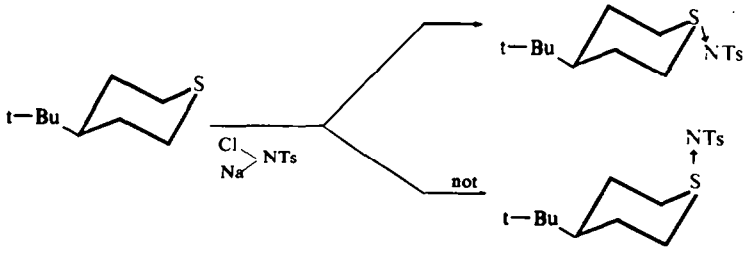
The addition of benzenesulphenyl chloride to *trans*-stilbene should give a *trans*-adduct, the *erythro* chlorosulphide II_E, since the addition of benzenesulphenyl chloride to ordinary olefins is known to be a *trans* addition.[7] Then the *erythro* chlorosulphide II_E, thus obtained was allowed to solvolyze by suspending it in MeOH at room temp with stirring for 50 hr. Although the stereochemistry of this reaction is not known,[8] the overall reaction is believed to result in net retention, after the initial formation of the thiiranium cation IV[9] of inverted configuration and the subsequent back side attack of MeOH on IV to give the *erythro*-III_E, like other anchimerically assisted solvolysis.



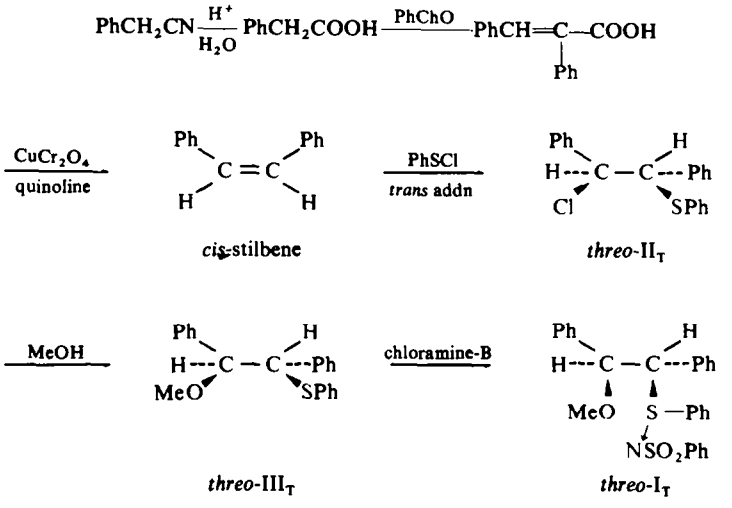
erythro II_E IV

erythro-III_E

Since the intermediate thiiranium cation IV is symmetrical, attack of MeOH at either carbon atom of the thiiranium ring ought to give the same product, *i.e.* the *erythro*-1-phenyl, methoxy-2-phenyl, phenylthia-ethane III_E. In fact the *erythro* sulphide III_E, was the only product obtained. The reaction of the *erythro* sulphide III_E with sodium benzenesulphonylchloramide (chloramine-B) gave only one diastereomeric racemate of the *erythro* sulphilimine I_E, though two diastereomeric racemates are theoretically expected. Perhaps since the sulphide III_E is substituted with many bulky groups, the reaction with chloramine-B proceeds stereospecifically as in the following reaction of 4-*t*-butylthian with chloramine-T.[10]



Thus, the *erythro* form of the sulphilimine I_E was obtained. The result of IR and NMR data are shown in Table I. Similarly, the *threo* isomer of the sulphilimine I_T was prepared in the following manner:

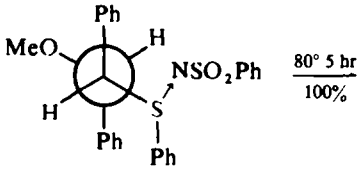


In this case too, the racemic *threo*-I_T isomer was obtained. The absolute configuration about S of I_E and I_T was not assigned in this experiment. The elimination reaction of both *erythro* I_E and *threo* I_T isomers of the sulphilimine was carried out in benzene at 80°. The rate of the reaction was found to be larger than that of phenyl ethyl sulphilimine. The olefins formed were isolated by passing through a silica gel column in which silica gel (pretreated with sodium carbonate solution and reactivated by heating at 150°) was packed in order to avoid hydrolysis of the vinyl olefins formed during the reaction thus giving unknown compounds. The olefins were analysed by measuring the NMR chemical shifts of Me protons of the OMe group. The

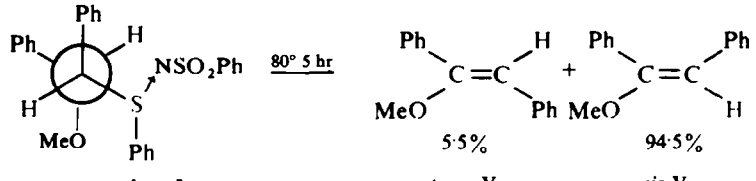
TABLE I. NMR CHEMICAL SHIFTS OF I_E ARE MEASURED FROM TMS INTERNAL STANDARD AS A REFERENCE PEAK IN $CDCl_3$ AND THE OTHER IN CCl_4. II_T WAS UNSTABLE AND NOT ISOLATED

	m.p.	NMR (ppm)				IR (cm^{-1})		
		HC		MeO	Ph protons			
I_E	125·5–126·5	4·10(d)	5·48(d)	3·28 (S)	7·10–8·20	(S–N) 965	(SO_2) 1140	(SO_2) 1285, 1087
I_T	96·5–97·0	4·66 (s)		3·27 (s)	6·70–8·05	(S–N) 965	(SO_2) 1150	(SO_2) 1295, 1090
II_E	92·0–93·0	4·55 (d)	5·22 (d)					
III_E	94·0–95·5	4·19 (d)	4·55 (d)	3·19 (s)	7·12		C–O 1100	
III_T	55·0–55·5	4·33 (d)	4·48 (d)	3·23 (s)	7·08–7·15		C–O 1100	
V_T	51·5–52·0	6·16 (s)		3·67 (s)	7·30–7·88		—	
V_C	liq.	5·84 (s)		3·83 (s)	7·09–7·36		—	
VI_E	115–116·5	4·62 (d)	4·98 (d)	3·22 (s)	7·35 (s)		—	
VI_T	84·5–85·5	4·47 (d)	4·98 (d)	3·35 (s)	7·25 (s)		—	

pyrolysis of the *erythro* isomer of the sulphilimine-I_E gave only the *trans*-olefin V_T quantitatively and hence the reaction is a completely stereospecific *cis*-elimination, whereas that of the *threo* sulphilimine-I_T gave the *trans*-olefin V_T and the *cis*-olefin V_C in the ratio of 1:17 in 80% of the total yield. The reaction is not as stereospecific as that for the *erythro* isomer but a predominantly stereoselective *cis*-elimination, similar to other *cis*-eliminations.[4,5]

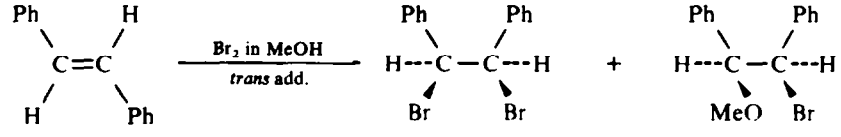


erythro-I_E *trans*-V_T

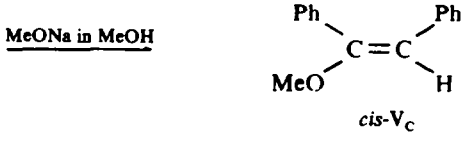


threo-I_T *trans*-V_T *cis*-V_C

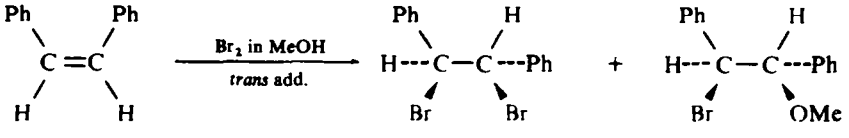
The structures of both olefins were determined by comparing authentic samples V_T and V_C prepared by the following procedures shown below.



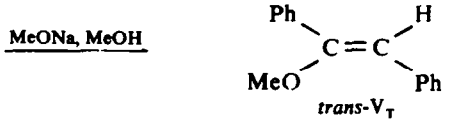
cis-stilbene *meso*-dibromide *erythro*-VI_E



cis-V_C



cis-stilbene d,l-dibromide *threo*-VI_T

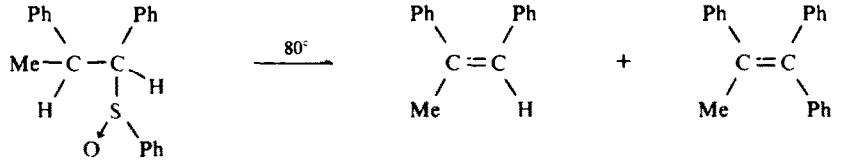


trans-V_T

Namely stilbenes were first allowed to react with Br_2 in MeOH to afford the corresponding dibromides and 1-bromo-2-methoxy compound VI. These reactions were found to proceed as completely stereospecific *trans* additions, though the stereochemistry of the addition to the *cis*-olefin has not been reported.

Thus, the *erythro* isomer VI_E, and the *threo* derivative VI_T, were obtained in pure form and then subjected to the usual *trans* elimination reaction with NaOMe in MeOH to generate both the *cis*-V_C and the *trans*-V_T olefins, respectively. The NMR and IR data of these *cis* and *trans* olefins obtained were in complete agreement with those derived from the *cis*-elimination reaction of the sulphilimines I. The rates of the elimination reaction of these *erythro* and *threo* sulphilimines were measured in benzene solution at 60°. The reactions display first order kinetics and the rate constants for the *threo*-I_T and the *erythro*-I_E were found to be $(1{\cdot}65 \pm 0{\cdot}04) \times 10^{-4}$ sec^{-1} and $(1{\cdot}01 \pm 0{\cdot}06) \times 10^{-4}$ sec^{-1} respectively.

These stereochemical results indicate that the reactions proceed *via* the stereospecific *cis*-elimination process. When these stereochemical data are compared with those of the sulphoxides reported by Cram *et al.*,[5] the pyrolysis of sulphilimines is a more stereoselective *cis*-elimination than those of the sulphoxides (VII) in which both the *erythro* and the *threo* (VII) gave the respective olefins with 90% stereoselectivity.



VII	*cis*-VIII	*trans*-VIII
erythro	10%	90%
threo	90%	10%

Namely the *erythro*-VII isomer gave a mixture of 90% *trans*-VIII and 10% *cis*-VIII and the *threo* VII *vice versa*. Thus the pyrolysis of these sulphilimines is more stereospecific than those of the corresponding sulphoxides and t-amine oxides.[11]

The observation that the rate of the pyrolysis of the *threo* isomer I_T is slightly higher than that of the *erythro* isomer I_E is in contrast to the general trend in ordinary E_2 type reactions in which the rate of elimination of the *erythro* isomer is larger than that of the *threo* isomer because of the large eclipsing effect by two bulky vicinal substituents of the *threo* isomer at the transition state.[12] The small difference in the rates of pyrolysis of the two isomers may be rationalized on the basis of different conformational changes between the E_2 and E_i reactions. In the E_2 reaction of the *threo* isomer, steric strain due to the two vicinal substituents usually increases in going from the ground state to the transition state, eventually retarding the rate. Whereas in the Ei reaction, the cyclic conformation of both the *erythro* and the *threo* isomers are so rigid and strained, there is not the usual increase of steric strain in going to the transition state.

Perhaps steric strain is released somewhat in the process, especially with the *threo* isomer. Similarly small but the *threo* favoured Ei reactions are known for sulphoxides and N-oxides. The relative rates of I_E and I_T to that of β-phenyl ethyl N-*p*-tolyl-sulphonylsulphilimine are 10^2 and $1{\cdot}5 \times 10^2$ respectively. This large rate enhancement by the substitution of an α-Ph group is undoubtedly due to the facile cleavage of the benzylic C—S bond at the transition state of the reaction.

Thus all these features of the reaction, such as, (i) the high yields of olefin formation: (ii) the moderate reaction conditions; (iii) the easy access and handle of a variety of sulphilimines and (iv) the high stereospecificity will be quite an advantage of sulphilimines when used as a source for the preparation of olefins.

EXPERIMENTAL

*Syntheses of erythro- and threo-*S-1-*phenyl*-2,2-*phenyl-methoxyl*-1-*ethyl*-N-*benzenesulphonylsulphilimines* (I) cis- *and* trans-*stilbenes. Cis* or *trans*-stilbene was synthesized from α-phenylcinnamic acid or benzaldehyde according to Buckles *et al.*[13] and Shriner *et al.*[14]

Cis-stilbene was obtained in 40% yield, b.p. 134–136°/10 mm. *Trans*-stilbene was obtained in 50% yield, m.p. 123–124°.

*Erythro- and threo-*S-*phenyl*-S-1-*phenyl*-2,2-*phenyl-chloro*-1-*ethyl-sulphide* (II). The CH_2Cl_2 solution (50 ml) of benzenesulphenyl chloride (0·05 mole) prepared by the reaction of thiophenol with Cl_2 in CH_2Cl_2 was added dropwise to a CH_2Cl_2 solution (50 ml) containing *trans* stilbene (0·05 mole) under cooling with ice-water. The mixture was allowed to stand at room temp for 3 hr and the solvent removed under red. press. The *erythro*-chloro-sulphide II_E was obtained from the residue by treatment with silica gel. The *threo*-chlorosulphide II_T (liquid) was obtained by the same procedure described above and used *in situ* for the preparation of *threo*-methoxyl-sulphide III_T.

*Erythro- and threo-*S-*phenyl*-S-1-*phenyl*-2,2-*phenyl-methoxyl*-1-*ethyl-sulphide* (III). The *threo*-chloro-sulphide II_T was suspended in MeOH with stirring at 30° for 40 hr and MeOH removed under reduced pressure. The *threo*-methoxy-sulphide III_T was obtained by treatment with silica gel from the residue. *Erythro*-methoxy-sulphide III_E was obtained from the *erythro*-chloro-sulphide II_E by the same procedure described above. (Calc. for $C_{21}H_{20}OS$: C, 78·72; H, 6·29. Found: C, 77·95; H, 6·26%).

*Erythro- and threo-*S-*phenyl*-S-1-*phenyl*-2,2-*phenyl-methoxyl*-1-*ethyl*-N-*benzenesulphonylsulphilimine* I. The *erythro*-III_E or the *threo*-methoxyl-sulphide III_T (0·01 mole) and chloramine-T (0·011 mole) were dissolved in MeOH (30 ml). To this solution was added dropwise 0·2 ml AcOH in 5 ml of MeOH at room temp. The mixture was allowed to stand at room temp. over night and poured into a cold dilute NaOH solution and a precipitate formed was collected. *Erythro*-I_E *or threo*-sulphilimine I_T was obtained by recrystallization from MeOH. Erythro-Sulphilimine I_E. (Calc. for $C_{27}H_{25}NO_3S_2$: C, 68·18; H, 5·30; N, 2·94. Found: C, 68·88; H, 5·34; H, 2·91%). Threo-Sulphilimine I_T. (Calc. for $C_{27}H_{25}NO_3S_2$: C, 68·18; H, 5·30; N, 2·94. Found: C, 67·92; H, 5·34; N, 2·91%).

Pyrolysis of erythro-I_E *and threo-sulphilimine* I_T. A benzene solution of the *erythro*-I_E or the *threo*-sulphilimine-I_T (0·02 mole/l) was heated in a sealed tube at 80° for 5 hr. The tube was opened, the contents were transferred to a chromatographic column containing neutralized silica gel treated with dil. Na_2CO_3 aq washed with H_2O repeatedly and reactivated by heating to 150°.

The column was washed with benzene–hexane (1:1, 100 ml), the eluent was evaporated completely under reduced pressure and weighed. The ratio of the olefins obtained was determined by measurement of the NMR chemical shifts of the Me protons in the OMe groups of the *cis*-V_C and the *trans*-olefins V_T. The pyrolysis of the *erythro*-sulfilimine I_E gave only *trans*-1,1-methoxyl-phenyl-2-phenyl-ethylene V_T quantitatively: λ_{max} 293 nm, ε_{max} = 24,000, (221 nm 11,740). The pyrolysis of the *threo*-sulfilimine I_T gave a mixture of the *trans*-V_T and *cis*-olefins V_C with the ratio of 1:17 in 80% yield. The *cis*-olefin V_C was a liquid and converted to the *trans*-isomer V_T by heating at 200° for 3 hr: λ_{max} 288 nm, ε_{max} = 13,700.

Syntheses of authentic cis- *and* trans-1,1-*phenyl-methoxyl*-2-*phenyl-ethylene* (V). Cis- *and* trans-1,1-*methoxyl-phenyl*-2-*phenyl-ethane* (VI) *Trans*-stilbene (0·01 mole) was suspended in MeOH (50 ml) and a MeOH solution of Br_2 (0·01 mole) was added dropwise with stirring at room temp and the mixture allowed to stand overnight and poured into ice-water.[15] The precipitate was collected, dried and extracted with

boiling EtOH (50 ml) 4 times. From the EtOH solution, *erythro*-1,1-bromo-phenyl-2,2-methoxy-phenyl-ethane VI_E was obtained (65%). Meanwhile the residue was found to be the corresponding *meso* dibromide m.p. 228° (dec.) after recrystallization from benzene.

Threo-1,1-bromo-phenyl-2,2-methoxyl-phenyl-ethane VI_T was obtained (50%) by treatment of the products with silica gel after the procedure described above; simultaneously the corresponding *d*,1-dibromide was obtained as a by-product, m.p. 107·0–108·0 (dec.) NMR chemical shift; H–C 5·50 (s), Ph protons 7·27 (s) ppm in CCl_4.

Cis- *and* trans-1,1-*methoxyl-phenyl-2-phenyl-ethylene* (V). The *erythro*- or the *threo*-derivative (0·005 mole) was added slowly to a NaOMe solution (0·02 mole) of MeOH (50 ml) with stirring at room temp and the mixture allowed to stand overnight, poured into ice-water, extracted with benzene, washed with water, dried ($MgSO_4$), and the solvent was removed. The residue was treated with neutralized silica gel. Thus the *cis*- V_C and *trans*-olefins V_T were obtained and their physical properties found to agree completely with those of the *cis*- and *trans*-olefins formed by the pyrolysis of *threo*- and *erythro*-sulphilimine.

Kinetics measurement by IR spectra. The benzene solution of either the *erythro*- or the *threo*-sulphilimine (0·025 mole/l) was placed in a flask stoppered to prevent evaporation of solvent and kept at constant temperature during the experiment. An aliquot (2–5 ml) of the mixture was taken from time to time (5–10 times) and the IR absorption at 3280 cm^{-1} due to the stretching of the NH group of the forming sulphenamide was followed.

REFERENCES

[1] Sulphilimine and Sulphoximine XII, Part XI, *Tetrahedron Letters* (1971)

[2] [a] S. Oae, K. Tsujihara and N. Furukawa, *Tetrahedron Letters* 2663 (1970);
[b] K. Tsujihara, N. Furukawa and S. Oae, *Tetrahedron* **27**, 4921 (1971)
[c] G. F. Whitfield, H. S. Beilan, D. Saika and D. Swern, *Tetrahedron Letters* 3543 (1970)

[3] D. V. Banthorpe, *Elimination Reactions*, p. 167. Elsvier, N.Y. (1963)

[4] [a] A. C. Cope, T. T. Foster, and P. H. Towle, *J. Am. Chem. Soc.* **71**, 3929 (1944);
[b] A. C. Cope, and E.R. Trumbull, *Organic Reactions* Vol. 11. 361 (1960)

[5] [a] C. A. Kingsbury and D. J. Cram, *J. Am. Chem. Soc.* **82**, 1819 (1960);
[b] D. W. Emerson and T. J. Korniski, *J. Org. Chem.* **34**, 4115 (1969);
[c] C. R. Johnson, *Quart. Reports on Sulphur Chem.* **4**, 33, (1969)

[6] K. Tsujihara, N. Furukawa and S. Oae, *Bull. Chem. Soc. Japan* **42**, 2631 (1969)

[7] [a] P. B. de la Mare and R. Bolton, *Electrophilic Addition Reactions to Unsaturated Systems* Elsvier Publish Co., London, N.Y. (1966)
[b] R. Fahey, *Topic in Stereochem.* Vol 11;
[c] W. H. Mueller, *Angew Chem. Int. Editn* **8**, 482 (1969)

[8] W. K. Kwok and S. I. Miller, *J. Am. Chem. Soc.* **92**, 4599 (1970); C. S. T. Lee, I. M. Mathai and S. I. Miller, Ibid. **92**, 4599 (1970); C. S. T. Lee, I. M. Mathai and S. I. Miller, *Ibid.* **92**, 4602 (1970)

[9] G. H. Schmid, and V. M. Szismadia, *Canad. J. Chem.* **44**, 1338 (1966)

[10] C. R. Johnson, and J. J. Rigan, *J. Org. Chem.* **33**, 4340 (1968)

[11] [a] D. J. Cram, J. E. McCarty, *J. Am. Chem. Soc.* **76**, 5740 (1954);
[b] M. R. V. Sahyun and D. J. Cram, *Ibid.* **85**, 1253, 1263 (1963)

[12] D. J. Cram, F. D. Greene, and C. H. DePuy, *Ibid.* **78**, 790 (1956)

[13] R. E. Buckles and N. G. Wheeler, *Org. Synth.*, Coll Vol. IV, 857, (1963)

[14] R. L. Shriner and A. Berger, *Ibid. Coll. Vol.* III, 786 (1955)

[15] D. S. Tarbell and P. B. Bartlett, *J. Am. Chem. Soc.* **58**, 466 (1936)