The Reactions of Isomeric 1-Chloro-2-methylthio-1, 2-diphenylethanes with the Base

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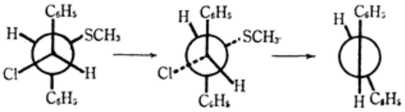
In the course of other study the authors encountered a striking difference in the reactivities of *erythro-* and *threo*-isomers. When isomers of 1-chloro-2-methylthio-1, 2-diphenylethane (I) were treated with potassium *t*-butoxide, the former gave *trans*-stilbene and the other, possibly α-methylthio-*trans*-stilbene (II). The results may be attributed to the different stabilities of the transition states, as will be described below.

trans-Stilbene oxide was treated with sodium methylmercaptide in ethanol to produce *erythro*-2-methylthio-1, 2-diphenyl-1-ethanol (III), m. p. 74°C (Found: C, 74.02; H, 6.66. Calcd. for $C_{15}H_{16}OS$: C, 73.75; H, 6.60%), which was converted into *erythro*-I, m. p. 123°C (Found: C, 68.59; H, 5.73. Calcd. for $C_{15}H_{15}ClS$: C, 68.40; H, 5.74%), by treating it with thionyl chloride in chloroform. Similarly, *threo*-III, which was characterized as acetate, m. p. 71.5—72°C (Found: C, 71.49; H, 6.27. Calcd. for $C_{17}H_{18}O_2S$: C, 71.30; H, 6.34%), and *threo*-I, m. p. 52.5°C (Found: C, 68.52; H, 5.76%), were prepared from *cis*-stilbene oxide.

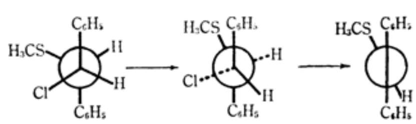
The stereochemistry of these compounds was established by the mode of preparation, since the ring opening of an epoxide proceeds in the trans fashion and the chlorination of an alcohol with thionyl chloride proceeds with the retention of the configuration.1) The results were further confirmed by the NMR spectra, in which *threo*-I shows a coupling constant of benzylic hydrogens of 7.5 c. p. s., whereas *erythro*-I shows one of 9.5—9.9 c. p. s.

The refluxing of a *t*-butyl alcohol solution of *erythro*-I with ca. 1 N potassium *t*-butoxide for 12 hr. yielded *trans*-stilbene as the sole product. Thus it is apparent that the elimination of methanesulfenyl chloride took place during this treatment. On the other hand, *threo*-I, upon similar treatment, gave II (NMR; τ 2.3—2.9 (multiplet), τ 8.05 (singlet), τ 3.23 (singlet): λ_{max} 308 mμ, ε 15000), which was then oxidized with peroxyacetic acid to α-methylsulfonyl-*trans*-stilbene (IV), m. p. 118—119°C (Found: C, 69.48; H, 5.61. Calcd. for $C_{15}H_{14}O_2S$: C, 69.74; H, 5.46%). Thus, the elimination of hydrogen chloride took place wih *threo*-I. The configuration of IV has not been firmly established, but from the mode of elimination, which will be discussed below, the trans configuration seems most probable.

Ground state Transition state Product



erythro-1-Chloro-2-methylthio-1, 2-diphenylethane (I) (V) *trans*-Stilbene



threo-1-Chloro-2-methylthio-1, 2-diphenylethane (I) (VI) α-Methylthio-*trans*-stilbene (II)

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1) E. L. Eliel, "Steric Effects in Organic Chemistry," Ed. by M. S. Newman, John Wiley & Sons, Inc., New York (1956), Chap. 2.

One possible explanation* of these results is that an E_2-type elimination occurs during this treatment. If so, the results could be interpreted as follows. *threo*-I, taking its most stable conformation, as is shown in the figure, will give II, in accord with expectations, through the transition state VI. *threo*-I must assume a transition state of high energy if it reacts to give *cis*-stilbene. On the other hand, a transition state which gives rise to the elimination of hydrogen chloride from *erythro*-I will be of too high an energy to be a major contribution, because the two bulky phenyl groups are opposed. It may be expected that the transition state V will be formed much more easily. Thus, instead of hydrogen chloride, methanesulfenyl chloride is eliminated from the *erythro* isomer, as is shown in the figure.

In this respect, it is very interesting that Helmkamp and Pettitt reported(2) recently that methanesulfenyl bromide was eliminated when two isomers of 2-bromo-3-methylthiobutane were treated with iodine, irrespective of their configurations.

The isomers of I also behave differently toward pyridine. The effect of the bulkiness of the substituent and/or base on the elimination and the effect of the acidities of α-hydrogens are now under investigation.

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* An alternative explanation will be an anchimeric assistance of a methylthio group to form a bridged cation as a transition state. However, this mechanism is less likely, because no sulfur-containining compound is isolated inspite of an expected competitive abstraction of CH_3S^+ or H^+.

2) G. K. Helmkamp and D. J. Pettitt, *J. Org. Chem.*, **29**, 3258 (1964).