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Reaction of *trans*-Stilbene with Methanesulfenyl Chloride

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We have treated *trans*-stilbene (**1**) with excess methanesulfenyl chloride and obtained a mixture of α-chloro-α-methylthiostilbenes which are formally the dehydrogenation products of the adduct. This paper presents characterization of the products and a discussion on the reaction.

Experimental

Reaction between trans-*Stilbene and Methanesulfenyl Chloride in 1: 1 Molar Ratio.* To a solution of 4.0 g. (0.022 mol) of *trans*-stilbene in 300 ml. of toluene was added 1.8 g (0.022 mol) of methanesulfenyl chloride at −78 °C. After the color of the chloride had faded, the mixture was warmed to room temperature and evaporated *in vacuo*. The remaining mixture was fractionally recrystallized from petroleum ether to give 48% *erythro*-1-chloro-2-methylthio-1,2-diphenylethane,[1] mp 123 °C.

Reaction of trans-*Stilbene with Excess Methanesulfenyl Chloride.* *trans*-Stilbene (4.5 g or 0.025 mol) was added to 6.2 g (0.075 mol) of methanesulfenyl chloride at −78 °C and the mixture was slowly warmed up to room temperature. During this period a vigorous reaction set in and evolution of hydrogen chloride took place. The excess of methanesulfenyl chloride was decomposed by pouring into methanol. The product chromatographed on alumina gave a mixture in 77% yield (by weight). NMR spectra of the mixture indicated that it consists of *cis*- and *trans*-α-chloro-α′-methylthiostilbenes, the composition being *ca.* 4: 1 in favor of the *cis*-isomer. Rechromatography of the mixture gave the *trans* compound, mp 74 °C, and the *cis*, mp 52 °C.[2]

trans-*α-Chloro-α-methylthiostilbene.* Methanesulfenyl chloride (5 g or 0.06 mol) was added to 9 g (0.05 mol) of tolane in 20 ml of ether containing 2 ml of boron trifluoride etherate. The mixture was washed with water, evaporated and chromatographed on alumina to give 70% *trans*-α-chloro-α′-methylthiostilbene, mp 74 °C, which was identical with one of the products obtained above. Found: C, 69.00; H, 5.19%. Calcd for $C_{15}H_{13}ClS$: C, 69.14; H, 5.01%.

trans- *and* cis-*α-chloro-α′-methylsulfonylstilbenes.* The corresponding thioethers were oxidized with peracetic acid in acetic acid at 70 °C for 1 hr. The *trans* form, mp 158.5—159 °C. Found: C, 61.40; H, 4.58%. The *cis* form, mp 123—126 °C. Found: C, 61.44; H, 4.52%. Calcd for $C_{15}H_{13}ClO_2S$: C, 61.53; H, 4.44%.

Reaction of erythro-*1-Chloro-2-methylthio-1,2-diphenylethane with Methanesulfenyl Chloride.* To a solution of 0.52 g (2 mmol) of *erythro*-1-chloro-2-methylthio-1,2-diphenylethane in 10 ml of carbon tetrachloride was added 0.33 g (4 mmol) of methanesulfenyl chloride at room temperature. After the reaction was over, as indicated by fading of the color, the solution was washed with aqueous sodium carbonate and the

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1) M. Ōki and A. Kimura, This Bulletin, **38**, 682 (1965).

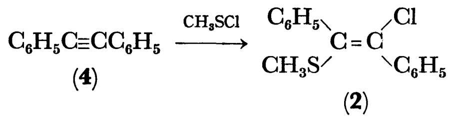
2) Since purification of this compound was rather tedious, elemental analysis was performed with the sulfone.

solvent was evaporated. NMR spectrum indicated the presence of *cis*- and *trans*-α-chloro-α′-methylthiostilbenes and dimethyl disulfide. The ratio of the isomers was paractically the same as the one obtained by the reaction of *trans*-stilbene with excess methanesulfenyl chloride.

Thermal Equilibration of α-Chloro-α′-methylthiostilbenes. The *trans* form of this compound was dissolved in carbon tetrachloride and sealed in an NMR sample tube. The whole was heated at 195 °C and the NMR spectra were determined at appropriate intervals. The *trans* compound had a sharp singlet at 1.77 ppm from internal TMS and a fairly sharp signal at 7.31 ppm, the latter being characteristic of *trans*-stilbene derivatives. After heating for 5 hr, the equilibrium was reached. The signals for the *cis* compound were observed at 1.83, 6.98, and 7.08 ppm. The latter two signals can be taken as an evidence for the *cis*-stilbene structure. The area ratio was *ca.* 2: 1 in favor of the *cis*.

Discussion

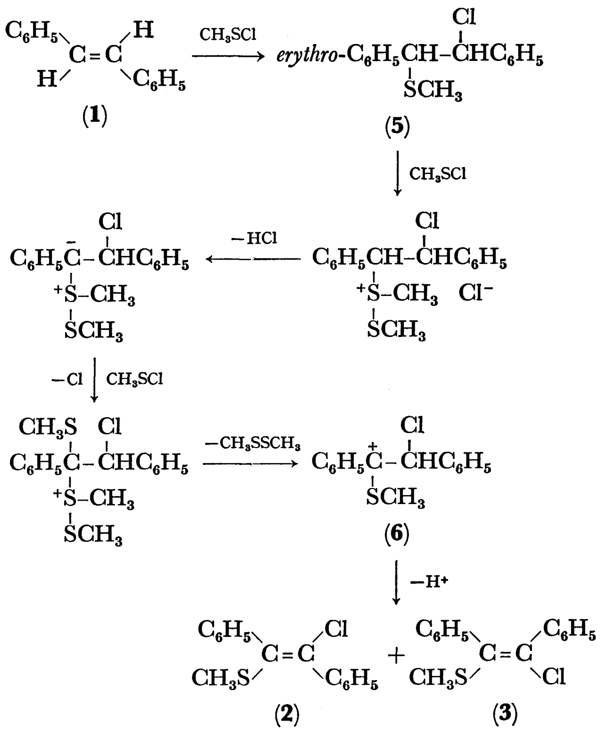
The reaction of *trans*-stilbene with excess methanesulfenyl chloride afforded a mixture of two compounds containing both sulfur and chlorine. One of the products was found to be identical with a product from the reaction of tolane with methanesulfenyl chloride. Since the ionic addition to tolane (**4**) has been known[3] to give mainly the *trans* isomer, it is most reasonable to assume that this compound is *trans*-α-chloro-α′-methylthiostilbene (**2**).



Analytical data of the other product suggest it to be an isomer of the *trans* compound, whose structure might be reasonably assigned to *cis*-α-chloro-α′-methylthiostilbene (**3**). Further evidence for the assignment of the structure was obtained by thermal equilibration with the *trans* compound and by refluxing the compound with Raney nickel in acetone: *cis*-stilbene, as identified by the corresponding signals in NMR spectra, was found.

The favored formation of the *cis* isomer over the *trans* is of interest. Although it is difficult to verify the reasons, there are many such examples. Among 1,2-dihaloethylenes, the *cis* isomer is known to be more stable than the *trans*.[4–6] In substituted enedithiol derivatives, the *cis* form is more stable,[7] although steric factor may operate to some extent in that *cis-trans* pair. Since the system in question possesses chlorine and sulfur atoms at both ends of the vinylene groups, the stability of the *cis* compound can be explained similarly. Thus the results appear as a result of thermodynamic control and the thermal equilibration agrees with expectation. The presence of hydrogen chloride, as one of the reaction products, will catalyze the equilibration between *cis*- and *trans*-isomers.

Since *erythro*-1-chloro-2-methylthio-1,2-diphenylethane (**5**), when treated with methanesulfenyl chloride, gives almost the same mixture as the products from *trans*-stilbene and excess methanesulfenyl chloride, the reaction may be assumed to proceed *via* compound **5**. The mechanism of the dehydrogenation reaction will then be similar to that reported:[8] a Pummerer type intermediate (**6**) intervenes and the deprotonation from beta to the sulfur atom takes place. A probable mechanism is as follows.



No evidence for further addition[9] of the sulfenyl chloride to **2** and **3** was obtained.

Note Added in Proof: Equilibration of *cis* and *trans* isomers of a similar system catalyzed by hydrogen chloride was reported recently. See G. Modena, G. Scorrano, and U. Tonellato, *J. Chem. Soc. Perkin II*, **1973**, 493.

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3) E. Bergmann, *J. Chem. Soc.*, **1936**, 402. Arenesulfenyl chlorides are also known to add in *trans* fashion to acetylenic bond: E. G. Kataev and T. G. Mannafov. *Zh. Org. Khim.*, **1970**, 1959; *Chem. Abstr.*, **74**, 12763s (1971).

4) H. Steinmetz and R. M. Noyes, *J. Amer. Chem. Soc.*, **74**, 4141 (1952).

5) K. S. Pitzer and J. L. Hollenberg, *ibid.*, **76**, 1493 (1954).

6) H. G. Viehe, *Chem. Ber.*, **93**, 1697 (1960).

7) M. Ōki and K. Kobayashi, This Bulletin, **43**, 1234 (1970).

8) M. Ōki and K. Kobayashi, *ibid.*, **43**, 1229 (1970).

9) M. Ōki and K. Kobayashi, *ibid.*, **46**, 687 (1973).