ENHANCED REACTIVITY OF FUSED THIIRENE SULFOXIDE IN CYCLOADDITIONS WITH ENOPHILES

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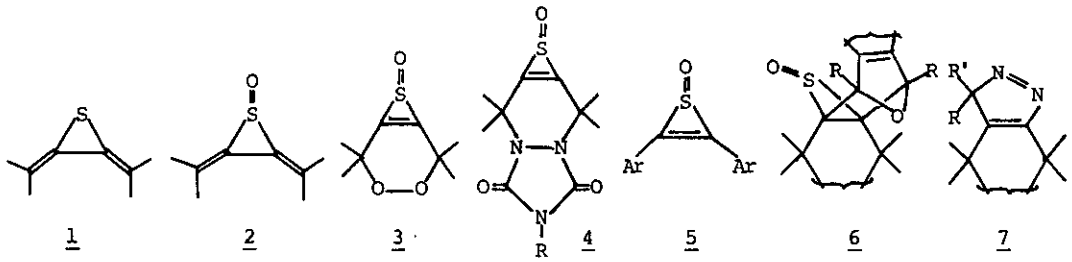
In the course of study on the chemistry of strained small ring heterocycles,[1] the authers have recently prepared a few thiirene sulfoxides 3[2] and 4[3] by means of [2+4]cycloaddition of thiiranoradialene sulfoxide 2[1] with appropriate dienophiles. The thiirene sulfoxides are fused with six-membered rings and so strained as to be expected to have extraordinarily high reactivity. Only known thiirene sulfoxide so far had been a diaryl type 5 whose reactions were seldom studied.[4] Here, as a beggining, several new cycloadditions of the fused thiirene sulfoxides were examined with dienes, diazo compounds and enamines.



1 2 3 4 5 6 7

The [2+4]cycloadditions with furan and 1,3-diphenylisobenzofuran smoothly proceeded to give stable adducts 6 bearing propellane skeltons in quantitative yields. The reactions, however, were not traced with diphenyl thiirene sulfoxide (5, Ar= Ph). Meanwhile, diazo compounds such as diphenyl diazomethane, ethyl diazoacetate and diethyl diazomalonate easily reacted with the fused thiirene sulfoxides to afford 2-pyrazole derivatives 7 with extrusion of SO. Cycloaddition also occurred with enamines.

Thus, the reactivity of the fused thiirene sulfoxides is newly clarified in cycloadditions with various enophiles, and further emphasized in comparison with that of diphenyl thiirene sulfoxide.

REFERENCES: 1) Syntheses of 1 and 2: W. Ando, Y. Hanyu, T. Takata, Tetrahedron Lett., 22, 4815(1981). 2) Y. Hanyu, T. Takata, W. Ando, The 47th Annual Meeting of Chemical Society of Japan, Kyoto, Apr. 1983, Abstract p. 1232. 3) W. Ando, Y. Hanyu, T. Takata, K. Ueno, J. Am. Chem. Soc., 104, 4981(1982). 4) L. A. Carpino, H.-W. Chen, J. Am. Chem. Soc., 101, 390(1979).