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# STEREOSPECIFICITY AND REGIOSELECTIVITY OF CYCLOADDITION REACTIONS OF o-THIOQUINONE METHIDE

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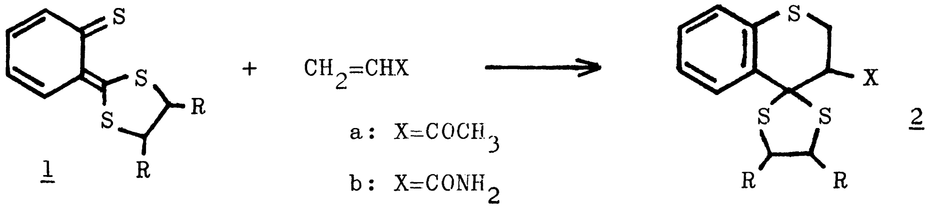
o-Thioquinone methide reacted with maleonitrile, fumaronitrile, methyl vinyl ketone, and acrylamide to give [4+2] cycloadducts. The former two reactions proceeded stereospecifically and the latter two regioselectively. The mode of these reactions are compared with those of the reactions with an enamine and of dimerization.

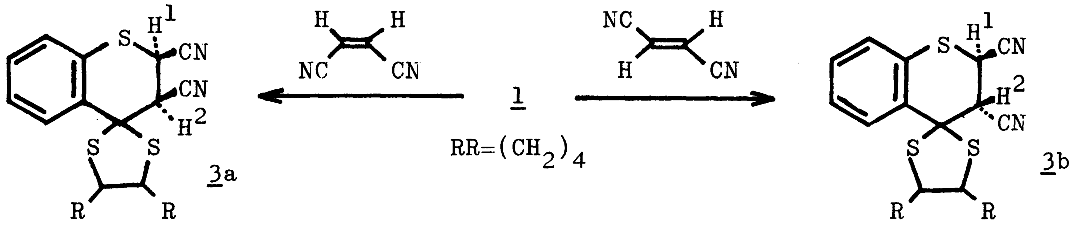
Stereospecificity and regioselectivity are the most fundamental problem in cycloaddition reactions. Thermal [4+2] cycloadditions usually proceed in a concerted manner leading to stereospecific six-membered products. In addition to the vast majority of these concerted reactions, however, there are also several examples of stepwise reactions involving dipolar intermediates.$^{1)}$ The fact that these stepwise reactions are observed when heterodienes and/or heterodienophiles are reaction components and hence the charge occurring in dipolar intermediates can be adequately stabilized prompted us to investigate the stereospecificity and regioselectivity in the cycloadditions of o-thioquinone methide (1) with olefins bearing electron-withdrawing substituents; 1 is the first stable representative of this class of compounds recently prepared by us.$^{2)}$



Reaction of the thioquinone methide (1) (RR=$(CH_2)_4$)$^{2)}$ with methyl vinyl ketone in refluxing benzene for 5 min resulted in a quantitative formation of [4+2] adduct (2a). A similar reaction with acrylamide afforded 2b in 64% yield.

Regioselectivity of the addition was established for 2a by desulfurization with Raney nickel leading to 3-methyl-4-phenyl-2-butanone (64%) and 3-methyl-4-phenyl-2-butanol (12%).

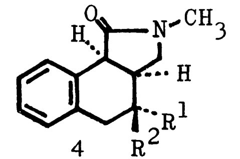
Upon reactions with maleonitrile and fumaronitrile (at room temperature, 1-2 days, $CH_2Cl_2$), 1 (RR=$(CH_2)_4$) yielded cis- (3a) (66%) and trans-adducts (3b) (88%) respectively. In the NMR spectra of the crude reaction mixtures, methine proton $H^1$ and $H^2$ for both 3a and 3b appear as two sets of double doublets of AX type;$^{3)}$ for 3a the intensity ratio of the two double doublets is about 4:1 with the coupling constant ($J_{AX}$) of 4 Hz, and for 3b the ratio is about 5:1 with $J_{AX}$ of 9 Hz. The two sets of the spectra are considered to correspond to two isomers with respect to the direction of the cyclohexane ring in view of isolation of such isomers in cycloaddition reactions of similar conjugated systems.[4)] Recrystallization of both the reaction mixtures leads to isolation of the major isomers. The coupling constants obtained for 3a and 3b clearly indicate they are cis- and trans-adducts respectively,[5)] thus demonstrating the stereospecificity of these cycloadditions.



Stereospecificity observed here is of special interest in view of the reaction mode of 1 recently observed in cycloaddition with enamines[6)] and in dimerization;[7)] these reactions most likely proceed in a stepwise manner via dipolar and diradical intermediates, respectively. We think such diverse reactivities of heterodiene 1 obviously stem from the presence of a thiocarbonyl group.

### References and Notes

1) Reviews: R. Gompper, Angew. Chem. Int. Ed. Engl., 8, 312 (1969); G. Desimoni and G. Tacconi, Chem. Rev., 75, 651 (1975).
2) R. Okazaki and N. Inamoto, Chem. Lett., 1974, 1439.
3) The chemical shifts ($\delta$) of these quartets are as follows; the major isomer of 3a: 4.06, 4.12, 5.07, and 5.13; the minor one of 3a: 4.12, 4.19, 4.92, and 4.99; the major one of 3b: 3.69, 3.84, 4.67, and 4.82; the minor one of 3b: 3.80, 3.94, 4.52, and 4.67. There was found no peak due to the other stereoisomer in each of the reaction mixture within the limits of detection (>5%).
4) R. Okazaki, M. O-oka, and N. Inamoto, J. Chem. Soc. Chem. Commun., 1976, 562; M. O-oka, A. Kitamura, R. Okazaki, and N. Inamoto, Bull. Chem. Soc. Jpn., 51, No. 2 (1978).
5) Examination of the molecular model based on reasonable assumptions that the dihydrothiopyran ring takes a half-chair conformation and the two cyano groups of 3b are in equatorial positions indicates that the dihedral angles of $H^1$-C-C-$H^2$ are about 50° for 3a and 170° for 3b, thus estimated $^3J$'s by Karplus equation being 3.3 and 8.5 Hz, respectively. The J values of 4.5 and 10 Hz are reported for 4a ($R^1$=H, $R^2$=Cl) and 4b ($R^1$=Cl, $R^2$=H), respectively. W. Oppolzer, J. Am. Chem. Soc., 93, 3833 (1971).



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6) F. Ishii, R. Okazaki, and N. Inamoto, Tetrahedron Lett., 1976, 4283; R. Okazaki, F. Ishii, and N. Inamoto, Bull. Chem. Soc. Jpn., 51, No. 2 (1978).
7) R. Okazaki, F. Ishii, K. Sunagawa, and N. Inamoto, the preceding paper.
8) Stereospecificity has been established for o-quinodimethanes. For example, see C.M. Bowes, D.F. Montecalvo, and F. Sondheimer, Tetrahedron Lett., 1973, 3181. For a review, see: R. Okazaki, Yuki Gosei Kagaku Kyokaishi, 34, 439 (1976).

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