Cycloaddition of Cycloheptatrienethione with Dienophiles

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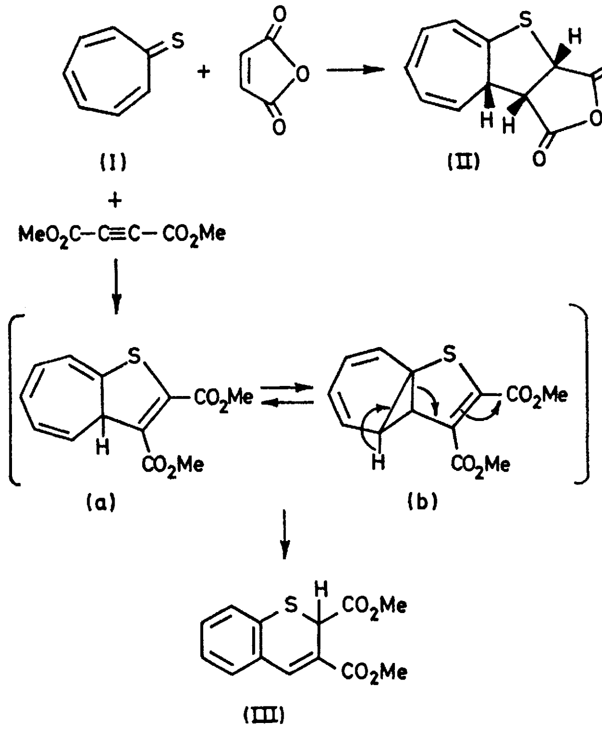
Summary The cycloaddition of cycloheptatrienethione (I) with maleic anhydride gives a rare $[_{\pi}8_s + {}_{\pi}2_s]$ type of adduct (II), while with dimethyl acetylenedicarboxylate it gives an unusual rearrangement product (III).

Although cycloheptatrienethione (I), the S-analogue of tropone, has been synthesized,[1] its thermal instability has so far precluded a detailed chemical study. We report here on its cycloaddition with dienophiles. Tropones have been reported to react normally with maleic anhydride and dimethyl acetylenedicarboxylate giving 1,4-cycloadducts.[2] We found that (I) reacted smoothly and rapidly,with immediate disappearance of the colour, with some dienophiles, undergoing a relatively rare $[_{\pi}8_s + {}_{\pi}2_s]$ type of cycloaddition.[3]

Reaction of (I) with maleic anhydride in benzene solution at 10° for 30 min gave a 1,8-cycloadduct (II), m.p. 98—99°, in quantitative yield; τ ($CDCl_3$, Me_4Si): 3·29—3·65 (3H, complex m, 6-, 7-, 8-H), 3·80 (1H, m, 5-H), 4·60 (1H, dd, *J* 9·0 and 5·5 Hz, 4-H), 5·00 (1H, d, *J* 9·0 Hz, 2-H), 5·72 (1H, dd, *J* 10·2 and 9·0 Hz, 3-H), and 6·93 (1H, ddt, *J* 10·2, 5·5, and 1·2 Hz, 3a-H).‡ Conversely, reaction of (I) with dimethyl acetylenedicarboxylate under similar conditions yielded the thiachromene (III), pale yellow prisms, m.p. 91—92° (*ca.* 65%); τ ($CDCl_3$, Me_4Si): 2·21 (1H, s, 4-H), 2·58—2·97 (4H, complex m, Ar-H), and 5·29 (1H, s, 2-H). Assignments and coupling constant values were confirmed by spin decoupling experiments.§ We suggest that (III) may be formed *via* the sequence shown in the Scheme. The cycloadduct (**a**) was not detected spectroscopically even at low temperature in CCl_4 solution. We feel that the [8 + 2] type of cycloadduct (**a**) should give rise to a norcaradiene intermediate (**b**) which could then smoothly rearrange owing to the electron-withdrawing group at C-2. It should be noted that a 1,8-cycloadduct of heptafulvene with dimethyl acetylenedicarboxylate, unlike the 1,8-cycloadduct (**a**), does not undergo further rearrrangement.[4]



Scheme

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‡ Satisfactory elemental analyses were obtained for all new compounds.

§ Detailed analyses of the decoupling will be reported elsewhere.

[1] Y. Kitahara, M. Funamizu, and T. Asao, Abstracts of the XVth Anniversary Meeting of the Chemical Society of Japan, 1962, p. 235; The preparation of $HgCl_2$ and $CdCl_2$ complexes of (I) have been reported briefly (T. Asao, and Y. Kikuchi, *Chemistry Letters*, 1972, 413).

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[4] W. von E. Doering, and D. W. Wiley, *Tetrahedron*, 1960, **11**, 183.

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