The chemistry of heterocyclic analogues of o-quinodimethane (o-QDM, 1) has attracted a great deal of attention recently, and several reports of the generation of the furan and pyrrole derivatives have appeared. The compounds 3,4-dimethylideneuracil 2, 3,4-dimethylidenethiophene 3 and 3,4-dimethylidenepyrrole 4 are π-conjugated non-Kekulé molecules that have aroused theoretical and synthetic interest. These 3,4-dimethylidene-heteroaromatics 2-4 were generated from the corresponding diazenes2 and have been detected by EPR, UV and NMR spectroscopy. They have also been shown by Berson and coworkers2 to react with a series of alkenes to form two types of cycloadducts: fused and bridged. The results are synthetically useful and have been elaborated upon by Takayama and coworkers in syntheses of multicentric compounds.1b,c

Diazene precursors are usually unstable at room temperature, therefore the search for possible substitutes becomes important. Various methods for generation of these highly reactive dienes have been developed.3,4 Among the many known methods for their preparation, that involving cheletropic elimination of SO2 from heteroaromatic-fused 3-sulfones 5-7 has drawn the most attention.1,4 Durst et al. were the first to generate o-QDM by thermal elimination of SO2 from a sultine, 1,4-dihydro-2,3-benzoxathiine 3-oxide.5 A significant advantage of using sultines is that their thermolysis occurs at a much lower temperature than that of corresponding sulfolenes (80–123 °C). Recently other papers on using sultines as precursors for nonclassical heteroaromatic molecules have appeared,6,7 however, the use of sultines in heteroaromatic analogues is still rare. We report here our work on the synthesis of furanosultine 8 with several dienophiles, and we detail its chemical reactivities other than pyrolysis. Our results show that thiophene-fused sulfolene 6 has very low reactivity compared to the corresponding sultine 9 in the Diels–Alder reaction.

The synthesis of 1,4-dihydrofuranol[3,4-d]-3,2-oxathiine 2-oxide 8, 5,7-dimethyl-1,4-dihydrothienol[3,4-d]-3,2-oxathiine 2-oxide 9 and 1,4-dihydro-6-tosylpyrrolo[3,4-d]-3,2-oxathiine 2-oxide 10, precursors for nonclassical heteroaromatic o-quinodimethanes, and their application in the Diels–Alder reactions are reported.

The Diels–Alder reactions of furan-fused sultine 8 with several dienophiles are presented in Table 1 (entries 1–5) and Scheme 2. Heating 8 with 3 equivalents of dimethyl acetylenedicarboxylate (DMAD) in benzene at 120–123 °C in a sealed tube for 1 h produced 5,6-dimethylidene-7-oxanorbornene 14a in 38% yield plus some polymer by-products (Table 1, entry 1). Essentially the same types of reactions were observed with diethyl fumarate (DEF), dimethyl maleate (DMM) and fumaronitrile (FN) (Table 1, entries 2–4). With N-phenylmaleimide (NPM), thermolysis at 134–140 °C gave a new type of product 15e in 24% yield. The low to medium yields of these reactions of furanosultine 8 with various dienophiles are disappointing, however, as their reaction products are different from those reported by Takayama and co-workers for the reactions of furan-fused sulfolene 5,8-10 where two types of products 14 and 15 were formed. Furthermore, the high yield of intractable polymers in all cases also implies that radical or biradical-initiated polymerization is involved.

Scheme 1 Reagents and conditions: i, AlCl3, diethyl ether, room temp.; ii, Rongalite, TBAB, DMF, 25 °C; iii, CICH2OMe, SnCl4–CS2

![Scheme 1](https://example.com/scheme1.png)
Alder reaction. Thus, in the reaction conditions studied here, the fused Diels–Alder adducts 16g–h can be obtained from the reaction of sultine 9 with dienophiles, but not from sulfolene 6. It is interesting to observe the great similarity between our results with sultines and those with diazenes reported by Berson et al.\(^2\) For example, in the thiophene–biradical 3 trapping experiments, the sole adducts found (85–100% yields) had the fused structure 16 rather than the bridged structure 14.

Reactions of N-tosylpyrrolosultine 10 with a series of dienophiles (3 equiv.) at 150–170 °C run smoothly to give three types of products: sulfolene 7 (20–40%), 1,2 Diels–Alder adducts 15 (0–42%) and fused adducts 16 (5–73%) (Table 1, entries 13–18). Basically the same reaction products are obtained even at 110 °C (Table 1, entry 15), however to our surprise, only 7 and the fused adduct 16i were obtained when DMAD was reduced to 1 equiv. (entry 14). The N-tosylpyrrolo-sulfolene 7 had been shown to be unreactive\(^10\) with dimethyl fumarate (DMF) even at 240 °C, however the N-tosylpyrrolosultine 10 reacted with DMF at 170 °C to give a fused adduct 16j (63%) and the isomerized 7 (32%) (Table 1, entry 16 vs. 20). It is also of interest to isolate the fused adduct 16i (5%) in the reaction of sultine 10 with DMAD compared with that of sulfolene 7,\(^10\) where 15i was the only product formed (entry 13 vs. 19).

These results can be explained by two mechanisms. The most obvious possibility is the formation of non-Kekulé biradicals (2–4), followed by Diels–Alder reaction with a dienophile to form either bridged (14) or fused adducts (16).\(^2\) Both adducts can add another dienophile to form the 1,2 adducts (15). Alternatively, a Diels–Alder reaction may first occur on the aromatic moieties of sultines 8–10 to give 17, from which SO\(_2\) trapping experiments, the sole adducts found (85–100% yields) had the fused structure 16 rather than the bridged structure 14.

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is eliminated instantaneously to give bridged adducts 14. Compound 14 further reacts with another dienophile to give the 1:2 adducts 15, and finally a retro-Diels-Alder reaction of 15 would occur to form 16 (Scheme 2). The latter mechanism was proposed by Takayama to explain results with corresponding sulfones 5 and 7. We conclude that the furano-, thieno- and N-tosylpyrrolo-fused sultines 8-10 reacted under milder condition than the corresponding sulfones 5-7 and their reaction products were different in many cases. When generated in the presence of a dienophile, they can provide elegant synthons for the formation of [4 + 2] cycloadducts. If less reactive trapping agents were used, the diene was recaptured by SO₂ to afford the sulfones 5-7 (path 3 in Scheme 2).¹¹

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Footnotes

2 Dichlorides 11, 12 and 13 have been reported in the literature and our samples correspond in all respects with the reported properties. For all products satisfactory spectral data were obtained. Selected data for 8: light yellow oil; ¹H NMR (300 MHz, CDCl₃) δ 7.40 (1 H, s), 7.36 (1 H, s), 5.28 (1 H, AB, J 14.4 Hz), 5.02 (1 H, AB, J 14.4 Hz), 3.87 (1 H, A'B', J 15.6 Hz) and 2.42 (3 H, s); ¹³C NMR, 145.50 (C₆), 135.54 (C₅), 130.15 (CH), 127.03 (CH), 119.19 (CH), 117.12 (C₆), 114.44 (CH), 110.97 (C₅), 55.99 (CH₂), 48.21 (CH₂) and 21.64 (CH₃); m/z 202 (M⁺), 138 100%; 111, 3671 and references cited therein.

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