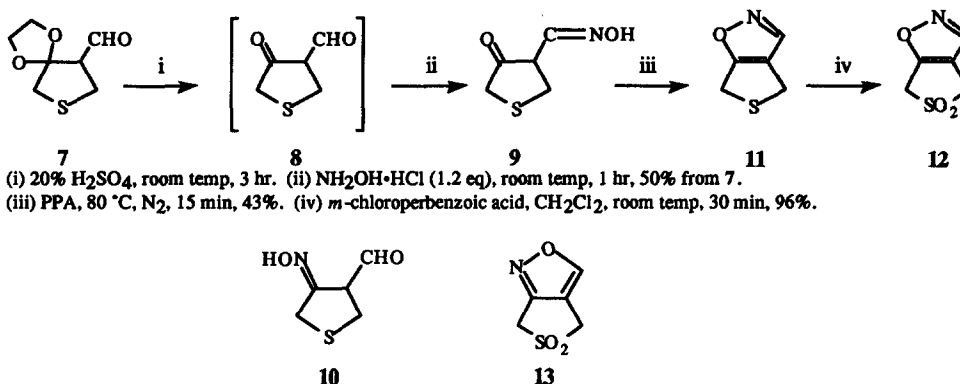




nitrogen. Subsequent oxidation with *m*-CPBA gave the target molecule **12** in 96% yield.<sup>13</sup> Spectral analyses revealed that the structural isomer **13** was not present.<sup>14</sup>

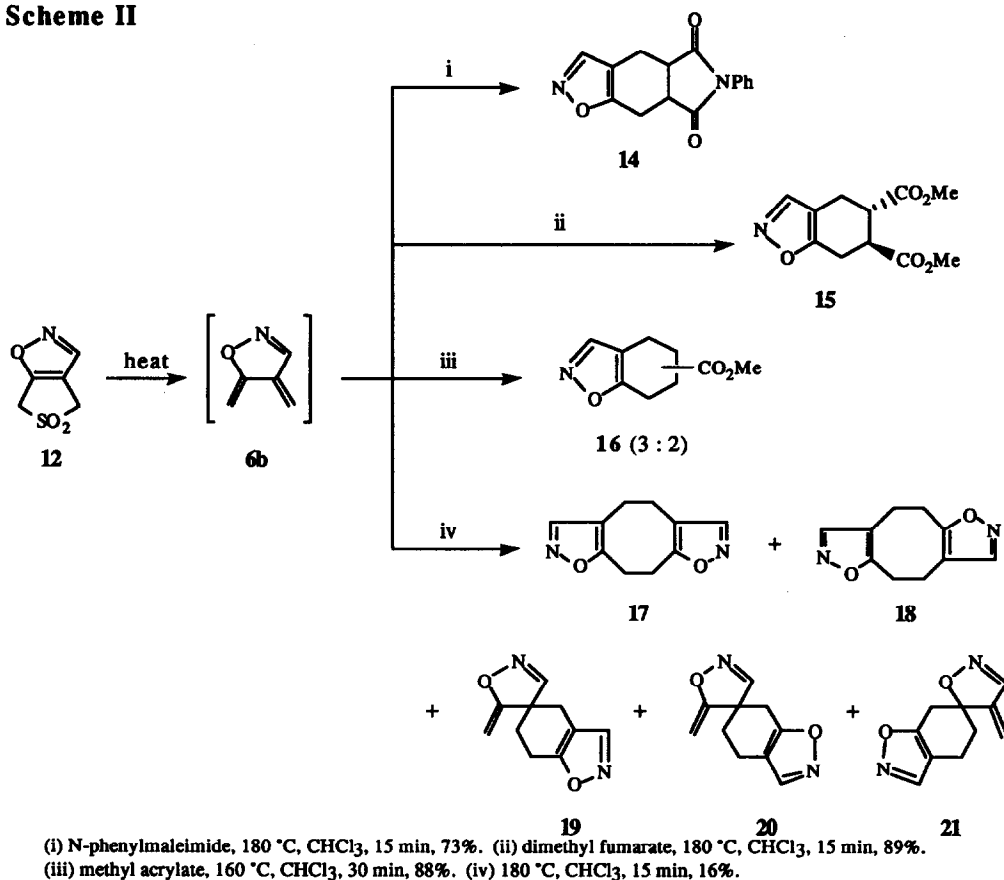
### Scheme I



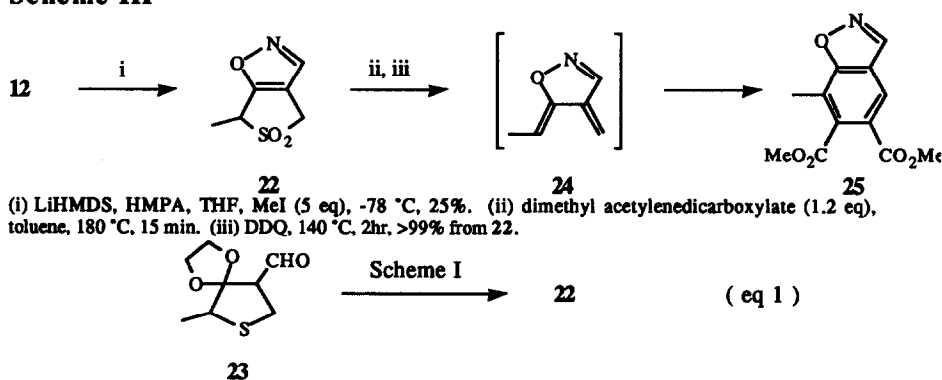
Heating the isoxazole-fused 3-sulfolene **12** in the presence of a suitable dienophile readily produced the [4+2] cycloadduct (Scheme II). This is consistent with that loss of SO<sub>2</sub><sup>15</sup> from **12** occurred in the first place to give the *o*-dimethylene isoxazole **6b** which was then intercepted by the dienophiles. When methyl acrylate, an unsymmetric dienophile, was used in this reaction, a 3 : 2 mixture of isomers of the cycloadduct **16** was produced showing little regioselectivity. When **12** was heated in the absence of a dienophile, the complex dimerization reactions of **6b** produced in low yield a mixture of two [4+4] dimers [**17** (10%), **18** (3%)] and three [4+2] dimers [**19**, **20**, **21** (3% altogether)]. The mode of dimerization of **6b** is quite different from those of other known *o*-dimethylene heterocycles. Only [4+2] dimers were obtained from dimethylene thiophene (**3**, X = S)<sup>3a-j</sup> and thiazole (**4**, X = S, R = H).<sup>10</sup> Whereas only head-to-head [4+4] dimers were formed from dimethylene furan (**3**, X = O),<sup>3b</sup> pyrrole (**3**, X = NSO<sub>2</sub>Ph),<sup>7</sup> and oxazole (**4**, X = O, R = H).<sup>4</sup> Furthermore, the dimers of some other *o*-dimethylene heterocycles, such as pyrazole<sup>5,11</sup> analogue, were never observed.

The 3-sulfolene ring of compound **12** not only serves as a masked functionality of *o*-dimethylene, but also is the 1-carbanion equivalent of the *o*-quinodimethane.<sup>16</sup> Thus, the deprotonation of **12** with lithium hexamethyldisilazide (LiHMDS) followed by treatment with excess MeI gave the  $\alpha$ -methylated product **22** (Scheme III). Although the yield was only moderate (25%), the alkylation reaction is regioselective that no other methylated isomers were obtained. The structural assignment was confirmed by an unambiguous synthesis of **22** from **23** (eq 1) following the same reaction sequence shown in Scheme I. Compound **22** should serve as the precursor for the substituted *o*-dimethylene isoxazole **24**. Indeed the reaction of compound **22** with dimethyl acetylenedicarboxylate at 180 °C produced a cycloadduct which was directly aromatized with DDQ to give the benzoisoxazole **25** in nearly quantitative yield. This example illustrates the broad synthetic applicability of **12** as the equivalent of *o*-dimethylene isoxazole **6b** because other alkylated derivatives of **6b** should also be preparable from **12**.

## Scheme II



## Scheme III



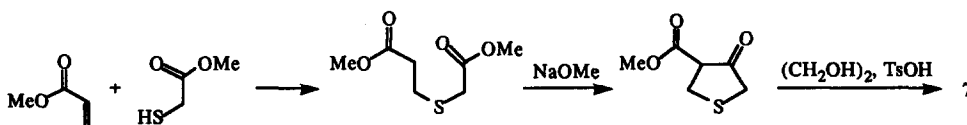
In summary, we have described herein the first success of the synthesis of the unsubstituted *o*-dimethylene isoxazole **6b** and its cycloaddition reactions. In addition, one can take advantage of the 3-sulfolene functionality of **12** to prepare the precursors of the alkylated derivatives of **6b** such as **22**.

It should also be noted that compound 7, containing a 1, 3-dicarbonyl functionality, should be a useful intermediate for the preparation of a number of other heterocycle-fused 3-sulfolenes, the precursors for *o*-dimethylene heterocycles.

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