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Novel Products from Thermolysis of 5,5-Dimethyl-2,2-diphenoxy-Δ^3-1,3,4-oxadiazoline in the Presence of DMAD

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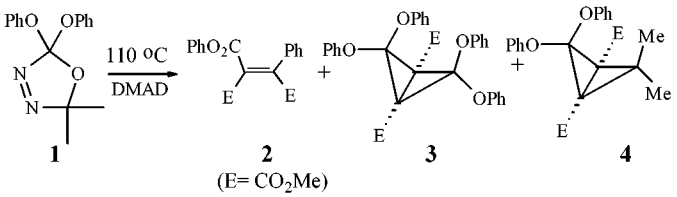
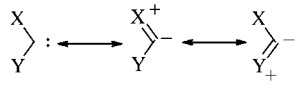
ABSTRACT



Thermolysis of 1 at 110 °C in benzene containing DMAD (dimethyl acetylenedicarboxylate) leads to triester 2 and bicyclo[1.1.0]butanes, 3 and 4.

The chemistry of nucleophilic carbenes continues to attract attention.[1−5] Nucleophilic carbenes are those in which one or more donor substituents at the carbene carbon feed electron density into the formally vacant orbital of the carbene singlet. Such donation can stabilize a carbene to the extent that it becomes persistent[6−8] and can give it nucleophilic properties,[9−12] Scheme 1. We were interested in

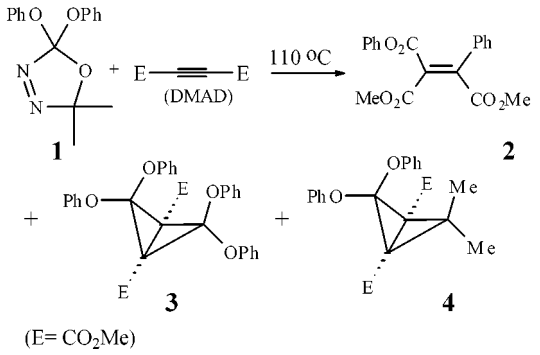
Scheme 1



replacing the substituents of the nucleophilic dialkoxycarbenes with aryloxy groups, not only to tune the nucleophilicity of the carbenes but also to look for new chemistry that might arise from reactions at the aromatic ring.

We now report that thermolysis of 5,5-dimethyl-2,2-diphenoxy-Δ^3-1,3,4-oxadiazoline (**1**) in the presence of DMAD affords products **2**−**4**, via diphenoxycarbene, Scheme 2.[13]

Scheme 2



Diphenoxycarbene was generated by thermolysis (sealed tube, 110 °C) of **1** (0.22 M) in benzene containing DMAD

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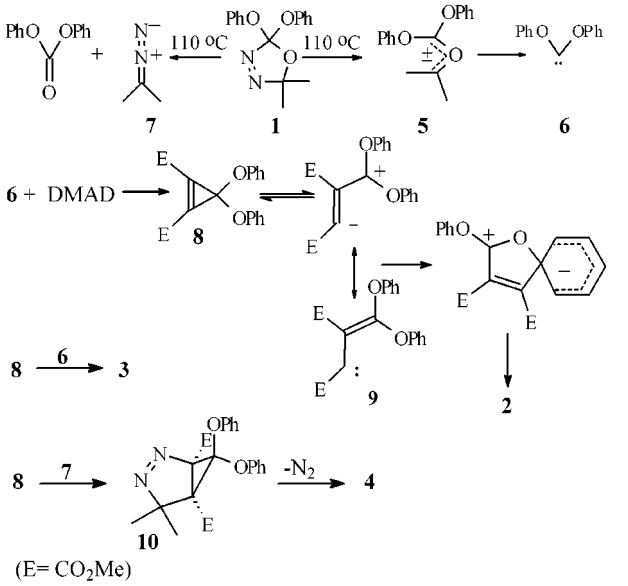
Scheme 3

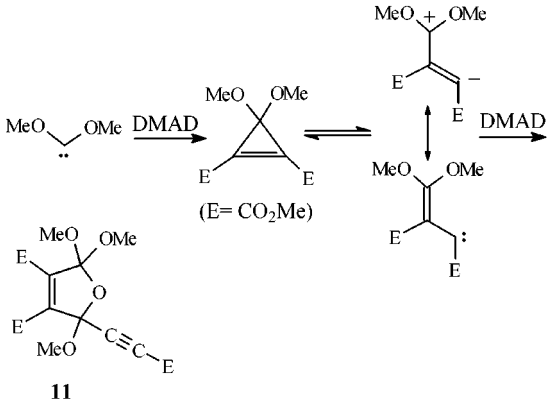


(0.20 M), Scheme 3. The thermolysis involves two competing 1,3-dipolar cycloreversions, one leading to N_2 and **5**[14] and the other to diphenyl carbonate and **7**, Scheme 3. Carbonyl ylide **5** fragments[14] to acetone and carbene **6**, and the latter adds to DMAD to make diphenoxycyclopropene **8**. Reversible opening of **8** to **9** leads to attack[15] at the *ipso* position of the phenoxy group,[16] to form phenyl (*E*)-2,3-bis(methoxycarbonyl)-3-phenyl propanoate (**2**) which was isolated in 40% yield by chromatography of the crude products. Addition of **6** to the reactive cyclopropene **8** would generate dimethyl 2,2,4,4-tetraphenoxybicyclo[1.1.0]butane-1,3-dicarboxylate (**3**), obtained in ca. 8% yield. Dimethyl 4,4-dimethyl-2,2-diphenoxybicyclo[1.1.0]butane-1,3-dicarboxylate (**4**) probably arises from cycloaddition of **7** to **8** to form pyrazoline **10** initially, Scheme 3. Loss of N_2 from **10** at 110 °C would lead to **4**, isolated in ca. 4% yield. Product **4** is unlikely to be the result of cycloaddition between **8** and 2-propylidene because the latter undergoes a 1,2 migration of H with $k \cong 10^7\ s^{-1}$ at ambient temperature.[17]

The three products provide indirect evidence for the equilibration of **8** with **9**, neither of which could be observed directly. Equilibration of cyclopropenes with vinylcarbenes has been proposed before,[18] and it is known to be facile for 3,3-dialkoxycyclopropenes.[19,20] Compound **2** presumably arises from intramolecular reaction of the ring-opened species, which can be viewed as a hybrid of a dipole and a π-delocalized vinylcarbene (**9**) (Scheme 3). Moreover, **3** and **4** are likely to be the result of cycloadditions (of **6** and **7**) to **8**.

Products **3** and **4** suggest that the phenoxy substituents, relative to alkoxy substituents, destabilize an intermediate such as **9**, thereby diverting some material through reactions of **8**. Analogous products that might be generated by addition to a cyclopropene intermediate are not obtained from reaction of dimethoxycarbene with DMAD. Dimethoxycarbene does react with DMAD[21] but to afford **11**, containing two units of DMAD and one of the carbene, Scheme 4. Compound

Scheme 4



11 is most likely derived from an acyclic intermediate analogous to **9**, rather than from a cyclic intermediate analogous to **8**.

Neither diacetals of bicyclo[1.1.0]butane-2,4-dione (e.g., **3**) nor acetals of bicyclo[1.1.0]butanone (e.g., **4**) have been reported previously. Other bicyclo[1.1.0]butanes have been studied intensely, in particular to try to discover which orbital of the system is the HOMO.[22] Often computational methods could not be supported by experiment because the relevant compounds had not been prepared.[22] Clearly, compounds **3** and **4** are of considerable interest, not only in their own right but also by reactions of the ester groups, for example, as precursors of other bicyclo[1.1.0] systems. Efforts to improve

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the yields, by increasing the concentration of DMAD to 0.80 M, led to enhancement of the yield of **3** to 32%. Further improvement may be possible.

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