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Communications to the Editor

Homolysis of Carbenes. Free Radicals from Dialkoxycarbenes

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We report the first clear cases of thermal fragmentation of acyclic dialkoxycarbenes in solution to radical pairs consisting of methoxycarbonyl and allylic radicals, Scheme 1, in which both the carbenes and the radicals could be trapped.

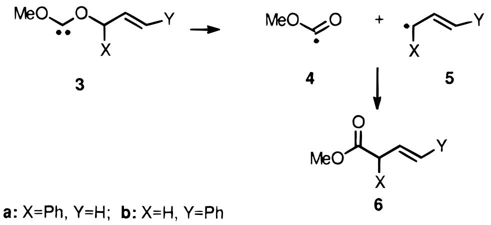
2-Methoxy-2-allyloxy-5,5-dimethyl-Δ^3-1,3,4-oxadiazolines (**2a**, **2b**) were prepared by the acid-catalyzed exchange reaction[1−4] of the 2-acetoxy-2-methoxy analogue (**1**) with 1-phenyl-2-propen-1-ol and with cinnamyl alcohol, respectively, Scheme 2. Thermolysis of **2** in benzene (sealed tube) at 110 °C afforded the esters (**6**), Scheme 3. Both **2a** and **2b** afforded **6a** and **6b** in 2:1 and 1:2 ratio, respectively (total yields 60%, isolated).

These results might be accounted for with competitive [1,2]-migrations and [2,3]-sigmatropic rearrangements of carbene intermediates or with another mechanism, possibly bypassing a carbene entirely. Carbene trapping with *t*-BuOH in benzene to afford the expected[5−7] orthoformate **7** in 70% yield (isolated), confirmed that carbene **3b** is indeed formed upon thermolysis of **2b** (Scheme 4). The yields of **6** and **7** as a function of [*t*-BuOH] were shown to be interdependent, Figure 1, indicating that the carbene **3b** is the precursor of radicals **4** and **5b**, a conclusion that was supported by interception of the radicals. Thus, thermolysis of **2b** in benzene containing TEMPO afforded adducts **8** and **9**, respectively (Scheme 5).[8] The yields of **6** dropped with increased [TEMPO], but traces of the esters could always be detected by GC. That is not surprising because TEMPO should not trap caged radical pairs and because TEMPO adducts of radicals can regenerate those radicals upon heating.[9]

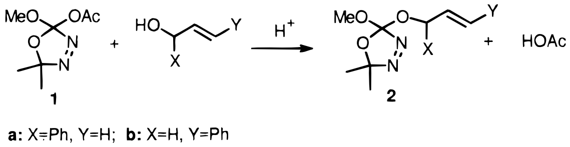
"*β*-Scissions" of alkylidenes to an alkyl radical and an unsaturated radical, analogous to the demonstrated fragmentations of Scheme 1, are very rare[10] for either carbenes with a triplet ground state or for ground-state singlets with a readily accessible triplet state. Ring opening of cyclic oxacarbenes to acyl alkyl biradicals (dotted arrow, Scheme 6) has been proposed,[11−12] and biradical combination, either from the photoreaction of cyclobutanones[14−19] or from diazenes,[12] to cyclic oxacarbenes (Scheme 6) is fairly well established. Good yields of alkenes that are apparently biradical-derived have been obtained from presumed cyclic dioxacarbenes.[20]

Analogous processes involving fragmentations of acyclic alkoxycarbenes, in condensed phase reactions, have been suggested to account for minor products. For example, methoxycarbene, generated in solution from a tosylhydrazone precursor, afforded traces of methane,[21] possibly from methyl radicals, and

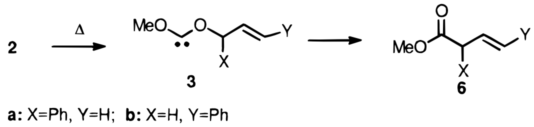
Scheme 1



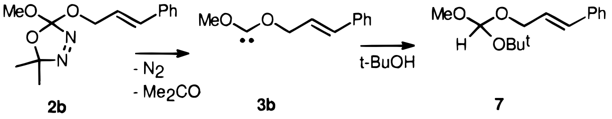
Scheme 2



Scheme 3



Scheme 4



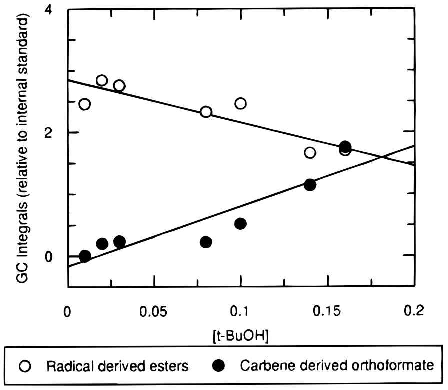


Figure 1. Relative yields of **2** and **7** as a function of [*t*-BuOH].

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[8] A trace amount of the methyl adduct of TEMPO, presumably from decarboxylation of the methoxycarbonyl radical, was detected also. Its identity was confirmed by comparison with an authentic sample, prepared by thermolysis of di-*tert*-butyl peroxide in the presence of TEMPO.

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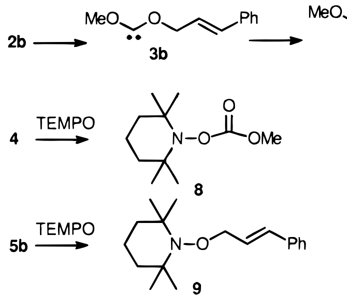
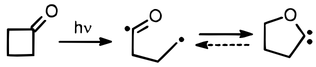
Scheme 5



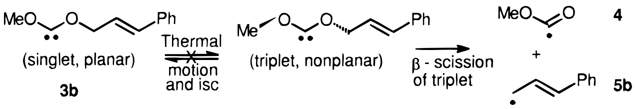
Scheme 6



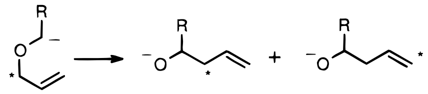
diethoxycarbene from a similar precursor afforded ethylene (1.5 parts) and ethane (1 part) out of 51.5 parts of identified gaseous products. Ethylene and ethane were attributed to ethyl radicals formed from diethoxycarbene, although neither the radical nor the carbene were trapped.[22] Carbenes **3b**, on the other hand, afford esters **6** as major products (60%, isol) and trapping of the carbene with *t*-BuOH and of radicals with TEMPO established that **6** are derived from the sequence oxadiazoline → dialkoxycarbene → radicals → esters. A further indicator of radical intermediates from both **2a** and **2b** was the formation of bibenzyl as a major coproduct of their thermolysis in toluene. Formation of bibenzyl must be attributed to attack of radicals on toluene.

Given that sigmatropic rearrangement of analogous (bisheteroatom)carbenes is well-known,[23−26] the fragmentation of carbenes **3** to radicals is surprising. One mechanism for the fragmentation would involve intersystem-crossing to the triplet carbene and formation of the double bond of the methoxycarbonyl radical by β-scission (Scheme 7). Although the singlet and triplet states of *nonplanar* dihydroxycarbene are almost degenerate at lower levels of theory[27] and separated by ca. 20−37 kcal mol^{-1} at higher levels of calculation,[28,29] there is a barrier between the *planar* singlet ground state and the nonplanar triplet state of ca. 76 kcal mol^{-1} (in dimethoxycarbene).[30] Thus the triplet mechanism is most unlikely. Moreover, it is difficult to accommodate the observed preference for the ester (**6**) that is most closely related to the geometry of the starting carbene with a triplet mechanism. That preference, although it is not understood at this time, implies very fast coupling, competitive with separation by diffusion. The [2,3]-Wittig rearrangement (Scheme 8), which occurs with partial retention of configuration,[31−33] is reminiscent of the "memory effect" observed here.

Scheme 7



Scheme 8



There have been only a few theoretical investigations of the mechanism by which dialkoxycarbenes dissociate into radical pairs.[15,34] Computation of the singlet and triplet potential energy surfaces of carbene **3b** is not possible at a currently reasonable cost, but calculations with the model system, $CH_2{=}CHCH_2O$-(HO)C:, are in progress.

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Supporting Information Available: Spectroscopic data for compounds **2a**, **2b**, **6a**, **6b**, **7**, **8**, **9**, and the methyl adduct of TEMPO (3 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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