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Extrusion Reactions of Carbon Dioxide from Orthoesters and Derivatives: An *ab initio* Study of Some Cyclic Carbenes

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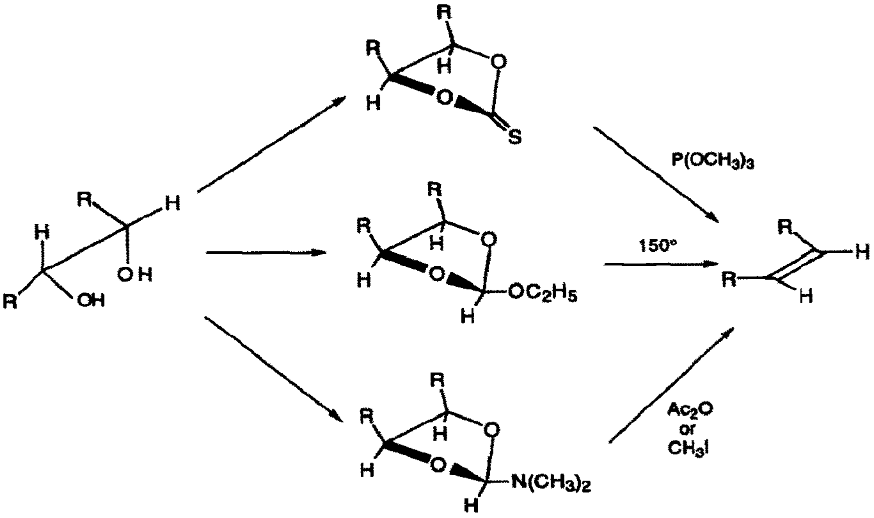
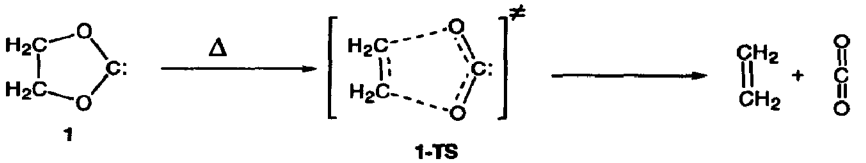
Abstract: ***ab initio*** Calculations showed that the loss of carbon dioxide from cyclic dioxocarbene **1** can proceed *via* a synchronous process with activation energy: $\Delta G^{\neq} =$ *ca*. 7.1 kcal/mol (MP2/6-31G**). The corresponding unsaturated analog **2** was calculated to be more stable: $\Delta G^{\neq} =$ *ca*. 25 kcal/mol (MP2/6-31G**) and its aromatic character was probed.

Deoxygenation of derivatives of 1.2-glycols by extrusion of carbon dioxide and other molecules from thiocarbonates, orthoesters, and amide acetals provides a versatile method for formation of carbon:carbon double bonds.[1,2] For example, alkene formation has been shown to proceed with retention of stereochemistry under mild conditions.[1, 2a,d] Relatively few details of the mechanisms of these reactions are known, but most authors have proposed cyclic dioxacarbenes (see below) as probable intermediates. Independent evidence for carbene formation has been presented in related reactions of orthoesters.[3]



An important question concerning these reactions is whether loss of CO_2 is in fact a viable reaction pathway from carbene intermediates (eq. 1). To answer this question, we carried out *ab initio* molecular orbital calculations[4] the objective of which was to characterize the transition structure **1-TS** and evaluate the activation



(eq. 1)

energy for the decomposition of **1**. The reaction pathway was treated as a synchronous cheletropic process with C_{2v} symmetry.[5] The calculations led to reasonable structures of **1** and **1-TS** (Figure 1), and the latter structure was characterized as a first-order saddle point by a normal coordinate analysis calculation that gave rise to one imaginary frequency corresponding to one negative eigenvalue. The changes in bond lengths and angles in the evolution of structure **1** to **1-TS** are consistent with expectation as CO_2 breaks away.

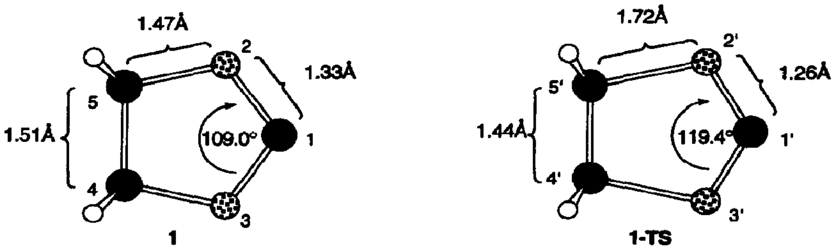


FIGURE I. Geometry of I and 1-TS: MP2/6-31G**

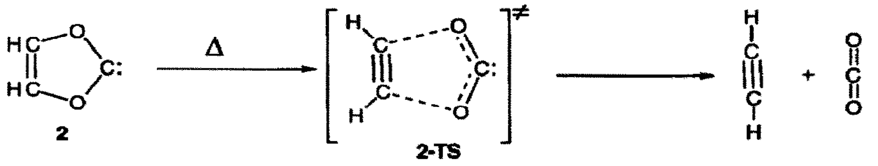
The calculations (Table 1) also demonstrate that the structure and energy of **1** and **1-TS** are sensitive to size of the basis sets invoked and the extent of electron correlation, but the results suggest that $\Delta E^{\neq}$ is in the range 10±1 kcal/mol. The free energy of activation for loss of CO_2 was calculated from thermodynamic data obtained by vibrational analyses of **1** and **1-TS** at the MP2/6-31G** level: $\Delta G^{\neq} = 6.3 + 0.0026T = 7.1$ kcal/mol at 298.15°.[6] This finding is consistent with mechanisms that involve facile thermal breakdown of carbene intermediates in these reactions since substituents at carbon 4 and 5 positions would not be expected to significantly influence the magnitude of the barrier.[7] In addition, these results suggest that attempts to trap carbene **1** at ambient temperatures will be problematic.

TABLE 1. Activation Energies for Eq. 1 and 2 and Structural Parameters for **1-TS**.

Computational Method	1-->1-TS				2-->2-TS
	$\Delta E^{\neq a}$	$C_1 \cdots O^b$	$O_2 \cdots C_5{}^b$	$O_2 \cdots C_1 \cdots O_3{}^c$	$\Delta E^{\neq a}$
HF / 3-21G	34.4	1.23	1.90	126.5	-
HF / 6-31G**	43.5	1.21	1.87	126.2	63.5
MP2 / 6-31G**	8.8	1.26	1.72	119.4	27.3
MP3 // MP2 / 6-31G**	17.1	-	-	-	37.3
MP4(DQ) // MP2 / 6-31G**	17.8	-	-	-	38.0
MP4(SDQ) // MP2 / 6-31G**	15.4	-	-	-	35.2
MP4(SDTQ) // MP2 / 6-31G**	9.7	-	-	-	27.9
QCISD(T) // MP2 / 6-31G**	11.3	-	-	-	30.1

[a] Electronic activation energy differences in kcal/mol. [b] Bond distance in Å. [c] Bond angle in degrees.

It was of interest to compare the calculated activation energy for the related reaction of the dioxolene system **2** with that for the saturated analog since the unsaturated carbene is a Hückel aromatic system with 6-π electrons in a cyclic array. To the extent that this results in stabilization one expects a corresponding increase in activation energy. The computed structures for **2** and **2-TS** (Figure 2) reveal minor differences from those of saturated analogs, the most interesting of which is the near identity of the ring bonds in **2**. The calculated[6] activation energy for eq.2 (MP2/6-31G**) is considerably larger than that for the saturated analog: 25.0 kcal/mol, and it is tempting to attribute at least part of this difference to loss of aromaticity in **2** as the transition structure evolves. As a test for aromaticity, we calculated the change in enthalpy for the isodesmic reaction described in eq. 3. The result,[8] -13.3 kcal/mol, is consistent with enhanced stability for **2**. Other data also lend support to the idea of delocalization in **2**. For example, calculated Mulliken charges on C_1 and O are almost identical for the two carbenes (Table 2), but more reliable routines lead to dramatic decreases in the amount of negative charge on $O_{2,3}$ and $C_{4,5}$ and smaller increases on C_1 that are consistent with delocalization in **2**.[9,10]



(eq. 2)

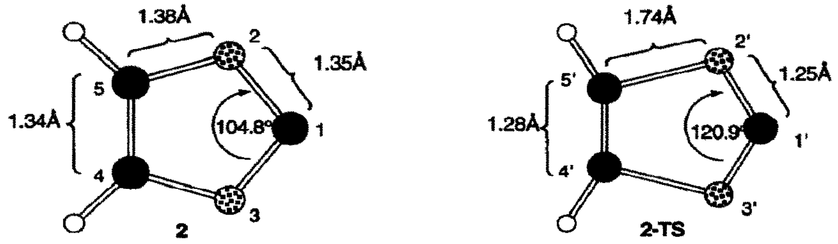
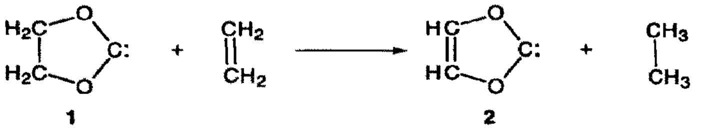


FIGURE 2. Geometry of 2 and 2-TS: MP2/6-31G**



ΔH = -13.2 kcal/mol (MP2/6-31G**) (eq. 3)

TABLE 2. Calculated Charge Distributions for **1** and **2**.

Atom Number(s)	1			2		
	Mulliken[a]	Chelpg[b]	M-K/S[c]	Mulliken[a]	Chelpg[b]	M-K/S[c]
C_1	.449	-.253	-.262	.449	-.296	-.305
$O_{2,3}$	-.576	-.159	-.185	-.546	-.0066	-.0041
$C_{4,5}$	.042	.448	.532	.118	.077	.057
H	.154	.080	-.107	.203	.078	.100

[a] Ref. 4. [b] Ref. 10. [c] Ref. 11.

In the more general context of carbene chemistry, the properties of **1** and **2** are consistent with those of open chain analogs in terms of expected carbene philicity.[7] The calculated HOMO-LUMO gaps for **1** and **2** are 15.4 eV and 14.8 eV, respectively, and compare favorably with that of the *all-cis-* dimethoxycarbene (15.0 eV).[7] It is of interest to note that the HOMO's of **1** and **2** are of different symmetry, however, the former being associated with the in-plane lone pair (A1) while the latter is associated with a cyclic π-system above and below the molecular plane (B1). This difference will affect the detailed correlation diagrams for decarboxylation and this aspect of these reactions will be reported subsequently.

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