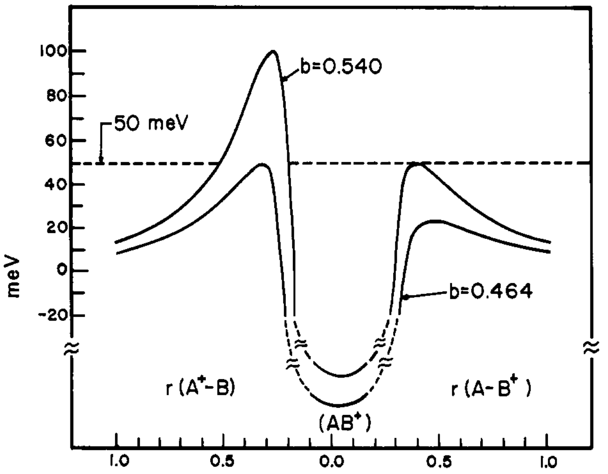

Figure 1. Effective potential for charge-transfer reactions $A^+ + B \rightleftarrows A + B^+$ at impact parameters of 0.540 nm (upper curve) and 0.454 nm (lower curve) when $\mu = 13.33$ au, $\alpha_A = 2\alpha_B = 10$ au, and $E = 50$ meV.

unequally.[7] The proposal of Ausloos and Lias,[1-4] however, leads to an equilibrium constant which must be corrected by the ratios of the forward and reverse collision frequencies. In the low temperature regime where all interactions except ion-induced dipole ones may be neglected, the collision frequencies are given by the polarization limit $Z_{A^+} = 2\pi e(\alpha_B/\mu)^{1/2}$ where e is the electronic charge and μ is the reduced mass of the system and is equal in both directions.[8] Since there is an equal probability for the charge to be on either species when the products separate, the equilibrium constant predicted by Ausloos and Lias is not unity but $K_{\text{int}} = {}^1/_2 Z_{A^+}/{}^1/_2 Z_{B^+} = (\alpha_B/\alpha_A)^{1/2}$ and $\Delta S = \Delta S_{\text{int}} = R \ln (\alpha_B/\alpha_A)^{1/2}$. The principle of equal a priori probabilities and the kinetic intermolecular correction are mutually exclusive.

The inclusion of such an intermolecular correction in this case also violates conservation of angular momentum. The dynamic model for ion–molecule reactions is well-established.[8-10] It may be applied to a charge-transfer reaction by restricting our demonstration system to one in which penetration of the centrifugal barrier (complex formation) is necessary for charge transfer, which should be the case at low temperatures. The description of an ion–molecule charge-transfer collision may then be based on defining the maximum angular momentum $L_{\max}$ (or the maximum impact parameter $b_{\max}$) at a given energy for which capture may occur. That is, only those encounters between A^+ and B for which the kinetic energy E exceeds the entrance rotational barrier, $V_{\text{rot in A}^+} = L^4/(8\alpha_B e^2\mu^2)$, may lead to capture and therefore collision. Conversely, the kinetic energy determines the maximum angular momentum $L_m = (8\alpha_B e^2\mu^2 E)^{1/4}$, or maximum impact parameter, $b_{\max} = [(2e^2\alpha_B)/E]^{1/4}$, for which collision may occur. This, however, defines only the collision frequency but does not speak of the number of encounters which may lead to products $A + B^+$. In order for these to be formed, the products must be able to separate, and this requires, of course,[11,12] that the (constant) energy exceed the rotation barrier in the exit direction $V_{\text{rot exit B}^+}$. Since α_B differs from α_A, $V_{\text{rot exit B}^+} = V_{\text{rot in A}^+}\alpha_A/\alpha_B$. When $\alpha_A = \alpha_B$ this is no problem in the forward direction because then the exit barrier is always smaller than the entrance barrier, but that is then not the case for the reverse reaction. Now $V_{\text{rot exit A}^+} = V_{\text{rot in A}^+}$ and the rate constant (rather than collision frequency) for the reverse reaction is exactly equal to the rate constant or collision frequency for the slower forward reaction. This is illustrated in Figure 1 which shows the effective potential V_e when $m_A = 40$ au, $m_B = 20$ au, $\alpha_A = 10$ au, $\alpha_B = 5$ au, and $E = 50$ meV for impact parameters of $b_{A^+} = 0.454$ and $b_{B^+} = 0.540$ nm, respectively. While impact parameters less than 0.454 nm permit charge exchange and complex formation in both directions, those between 0.454 and 0.540 au allow the formation of the collision complex from A and B^+, but the complex cannot penetrate the rotational exit barrier to A^+ and B, and the complex *must* redissociate to A and B^+. Therefore, $k_f/k_r = K = 1$, and $\Delta S_{\text{int}} = \Delta S = 0$, and not $R \ln (\alpha_A/\alpha_B)^{1/2}$ as required by the correction hypothesis. This simple, well-established dynamic argument, which is another expression of the principle of detailed balancing, clearly demonstrates that intermolecular entropy effects are excluded on the basis of simple physical laws alone. It is an interesting conclusion that the effective collision rates of the forward and reverse reactions in equilibria must be the same.

If A and B represent molecular entities, the matter is more complicated because the total angular momentum J is conserved, and the rotational distributions of reactants and products must be considered also. The formalism is now more complex and requires assumptions[5,12] which make the argument less stringent.

It remains to be understood why some experimental measurements appear to require a collisional correction to yield entropy data consistent with other information. It is possible that the experiments in question may not have been performed under true equilibrium conditions and that a kinetic component remained; when ions are sampled within 20 collisions of their formation,[13] the rate of formation in the reverse direction may become an influencing factor. Indeed, equilibrium measurements are also sensitive to relatively minor potential errors in the measurement of gas composition, mass-dependent ion-detector response, etc.[14]

Acknowledgment. The support of the Department of Energy under contract DEAS02-76-ERO-2567 is acknowledged gratefully.

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(7) At low density, such a stabilization would be independent of the nature of the ion but dependent on density and composition because it corresponds to the integral over attraction terms with all neutrals in the system. Those should become unequal for the two ions only at densities approaching those of the condensed phase.

(8) G. Gioumousis and D. P. Stevenson, *J. Chem. Phys.*, **29**, 294 (1958).

(9) E. W. McDaniel, "Collision Phenomena in Ionized Gases", Wiley, New York, 1964, p 60 ff.

(10) M. Henchman, "Ion-Molecule Reactions", Vol. 1, J. L. Franklin, Ed., Plenum Press, New York, 1972, p 101.

(11) This limitation was first pointed out by H. M. Rosenstock, U.S. AEC Report JLI-650-3-T, TID-4500 (1959). It is a precursor of the phase space theory; J. C. Light, *J. Chem. Phys.*, **40**, 3321 (1964).

(12) G. G. Meisels, H. J. Weiss, G. M. L. Verboom, and T. Hsieh, *J. Am. Chem. Soc.*, **101**, 7189 (1979).

(13) S. G. Lias, private communication.

(14) A. J. Illies and G. G. Meisels, to be published.

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Facile Generation of a Reactive Palladium(II) Enolate Intermediate by the Decarboxylation of Palladium(II) β-Ketocarboxylate and Its Utilization in Allylic Acylation

Sir:

A reactive palladium(II)–enolate complex[1] is a useful reaction intermediate in organic synthesis.[2] Here we report a facile generation of the reactive palladium(II) enolate intermediate by the decarboxylation of a palladium(II)–β-ketocarboxylate complex under a mild condition and its utilization in allylic acylation. Thus, a catalytic amount of Pd(PPh$_3$)$_4$ induced the decarboxylation of allylic β-ketocarboxylates to produce α-allylic ketones via π-al-

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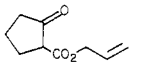
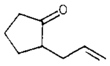
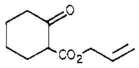
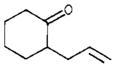
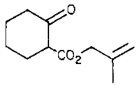
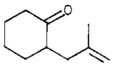
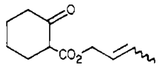
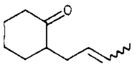
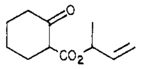
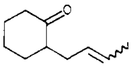
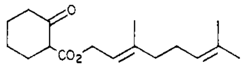
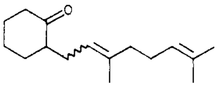
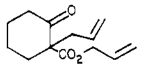
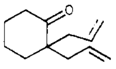
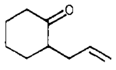
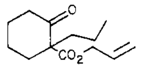
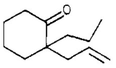
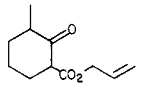
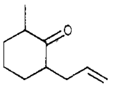
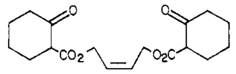
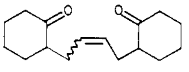
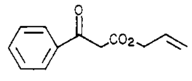
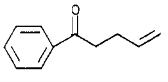
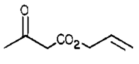
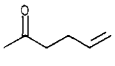
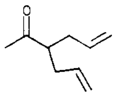
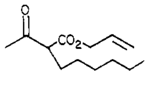
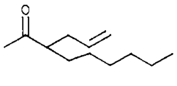
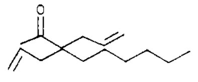
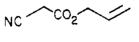
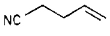
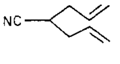
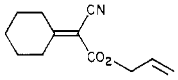
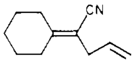
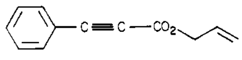
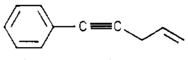
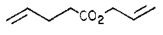
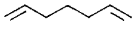
(1) The palladium(II)–enolate complex may be formally expressed in three structures: palladium(II)–enolate, oxa-π-allylpalladium(II), and 2-oxoalkylpalladium(II) complexes. As sufficient information to discriminate these three structures is not presently available, we tentatively expressed it as the palladium(II)–enolate complex.

(2) Theissen, R. J. *J. Org. Chem.* **1971**, *36*, 752. Ito, Y.; Hirao, T.; Saegusa, T. *Ibid.* **1978**, *43*, 1011. Ito, Y.; Aoyama, H.; Hirao, T.; Mochizuki, A.; Saegusa, T. *J. Am. Chem. Soc.* **1979**, *101*, 494.

Table I. Gd(0)-Catalyzed C–C Bond Formations by the Decarboxylations of Allylic β-Ketocarboxylates and Related Compounds[a]

entry	ester	temp, °C	time,[b] h	CO_2 evolved, %	products[c] (yields,[d] %)			
1		room temp	3	100		(88)		
2		room temp	0.5	99		(96)		
3		room temp	1	97		(92)		
4		room temp	1	96		(75)		
5		room temp	1	94		(72)		
6		50	1	99		(39)		
7		room temp	2	94		(67)		(9)
8		room temp	2	91		(67)		
9		room temp	1	98		(94)		
10		room temp	2	87		(41)		
11		room temp	1	100		(92)		
12		room temp	2	81		(37)		(16)
13		room temp	1.5	93		(32)		(16)
14		50	2			(69)		(16)
15		50	2	98		(63)		
16		50	3	72		(21)		
17		120	3	18		(23)		

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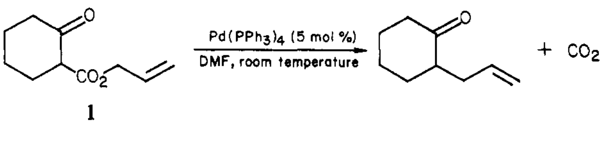
[a] Reactions were carried out under nitrogen with 1.0–1.5 mmol of allylic esters and 5.0 mol % of $Pd(PPh_3)_4$ in 5 mL of DMF. [b] The reactions carried out at room temperature evolved CO_2 quantitatively within 30 min. [c] All products were identified by spectral data. Byproducts detected by GLPC analysis in yields of less than 5% were not identified. [d] Yield was determined by GLPC analysis and was based on allylic ester. [e] The reaction was carried out by using 0.26 mmol of allyl cyanoacetate and 5.0 mol % of $Pd(PPh_3)_4$ in 30 mL of benzene. CO_2 analysis was not carried out.

lylpalladium(II)–enolate complexes.

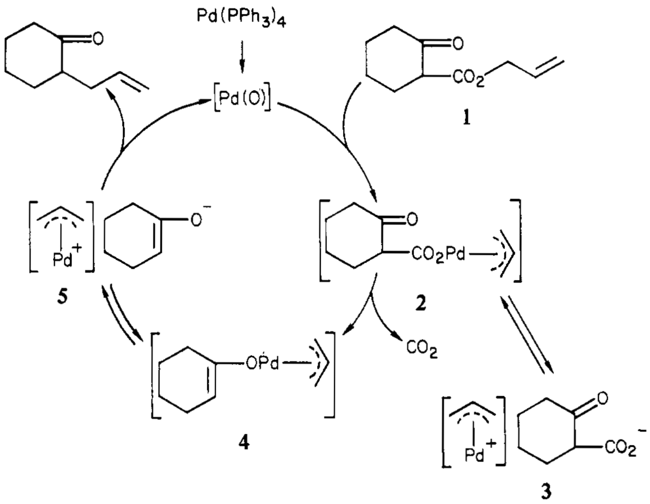
All experimental operations described below were carried out under nitrogen. A typical procedure is as follows. Allyl cyclohexanone-2-carboxylate (**1**) (1.23 mmol) was added to 5 mL of dimethylformamide (DMF) containing 5 mol % of $Pd(PPh_3)_4$ at ambient temperature. A rapid and quantitative evolution of CO_2 took place in 0.5 h. GLPC analysis of the resulting reaction mixture showed the formation of 2-allylcyclohexanone in a yield of 96% (eq 1). Table I summarizes the results of various allylic β-ketocarboxylates. It is seen that the catalytic amount of $Pd(PPh_3)_4$ induced the decarboxylation of β-ketocarboxylates to produce carbon–carbon bond-coupling products of α-allylic ketones under mild conditions. In other words, the $Pd(PPh_3)_4$-catalyzed decarboxylation of β-ketocarboxylates provides an excellent procedure for allylic acylation. The yields of α-allylic ketones are satisfactory, except for the case of allyl acetoacetate where a diallylated product formed concomitantly (entries 12 and 13). The alkylation takes place regioselectively at the carbon atom bearing the carboalkoxy group originally (entries 7–9). The results of entries 7 and 8 indicate that the present allylic acylation reaction offers a useful method for a regiospecific α,α-dialkylation of



1

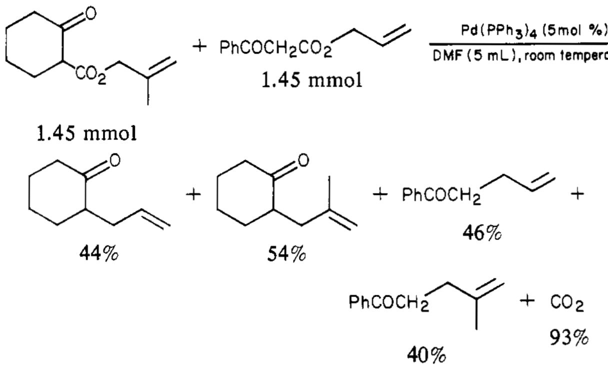
(1)

Scheme I



ketones, for which the general methods are scarce.[3] Elaboration of the starting β-ketocarboxylate may permit the preparation of various types of carbonyl compounds. For example, the reaction with the di-β-keto ester of 2-butene-1,4-diol produced a diketonic compound (entry 10). The present novel palladium(0)-catalyzed carbon–carbon bond-coupling reaction is characterized by its rapidness under mild conditions and is unique among the reported palladium-catalyzed carbon–carbon bond-forming reactions from the viewpoint of the decarboxylation used as the key step.

2-Buten-1-yl cyclohexanone-2-carboxylate and 3-buten-2-yl cyclohexanone-2-carboxylate gave the same product (entries 4 and 5). This finding suggests an intermediacy of a π-allylpalladium(II) complex. The assumed reaction path for the reaction of **1** as a representative is shown in Scheme I.[4] The reaction is initiated by the oxidative addition of **1** to $Pd(PPh_3)_4$ to produce a π-allylpalladium(II)–cyclohexanone-2-carboxylate complex (**2**), which undergoes decarboxylation to generate a π-allylpalladium(II) enolate intermediate (**4**). No reaction took place in methyl or benzyl cyclohexanone-2-carboxylate, which cannot react with $Pd(PPh_3)_4$ at ambient temperature. Experiments of entries 14–17 show that an electron-withdrawing functional group at the α carbon atom of an acid moiety is necessary for the facile decarboxylation of palladium(II) carboxylate. Further reaction of **4** to form the carbon–carbon coupling product may be understandable on the basis of the studies of the nucleophilic attack on π-allylpalladium(II) cationic complexes by Trost et al.[5] Thus, the dissociation of the enolate ligand in **4** takes place to form a cationic π-allylpalladium(II) complex (**5**) followed by the nucleophilic attack of the enolate anion on the π-allyl group to produce 2-allylcyclohexanone and the palladium(0) catalyst. The result of the cross-coupling experiment shown in eq 2 is compatible with the assumed reaction path involving **5**.[6]

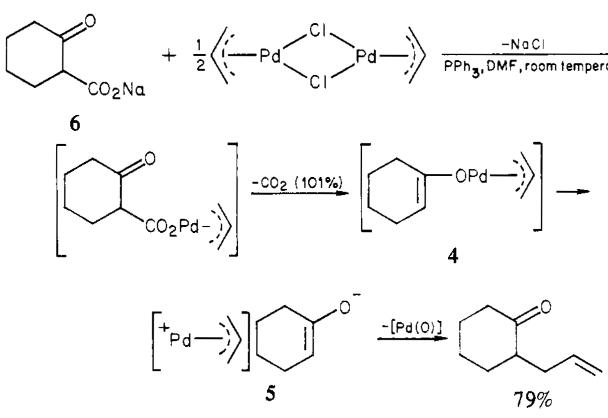


(2)

Allylic acylation is a useful transformation reaction in organic synthesis.[5] However, it is generally known that simple enolates derived from ketones react with π-allylpalladium(II) cationic complexes in a stoichiometric reaction to give mainly decomposition products,[5] although cyclization reaction by intramolecular nucleophilic attack of such enolate anions on the cationic π-allylpalladium(II) moiety has been reported very recently.[7] Thus, the present study provides a convenient and efficient method of allylic acylation with the π-allylpalladium(II) complexes. Allylic β-ketocarboxylate as a starting compound has both the enolate and allylic parts in the same molecule. The effective palladium(0)-catalyzed allylic acylation with β-ketocarboxylate is presumably ascribed to the efficient and simultaneous generation of the enolate anion and the π-allylpalladium(II) cationic complex **5** by the decarboxylation of π-allylpalladium(II) β-ketocarboxylate **2**.

Another route for the formation of palladium(II) β-ketocarboxylate is a metathesis reaction between sodium β-ketocarboxylate and a palladium(II) chloride complex. The reaction of sodium cyclohexanone-2-carboxylate (**6**) and a π-allyl-palladium(II) chloride complex gave 2-allylcyclohexanone (eq 3). This result supports the participation of **2** in Scheme I. **6** alone did not evolve CO_2 in DMF at ambient temperature, which suggests that the key intermediate of the decarboxylation reaction is not **3** but **2**.

The palladium(II)–enolate complex having a chloride ligand instead of the π-allyl group undergoes reductive elimination of hydrogen chloride to produce enone. An equimolar reaction of **6** and $PdCl_2(PPh_3)_2$ in DMF at room temperature in the presence of 5 equiv of sodium acetate acting as an acceptor of HCl produced



(3)

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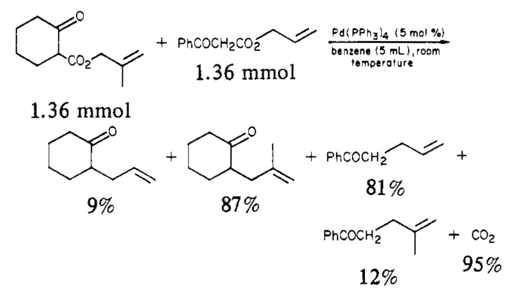
(3) Coates, R. M.; Sowerly, R. L. *J. Am. Chem. Soc.* **1971**, *93*, 1027. Miller, R. B. *Synth. Commun.* **1972**, *2*, 267. Nicholas, K. M.; Mulvaney, M.; Bayer, M. *J. Am. Chem. Soc.* **1980**, *102*, 2508.

(4) Due to the uncertainty of the structures of intermediate palladium complexes, we omitted the PPh_3 ligand in the expression of them.

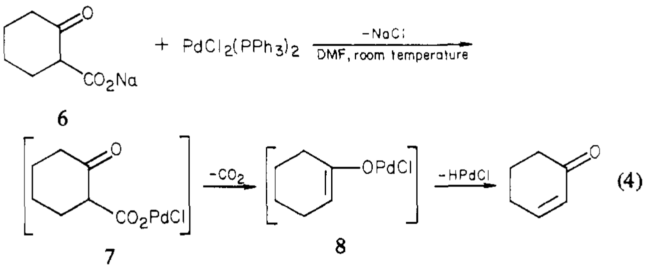
(5) Trost, B. M. *Tetrahedron* **1977**, *33*, 2615. Trost, B. M.; Weber, L.; Strege, P. E.; Fullerton, T. J.; Dietsche, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 3416, 3426.

(6) The reaction in benzene suppressed the formation of the cross-coupled products compared to the reaction in DMF. This finding suggests that the reaction mechanism may be varied according to the reaction conditions. Attempts to establish the mechanism of the present allylic acylation are now in progress.



(7) Trost, B. M.; Chan, D. M. T. *J. Am. Chem. Soc.* **1979**, *101*, 6429, 6432.

cyclohexenone in 91% yield, presumably via a palladium(II) chloride–enolate complex (**8**) (eq 4). In the presence of $CuCl_2$, cyclohexenone was produced with a catalytic amount of $PdCl_2(PPh_3)_2$.



(4)

As the starting β-ketocarboxylates are accessible,[8] the decarboxylation of palladium(II) β-ketocarboxylates provides a convenient way to produce the synthetically useful palladium(II) enolate intermediates. Other low-valent transition-metal complexes such as $Ni(PPh_3)_4$ and $RhCl(PPh_3)_3$ also caused the decarboxylation of **1** to produce 2-allylcyclohexanone.

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[8] Rathke, M. W.; Deitch, J. *Tetrahedron Lett.* **1971**, 2953. Ainsworth, C.; Kuo, Y. N. *J. Organomet. Chem.* **1972**, *46*, 73. Wierenga, W.; Skulnich, H. I. *J. Org. Chem.* **1979**, *44*, 310.

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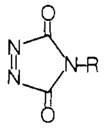
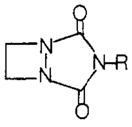
Mechanism of Triazolinedione–Olefin Reactions. Ene and Cycloaddition

Sir:

In the course of efforts to synthesize diazetines[1] (four-membered ring cyclic azo compounds), we have been attracted to the reactions of triazolinediones, TAD (**1**). These species react with dienes to afford Diels–Alder adducts,[2a] with mono olefins to afford products of an ene reaction,[2b,c] and occasionally with olefins to afford products corresponding to [2 + 2] cycloaddition, diazetidine derivatives **2**.[2d,e]

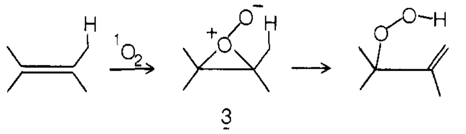


1



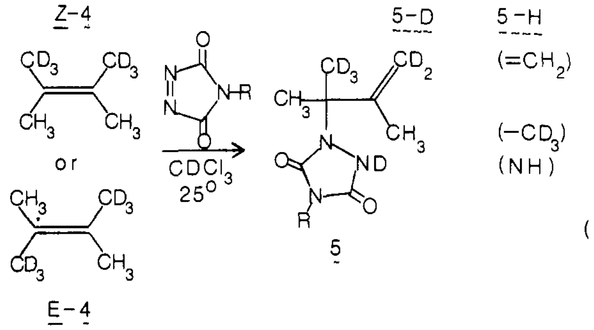
2

We have been struck by the variety of reactions of TAD, and by similarities in reactions of TAD and singlet oxygen, which also undergoes the above three reactions.[3] By an elegant isotope effect experiment, Stephenson has provided evidence for an intermediate, a perepoxide **3** or a complex with the structural characteristics of a perepoxide,[4a] in the ene reaction (eq 1) of singlet oxygen with (*Z*)- and (*E*)-2,3-bis(trideuteriomethyl)-2-butene (**4**).[4b]



(1)

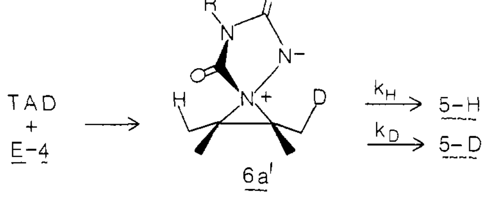
We have applied this Stephenson test to the reaction of TAD with (*Z*)- and (*E*)-**4** (eq 2). Reaction of TAD with **4** affords the ene product **5**.[5] Determination of the location and amount of deuterium is easily made by NMR,[5] leading to the following isotope effects.



(2)

	TAD, 1	k_H/k_D
(*Z*)-4	R = CH_3	1.08 ± 0.1
	R = C_6H_5	1.1
(*E*)-4	R = CH_3	3.8 ± 0.2
	R = C_6H_5	3.7

The observation of an isotope effect only when CH_3 is cis to CD_3 [olefin (*E*)-**4**] but not when CH_3 is trans or geminal to CD_3 implies rate-determining conversion of olefin **4** and TAD to an intermediate in which little or no breaking of an allylic carbon–protium bond has taken place. In a subsequent step, isotopic discrimination occurs if the "allylic" carbon–protium atoms are cis to each other (eq 3). Species **6a**, an aziridinium imide,[6]



(3)

appears to be a possible representation for the intermediate. The isotope effects place some further restrictions on **6a**: conversion

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[1] White, D. K.; Greene, F. D. *J. Am. Chem. Soc.* **1978**, *100*, 6760.

[2] (a) See: Burrage, M. E.; Cookson, R. C.; Gupte, S. S.; Stevens, I. D. R. *J. Chem. Soc., Perkin Trans. 2* **1975**, 1325, and references therein. (b) See: Hoffmann, H. M. R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 556. (c) See: Gopalan, A.; Moerck, R.; Magnus, P. *J. Chem. Soc., Chem. Commun.* **1979**, 548, and references therein. (d) von Gustorf, E. K.; White, D. V.; Kim, B.; Hess, D.; Leitich, J. *J. Org. Chem.* **1970**, *35*, 1155. (e) Pasto, D. J.; Chen, F-T. *Tetrahedron Lett.* **1973**, 713.

[3] (a) Frimer, A. A. *Chem. Rev.* **1979**, *79*, 359. (b) Harding, L. B.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1980**, *102*, 439. (c) Schulte-Elte, K. H.; Rautenstrauch, V. *Ibid.* **1980**, *102*, 1738.

[4] (a) Stephenson, L. M. *Tetrahedron Lett.* **1980**, *21*, 1005. (b) Grdina, B.; Orfanopoulos, M.; Stephenson, L. M. *J. Am. Chem. Soc.* **1979**, *101*, 3111.

[5] Compound **5**, undeuterated (R = CH_3); mp 95–96 °C. Pirkle, W. H.; Stickler, J. C. *Chem. Commun.* **1967**, 760. ^1H NMR ($CDCl_3$): δ 1.58 (s, 6 H), 1.82 (s, 3 H), 3.04 (s, 3 H), 4.99 (s, 2 H), 7.90 (s, br, 1 H). Compound **5** (R = C_6H_5): mp 127–128 °C; IR 1760, 1695 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.60 (s, 6 H), 1.82 (s, 3 H), 4.95 (s, 1 H), 4.99 (s, 1 H), 7.38 (m, 5 H), 7.90 (s, br, 1 H); anal. C, H, N.

[6] An isolable species of known structure (X-ray analysis) and bearing some resemblance to **6a** has been reported; 1-(diphenylhydrazono)-3,5-dioxo-4-phenyl-1,2,4-triazolidinium hydroxide, inner salt: Weidenborner, J. E.; Fahr, E.; Richter, M. J.; Koch, K.-H. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 236.