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lyzed in a sealed tube at the much higher temperature of 250 °C for 50–75 min, this tricyclic diene was partially converted to I, II (probable stereochemistry indicated), and two unidentified products. We are grateful to Professor Vogel for making a copy of the Frey dissertation available to us.

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Pressure Dependence of the Thermolysis of Tetramethyl-1,2-dioxetane: the Volume of Activation and Its Mechanistic Implications

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Abstract: The thermal decomposition of tetramethyl-1,2-dioxetane (TMD) and its indirect chemiluminescence via 9,10-dibromoanthracene (DBA) was studied in different solvents at pressures ranging from 1 to 1000 atm. The pressure dependence of the rate constants of decomposition of TMD at 60 °C permits the calculation of the volumes of activation, ΔV^{\ddagger}_D , amounting to 9 ± 2 cm³/mol in toluene and 11 ± 3 cm³/mol in chlorobenzene. Apparent volumes of activation, ΔV^{\ddagger}_{Ch} , were obtained from the pressure dependence of the intensity of chemiluminescence at 40 °C on the system TMD-DBA and amount to 8 ± 1 cm³/mol in toluene, 10 ± 1 cm³/mol in chlorobenzene, and 11 ± 2 cm³/mol in benzonitrile, respectively. These data are discussed in connection with literature values for homolytic bond cleavages. They cannot exclude a biradical mechanism, but favor a concerted pathway for the decomposition. Partial molar volumes of the TMD and acetone in toluene were determined and a volume profile for the reaction is presented. Thus one can deduce that the transition state is placed much closer to the side of the educt.

Although substituted dioxetanes have been known for only several years,¹⁻³ their thermal decompositions, together with their direct or indirect chemiluminescence, are frequently investigated reactions.⁴⁻⁷

Using different methods to follow the thermal decomposition reactions, it was shown that they obey first-order kinetics in diluted, air-saturated solutions. The reactions are autocatalyzed, however, in degassed or concentrated solutions.^{4,8,9} Transition metal ions catalyze the decomposition.^{10,11} Products of the thermolysis of dioxetanes are the corresponding carbonyl compounds in their ground states as well as in their excited states, the latter being responsible for the appearance of the direct and indirect chemiluminescence.⁷ According to product analysis and physical investigations, the product of the thermal decomposition of TMD was identified as acetone, of which ca. 50% is in its ground state, ca. 0.2% in its excited singlet state, and ca. 50% in its excited triplet state.^{9,12}

The appearance of acetone in an electronically excited state can be understood, if one takes into account thermochemical data,¹³ activation parameters of the thermolysis,¹⁴ and thermodynamic considerations.¹⁵ This possibility of transferring molecules into their electronically excited states by means of a chemical reaction rather than irradiation initiated a series of investigations about energy transfer processes and photochemical reactions.^{5,16-21}

Despite the host of information on the thermolysis of TMD, the mechanism of the primary rate-determining step of the reaction is still ambiguous. Two mechanisms, schematically shown in Figure 1, are both being discussed. Mechanism A represents a one-step process with the synchronous cleavage of the carbon-carbon and the oxygen-oxygen bonds, whereas

mechanism B consists of a two-step reaction including a biradical intermediate following the peroxide bond cleavage.

A very small observed solvent effect on the decomposition¹⁰ excludes any mechanism involving polar transition states and/or intermediates. However, it is compatible with both mechanisms depicted in Figure 1. Applications of correlation diagrams with regard to symmetry rules²¹⁻²⁶ are consistent with a concerted mechanism. On the other hand, activation parameters in connection with thermochemical considerations²⁷⁻³¹ support the formation of a biradical. Recently a biradical mechanism for the decomposition of trimethyldioxetane was proposed by Stauff.³²

With the present investigations further data on the kinetics and chemiluminescence of TMD thermolysis under pressure are presented and discussed in view of the possible mechanisms.

Experimental Section

Materials. TMD was prepared and purified as previously described.¹⁷ The Aldrich-Europe product DBA was repeatedly recrystallized from ethanol for purification. Commercially available solvents like toluene, chlorobenzene, and benzonitrile of highest purity were redistilled before use. Additions of ethylenediaminetetraacetic acid (EDTA) to the solvents in order to complex any possibly present, and catalytically active, transition metal ions^{10,30} showed no influence on the results.

High-Pressure Measurements of Thermal Decomposition and Luminescence. The thermolysis reaction of TMD was followed by recording the time dependence of the intensity of the indirect chemiluminescence of DBA, which is excited mainly by triplet-singlet energy transfer via triplet-excited acetone.¹⁷ Air saturated solutions with

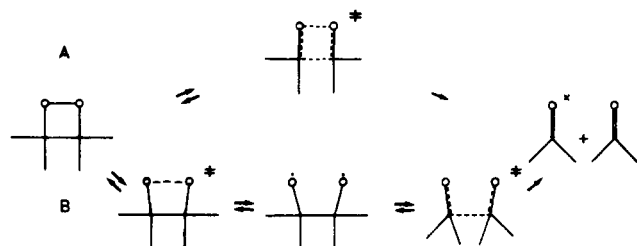


Figure 1. Scheme of possible mechanisms for the thermal decomposition of TMD.

concentrations of 10^{-3} M in DBA and 10^{-3} to 10^{-2} M in TMD were placed in a high-pressure cuvette described earlier.³³ One of the two sapphire windows of the cuvette was blocked. A photomultiplier (Hamamatsu R 456) was directly mounted to the other window. The cuvette was thermostated to 60.0 ± 0.1 °C or 40.0 ± 0.1 °C during the measurements.

It is known that the fluorescence light of a system usually experiences a small red shift under the influence of pressure. For instance, the maximum emission band of anthracene is shifted to longer wavelengths by about 1 nm at 1000 atm.³⁴ The spectral sensitivity of the photomultiplier used here changes, however, in the range of 400–500 nm by less than 50%. Therefore, the change in intensity of the photomultiplier signal under pressure was less than 1% at 1000 atm and thus could be neglected.

Density Measurements. A Paar density meter (DMA 02/C) was used for the determination of the apparent molar volumes of the educt (TMD) and product (acetone) of the reaction. The apparatus was thermostated at 25.000 ± 0.001 °C, using a specially designed temperature control unit in connection with a thermistor. The temperature was measured by a Hewlett Packard quartz thermometer.

Results

The decrease in the intensity of the indirect luminescence during thermolysis of TMD at 60 °C was followed over at least two half-lives. Rate constants were determined in two solvents and at five different pressures ranging from 1 to 1000 atm and the results are listed in Table I. The rate constants in benzonitrile did not show sufficient reproducibility to elucidate a pressure coefficient.

In toluene the rate constant for the decomposition at 1 atm and 40 °C amounted to $k = 7.64 \times 10^{-6} \text{ s}^{-1}$. Combining this value with the corresponding rate constant at 60 °C, the following activation parameters were determined: $\Delta H^\ddagger = 27.0 \pm 1$ kcal/mol, $\Delta S^\ddagger = 4 \pm 3$ eu, and $E_a = 27.6 \pm 1$ kcal/mol. The value of E_a compares well with those reported in the literature, e.g., 27.9 kcal/mol¹⁴ in acetonitrile, 26.5 kcal/mol¹⁰ in benzene, and 25.7 kcal/mol¹⁰ in ethanol.

The decomposition reaction of TMD is quite slow at 40 °C. Its half-life in toluene amounts to approximately 25 h under these conditions. Therefore, it was possible to determine the pressure dependence of the relative intensities of the chemiluminescence for the system TMD–DBA at this temperature. During these experiments the pressure on a given sample was varied in a stepwise manner. After each pressure regulation enough time was given for the dissipation of the heat of compression or decompression before the intensity reading was taken. The same results were obtained for sets of increasing and decreasing pressures in all three solvents. The data are summarized in Table II.

Upon correction of the relative intensities of chemiluminescence resulting from the change in concentration due to the compressibility of the solvents, the relative yields of luminescence are expressed in the form $\Phi_P^{\text{CH}}/\Phi_1^{\text{CH}}$. This correction can be derived by using the relation

$$\ln c_P/c_1 = \int_1^P \kappa \, dP \quad (1)$$

in which c_P and c_1 are the concentrations at pressures P and 1 atm and κ is the compressibility of the solvent. The pressure

Table I. Pressure Dependence of the Rate Constant of the Thermolysis of TMD at 60 °C

P , atm	Toluene		Chlorobenzene	
	$10^4 \times k_{\text{obsd}}$, s^{-1}	No. of runs	$10^4 \times k_{\text{obsd}}$, s^{-1}	No. of runs
1	1.091 ± 0.014	8	1.32 ± 0.03	8
200	1.024 ± 0.003	5	1.21 ± 0.02	4
400	0.995 ± 0.009	4	1.14 ± 0.02	4
600	0.967 ± 0.004	4	1.12 ± 0.01	4
1000	0.933 ± 0.006	2	1.05 ± 0.01	2

dependence of κ can in turn be expressed by eq 2, which is analogous to the Tait equation and contains the constants K and L :

$$\kappa = K/(L + P) \quad (2)$$

Thus the correction can be expressed by the equation:

$$\ln c_P/c_1 = K \ln [(L + P)/(L + 1)] \quad (3)$$

Values for the constants L and K were taken from literature.³⁵

In order to obtain the volume of reaction, $\Delta \bar{V}_R$, for the thermolysis of TMD in one solvent, the partial molar volumes \bar{V} of acetone and TMD in toluene were determined. The apparent molar volumes ζ of the educt and product, at different concentrations, were obtained from precision density measurements and are shown in Table III, together with the extrapolated partial molar volumes.

The dependence of $\ln(k_P/k_1)$ vs. pressure is shown in Figure 2. According to eq 4 the slopes of these curves at any pressure are equal to $-\Delta V^\ddagger/RT$

$$(d \ln(k_P/k_1)/dP)_T = -\Delta V^\ddagger/RT \quad (4)$$

Consequently the volumes of activation, ΔV^\ddagger_D , at 1 atm and 40 °C were calculated to be 9 ± 2 cm³/mol in toluene and 11 ± 3 cm³/mol in chlorobenzene.

In Figure 2 an analogous representation of the relative yields of chemiluminescence vs. pressure is shown. From these plots the apparent volumes of activation of chemiluminescence, $\Delta V^\ddagger_{\text{Ch}}$, of 8 ± 1 cm³/mol in toluene, 10 ± 1 cm³/mol in chlorobenzene, and 11 ± 2 cm³/mol in benzonitrile were derived.

Discussion

Influence of Solvent on the Volume of Activation. Since at 40 °C and below the reaction rate of the thermolysis of TMD is very slow, the concentration of TMD does not change during the time of analysis. Therefore, the intensity of the chemiluminescence, I^{Ch} , of a solution of TMD and DBA at this temperature is constant, too, and can be expressed by the equation:

$$I_{40^\circ\text{C}}^{\text{Ch}} = Ak[\text{TMD}]_0 \Phi^* \Phi^{\text{ET}} \Phi^{\text{Fl}} \quad (5)$$

Herein A represents a constant; k the rate constant of the thermolysis of TMD; Φ^* the yield of formation of excited acetone; Φ^{ET} the yield of energy transfer from acetone to DBA; and Φ^{Fl} the quantum yield of fluorescence of DBA. Naturally, Φ^* and Φ^{ET} differ depending on the two spin states in question.¹⁷

At higher temperatures, e.g., at 60 °C, the thermal decomposition of TMD is faster and consequently the intensity of the chemiluminescence of the system, which is proportional to the respective concentration of TMD, changes during the recording time. According to the first-order decomposition process the intensity of the chemiluminescence can now be

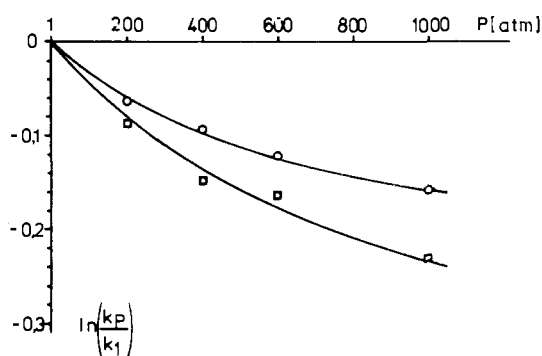
Table II. Pressure Dependence of the Relative Intensity of Chemiluminescence of the System TMD-DBA in Various Solvents at 40 °C^{a,b}

P, atm	Toluene			Chlorobenzene			Benzonitrile		
	$\ln \left(\frac{I_P^{\text{Ch}}}{I_1^{\text{Ch}}} \right)$	$\ln \left(\frac{c_P}{c_1} \right)$	$\ln \left(\frac{\Phi_P^{\text{Ch}}}{\Phi_1^{\text{Ch}}} \right)$	$\ln \left(\frac{I_P^{\text{Ch}}}{I_1^{\text{Ch}}} \right)$	$\ln \left(\frac{c_P}{c_1} \right)$	$\ln \left(\frac{\Phi_P^{\text{Ch}}}{\Phi_1^{\text{Ch}}} \right)$	$\ln \left(\frac{I_P^{\text{Ch}}}{I_1^{\text{Ch}}} \right)$	$\ln \left(\frac{c_P}{c_1} \right)$	$\ln \left(\frac{\Phi_P^{\text{Ch}}}{\Phi_1^{\text{Ch}}} \right)$
200	-0.046 ± 0.005	0.018	-0.064	-0.055 ± 0.005	0.016	-0.071	-0.055 ± 0.016	0.018	-0.073
400	-0.092 ± 0.005	0.033	-0.125	-0.121 ± 0.005	0.029	-0.148	-0.139 ± 0.005	0.033	-0.172
600	-0.150 ± 0.005	0.047	-0.197	-0.192 ± 0.005	0.041	-0.233	-0.223 ± 0.005	0.047	-0.270
800	-0.212 ± 0.010	0.058	-0.270	-0.260 ± 0.005	0.052	-0.312	-0.294 ± 0.005	0.058	-0.352
1000	-0.274 ± 0.010	0.068	-0.342	-0.335 ± 0.005	0.061	-0.396	-0.371 ± 0.010	0.068	-0.439

^a The pressure dependence of the chemiluminescence is independent of the concentration of TMD in the range used: $10^{-3} \text{ M} \leq [\text{TMD}] \leq 10^{-2} \text{ M}$; $[\text{DBA}] = 10^{-3} \text{ M}$. ^b The number of individual measurements ranges between two and five.

Table III. Apparent Molar Volumes ζ and Partial Molar Volumes \bar{V} of TMD and Acetone in Toluene at 25.000 ± 0.001 °C

Compd	Concn, mol/l.	ζ , ml/mol	\bar{V} , ml/mol
TMD	9.627×10^{-2}	133.1	128 ± 2
	4.706×10^{-2}	126.6	
	8.335×10^{-3}	129.6	
Acetone	8.795×10^{-2}	73.0	79.0 ± 0.5
	4.587×10^{-2}	75.0	
	1.394×10^{-2}	78.4	

**Figure 2.** Pressure dependence of the relative rate constants of the thermal decomposition reaction of TMD in toluene (O) and chlorobenzene (□) at 60 °C.

described by:

$$I_{60^\circ\text{C}}^{\text{Ch}} = \{Ak[\text{TMD}]_0 \Phi^* \Phi^{\text{ET}} \Phi^{\text{FI}}\} e^{-kt} \quad (6)$$

Pressure influences the rate constant k in the exponential term as well as in the preexponential term. The concentration $[\text{TMD}]_0$ also changes slightly with pressure. The product $\Phi^{\text{ET}} \Phi^{\text{FI}}$ is pressure dependent, while Φ^* and A are pressure independent.³⁶ Thus for a given pressure the preexponential term remains constant and the rate constant k can be determined from the half-life of the decay of the chemiluminescence.

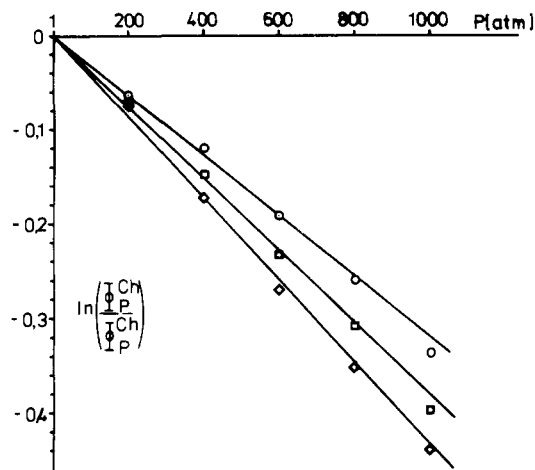
The relative yields of chemiluminescence at 40 °C reduce to

$$\left(\frac{\Phi_P^{\text{Ch}}}{\Phi_1^{\text{Ch}}} \right)_{40^\circ\text{C}} = \left(\frac{k_P \Phi_P^{\text{ET}} \Phi_P^{\text{FI}}}{k_1 \Phi_1^{\text{ET}} \Phi_1^{\text{FI}}} \right)_{40^\circ\text{C}} \quad (7)$$

and

$$\ln \left(\frac{\Phi_P^{\text{Ch}}}{\Phi_1^{\text{Ch}}} \right)_{40^\circ\text{C}} = \ln \left(\frac{k_P}{k_1} \right)_{40^\circ\text{C}} + \ln \left(\frac{\Phi_P^{\text{ET}} \Phi_P^{\text{FI}}}{\Phi_1^{\text{ET}} \Phi_1^{\text{FI}}} \right)_{40^\circ\text{C}} \quad (8)$$

The pressure dependence of $\ln \left(\Phi_P^{\text{Ch}} / \Phi_1^{\text{Ch}} \right)$ is caused by a pressure dependence of both right-hand-side terms of eq 8. This can be seen from a comparison of the curves of Figure 2 with

**Figure 3.** Pressure dependence of the relative yields of chemiluminescence of the system TMD-DBA in toluene (O), chlorobenzene (□), and benzonitrile (◇) at 40 °C.

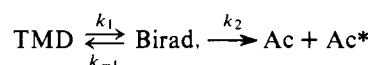
those of Figure 3, assuming that the curvatures of $\ln k_P/k_1$ vs. pressure plots prevail at 40 °C.

If one assumes, however, that the pressure dependence of the product of yields is similar in all solvents used, then variations in ΔV_D^\ddagger and $\Delta V_{\text{Ch}}^\ddagger$ with solvent should be the same. This is borne out in a comparison of the data obtained in toluene and chlorobenzene. The ΔV_D^\ddagger value for the benzonitrile solution can thus be estimated to be $12 \pm 3 \text{ cm}^3/\text{mol}$, being close to $9 \pm 2 \text{ cm}^3/\text{mol}$ for toluene and $11 \pm 3 \text{ cm}^3/\text{mol}$ for chlorobenzene solutions. In conclusion, the volume of activation for the thermal decomposition of TMD shows almost no solvent dependence, as do the rate constants, averaging approximately to $11 \pm 3 \text{ cm}^3/\text{mol}$. The usual presentation of the volume of activation is given by

$$\Delta V_{\text{expt}}^\ddagger = \Delta V_{\text{intr}}^\ddagger + \Delta V_{\text{solv}}^\ddagger \quad (9)$$

Equation 9 implies that the experimentally obtained value of $\Delta V_{\text{expt}}^\ddagger$ consists in a first approximation of an intrinsic contribution, $\Delta V_{\text{intr}}^\ddagger$, due to bond formation or cleavage during the rate determining step, and a solvation contribution, $\Delta V_{\text{solv}}^\ddagger$, originating from a change of solvation during the development of the transition state. The latter contribution appears to be negligible for the system studied here. The resulting intrinsic contribution, $\Delta V_{\text{expt}}^\ddagger \approx \Delta V_{\text{intr}}^\ddagger$, can then be discussed in terms of the mechanisms of Figure 1, provided the k values determined can be associated with the primary steps of the decomposition of TMD.

Kinetic Considerations. In agreement with Figure 1 the decomposition of TMD via biradical can be described by the scheme



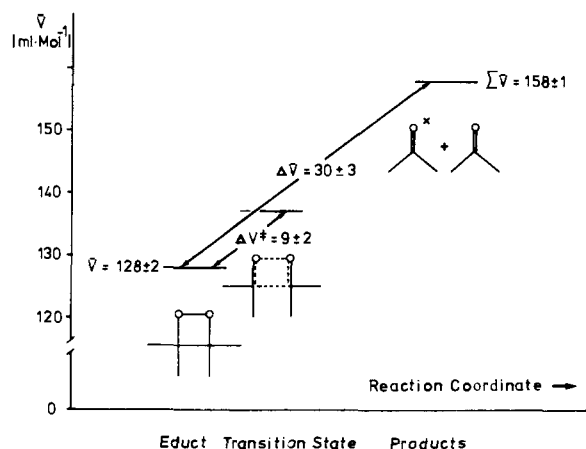


Figure 4. Volume profile for the thermolysis reaction of TMD in toluene.

in which Birad. represents the intermediate, and Ac and Ac* stand for acetone in its ground and electronically excited state, respectively. The application of steady-state conditions yields the rate law:

$$-d[\text{TMD}]/dt = (k_1 k_2 / (k_{-1} + k_2)) [\text{TMD}] = k_{\text{obsd}} [\text{TMD}] \quad (10)$$

According to the thermochemical calculations on the biradical mechanism by Richardson and co-workers,²⁷⁻³¹ the relation $k_2 \gg k_{-1}$ must hold. In this case the experimentally determined value for the volume of activation, ΔV^\ddagger_D , is equal to the volume of activation (ΔV^\ddagger_1) of the first step. As Neuman^{37,38} was able to show, the homolytic cleavage of a covalent bond without complication caused by recombination of the products yields a ΔV^\ddagger value of approximately 5 cm³/mol. Since the experimentally determined activation volume $\Delta V^\ddagger_D = 11 \pm 3$ cm³/mol is not in agreement with these expectations, we are led to the following alternative conclusions:

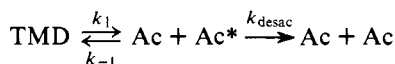
(1) If the thermolysis of TMD follows a biradical pathway, then the calculation by Richardson ($k_2 \gg k_{-1}$) is not valid. The observed large value of ΔV^\ddagger_D should be explained, therefore, by a competition of ring closure and dissociation of the intermediate biradical, i.e., $k_2 \approx k_{-1}$. Based on Neuman's results,^{37,38} in this case ΔV^\ddagger_D is given by the more complicated expression:

$$\Delta V^\ddagger_D = \Delta V^\ddagger_1 + RT(d \ln(1 + k_{-1}/k_2)/dP) \quad (11)$$

which could result in a ΔV^\ddagger_D value larger than 5 cm³/mol.

(2) If Richardson's calculations based on Hammond's postulate ($k_2 \gg k_{-1}$) reflect truly the energy surface of the biradical pathway of 1,2-dioxetane decomposition, our results must be interpreted by a concerted mechanism. Then, however, the observed ΔV^\ddagger_D does not agree with Neuman's results,³⁹ according to which $\Delta V^\ddagger_D \approx 5$ cm³/mol, regardless whether a one-bond or a simultaneous two-bond cleavage occurs.

The concerted mechanism requires a simple reaction scheme:



with the corresponding rate law:

$$-d[\text{TMD}]/dt = k_1[\text{TMD}] - k_{-1}[\text{Ac}][\text{Ac}^*] \quad (12)$$

Due to the very short lifetime of excited acetone molecule ($\tau \ll 10^{-7}$ s for the conditions applied¹⁸) the steady-state concentration of [Ac*] is extremely small. Thus the reverse reaction forming TMD can be neglected and, in fact, has never been observed during the irradiation of acetone. Consequently, the experimentally determined rate constant corresponds to

k_1 , the primary step during the decay process, and the volume of activation, ΔV^\ddagger_D , reflects the simultaneous stretching of the oxygen-oxygen bond as well as the carbon-carbon bond.

The experimentally determined value of V^\ddagger_D is about twice the amount one usually finds for a simple bond cleavage without additional complications such as cage reactions.^{37,38} This result supports in our opinion a concerted mechanism for the thermal decomposition of TMD with a simultaneous two-bond cleavage, which should produce a larger V^\ddagger_D than for a one-bond cleavage. This mechanism in turn is reconcilable with the high yield of acetone molecules in their excited state.

In view of the preceding discussion the determination of the partial molar volumes of educt and product in toluene, together with the use of the volume of activation, permits the drawing of a total volume profile for the thermolysis in at least one solvent as shown in Figure 4. The use of the partial molar volume of acetone in its ground state instead of the excited state and the combination of the partial molar volume data obtained at 25 °C with an activation volume determined at 40 °C may cause small corrections of the profile. Nevertheless, it is safe to conclude from the results that the transition state is placed closer to the side of the educt than of the products on the reaction coordinate. The polar carbonyl groups are probably not formed in the transition state or at the most only slightly developed, which explains the rather small or negligible solvent effect.

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 (36) Φ^* is constant regardless of the solvent used (e.g. *n*-hexane vs. acetonitrile);

- the difference of internal pressure of these solvents is larger than the pressure change in our experiments (N. J. Turro and H.-C. Steinmetzer, unpublished results; see also ref 10).
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Studies on the Syntheses of Heterocyclic Compounds. 675.¹ A Facile Regiospecific and Stereocontrolled Synthesis of a Diterpene Alkaloid Intermediate from Benzocyclobutenes

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Abstract: Thermolysis of 1-cyano-4-methoxy-1-(4-methoxycarbonyl-4-vinyl)pentylbenzocyclobutene (**3**), derived from methyl methylacetoacetate (**7**) in five steps, gave (\pm)-4 α -cyano-1,2,3,4,4a,9,10,10 α -octahydro-7-methoxy-1 α -methoxycarbonyl- β -methylphenanthrene (**19**) in a stereocontrolled manner, which was converted into the epimer (**26**) by oxidation, bromination, dehydrobromination, and hydrogenation. Catalytic reduction of **26** gave the lactam (**27**), whose reduction with lithium aluminum hydride afforded 16,17-imino-13-methoxy-5 β ,10 α -podocarpene-8,11,13-triene (**1**). The 5 α -epimer (**22**) of **1** was also synthesized from **21**.

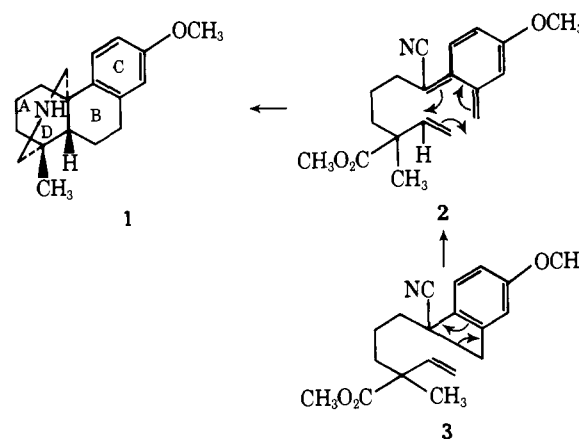
The synthetic challenge of diterpenes² and diterpene alkaloids^{3,4} has attracted much attention by many investigators. A crucial step in the synthesis of these types of natural products is the introduction of a functionalized carbon unit at the C-4a angular position in combination with C-1 substituents with appropriate stereochemical control in the phenanthrene ring.⁵ Hitherto, two general methods have been available; one is an introduction of a suitable group into the C-4a angular position of hydrophenanthrene,^{6,7} and the other is a direct synthesis from β -tetralone derivatives having a functionalized group at the α position by Robinson annelation.^{7,8}

Previously, we have reported a simple total synthesis of the isoquinoline alkaloids⁹⁻¹³ by a regioselective electrocyclic reaction or cycloaddition of the cyanated *o*-quinodimethane to imines¹⁴ and olefins.¹⁵ In connection with our interest in a simple total synthesis of other types of natural products, we have investigated a new type of synthetic method of C-4a-substituted hydrophenanthrenes by our method. Herein, we wish to report an unusually simple and stereocontrolled synthesis of (\pm)-16,17-imino-13-methoxy-5 β ,10 α -podocarpene-8,11,13-triene (**1**),^{4,5,7,15} which has already been correlated with atisine,^{6,8} veatchine,¹⁷ garryine,¹⁶ and gibberellin A₁₅.¹⁸ The method involves an intramolecular cycloaddition reaction of the *o*-quinodimethane derivative **2**¹⁹ derived from the benzocyclobutene **3** as a key reaction (Scheme I).

Our synthesis was designed on the basis of the idea that a hydrophenanthrene derivative which has two functional groups would be most effective for construction of the D ring of **1**, and that such an intermediate could be prepared in one step by an intramolecular cycloaddition reaction of an *o*-quinodimethane derivative. The benzocyclobutene **3** was chosen as a suitable starting material because this compound forms an *o*-quinodimethane on heating¹⁹ and also has cyano and carbomethoxyl groups which are necessary for building up the D ring.

However, there are two regioselectively different routes for the intramolecular cycloaddition reaction of the *o*-quinodimethane **4** as shown in Scheme II. One is a formation of the

Scheme I



Scheme II

