interpretation of overlapping multiplets at conventional field strengths.

Experimental Section

All spectra were recorded on a Varian XL-300 spectrometer utilizing a Varian 5-mm broad-band switchable probe at 25.0 °C controlled to ±0.2 °C by the standard variable-temperature hardware. All samples were 80 ± 10 mM in 0.5 mL of $CDCl_3$. No weighting functions were applied to any of the spectra presented. Benzo[*a*]pyrene-7,10-dione was prepared by electrochemical oxidation of 7-hydroxybenzo[*a*]pyrene provided by the National Cancer Institute (NCI) Repository. The 10-methylbenzo[*a*]pyrene was also provided by the NCI Repository, and the 6-acetoxybenzo[*a*]pyrene was prepared by manganic acetate oxidation of benzo[*a*]pyrene.[19]

Acknowledgment. We thank T. Apple and P. Gannett for useful discussions, Jan Leemkuil and Julie Caniglia for the preparation of this manuscript, the NCI Repository for the chemicals mentioned, and S. Patt and Varian Associates for providing the phase-pulse software. This work was supported in part by NIH Research Grants CA32513 and CA36727 from the National Cancer Institute and by NIH Research Grant RR01968.

Registry No. BP-7,10-dione, 71241-25-3; 10-Me-BP, 63104-32-5; 6-acetoxy-BP, 53555-67-2.

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Thermolysis of 3,4-Cyclic 1,2-Dioxetanes: Effect of 6-Ring Conformation on the Activation Parameters

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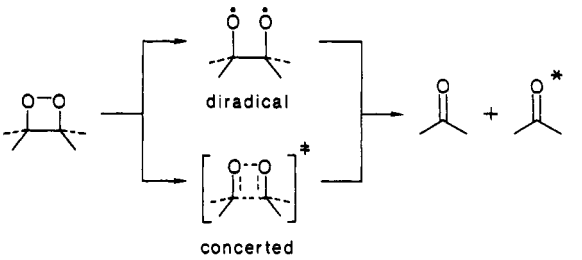
2a,3,8,8a-Tetrahydronaphtho[2,3-*c*]-1,2-dioxete (1) and 2a,3,4,8b-tetrahydronaphtho[1,2-*c*]-1,2-dioxete (2) were synthesized by the Kopecky method. The dioxetanes, purified by low-temperature chromatography, were characterized by ^1H NMR spectroscopy and by analysis of their thermolysis products. The activation parameters for the thermolysis of 1 and 2 in xylenes were determined by the chemiluminescence method [1: E_a = 27.4 kcal/mol, log A = 14.4, $k_{60°}$ = 2.8 × 10^{-4} s^{-1}. 2: E_a = 24.5 kcal/mol, log A = 12.8, $k_{60°}$ = 5.1 × 10^{-4} s^{-1}]. The thermal decomposition of both dioxetanes produced (directly) much higher yields of excited triplet carbonyl products than excited singlet products. The total yields of excited states were 1% for both dioxetanes, much less than normal for disubstituted dioxetanes. Molecular mechanics (MM2) calculations were carried out. The most stable conformation of 1 was predicted to be a boat with a O–C–C–O torsion angle of 0°. 3,4-Tetramethylene-1,2-dioxetane (3) was predicted to favor a "twist-boat" conformation with a dioxetane ring torsion angle of 10°. The conformation of 2 was calculated to be intermediate with a dioxetane ring torsion angle of 4°. The relative stabilities of the dioxetanes seem to correlate with ring conformation and dioxetane (O–C–C–O) torsion angle.

The thermal decomposition of 1,2-dioxetanes[2] results in the quantitative cleavage of the 4-membered ring peroxide into two carbonyl fragments, one of which may be produced in an excited state. The thermolysis of dioxetanes that contain "easily oxidized" groups has been shown to directly produce high yields of excited singlet carbonyls and appears to be well described[3] by the CIEEL or electron-transfer type mechanism.[2] On the other hand, the mechanism of thermolysis of simple (alkyl, aryl, alkoxy) dioxetanes (direct production of high yields of excited triplet products) remains controversial and of high theoretical interest. Historically, two mechanistic extremes have been postulated to explain this unique process: (a) diradical; (b) concerted (Scheme I).

Scheme I[a]



[a] Asterisk denotes excited state.

Most of the experimental evidence has been interpreted[4] to be consistent with a diradical-like process. However, in recent years the distinctions between the two mechanisms have become blurred and the concept of a merged mechanism has arisen.[5] Results for dioxetanes with cyclic substituents[6] were interpreted to be indicative of a twisting

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(2) For reviews, see: (a) Wilson, T. *Int. Rev. Sci.: Phys. Chem., Ser. Two* **1976**, *9*, 265. (b) Adam, W. *Adv. Heterocycl. Chem.* **1977**, *21*, 437. (c) Horn, K. A.; Koo, J.; Schmidt, S. P.; Schuster, G. B. *Mol. Photochem.* **1978–1979**, 9(1), 1. (d) Bartlett, P. D.; Landis, M. E. In *Singlet Oxygen*; Wasserman, H. H., Murray, R. W., Eds.; Academic: New York, 1979; p 243. (e) Schuster, G. B.; Schmidt, S. P. *Adv. Phys. Org. Chem.* **1982**, *18*, 187. (f) Adam, W. In *Chemical and Biological Generation of Electronically Excited States*; Cilento, G., Adam, W., Eds.; Academic: 1982; Chapter 4. (g) Baumstark, A. L. In *Singlet Oxygen*; Frimer, A., Ed.; Uniscience, CRC Press: Cleveland, OH, 1985, Vol. 2, p 1.

(3) The unique electron-transfer mechanism(s) that occurs for certain peroxides does not occur readily with simple dioxetanes. See: (a) Schuster, G. B.; Dixon, B.; Koo, J.-Y.; Schmidt, S. P.; Smith, J. P. *Photochem. Photobiol.* **1979**, *30*, 17. (b) Zaklika, K. A.; Kissel, T.; Thayer, A. L.; Burns, P. A.; Schaap, A. P. *Ibid.* **1979**, *30*, 35. (c) Wilson, T. *Ibid.* **1979**, *30*, 177. (d) Adam, W.; Cueto, D.; Yang, F. *J. Am. Chem. Soc.* **1978**, *100*, 2587. (e) McCapra, F. *Chem. Commun.* **1977**, 946.

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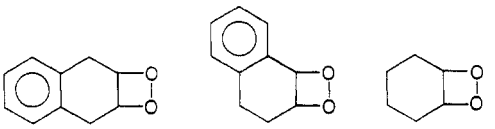
mode of O–O bond scission. The twisting hypothesis has gained support in studies of additional polycyclic dioxetanes.[7] A modification of the twisting concept during thermolysis has been employed on acyclic systems as well.[5] However, the original twisting hypothesis[6b] was formulated to explain the unusual instability of a dioxetane with a 6-ring substituent. Thus, it is not clear as to whether this process (twisting) is applicable to the thermolysis of stable compounds. We report here the synthesis and characterization of two 3,4-cyclic 1,2-dioxetanes **1** and **2**, in which the conformation of the 6-ring substituent has been altered as well as the light yields for the thermolysis of **1–3**, which provide new insights into the dynamics of O–O bond scission.

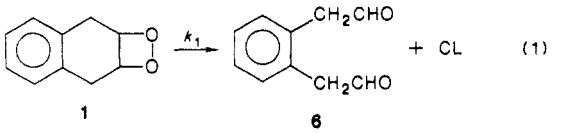


1 **2** **3**

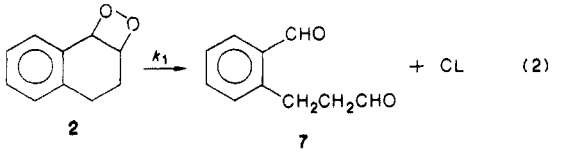
Results

Dioxetanes **1** and **2** were synthesized by the Kopecky method.[2,4f] 1,4-Dihydronaphthalene and 1,2-dihydronaphthalene were converted into the β-bromo hydroperoxides **4** and **5** by the standard procedure developed by Kopecky. The dioxetanes 2a,3,8,8a-tetrahydronaphtho-[2,3-*c*]-1,2-dioxete (**1**) and 2a,3,4,8b-tetrahydronaphtho-[1,2-c]-1,2-dioxete (**2**) were synthesized in low yield by closure of the β-bromo hydroperoxides with base at low temperature (see Scheme II). The synthesis and characterization of 3,4-tetramethylene-1,2-dioxetane (**3**) has been previously reported.[6b]

Dioxetanes **1** and **2** were purified by low-temperature chromatography on silica gel. Dioxetane **2** was obtained as a yellow oil. Dioxetane **1** was obtained in pure form (yellow needles) by crystallization. The dioxetanes were characterized by ^{1}H NMR spectroscopy. Thermolysis of **1** and **2** in CCl_4 produced the expected dialdehyde cleavage products **6** and **7**, in essentially quantitative yield (reactions 1 and 2). The products were characterized by ^{1}H NMR spectroscopy and by their conversion to known derivatives.



1 **6**

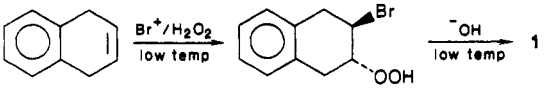


2 **7**

CL = chemiluminescence

The rates of thermolysis of **1** and **2** in xylenes were determined by the chemiluminescence method. The rates of dioxetane decomposition were not affected by variation in the concentrations of added fluorescers (DPA, DBA) and were of the first order for greater than 3 half-lives. The first-order rate constants (k_1) were determined over a 50 °C+ temperature range. Over the entire temperature range investigated, the k_1 values for **1** and **2** were found to be much smaller than those for **3**. The activation parameter data for **1** and **2**, determined by the Arrhenius method, are listed in Table I. Data[6b] for 3,4-tetramethylene-1,2-dioxetane (**3**, 7,8-dioxabicyclo[4.2.0]octane) are included for comparison.

Scheme II



4

Table I. Activation Parameters[a] for the Thermolysis of Dioxetanes 1 and 2 in Xylenes

dioxetane	$\Delta H^{\ddagger}$,[b] kcal/mol	$\Delta S^{\ddagger}$, eu	$k_{60°}$, s^{-1}
1	26.7 ± 0.4	+1.1	2.8×10^{-4}
2	23.8 ± 0.4	−2.3	5.1×10^{-4}
3[c]	21.8 ± 0.3	−2.2	1.1×10^{-2}

[a] Calculated at 60 °C. [b] $\Delta H^{\ddagger} = E_a - RT$; 95% confidence limits. [c] Taken from ref 6b.

Table II. Singlet and Triplet Excitation Yields[a] for the Decomposition of Dioxetanes 1–3 in Xylenes

dioxetane	$^3\phi$ DBA	$^1\phi$ DPA
1	0.003 ± 0.001	0.000 02 ± 0.000 01
2	0.001 ± 0.0005	0.000 006 ± 0.000 003
3	0.006 ± 0.003	≥0.000 01

[a] Einstein/mol; DBA/DPA method at 60 °C; instrument calibrated with tetramethyl-1,2-dioxetane.

The thermolysis of **1–3** in xylenes without added fluorescers exhibited only weak chemiluminescence. Addition of 9,10-dibromoanthracene (DBA) or 9,10-diphenylanthracene (DPA) resulted in large increases in the chemiluminescence intensity without affecting the rate of dioxetane decomposition. The yields of excited carbonyl fragments directly produced during the thermolysis of **1–3** were determined by the DBA/DPA method (varying the concentration of added fluorescer at constant temperature and dioxetane concentration). As expected,[2] the thermal decomposition of **1–3** produced (directly) greater yields of excited triplet carbonyl products than yields of excited singlets. However, the total light yields for **1–3** are less than 1% rather than the expected values of 5–10% observed for most 3,4-disubstituted dioxetanes.[2] The data for dioxetanes **1–3** are listed in Table II.

Discussion

The activation parameter data for **1–3** show a large variation in activation energies despite the apparent similarity in degree of dioxetane substitution. As usual for simple dioxetanes,[2g] the $\Delta S^{\ddagger}$ terms for all three compounds are close to zero and within experimental error of one another. Thus, the relative stabilities of the compounds can be discussed in terms of E_a or $\Delta H^{\ddagger}$. Dioxetane **1**, which is similar in stability to that of tetramethyl-1,2-dioxetane,[2,4e] is the most stable cis-3,4-disubstituted dioxetane synthesized to date while **3** remains the least stable compound of this type. **2** is of normal stability, similar to that of *cis*-3,4-diethyl-1,2-dioxetane.[6b] Since steric interactions are expected to be roughly constant and electronic effects are not applicable,[2] the relative stabilities must be the consequences of conformational differences.

Unfortunately, little structural information is available on simple dioxetanes.[2] Attempts at X-ray analysis on **1** have shown the crystals to be unsatisfactory. However, molecular mechanics calculations (MM2)[8a] can be carried

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Scheme III

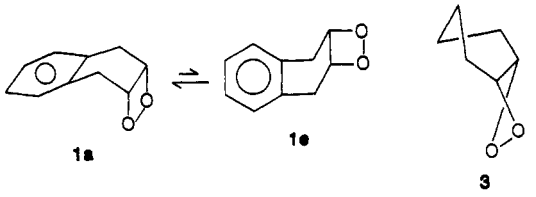

Table III. Molecular Mechanics (MM2) Results for Dioxetanes 1-3 and the Corresponding Diradicals

compd	6-ring conformation	torsion angle C–O–O–C, deg	diradical torsion angle ·O–C–C–O·, deg
1a	boat	0	2
1e	boat	0	4
2	intermediate	4	43
3	"twist-boat"	10	56

out to gain insight into possible conformational differences.[8b] The molecular mechanics calculations on dioxetane 1 predicted the most stable conformation (**1a**) to be a boat with the dioxetane ring in a pseudo-endo position (Scheme III). In addition, the O–C–C–O torsion angle was determined to be 0°. A boat conformation (**1e**) with the dioxetane ring in a pseudo-exo position was calculated to be 2 kcal/mol less stable. In contrast, the most stable conformation of dioxetane **3** was determined to be of a twist-boat type with an O–C–C–O torsion angle of 10° (see Scheme III). Compound **2** was calculated to be of intermediate conformation with a dioxetane ring torsion angle of 4°. The results are summarized in Table III.

Interestingly the MM2 results seem to confirm the earlier speculation that **3** was in a twist-boat conformation. The MM2 results correlate with the notion that the instability of a dioxetane is related to the degree of torsion twisting of dioxetane ring. Torsion angles (·O–C–C–O·) for the diradicals that would result from homolysis of **1–3** were also calculated by the molecular mechanics method (see Table III). The conformation of the 6-ring in the diradical generated from **1** remains a boat. However, those for diradicals from **2** and **3** begin to approach a chair conformation. On the assumption of a diradical model, these calculations suggest that dioxetane **1** undergoes thermolysis without twisting. Thus, restriction of twisting motions leads to substantial increases in the activation energy of the dioxetane.

Structural investigations (X-ray) of the extremely stable dioxetanes derived from diadamantylene[9] and a hindered cyclobutadiene[10] yielded dioxetane ring torsion angles (puckering) of 21 and 0°, respectively. Subsequent X-ray data by Adam[11] on three additional dioxetanes yielded torsion angles of ~10–15°. The authors concluded[11] that for these dioxetanes the degree of puckering of the peroxide ring did not affect the thermal stability but also pointed out that fused bicyclic dioxetanes should be tested. A recent study[7b] on dioxetanes of benzo-1,4-dioxenes and related compounds found the dioxetane ring to be planar with the 1,4-dioxene rings in a boatlike conformation. In these cases, the 1,4-dioxene ring was thought[11] to control the conformation of the peroxide ring. The present results show that for annulated dioxetanes the conformation of the substituent ring affects the torsion angle of the peroxide ring and the relative stability.

The total light yields for **1–3** were less than 1% rather than the expected values of 5–10% observed for most 3,4-disubstituted compounds. The triplet/singlet ratios were high and appear normal for this type of dioxetane. Kopecky[7a] has noted a low light yield for a 6-ring-substituted dioxetane, 3,4:3,4-dibutano-1,2-dioxetane. The present data indicate that a low light yield is general for this type of polycyclic dioxetane. In addition, the light yields do not seem to depend on the stability of the dioxetane. No theory adequately explains the low light yields for this type of polycyclic dioxetane.

Experimental Section

All solvents were of reagent grade. ^{1}H NMR spectra were recorded on a Varian EM 360 NMR spectrometer and a JEOL GX-270 NMR spectrometer. 1,2-Dihydronaphthalene[12] and 1,4-dihydronaphthalene[13] were prepared by literature procedures. 9,10-Diphenylanthracene (Aldrich) was used without further purification. 9,10-Dibromoanthracene (Aldrich) was recrystallized from xylenes (Aldrich) before use. Molecular mechanics calculations were carried out on a Vax 11750 (VMS operating system) using the MM2 program model (version 1.3) available from Prof. C. Still, Columbia University.

Dioxetane Synthesis and Purification. The purified (no metal ions!) alkenes (70 mmol) were converted to the corresponding β-bromo hydroperoxides in ~70% yield by the standard procedure developed by Kopecky.[4f] The β-bromo hydroperoxides (white solids) **4** and **5** were crystallized from CCl_4–pentanes, at −30 °C and room temperature, respectively. **4**: mp 37–38 °C. Anal. Calcd C, 49.41; H, 4.56. Found: C, 49.34; H, 4.59. **5**: mp 79–80 °C. Anal. Calcd: C, 49.41; H, 4.56. Found: C, 49.35; H, 4.59. Proton NMR ($CDCl_3$): 2-hydroperoxy-3-bromo-1,2,3,4-tetrahydronaphthalene (**4**) δ 3.0–3.6 (m, 4 H), 4.35–4.75 (m, 2 H), 7.1 (br s, 4 H), 8.2 (s, 1 H); 1-hydroperoxy-2-bromo-1,2,3,4-tetrahydronaphthalene (**5**) δ 2.2–3.1 (m, 4 H), 4.7–5.0 (m, 1 H), 5.1 (br d, 1 H), 7.1–7.4 (m, 4 H), 8.0 variable (s, 1 H) [The signals for the hydroperoxy protons varied in chemical shift and linewidth from sample to sample]. ^{13}C NMR ($CDCl_3$): **4**, δ 132.4, 131.9, 128.6, 128.1, 126.4, 126.1, 82.8, 46.4, 36.1, 30.8; **5**, δ 137.0, 130.7, 128.8, 128.6, 126.1, 85.2, 47.9, 26.8, 25.7. IR (melt) for **4** and **5**: 3450 (s), 3065 (w), 3015 (w), 2915 (w).

The following procedure was employed in the synthesis of dioxetanes **1** and **2**. A 1.0-g portion of β-bromo hydroperoxide was dissolved in 10 mL of CH_2Cl_2 and the resultant cooled to −15 °C. To the rapidly stirring (magnetically) solution was added 3.0 g of KOH in 10 mL of deionized water (1% $EDTA^{2-}$) dropwise. The mixture was stirred until the solution warmed to 10 °C. The organic layer was separated and dried with $MgSO_4$. The solvent was removed under reduced pressure. The temperature of all dioxetane-containing samples was maintained at 0 °C or less. The dioxetanes were purified by low-temperature chromatography following the procedure described by Baumstark.[2g] Dioxetane **1** crystallized from CCl_4 at −15 °C, as light yellow needles, in 2.5% yield: NMR (CCl_4) δ 2.84 (dd, J_{gem} = 17 Hz, J_{vic} = 0.8 Hz, 2 H), 3.09 (dd, J_{gem} = 17 Hz, J_{vic} = 1.1 Hz, 2 H), 5.87 (m, 2 H), 7.28 (br s, 4 H). Dioxetane **2** was difficult to purify. The major impurity in samples of **2** was the corresponding epoxide, 1,2-dihydronaphthalene oxide (formed in side reactions), which could be separated by repeated low-temperature chromatography. Pure dioxetane **2** was obtained as a yellow oil in ~2% yield: NMR (CCl_4) δ 2.31 (m, 4 H), 5.5 (m, 1 H), 6.25 (d, J = 7 Hz, 1 H), 7.3 (br 4 H). Dioxetane **3** (yellow oil) was prepared as previously reported.[6b]

Product Studies. The following procedure was employed for dioxetanes **1** and **2**. A solution of the purified dioxetane (~0.1 M) in CCl_4 was heated at 60 °C in a 5-mm NMR sample tube

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until the yellow color disappeared. The corresponding dialdehydes (see reactions 1 and 2) were the only products detected. ^{1}H NMR (CCl_4): 1,2-benzenediacetaldehyde (**6**), δ 3.68 (d, J = 2.0 Hz, 4 H), 7.23 (m, 4 H), 9.63 (t, J = 2.0 Hz, 2 H); 3-(2-formylphenyl)propanol (**7**), δ 2.7 (dt, J = 7 Hz, J = 0.8 Hz, 2 H), 3.28 (t, J = 7 Hz, 2 H), 7.38 (m, 4 H), 9.7 (t, J = 0.8 Hz, 1 H), 10.06 (s, 1 H). Dialdehyde **6** was converted to the corresponding bis(semicarbazone): light yellow crystals from ethanol/H_2O; mp 214-215 °C (lit.[14] mp 215 °C). Dialdehyde **7** was isolated as the bis(2,4-dinitrophenyl)hydrazone derivative: orange crystals from ethanol; mp 204-205 °C (lit.[15] mp 204 °C).

Thermolysis Studies. The chemiluminescence monitoring apparatus is essentially identical with that previously described.[16] The temperature (±0.3 °C) of the reaction mixture in the apparatus was monitored directly by use of a YSI Model 425C Tele-Thermometer with a #423 probe before and after each run. The jacketed cell was pretreated with aqueous Na_2EDTA solution. All experiments were carried out in xylenes (Aldrich) as solvent. In a typical run, 10 μL of a dioxetane solution (~0.1 M) in CCl_4 was added to 1.0 mL of xylenes containing a known concentration of DBA or DPA as added fluorescer. The solution was mixed by bubbling air via pipet. Experiments carried out without added fluorescer were of the first order for at least 3 half-lives and showed no dependence on the amount or type of added fluorescer. Initial dioxetane concentrations must be kept at 10^{-3} M or lower to avoid complications due to induced decomposition.[2]

Yields of Excited States. The relative yields of excited states produced upon dioxetane thermolysis were determined at 60.0 °C by variation of the concentration of the appropriate fluorescer (DBA/DPA method) at constant dioxetane concentration. The dioxetane concentration was determined by the ^{1}H NMR spectroscopic method with an added internal standard. Concentrations determined by the NMR method were in good agreement with those calculated on the basis of weight of sample. The instrument was calibrated by setting the yield of triplet products from the thermolysis of tetramethyl-1,2-dioxetane at 0.30. The method of calculation has been discussed in detail.[2]

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Palladium-Catalyzed Reaction of 1,3-Diene Monoepoxides with β-Keto Acids. Allylic Alkylation and Isomerization of 1,3-Diene Monoepoxides

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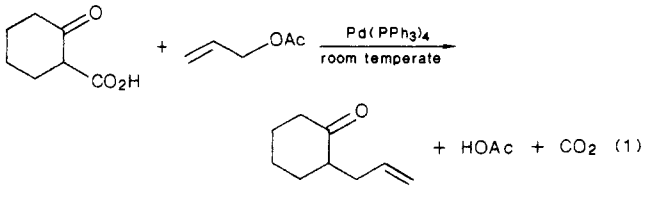
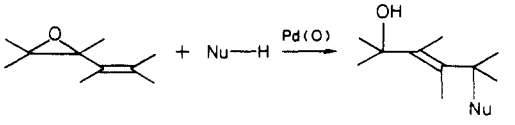
Tetrakis(triphenylphosphine)palladium catalyzed the decarboxylative allylic alkylation of 1,3-diene monoepoxides with β-keto acids at ambient temperature to produce keto allylic alcohols in moderate to good yields. 1,3-Diene monoepoxides employed in this reaction were 3,4-epoxy-1-butene (**2**), 3,4-epoxy-2-methyl-1-butene (**3**), 4,5-epoxy-2-hexene (**4**), and 3,4-epoxy-4-methyl-1-pentene (**5**). As β-keto acids, 1-oxocyclohexane-2-carboxylic acid, benzoylacetic acid (**1**), and 1,3-acetonedicarboxylic acid were used. The allylic alkylation of 1,3-diene monoepoxide took place regioselectively at the allylic carbon atom distal to the hydroxyl group. The stereochemistry of the resultant carbon-carbon double bond was predominantly to exclusively *E*. On the contrary, 3,4-epoxy-2,3-dimethyl-1-butene (**6**), 4,5-epoxy-2,5-dimethyl-2-hexene (**7**), and 3,4-epoxy-1-cyclohexene (**8**) took a different course of the reaction to undergo the palladium-catalyzed isomerization. The isomerization of **6** and **7** was accelerated by **1**, but that of **8** was not. The effect of the structure of 1,3-diene monoepoxides upon the reaction course and the role of β-keto acid in the isomerization were discussed.

Very recently we reported palladium-catalyzed decarboxylative allylic alkylation of allylic acetates with β-keto acids (eq 1).[1] Use of other allylic compounds may expand



the scope of this type of decarboxylative allylic alkylation reaction.[2] Palladium-catalyzed reactions of 1,3-diene monoepoxides as allylic ethers are a recent subject of considerable interest.[3] The palladium-catalyzed regio- and stereoselective allylic alkylation of 1,3-diene monoepoxides with the stabilized nucleophiles generated in situ from carbon acids (NuH) has been reported (eq 2).[3b,c] The



allylic alkylation takes place at the allylic carbon atom distal to the hydroxyl group, and the allylic alkylation

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