for 2 h, the mixture was then stirred at room temperature for 5 h, poured onto ice, and extracted with EtOAc (150 mL), and the organic phase was washed with water (50 mL), brine (50 mL), and dried (Na_2SO_4). The residual oil was purified by Kugelrohr distillation, 128-134 °C (0.08 Torr), to give the product (13, 3 g, 40%): IR (neat) 1355 and 1180 cm^{-1}; ^1H NMR 1.17 (t, 3 H, J = 7 Hz), 1.3-1.8 (m, 6 H), 2.43 (s, 3 H), 3.36 (t, 2 H, J = 7 Hz), 3.42 (q, 2 H, J = 7 Hz), 4.0 (t, 2 H, J = 6 Hz), 7.28 (d, 2 H, J = 8 Hz), and 7.76 ppm (d, 2 H, J = 8 Hz).

5-(Tetrahydropyranyloxy)pentan-1-ol (14). To a mixture of pentane-1,5-diol (5.2 g, 0.05 mol) and *p*-TsOH (0.1 g, 0.53 mmol) in CH_2Cl_2 (120 mL) was added slowly dihydropyran (4.6 g, 0.055 mol) in CH_2Cl_2 (30 mL) at 0 °C. After the mixture was stirred for 2 h at 0 °C and 1 h at room temperature, saturated $NaHCO_3$ (50 mL) was added to the reaction mixture. The CH_2Cl_2 layer was washed with saturated $NaHCO_3$ (50 mL) and water (50 mL) and dried ($MgSO_4$). The residue was purified by column chromatography on silica gel with EtOAc-hexane (1:1,v/v) and Kugelrohr distillation at 80-85 °C (0.1 Torr) to give the product (14, 5.1 g, 54%): IR (neat) 3450 (br) and 1135 cm^{-1}; ^1H NMR 1.3-1.9 (m, 12 H), 2.4 (br s, 1 H), 3.3-3.9 (m, 6 H), and 4.58 ppm (m, 1 H).

6,12-Dioxatetradecan-1-ol (16). The reaction of compound 13 (2.86 g, 0.01 mol) and compound 14 (1.88 g, 0.01 mol) in the presence of NaH (0.4 g, 0.011 mol) in dry THF (70 mL) was carried out in the same manner as described above. The crude oil was chromatographed on silica gel to give a mixture (2.4 g) of the starting material (13) and compound 15 (40:60). To this mixture in MeOH (50 mL) was added *p*-TsOH (28 mg), and the reaction mixture was stirred for 3 h at room temperature. After evaporation of the solvent, the residue was dissolved in EtOAc (150 mL). The organic phase was washed with 5% $NaHCO_3$ (2 × 50 mL), water (50 mL), and brine (50 mL) and dried (Na_2SO_4). The residue was purified by column chromatography on silica gel with EtOAc-hexane (1:1) and Kugelrohr distillation at bp 88-92 °C (0.05 Torr) to give the product (16, 0.8 g, total yield 37%): IR (neat) 3460 (br) and 1115 cm^{-1}; ^1H NMR 1.18 (t, 3 H, J = 7 Hz), 1.3-1.8 (m, 12 H), 2.1 (br s, 1 H), 3.38 (t, 8 H, J = 6.5 Hz), and 3.43 ppm (q, 2 H, J = 7 Hz).

6,12-Dioxatetradecanoic Acid (1). Kiliani reagent[25] was prepared in situ by dissolving $Na_2Cr_2O_7 \cdot 2H_2O$ (3 g) in a cold solution of H_2SO_4 (4 g) and water (13.5 g). To a solution of compound 16 (1.2 g, 5.5 mmol) in AcOH (28 mL) was added Kiliani reagent (20 g) at 0 °C. The reaction mixture was stirred for 7 h at room temperature. Water (120 mL) was added to the mixture and then extracted with EtOAc (2 × 100 mL). The organic phase was washed with water (2 × 30 mL) and dried (Na_2SO_4). The residual oil was purified by column chromatography on silica gel with $CHCl_3$-MeOH (7:1) and subsequent Kugelrohr distillation at bp 128-132 °C (0.1 Torr) to give the product (1) (0.7 g, 52%): IR (neat) 3000 (br) and 1730 cm^{-1}; ^1H NMR 1.23 (t, 3 H, J = 7.4 Hz), 1.3-1.8 (m, 10 H), 2.38 (t, 2 H, J = 5.4 Hz), 3.3-3.6 (m, 8 H), and 9.98 ppm (br s, 1 H). Anal. Calcd for $C_{12}H_{24}O_4$: C, 62.04; H, 10.41. Found: C, 61.95; H, 10.43%.

Acknowledgment. This project was supported by grants from the Monsanto Company (B.D. and S.P.A.) and the National Institutes of Health (J.I.G. and G.W.G.) AI27179.

Supplementary Material Available: NMR spectra of relevant compounds (11 pages). Ordering information is given on any current masthead page.

Nazarov Reaction of Trisubstituted Dienones: Mechanism Involving Wagner-Meerwein Shift

Jiro Motoyoshiya,* Toshikazu Yazaki, and Sadao Hayashi

Department of Material Creation Chemistry, Faculty of Textile Science and Technology, Shinshu University, Ueda, Nagano 386, Japan

Received December 4, 1989

The Nazarov reactions of trisubstituted α,α'-dienones were studied. Whereas α,β-dimethyl-β'-alkyl α,α'-dienones gave 2,3-dimethyl-4-alkyl-2-cyclopentenones when heated in concentrated sulfuric acid, the reaction of β,β-dimethyl-β'-alkyl α,α'-dienones afforded 3,4-dimethyl-4-alkyl-2-cyclopentenones as the rearranged products. A mechanistic investigation using two deuterated dienones suggests that the Nazarov reactions of the latter dienones are accompanied by Wagner-Meerwein shifts to form the most stable carbocations.

There have been many investigations on the Nazarov reaction[1,2] from mechanistic and synthetic viewpoints. The original Nazarov reaction is the ring closure of α,α'-dienones (divinyl ketones) or α,β'-dienones (allyl vinyl ketones) in strongly acidic media. This reaction proceeds via conrotatory 4π electronic cyclization of pentadienyl cations[3] and provides an efficient route to 2-cyclopentenones, useful intermediates for organic synthesis.[4] Among the many studies of this reaction, a few examples of abnormal Nazarov reactions with rearrangements were found in substituted dienones.[5] These are considered to occur by rearrangement of the cyclopentenyl cations formed by a normal electronic cyclization of the 4π system to the most stable cyclopentenyl cations, which give the final products. These competing rearrangements are often regarded as a shortcoming of the Nazarov reaction but are suggestive,

(1) Nazarov, I. N.; Zaretskaya, I. I.; Sorkia, T. I. *Zh. Obshch. Khim.* **1960**, *30*, 746; *Chem. Abstr.* **1961**, *55*, 524h. Nazarov, I. N.; Zaretskaya, I. I. *Zh. Obshch. Khim.* **1957**, *27*, 693. For a recent review, see: Santelli-Rouvier, C.; Santelli, M. *Synthesis* **1983**, 429.

(2) Recent papers for the Nazarov reaction, see: (a) Denmark, S. E.; Jones, T. K. *J. Am. Chem. Soc.* **1982**, *104*, 2642. (b) Marino, J. P.; Linderman, R. J. *J. Org. Chem.* **1981**, *46*, 3696. (c) Jacobson, R. M.; Lahm, G. P.; Clader, J. W. *Ibid.* **1980**, *45*, 395. (d) Shoppee, C. W.; Cooke, B. J. *J. Chem. Soc., Perkin Trans. I* **1972**, 2271.

(3) Shoppee, C. W.; Cooke, B. J. *J. Chem. Soc., Perkin Trans. I* **1973**, 1026.

(4) For a review on the synthesis of 2-cyclopentenones, see: (a) Ramaiah, M. *Synthesis* **1984**, 529. (b) Ellison, R. A. *Synthesis* **1973**, 397.

(5) (a) Paquette, L. A.; Fristad, W. E.; Dime, D. S.; Bailey, T. R. *J. Org. Chem.* **1980**, *45*, 3017. (b) Hirano, S.; Takagi, S.; Hiyama, T.; Nozaki, H. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 169. (c) Hirano, S.; Hiyama, T.; Nozaki, H. *Tetrahedron Lett.* **1974**, 1429.

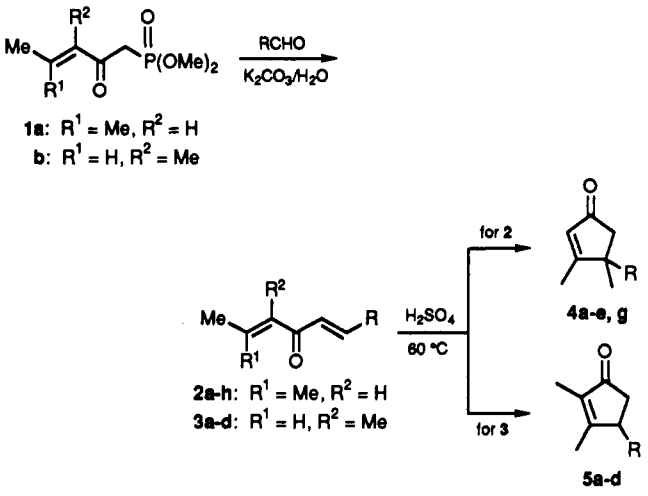
0022-3263/91/1956-0735$02.50/0

Table I. Preparation and Nazarov Reaction of α,α′-Dienones

α,α′-dienone	R	R^1	R^2	yield (%)[a]	2-cyclopentenone[a]	yield (%)
2a	Me	Me	H	68	**4a**	41
2b	Et	Me	H	83	**4b**	55
2c	*n*-Pr	Me	H	59	**4c**	39
2d	*i*-Pr	Me	H	73	**4d**	31
2e	*n*-Bu	Me	H	55	**4e**	47
2f	*t*-Bu	Me	H	10[b]	**4f**	*d*
2g	*n*-Pent	Me	H	55	**4g**	47
2h	Ph	Me	H	59[c]	**4h**	*d*
3a	Me	H	Me	40	**5a**	61
3b	Et	H	Me	44	**5b**	37
3c	*i*-Pr	H	Me	49	**5c**	58
3d	*n*-Bu	H	Me	45	**5d**	63
6a	CD_e	Me	H	47	**7a + 7b**	55
6b	Me	CD_3	CD_3	51	**8a + 8b**	20

[a] Isolated yields. [b] Reaction condition, 70 °C for 48 h. [c] Reaction condition, 2 days at room temperature. [d] No cyclopentenone was isolated.

Scheme I



on the other hand, that in a strongly acidic medium the Nazarov reactions of suitably substituted dienones would give rearranged 2-cyclopentenones.[6] In order to obtain a better understanding of rearrangements in Nazarov reactions, we have studied reactions of several trisubstituted dienones and now wish to report the results of some aspects of the mechanism.

Results and Discussion

Preparation of Trisubstituted α,α′-Dienones. Many methods for the preparation of α,α′-dienones[4a] have been developed. The readily available γ,δ-unsaturated β-keto phosphonates[7] are regarded as suitable reagents for this purpose. Thus, dimethyl keto phosphonates **1a**[8] and **1b** were synthesized from the reactions of copper(I) (dimethylphosphono)methanide[7a] and senecyl acid chloride or tiglic acid chloride, respectively. The Horner–Wadsworth–Emmons reaction of phosphonates **1a** or **1b** with

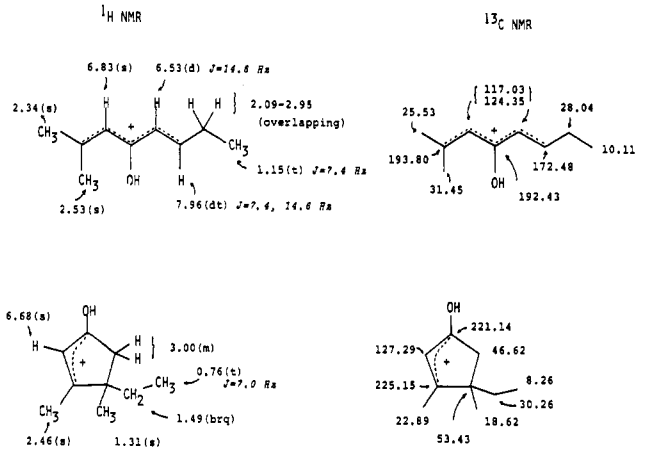


Figure 1. Chemical shifts of carbocation intermediates **2b** → **4b** measured in concentrated H_2SO_4. Me_4Si as an external standard.

aldehydes proceeded smoothly in an aqueous medium[9] in the presence of potassium carbonate to give α,α′-dienones **2a–h** and **3a–d**, respectively (Scheme I and Table I). In these compounds, all newly formed double bonds have the *E* configuration as generally seen in this class of reactions.[10]

Nazarov Reactions of α,α′-Dienones. When α,α′-dienones **2a–h** were heated in concentrated H_2SO_4 at 60 °C for 6 h, the rearranged 2-cyclopentenones **4a–e,g** were obtained without any normal Nazarov reaction products, while the normal cyclization products **5a–d** were obtained from **3a–d** (Table I and Scheme I). Although the yields of these cyclopentenones are low to moderate, they are comparable to those of previously reported Nazarov reactions.[11,12] The structures of the rearranged 2-cyclopentenones were confirmed by ^1H and ^{13}C NMR spectral data; in the ^1H NMR spectrum, the nonequivalence of 5-methylene protons in rearranged 2-cyclopentenones **4a–e,g** is clearly established by these spectral data and further the NOE between 4-methyl protons and the higher field 5-methylene proton allows us to assign this 5-proton to be cis to 4-methyl group (See Experimental Section).

In the case of **2f** and **2h**, only decomposition resulted instead of cyclization. Steric hindrance of the tertiary butyl group would obstruct cyclization in **2f** and the conjugated phenyl group of **2h** would extend the positive charge to stabilize the initially formed pentadienyl cation, which would slow its cyclization leading to decomposition.

The reaction of **2b** was monitored by ^1H and ^{13}C NMR spectroscopy in concentrated H_2SO_4, and signals of each carbocation are assigned as described in Figure 1. In these spectra only the signal of the initial pentadienyl cation and the final 1-hydroxyallyl cation formed by a rearrangement could be clearly distinguished. In both cases the signals from the final carbocation gradually grew in with in-

(6) For examples of rearrangement in dehydration of 2-hydroxycyclopentanones, see: Agosta, W. C.; Smith, A. B., III. *J. Am. Chem. Soc.* **1971**, *93*, 5513. Bellamy, A. J. *J. Chem. Soc. B* **1969**, 449.

(7) For the preparation of γ,δ-unsaturated β-keto phosphonates, see: (a) Savignac, P.; Mathey, F. *Tetrahedron Lett.* **1976**, 2829. (b) Mathey, F.; Savignac, P. *Tetrahedron* **1978**, 649. For the synthesis of α,α′-dienones from [(alkylideneacetyl)methylidene]triphenylphosphoranes, see: Bestmann, H. J.; Schlosser, W. *Synthesis* **1979**, 201.

(8) Motoyoshiya, J.; Miyajima, M.; Hirakawa, K.; Kakurai, T. *J. Org. Chem.* **1985**, *50*, 1326.

(9) For recent papers on the Horner-Wittig reaction in an aqueous medium, see: Villieras, J.; Rambaud, M.; Graff, M. *Tetrahedron Lett.* **1985**, *26*, 53. Coutrot, Ph.; Grison, C. *Ibid.* **1988**, *29*, 2655.

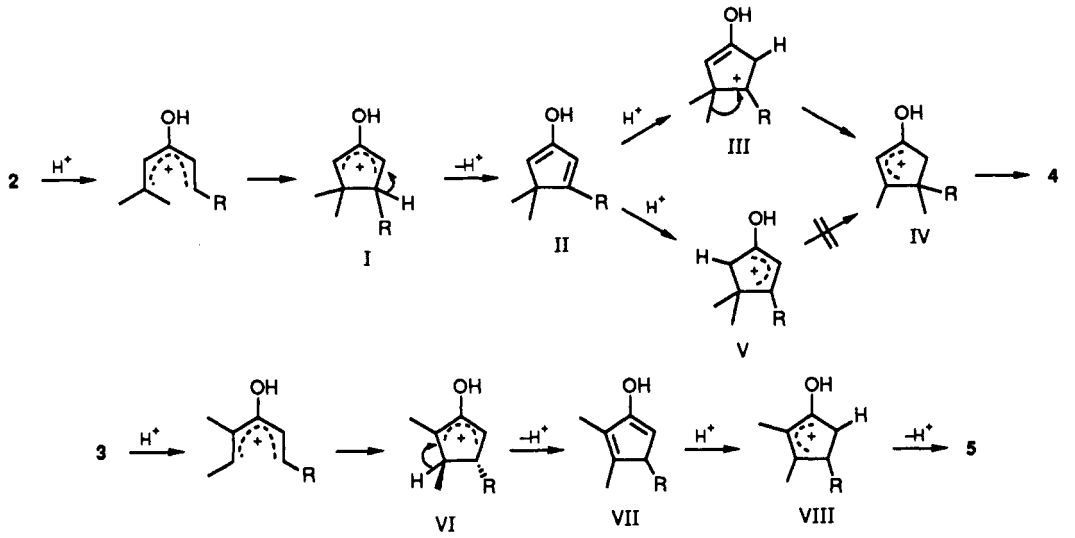
(10) For reviews on the Horner–Wadsworth–Emmons reaction, see: (a) Maryanoff, B. E.; Reitz, A. B. *Chem. Rev.* **1989**, *89*, 863. (b) Wadsworth, W. J., Jr. *Organic Reactions*; Wiley: New York, 1977; Vol. 25, Chapter 2. (c) Boutagy, J.; Thomas, R. *Chem. Rev.* **1974**, *74*, 87.

(11) (a) Hacini, S.; Pardro, P.; Santelli, M. *Tetrahedron Lett.* **1979**, 4454. (b) Cooke, F.; Schwindeman, J.; Magnus, P. *Ibid.* **1979**, 1995.

(12) Recently, silicon- or tin-directed Nazarov reactions have been reported to afford monocyclic cyclopentenones in good yields: (a) Johnson, C. R. *Tetrahedron Lett.* **1986**, *27*, 5947. (b) Denmark, S. E.; Jones, T. K. *Helv. Chim. Acta* **1983**, *66*, 2377.

(13) For an example of cyclization in carbonium ions accompanied by the Wagner–Meerwein shift, see: Smith, A. B., III; Toder, B. H.; Stephen, J. B.; Dieter, R. K. *J. Am. Chem. Soc.* **1981**, *103*, 1996.

Scheme II



creasing reaction time. The spectra of the final cyclopentenyl cation agree with those of protonated 2-cyclopentenone **4b** measured in concentrated H_2SO_4. In the case of **3c** the final carbocation was also identified to be the 1-hydroxyally cation, which agrees with the protonated **5c** in concentrated H_2SO_4.

On the basis of these results, a plausible mechanism for these reactions is suggested in Scheme II. The cyclopentenyl cation I, formed from **2** by conrotatory cyclization of the pentadienyl cation, would be transformed to cross-conjugated dienol II by deprotonation. The following protonation would take place not at the enol carbon but at the other α-carbon to give carbocation III, which would produce the final carbocation IV by a Wagner–Meerwein shift. The direct formation of III from I by a 1,2-hydride shift also cannot be excluded. The strong acid medium might make the preferential formation of III possible and in fact the reaction of **2b** in a weaker acid such as a mixture of formic and phosphoric acids gave a mixture of rearranged and nonrearranged 2-cyclopentenones in an almost equal ratio. Although dienol II could also afford 1-hydroxyallyl cation V by protonation on the enol carbon as seen in general Nazarov reactions, this pathway to IV should be excluded because this carbocation, independently generated from 3-ethyl-4,4-dimethyl-2-cyclopentenone[14] in concentrated H_2SO_4, did not give any rearranged carbocation after being heated for a long time. In comparison of V with IV, IV seems to be more stable owing to increased hyperconjugation[15] of the methyl group compared to that of the other alkyl groups and this would lower the activation energy for the rearrangements. On the other hand, VI, formed from **3**, would also be converted to the dienol VII, which gives the stable carbocation VIII as a final intermediate, and thus this is the normal Nazarov reaction product **5**.

Nazarov Reaction of Deuterated α,α'-Dienones. In order to clarify the course of the rearrangement, two deuterated dienones, **6a** and **6b**, were synthesized and employed in the Nazarov reaction under the same conditions (heated in concentrated H_2SO_4 at 60 °C for 6 h). As expected, a predominance of rearrangement was found in the reaction of **6a**. The integration of geminal methyl protons at δ 1.22 (nonlabeled methyl group in **7a** and **7b**) and vinyl methyl protons at δ 2.04 (nonlabeled methyl group only in **7a**) was compared in the ^1H NMR spectrum (Figure 2) to determine the ratio of a mixture of **7a** and **7b** (Scheme III). The ratio of these integrations was measured as 16.2:12.7, so the ratio of **7a**:**7b** is calculated to be ca. 9:1. Additionally, the inverse-gated heteronuclear decoupled ^{13}C NMR measurements also allowed the calculation of the ratio of **7a** and **7b**. Thus the ratio 8.0:7.2 of the integrations of geminal methyl carbon at δ 13.90 and vinyl methyl carbon at δ 26.66 led the ratio of **7a** and **7b** as ca. 16:1 (see Experimental Section). Although the exact ratio is uncertain, the predominance of rearranged product **7a** is clear. Partial exchange of the 5-methylene protons with deuterium in the products was also evident from their ^1H and ^{13}C NMR spectra as well as their high resolution mass spectra (see Experimental Section). On the other hand, in the reaction of **6b**, the ratio of rearranged and nonrearranged products could not be determined accurately because of a significant amount of deuterium exchange during the synthesis of **6b**. However, the ratio of rearrangement to nonrearrangement **8a**:**8b** $\simeq$ 2.4:1 was estimated from the ^1H NMR spectrum of the resulting mixture.

The different ratios observed in the products from **6a** and **6b** should reflect isotope effects[16] during the course of the reactions involving rearrangements (Scheme III). Reactions of **6a** and **6b** should, in principle, proceed similarly to the nondeuterated dienones as discussed above. Thus, dienols X and XIV would afford preferentially XI and XV by protonation, which would be in equilibrium with the dienols. The following migration step provides the same situation observed by Schubert et al., where migrational and nonmigrational isotope effects were found in neopentyl arenesulfonate solvolysis[17] and pinacol rearrangement[18] containing deuterated methyl groups, and this migration is one of the rate-determining steps pointed out by them. Therefore, the transformation of XI to XII would be faster than that of XV to XVI, which resulted in a much higher ratio of rearrangement in the reaction of **6a** than in **6b**. Additionally, a comparison of the stability of XIII and XVII also explains the higher rear-

(14) This cyclopentenone was prepared by a known method: Greene, A. E.; Depres, J.-P. *J. Am. Chem. Soc.* **1979**, *101*, 4003.
(15) (a) Olah, G. A.; Pittman, C. U., Jr.; Sorensen, T. S. *J. Am. Chem. Soc.* **1963**, *85*, 2331. (b) Deno, N. C.; Friedman, N.; Hodge, J. D.; Houser, J. J. *Ibid.* **1963**, *85*, 2995.
(16) For a review on kinetic isotope effects, see: Scheppele, S. E. *Chem. Rev.* **1972**, *72*, 511.
(17) Schubert, W. M.; Henson, W. L. *J. Am. Chem. Soc.* **1971**, *83*, 6299.
(18) Schubert, W. M.; LeFevre, P. H. *J. Am. Chem. Soc.* **1972**, *94*, 1639.

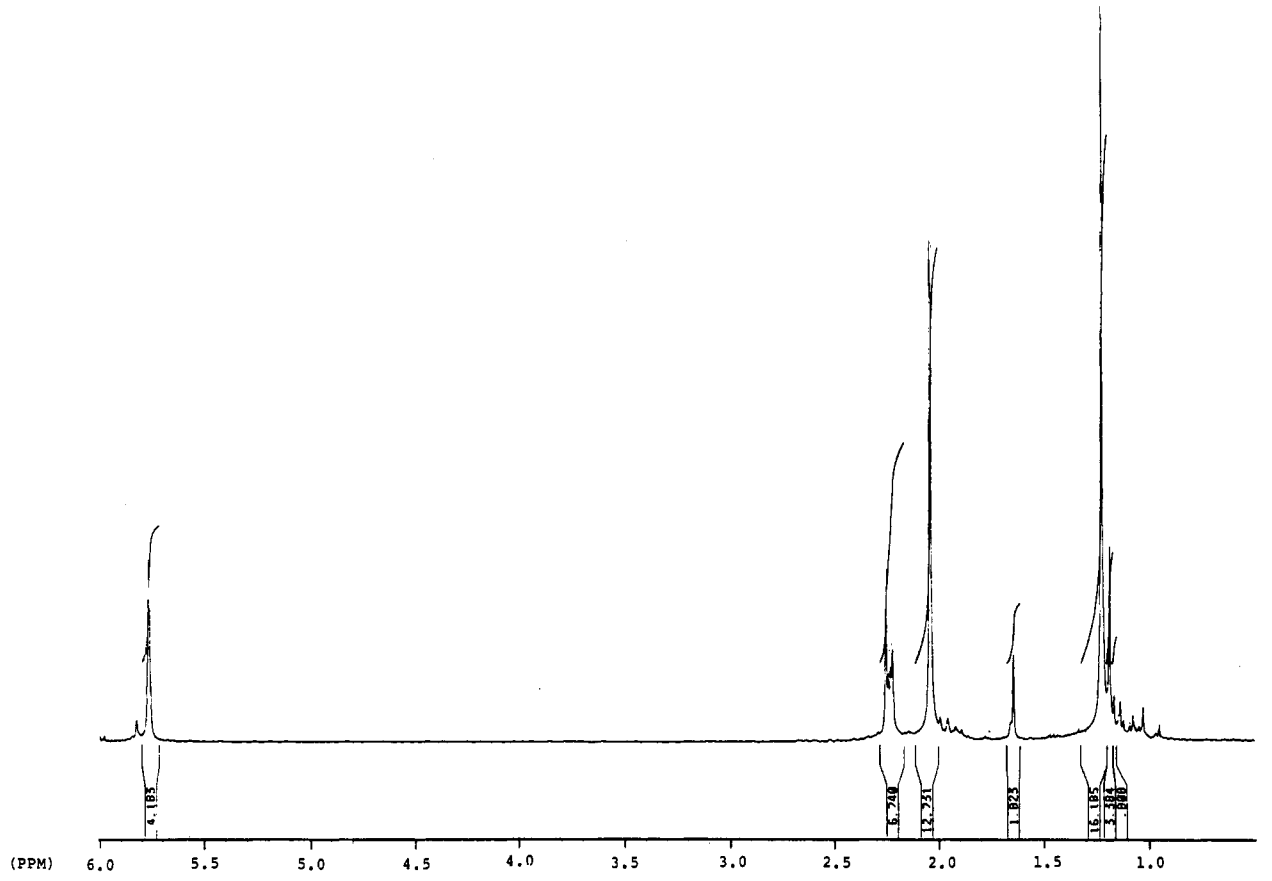
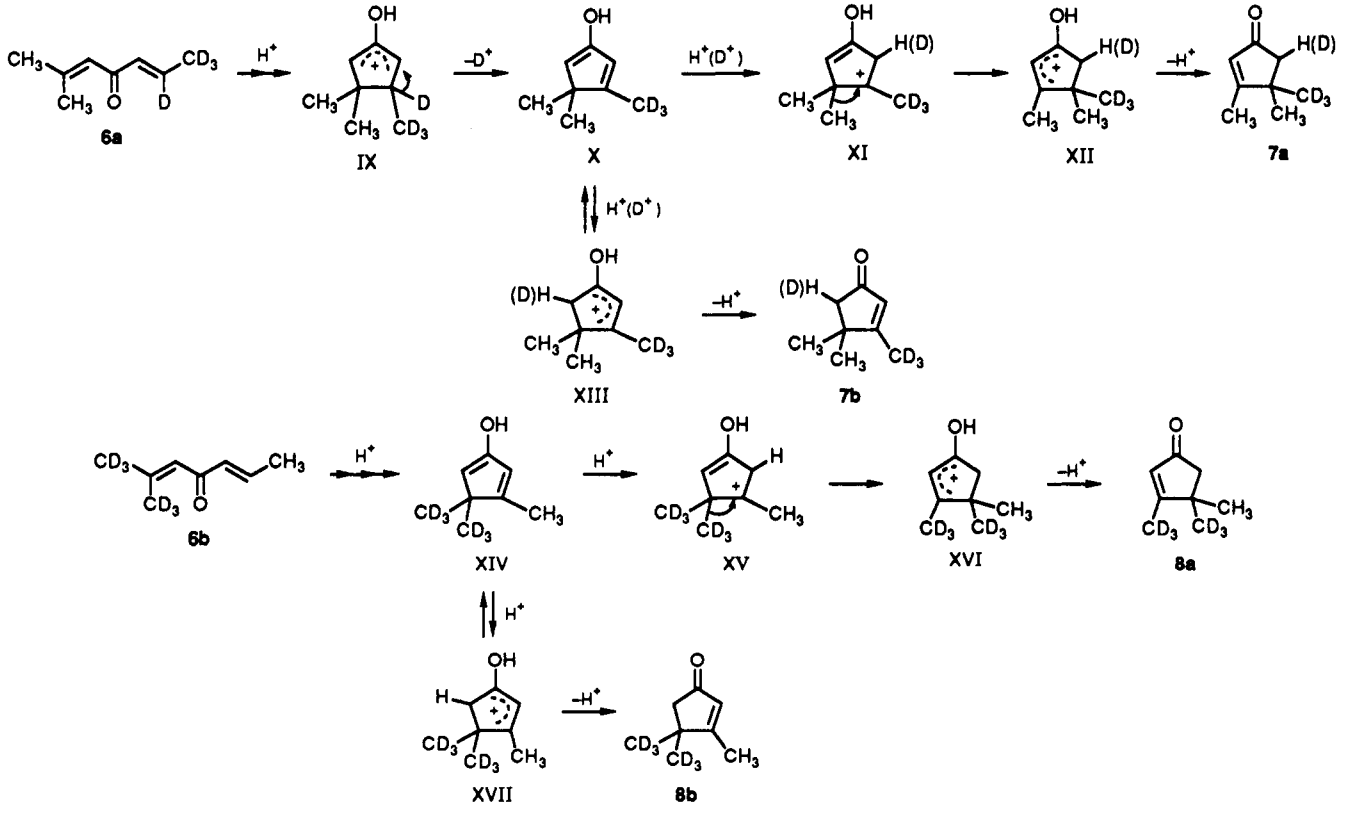


Figure 2. ^{1}H NMR spectrum of the deuterated cyclopentenones, a mixture of **7a** and **7b**.

Scheme III



rangement ratio from **6a**, namely, a β-D secondary isotope effect diminishes the stabilization from hyperconjugation in XIII compared to XVII, in accord with the observed predominance of the rearrangement pathway with **6a**.

This study using deuterated dienones supports the mechanism of the Nazarov reaction of dienones **2** involving rearrangements described in Scheme II. The important role of hyperconjugation from the methyl groups in de-

termining the extent of rearrangement is stressed.

Experimental Section

^1H NMR spectra were recorded at 60 or 250 MHz in CCl_4 and ^{13}C NMR spectra were recorded at 62 MHz. For ^1H and ^{13}C NMR spectral measurements in concentrated H_2SO_4, tetramethylsilane was used as an external standard in a glass capillary. Commercially available concentrated sulfuric acid (assay 98%, for analytical use) was used for the Nazarov reactions.

Dimethyl (4-Methyl-2-oxo-3-pentenyl)phosphonate (1a)[8] and Dimethyl ((*Z*)-3-Methyl-2-oxo-3-pentenyl)phosphonate (1b). These phosphonate reagents were synthesized according to an established procedure.[7a,8] The data for the newly prepared phosphonate **1b** follow: bp 119 °C (1.5 mm); IR (cm^{-1}) 1650; ^1H NMR (60 MHz) δ 1.78 (s, 3 H, 3-CH_3), 1.92 (d, 3 H, CH_3CH=, J_{HH} = 6 Hz), 3.20 (d, 2 H, PCH_2CO, J_{HP} = 22.5 Hz), 3.70 (d, 6 H, $POCH_3$, J_{HP} = 12 Hz), 6.82 (q, 1 H, CH=C, J_{HH} = 19 Hz); HRMS, *m/z* 206.0723 (calcd for $C_8H_{15}O_4P$, 206.0707).

Dimethyl (4-(Methyl-*d*$_3$)-2-oxo-3-pentenyl-*5,5,5-d*$_3$)-phosphonate (1c). To a suspension of NaH (50% in oil, 1.14g, 28.6 mmol) in THF (30 mL) was added triethyl phosphonoacetate (6.40 g, 28.6 mmol). After evolution of H_2 was ceased, acetone-d_6 (99% *d*, 2.4 mL, 33 mmol) in THF (10 mL) was added dropwise to the above solution and then heated under reflux for 2 h. After removal of the solvent, brine (30 mL) was added, and the organic layer was extracted with ether (3 × 30 mL) and dried (Na_2SO_4). Distillation gave ethyl 2-(methyl-d_3)-butenoate-*4,4,4-d*$_3$ (2.23 g, 58%, bp 48 °C at 25 mmHg). Saponification of this ester (3.59 g, 27 mmol) with KOH (1.51 g, 27 mmol) in ethanol (20 mL) at ambient temperature and acidification with concentrated HCl followed by a reaction with $SOCl_2$ (3.57 g, 30 mmol) for 30 min at 60 °C yielded the acid chloride (1.34 g) in 40% overall yield. The acid chloride was reacted with copper(I) (dimethylphosphono)methanide according to the literature method[7,8] to afford phosphonate **1c** (0.62 g, 20%): bp. 120 °C (1 mm) (oven temperature, Kugelrohr distillation); IR (cm^{-1}) 1670, 1600; ^1H NMR (60 MHz) δ 1.73, 2.12 (two m, 1.25 H, CH_3C=), 2.88 (d, 2 H, PCH_2CO, J_{HP} = 23 Hz) 3.73 (d, 6 H, CH_3OP, J_{HP} = 11 Hz), 6.22 (m, 0.17 H, CH=C); HRMS, *m/z* 210.0948 (calcd for $C_8H_9D_5O_4P$, 210.0943). As revealed by ^1H NMR spectral data, the percentage of deuterium was calculated as ca. 79%.

Preparation of α,α′-Dienones by the Horner–Wadsworth–Emmons Reaction. Typical Procedure. (*E*)-2-Methyl-2,5-heptadien-4-one (2a). To a solution of the phosphonate **1a** (1.0 g, 4.9 mmol) and K_2CO_3 (1.02 g, 7.4 mmol) in 10 mL of water was added excess acetaldehyde (0.43 g, 9.8 mmol). After being stirred at ambient temperature for 15 min, the organic layer was extracted with ether and dried (Na_2SO_4). After removal of solvent and Kugelrohr distillation, α,α′-dienone **2a** (1.18 g, 68%) was obtained as a liquid, bp (oven temperature) 82 °C (20 mm) (lit.[19] bp 75–85 °C; 15 mmHg). The spectral data of this compound are in good agreement with those reported.[19]

The following dienones were prepared in a similar manner. The boiling points given below are oven temperatures of Kugelrohr distillation.

(*E*)-2-Methyl-2,5-octadien-4-one (2b): bp 85 °C (1 mm); IR (cm^{-1}) 1680, 1655, 1625, 1605; ^1H NMR (60 MHz) δ 1.04 (t, 3 H, CH_3CH_2, *J* = 7.5 Hz), 1.82 (s, 3 H, CH_3C=), 2.02 (s, 3 H, CH_3C=), 2.06–2.36 (m, 2 H, CH_3CH_2), 5.72 (dt, 1 H, CH_2CH=C*H*, *J* = 1.5, 16 Hz), 5.82–5.98 (m, 1 H, CH_3C=C*H*), 6.51 (dt, 1 H, CH_2CH=, *J* = 6, 16 Hz); HRMS, *m/z* 138.1017 (calcd for $C_9H_{14}O$, 138.1043).

(*E*)-2-Methyl-2,5-nonadien-4-one (2c): bp 85 °C (1 mm); IR (cm^{-1}) 1675, 1650, 1620, 1600; ^1H NMR (60 MHz) δ 0.97 (t, 3 H, CH_3CH_2, *J* = 7 Hz), 1.20–1.70 (m, 2 H, CH_3CH_2), 1.90 (s, 3 H, CH_3C=), 2.13 (s, 3 H, CH_3C=), 2.23–2.60 (m, 2 H, CH_2), 5.96 (dt, 1 H, CH_2CH=C*H*, *J* = 1.5, 16 Hz), 6.03–6.23 (m, 1 H, CH_3C=C*H*), 6.72 (dt, 1 H, CH_2CH=CH, *J* = 6, 16 Hz); HRMS, *m/z* 152.1219 (calcd for $C_{10}H_{16}O$, 152.1200).

(*E*)-2,7-Dimethyl-2,5-octadien-4-one (2d): bp 90 °C (1 mm); IR (cm^{-1}) 1690, 1620; ^1H NMR (60 MHz) δ 1.00 (d, 6 H, $(CH_3)_2CH$, *J* = 6.0 Hz), 1.90 (s, 3 H, CH_3C=), 2.12 (s, 3 H, CH_3C=), 2.47 (m, 1 H, $(CH_3)_2CH$), 5.92 (d, 1 H, CHCH=C*H*, *J* = 16 Hz), 6.08 (m, 1 H, CH_3C=C*H*), 6.63 (dd, 1 H, CHC*H*=CH, *J* = 7.0, 16 Hz); HRMS, *m/z* 152.11746 (calcd for $C_{10}H_{16}O$, 152.1200).

(*E*)-2-Methyl-2,5-decadien-4-one (2e): bp 115 °C (0.3 mm); IR (cm^{-1}) 1680, 1660, 1630, 1610; ^1H NMR (60 MHz) δ 0.90 (t, 3 H, CH_3CH_2, *J* = 6 Hz), 1.10–1.73 (m, 4 H, $CH_3(CH_2)_2CH_2$), 1.87 (s, 3 H, CH_3C=), 2.12 (s, 3 H, CH_3C=), 2.15–2.40 (m, 2 H, CH_2CH=), 5.88 (dt, 1 H, CH_2CH=C*H*, *J* = 1.5, 16 Hz), 5.97–6.17 (m, 1 H, $(CH_3)_2C$=C*H*), 6.50 (dt, 1 H, CH_2CH=CH, *J* = 6, 16 Hz); HRMS, *m/z* 166.1369 (calcd for $C_{11}H_{18}O$, 166.1357).

(*E*)-2,7,7-Trimethyl-2,5-octadien-4-one (2f): bp 100 °C (1 mm); ^1H NMR (60 MHz) δ 1.12 (s, 9 H, $(CH_3)_3C$), 1.92 (s, 3 H, CH_3C=), 2.13 (s, 3 H, CH_3C=), 5.93 (d, 1 H, CCH=C*H*, *J* = 16 Hz), 6.03–6.23 (m, 1 H, CH_3C=C*H*), 6.72 (d, 1 H, CC*H*=CH, *J* = 16 Hz); HRMS, *m/z* $M^+ - CH_3$, 151.1162 (calcd for $M^+ - CH_3$, $C_{10}H_5O$).

(*E*)-2-Methyl-2,5-undecadien-4-one (2g): bp 130 °C (1.5 mm); IR (cm^{-1}) 1675, 1655, 1625, 1605; ^1H NMR (60 MHz) δ 0.92 (t, 3 H, CH_3CH_2, *J* = 4 Hz), 1.1–1.63, 2.0 (m, 8 H, CH_3CH_2), 1.88 (s, 3 H, CH_3C=), 2.10 (s, 3 H, CH_3C=), 5.97 (d, 1 H, CH_2CH=C*H*, *J* = 14 Hz), 6.08 (m, 1 H, CH_3C=C*H*), 6.67 (dt, 1 H, CH_2CH=CH, *J* = 7, 14 Hz); HRMS, *m/z* 180.1520 (calcd for $C_{12}H_{20}O$, 180.1513).

(*E*)-2-Methyl-6-phenyl-2,5-hexadien-4-one (2h): bp 150 °C (1 mm); IR (cm^{-1}) 1665, 1640, 1640, 1620; ^1H NMR (60 MHz) δ 1.80, 2.18 (s, 6 H, CH_3C=CH), 6.20 (m, 1 H, CH_3C=C*H*), 6.63 (d, 1 H, C*H*=CHPh, *J* = 16.5 Hz), 7.41 (d, 1 H, CH=C*H*Ph, *J* = 16.5 Hz); HRMS, *m/z* 186.1035 (calcd for $C_{13}H_{14}O$, 186.1044).

(*E,E*)-3-Methyl-2,5-heptadien-4-one (3a): bp 75 °C (0.2 mm) (lit.[19] bp 75–87 °C; 15 mmHg). The spectral data were in good agreement with those reported.[19] HRMS: *m/z* 124.0893 (calcd for $C_8H_{12}O$, 124.0887).

(*E,E*)-3-Methyl-2,5-octadien-4-one (3b): bp 95 °C (0.1 mm); IR (cm^{-1}) 1655, 1605; ^1H NMR (60 MHz) δ 1.10 (t, 3 H, CH_3CH_2, *J* = 7 Hz), 1.75 (s, 3 H, 3-CH_3), 1.85 (d, 3 H, CH_3CH=C, *J* = 6 Hz), 2.23 (m, 2 H, CH_3CH_2), 6.47 (d, 1 H, CH_2CH=C*H*, *J* = 16 Hz), 6.57 (m, 1 H, CH_3CH=CCH_3, overlapping signal), 6.68 (dt, 1 H, CH_2CH=CH, *J* = 6.0, 16 Hz); HRMS, *m/z* 138.1042 (calcd for $C_9H_{14}O$, 138.1043).

(*E,E*)-3,7-Dimethyl-2,5-octadien-4-one (3c): bp 85 °C (0.1 mm); IR (cm^{-1}) 1660, 1620; ^1H NMR (60 MHz) δ 1.08 (d, 6 H, $(CH_3)_2CH$, *J* = 6 Hz), 1.77 (s, 3 H, 3-CH_3), 1.83 (d, 3 H, CH_3CH=, *J* = 6 Hz), 2.4 (m, 1 H, $(CH_3)_2CH$), 6.40 (d, 1 H, CHCH=C*H*, *J* = 16 Hz), 6.57 (m, 1 H, CH_3CH=, overlapping signal), 6.80 (dd, 1 H, CHC*H*=CH, *J* = 6, 16 Hz); HRMS, *m/z* 152.1209 (calcd for $C_{10}H_{16}O$, 152.1200).

(*E,E*)-3-Methyl-2,5-decadien-4-one (3d): bp 110 °C (0.2 mm); IR (cm^{-1}) 1660, 1620; ^1H NMR (60 MHz) δ 0.93 (t, 3 H, CH_3CH_2), 1.43 (m, 4 H, CH_3CH_2), 1.80 (s, 3 H, 3-CH_3), 1.87 (d, 3 H, CH_3-CH=, *J* = 6 Hz), 2.23 (m, 2 H, CH_2CH=), 6.47 (d, 1 H, =C*H*CO, *J* = 16 Hz), 6.63 (m, 1 H, CH_3CH=, overlapping signal), 6.80 (dt, 1 H, CH_2CH=CH, *J* = 6, 16 Hz); HRMS, *m/z* 166.1371 (calcd for $C_{11}H_{18}O$, 166.1356).

Nazarov Reaction of α,α′-Dienones. Typical Procedure. 3,4,4-Trimethyl-2-cyclopentenone (4a). A solution of **2a** (0.50 g, 4 mmol) in 5 mL of concentrated H_2SO_4 was heated at 60 °C with magnetically stirring for 6 h in a 30-mL round-bottomed flask protected from moisture by a calcium chloride tube. After cooling to room temperature, the reaction mixture was diluted by adding it slowly into ca. 30 mL of ice–water and then it was neutralized carefully with saturated $NaHCO_3$ solution (ca. 15 mL). The organic layer was extracted with ether (3 × 20 mL) and dried (Na_2SO_4). Removal of the solvent and vacuum distillation gave **4a** (0.23 g, 46%): bp 27 °C (0.18 mmHg). The spectral data are in good agreement with those reported.[20] HRMS: *m/z* 124.0884 (calcd for $C_8H_{12}O$, 124.0886). Anal. Calcd for $C_{14}H_{15}O_4N_4$ as (2,4-dinitrophenyl)hydrazone of **4a** (mp 161–162 °C): C, 55.25; H, 5.30; N, 18.41. Found: C, 55.09; H, 5.23; N, 18.03.

The following 2-cyclopentenones were prepared in a similar manner to that described above. The boiling points given below are oven temperatures from Kugelrohr distillations.

4-Ethyl-3,4-dimethyl-2-cyclopentenone (4b): bp 95° C (2 mm); IR (cm^{-1}) 1700, 1625; ^1H NMR (250 MHz) ($CDCl_3$) δ 0.77 (t, 3 H, CH_3CH_2, *J* = 7.5 Hz), 1.20 (s, 3 H, 4-CH_3), 1.49, 1.59 (q, 2 H, CH_3CH_2, *J* = 7.5 Hz), 1.99 (d, 3 H, CH_3C=, *J* = 1.0 Hz),

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2.12 and 2.36 (AB system, 2 H, CH_AH_B, J = 18.5 Hz), 5.86 (m, 1 H, CHC=, J = 1.0 Hz); NOE (7%) observed between C4-CH_3 and CH_2 at C5 resonated at higher field (δ 2.12); ^{13}C NMR ($CDCl_3$) δ 8.89, 14.28, 25.58, 30.91, 47.72, 130.57, 184.53, 208.10; HRMS, m/z 138.1068 (calcd for $C_9H_{14}O$, 138.1044). Anal. Calcd for $C_{15}H_{17}O_4N_4$ as (2,4-dinitrophenylhydrazone) of **4b** (mp 119–122 °C): C, 56.59; H, 5.70; N, 17.60. Found: C, 56.43; H, 5.60; N, 17.35.

4-Propyl-3,4-dimethyl-2-cyclopentenone (4c): bp 90 °C (0.8 mm); IR (cm^{-1}) 1700, 1610, ^1H NMR (60 MHz) δ 0.93, 1.00 (t, 3 H, CH_3CH_2), 1.18 (s, 3 H, 4-CH_3), 1.12–1.65 (m, 4 H, CH_3CH_2), 1.97 (d, 3 H, CH_3C=), 2.03 and 2.24 (AB system, 2 H, CH_AH_B, J = 18 Hz), 5.73 (m, 1 H, CHC=); HRMS, m/z 152.1179 (calcd for $C_{10}H_{16}O$, 152.1199).

4-(1-Methylethyl)-3,4-dimethyl-2-cyclopentenone (4d): bp 90 °C (1 mm); IR (cm^{-1}) 1690, 1620; ^1H NMR (60 MHz) δ 0.70, 0.93 (d, 6 H, $(CH_3)_2CH$, J = 6 Hz), 1.20 (s, 3 H, 4-CH_3), 1.76 and 2.24 (AB system, 2 H, CH_AH_B, J = 18 Hz), 1.9 (m, 1 H, $(CH_3)_2CH$), 1.93 (d, 3 H, 3-CH_3, J = 1.0 Hz), 5.75 (m, 1 H, CHC=); ^{13}C NMR ($CDCl_3$) δ 14.44, 17.61, 17.97, 24.99, 32.59, 43.47, 49.95, 130.17, 185.44, 208.60; HRMS, m/z 152.1203 (calcd for $C_{10}H_{16}O$, 152.1200).

4-Butyl-3,4-dimethyl-2-cyclopentenone (4e): bp 90 °C (0.2 mm); IR (cm^{-1}) 1700, 1610; ^1H NMR (250 MHz) δ 0.88 (t, 3 H, CH_3CH_2), 0.96–1.66 (m, 6 H, CH_3CH_2), 1.20 (s, 3 H, 4-CH_3), 1.96 (s, 3 H, 3-CH_3), 2.14 and 2.38 (AB system, 2 H, CH_AH_B, J = 18 Hz), 5.73 (m, 1 H, CHC=); NOE (3%) observed between 4-CH_3 and CH_2 at C5 resonated at higher field (δ 2.14); HRMS, m/z 166.1376 (calcd for $C_{11}H_{18}O$, 166.1357).

4-Pentyl-3,4-dimethyl-2-cyclopentenone (4g): bp 130 °C (1.5 mm); IR (cm^{-1}) 1700, 1610; ^1H NMR (250 MHz) δ 0.87 (t, 3 H, CH_3CH_2), 1.02–1.65 (m, 8 H, CH_3CH_2), 1.18 (s, 3 H, 4-CH_3), 1.95 (d, 3 H, 3-CH_3, J = 1.0 Hz), 1.95 and 2.20 (AB system, 2 H, CH_AH_B, J = 18 Hz), 5.73 (q, 1 H, CHC=, J = 1.0 Hz); ^{13}C NMR ($CDCl_3$) δ 14.02, 14.30, 22.51, 24.33, 25.84, 32.25, 38.37, 46.41, 48.24, 130.36, 184.78, 208.13; HRMS, m/z 180.1548 (calcd for $C_{12}H_{20}O$, 180.1513).

2,3,4-Trimethyl-2-cyclopentenone (5a): bp 80 °C (0.1 mm). The spectral data are in good agreement with those reported.[21] ^{13}C NMR ($CDCl_3$): δ 7.99, 14.80, 19.02, 37.27, 42.98, 135.77, 173.88, 208.88. HRMS: m/z 124.0895 (calcd for $C_8H_{12}O$, 124.0888).

4-Ethyl-2,3-dimethyl-2-cyclopentenone (5b): bp 90 °C (3 mm); IR (cm^{-1}) 1700, 1640; ^1H NMR (60 MHz) δ 0.87 (t, 3 H, CH_3CH_2, J = 7.0 Hz), 1.07–1.73 (m, 2 H, CH_3CH_2), 1.63 (s, 3 H, 2-CH_3), 1.93 (s, 3 H, 3-CH_3), 2.22 (d, 1 H, C5-H, J = 7.0 Hz), 2.40–2.73 (m, 2 H, C4- and C5-H); HRMS, m/z 138.1046 (calcd for $C_9H_{14}O$, 138.1044).

4-(1-Methylethyl)-2,3-dimethyl-2-cyclopentenone (5c): bp 140 °C (15 mm). The spectral data are in good agreement with those reported.[22] ^{13}C NMR ($CDCl_3$): δ 7.86, 14.74, 15.19, 21.62, 27.66, 34.93, 48.37, 137.07, 172.20, 209.20. HRMS: m/z 152.1200 (calcd for $C_{10}H_{16}O$, 152.1200).

4-Butyl-2,3-dimethyl-2-cyclopentenone (5d): bp 95 °C (0.2 mm); IR (cm^{-1}) 1700, 1640; ^1H NMR (60 MHz) δ 0.9 (t, 3 H, CH_3CH_2), 1.06–1.83 (m, 6 H, CH_3CH_2), 1.60 (s, 3 H, 2-CH_3), 1.93 (s, 3 H, 3-CH_3), 2.27 (d, 1 H, C5-H, J = 7.0 Hz), 2.33–2.77 (m, 2 H, C4- and C5-H); HRMS, m/z 166.1372 (calcd for $C_{11}H_{18}O$, 166.1356).

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2-Methyl-2,5-heptadien-4-one-*6,7,7,7-d*$_4$ (6a). To an aqueous solution (20 mL) of K_2CO_3 (1.02 g 7.4 mmol) was added the phosphonate **1a** (1.0 g, 4.85 mmol). After being stirred for 5 min at ambient temperature, acetaldehyde-d_4 (0.28 g, 4.85 mmol), prepared by oxidation of ethanol-d_4 (99% d, 2 mL, 35 mmol) with $Na_2Cr_2O_7 \cdot 2H_2O$ (3.58 g, 12 mmol) in concentrated H_2SO_4 (2.6 mL) and water (22 mL), was added to the above solution, which was stirred for 1 h. Usual workup gave the dienone **6a** (0.29 g, 47%): bp 60 °C (2 mm); ^1H NMR (60 MHz) δ 1.90 (s, 3 H, CH_3C=), 2.30 (s, 3 H, CH_3C=), 5.96–6.20 (m, 2 H, =CHCOCH=, overlapping signals). Other signals due to nondeuterated methyl and vinyl protons were not observed. HRMS: m/z 128.1144 (calcd for $C_8H_8OD_4$, 128.1139).

2-Methyl-2,5-heptadien-4-one-*1,1,1,2-d*$_4$ (6b). A reaction similar to that described above using potassium carbonate (0.44 g, 3.2 mmol), the phosphonate **1c** (0.45 g, 2.12 mmol), and aqueous acetaldehyde (5 mL) gave the dienone **6b** (0.35 g, 51%): bp 105 °C (14 mm); ^1H NMR (60 MHz) δ 1.85 (dd, 3 H, CH_3CH=, J = 1.2, 6 Hz), 1.76–2.13 (m, 1.16 H, protons due to nondeuterated methyl groups), 5.97 (dq, 1 H, CH=CHCO, J = 1.2, 16 Hz), 6.07 (m, 0.2 H, CD_3C=CHCO), 6.67 (dq, 1 H, CH_3CH=CHCO, J = 6, 16 Hz). As there were 1.16 protons among δ 1.76–2.13 that would have been exchanged by protium during base-mediated reactions, the percentage of deuteration was calculated as 72%. HRMS: m/z 130.1326 (calcd for $C_8H_6OD_6$, 130.1263).

Tetradeuterated 2-Cyclopentenones 7a + 7b. The deuterated dienone **6a** (0.20 g, 1.56 mmol) was heated in concentrated H_2SO_4 at 0 °C for 6 h. After workup similar to that described in the typical procedure, a mixture of **7a** and **7b** (0.11 g, 55%) was obtained: bp 55 °C (2 mm); IR (cm^{-1}) 1700, 1600, ^1H NMR (250 MHz) (CCl_4 and $CDCl_3$) δ 1.22 (s, 3.36 H, 4-CH_3), 2.04 (d, 2.65 H, 3-CH_3), 1.97–2.2 (m, 1.61 H, C5-H), 5.67 (m, 1 H, CH=); ^{13}C NMR (CCl_4 + $CDCl_3$); the inverse-gated heteronuclear decoupling measurement, 13.90 (relative intensity, 8.04), 5.83, 26.14 (4.61), 26.66 (7.17), 26.87 (1.62), 42.35 (4.53), 50.19, 50.44 (4.75), 50.76, 51.08 (3.41), 129.38 (9.34), 183.92 (4.74), 206.01 (4.15); HRMS, m/z 128.1166 (calcd for $C_8H_8OD_4$, 128.1139).

Hexadeuterated 2-Cyclopentenones 8a + 8b. The deuterated dienone **6b** (0.14 g, 1.08 mmol) was heated in concentrated H_2SO_4 at 60 °C for 6 h. After workup similar to that described in a typical procedure, a mixture of **8a** and **8b** (0.02 g, 20%) was obtained with a significant amount of loss in Kugelrohr distillation: bp 110 °C (15 mm); IR (cm^{-1}) 1700, 1605; ^1H NMR (60 MHz) δ 1.07 (s, 4.37 H, 4-CH_3), 2.0 (s, 1.85 H, 3-CH_3), 2.15 (s, 2 H, C5-H), 5.67 (br, 1 H, CH=); HRMS, m/z 130.1281 (calcd for $C_8H_6OD_6$ 130.1264).

Acknowledgment. We are indebted to Mrs. Kyoko Hokari, Kimio Miyahara, and Kazue Nishikawa for a part of the experiment, Prof. Ryozo Irie and Mrs. Hiromi Karasawa (Faculty of Agriculture, Shinshu University) for 250-MHz ^1H and ^{13}C NMR measurements, and Mrs. Eiko Tsuchida (Faculty of Engineering, Shinshu University) for high-resolution mass spectral measurements. We also thank a reviewer for valuable comments concerning the mechanisms.

Supplementary Material Available: NMR spectra for compounds **1b,c**, **2b–e,g**, **3b–d**, **6a,b**, **4b–e,g**, **5b–d**, **7a,b**, and **8a,b** (28 pages). Ordering information is given on any current masthead page.