Hz, 1 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 41.3 (d), 42.8 (d), 43.3 (t), 44.6 (d), 44.9 (2 C, d), 49.6 (d), 54.7 (d), 59.1 (d), 84.7 (d), 121.2 (s); mass spectrum, $m/e$ (relative intensity) (no molecular ion), 159 (100).

Anal. Calcd for $C_{11}H_{11}NO_3$: C, 64.38; H, 5.40. Found: C, 64.30; H, 5.47.

**Reduction of 1 with Sodium Cyanoborohydride.** Compound 1 was prepared by reacting pentacyclo[5.4.0.0$^{2,6}$.0$^{3,10}$.0$^{5,9}$]undecane-8,11-dione (5.00 g, 28.7 mmol) with benzylamine (3.20 g, 30 mmol) according to the procedure described by Sasaki et al.[2] The material thereby prepared was used without further purification; it was immediately dissolved in a solution of acetic acid (15 mL) in dry methanol (250 mL). To the resulting solution was added sodium cyanoborohydride (2.0 g, 32 mmol) portionwise with stirring at room temperature during 5 min. The resulting mixture was stirred at room temperature for 2 h. The reaction mixture was then concentrated in vacuo, and water (100 mL) was added to the residue. The resulting suspension was stirred, and solid sodium bicarbonate was added portionwise until evolution of carbon dioxide ceased. Excess solid sodium bicarbonate (2.0 g) was added, and the aqueous suspension was extracted with methylene chloride (4 × 50 mL). The combined extracts were washed with water (2 × 100 mL), dried (anhydrous magnesium sulfate), and filtered, and the filtrate was concentrated in vacuo. A yellow microcrystalline solid was thereby obtained. This material was recrystallized from benzene to afford pure **3** (5.30 g, 70%) as a colorless microcrystalline solid: mp 157-158 °C; IR (KBr) 3115 (br, vs), 3043 (w), 3019 (w), 2948 (s), 2864 (s), 2832 (s), 1603 (m), 1498 (m), 1326 cm$^{-1}$ (vs); $^1$H NMR ($CDCl_3$) $\delta$ 1.43 (*AB*, $J_{AB}$ = 10.5 Hz, 1 H), 1.76 (*AB*, $J_{AB}$ = 10.5 Hz, 1 H), 2.2-2.6 (m, 8 H), 3.29 (t, $J$ = 5.0 Hz, 1 H), 3.37 (*AB*, $J_{AB}$ = 10.5 Hz, 1 H), 3.91 (*AB*, $J_{AB}$ = 10.5 Hz, 1 H), 4.93 (br s, 1 H), 7.3 (m, 5 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 41.7 (t), 41.8 (d), 42.6 (d), 43.2 (d), 44.9 (d), 45.5 (d), 50.8 (d), 51.7 (t), 53.4 (d), 55.1 (d), 64.9 (d), 110.8 (s), 126.7 (d), 128.4 (d), 128.5 (d), 139.2 (s).

Anal. Calcd for $C_{18}H_{19}NO$: C, 81.47; H, 7.74. Found: C, 81.55; H, 7.50.

**Reduction of 1 with Lithium Aluminum Hydride.** Compound 1 was prepared by reacting pentacyclo[5.4.0.0$^{2,6}$.0$^{3,10}$.0$^{5,9}$]undecane-8,11-dione (5.00 g, 28.7 mmol) with benzylamine (3.20 g, 30 mmol) according to the procedure described by Sasaki et al.[2] The material thereby prepared was used without further purification; it was immediately dissolved in dry THF (100 mL). To the resulting solution was added lithium aluminum hydride (2.3 g, 60 mmol) portionwise with stirring at room temperature during 10 min. After the addition of the reducing agent had been completed, the reaction mixture was refluxed for 2 h. The reaction mixture was then cooled to room temperature and quenched by cautious, dropwise addition of water (50 mL). Diethyl ether (200 mL) was added, and the resulting mixture was stirred for 15 min. The mixture was filtered, and the residue was washed with ether (25 mL). The combined filtrates were diluted with water (50 mL), and the layers were separated. The aqueous layer was extracted with ether (2 × 50 mL). The combined ethereal solutions were washed with water (50 mL), dried (anhydrous magnesium sulfate), and filtered, and the filtrate was concentrated in vacuo to afford a pale yellow oil. This oil was purified via column chromatography (silica gel stationary phase, diethyl ether as eluent). The first fraction afforded an intractable oil (1.3 g). Continued elution of the chromatography column afforded a second fraction, which contained **2** (780 mg, 10%). Further elution of the chromatography column with 1:10 methanol-methylene chloride mixed solvent afforded a third fraction, from which a yellow microcrystalline solid could be obtained (2.2 g, 29%). This material was recrystallized from methanol-hexane mixed solvent, thereby affording pure **7** as a colorless microcrystalline solid: mp 129.5-130 °C; IR (KBr) 3600-2700 (br, vs), 1604 (w), 1478 (m), 1362 (m), 1112 (m), 1078 cm$^{-1}$ (m); $^1$H NMR ($CDCl_3$) $\delta$ 1.37 (*AB*, $J_{AB}$ = 11.3 Hz, 1 H), 1.68 (*AB*, $J_{AB}$ = 11.3 Hz, 1 H), 2.2-2.35 (m, 2 H), 2.4-2.5 (m, 2 H), 2.6-2.7 (m, 4 H), 3.47 (s, 1 H), 3.73 (s, 2 H), 3.91 (t, $J$ = 4.0 Hz, 1 H), 3.99 (s, 1 H), 5.32 (s, 1 H), 7.2-7.4 (m, 5 H); $^{13}$C NMR ($CDCl_3$) $\delta$ 34.7 (t), 38.6 (d), 39.5 (d), 40.1 (d), 40.5 (d), 43.2 (d), 44.2 (d), 46.4 (d), 46.6 (d), 51.2 (t), 58.3 (d), 73.8 (d), 126.6 (d), 128.0 (d), 128.2 (d), 140.8 (s).

Anal. Calcd for $C_{18}H_{21}NO$: C, 80.86; H, 7.92. Found: C, 80.67; H, 8.02.

**Single-Crystal X-ray Structural Analysis of 7.** A crystal of dimensions 0.10 × 0.33 × 0.50 mm was mounted on a Nicolet R3m/$\mu$ update of a P2$_1$ diffractometer. Data were collected in the Wyckoff mode (4° ≤ 2$\theta$ ≤ 45°, 2$\theta$ fixed $\omega$ varied) with a scan rate of 4-29.3 deg min$^{-1}$ using Mo K$\alpha$ radiation ($\lambda$ = 0.71073 Å). Lattice parameters were obtained from a least-squares refinement of 25 centered reflections (31.29° ≤ 2$\theta$ ≤ 40.52°). Systematic absences and Laue symmetry 2/$m$ were consistent with space group $C2/c$. A total of 1792 independent reflections were collected, of which 1254 were ≥3.0$\sigma(I)$. Lorentz-polarization and $\psi$-scan empirical absorption corrections were applied. The structure was solved by direct-methods techniques and refined by anisotropic block-cascade least-squares techniques (H atoms refined isotropically) to a final $R$ of 0.0489, $wR$ = 0.0483 (256 parameters), $S$ = 1.126, and $(\Delta/\sigma)_{max}$ = 0.019. The largest peaks in the final difference map were +0.21 and -0.17 e Å$^{-3}$. The function minimized was $\sum w(|F_o|-|F_c|)^2$ where $w = [\sigma^2(F_o) + 0.000\,63F_o^2]^{-1}$. The mass absorption coefficient, $\mu$, was determined to be 0.79 cm$^{-1}$ (Mo K$\alpha$). All computer programs were supplied by Nicolet for Desktop 30 Microeclipse and Nova 4/C configuration. Atomic scattering factors and anomalous dispersion corrections were taken from the International Tables for X-ray Crystallography.[10]

**Acknowledgment.** We gratefully acknowledge the assistance of Dr. Sanjay Basak with the synthesis and characterization of **6**. We thank the Air Force Office of Scientific Research (Grant AFOSR-84-0085), the Robert A. Welch Foundation (Grant B-963 to A.P.M., Grant P-074 to W.H.W.), and the University of North Texas Faculty Research Committee for financial support of this study.

**Supplementary Material Available:** Tables of atomic coordinates and isotropic thermal parameters, bond lengths, bond angles, torsion angles, anisotropic thermal parameters, H-atom coordinates, and isotropic thermal parameters (9 pages); observed and calculated structure factors (11 pages). Ordering information is given on any current masthead page.

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## Structural Assignment of a Methylcyclopentadiene-Toluquinone Diels-Alder Cycloadduct. Analysis of the Two-Dimensional NMR Spectrum of 1,6-Dimethyl-1$\alpha$,4$\alpha$,4a$\alpha$,5$\alpha$,8$\beta$,8a$\alpha$-hexahydro-1,4-methanonaphthalene-5,8-diol

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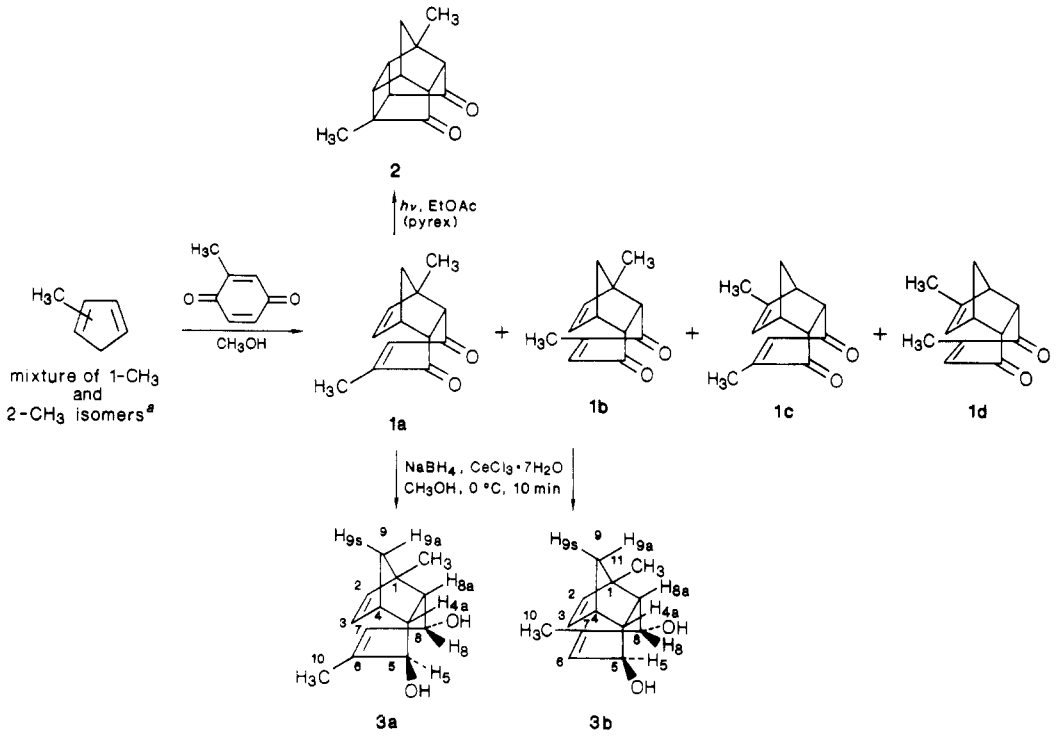
The tricyclic compounds that result via Diels-Alder cycloaddition of substituted cyclopentadienes to substituted *p*-benzoquinones are of considerable interest as intermediates in the synthesis of natural products.[1-3] As

(1) Smith, W. B.; Marchand, A. P.; Suri, S. C.; Jin, P.-w. *J. Org. Chem.* **1986**, *51*, 3052.

0022-3263/88/1953-2647$01.50/0 

**Scheme I**[a]




[a] Reference 6.

part of a program that is involved with the synthesis of novel, functionalized pentacyclo[5.4.0.0$^{2,6}$.0$^{3,10}$.0$^{5,9}$]undecanes,[4] we have undertaken a study of the Diels–Alder cycloaddition of methylcyclopentadienes to toluquinone.

Thermal cracking of methylcyclopentadiene dimer[5] affords a mixture of 1-methyl- and 2-methylcyclopentadienes.[6] Diels–Alder cycloaddition of this diene mixture to toluquinone afforded a corresponding mixture of isomeric (4 + 2) cycloadducts, which could be separated conveniently via flash column chromatography. A single, isomerically pure cycloadduct, **1**, mp 95–96 °C, was thereby obtained (see Experimental Section). That this cycloadduct possesses the endo configuration was demonstrated via its facile intramolecular photochemical cyclization to the corresponding dimethylpentacyclo[5.4.0.0$^{2,6}$.0$^{3,10}$.0$^{5,9}$]-undecane-8,11-dione (**2**).

Simple integration of the proton NMR spectrum of this cycloadduct revealed that only one of the vinylic carbon atoms bears a methyl group. Hence, of the four possible isomeric endo cycloadducts that might have been formed (**1a–d**, Scheme I),[7] the material that was isolated via column chromatography must possess either structure **1a** or **1b**. Further structural information was made available via analysis of the two-dimensional NMR spectrum of the corresponding exo,exo diol (**3**, which must possess either structure **3a** or **3b**). Diol **3** was synthesized via stereospecific reduction of the Diels–Alder cycloadduct (**1a** or

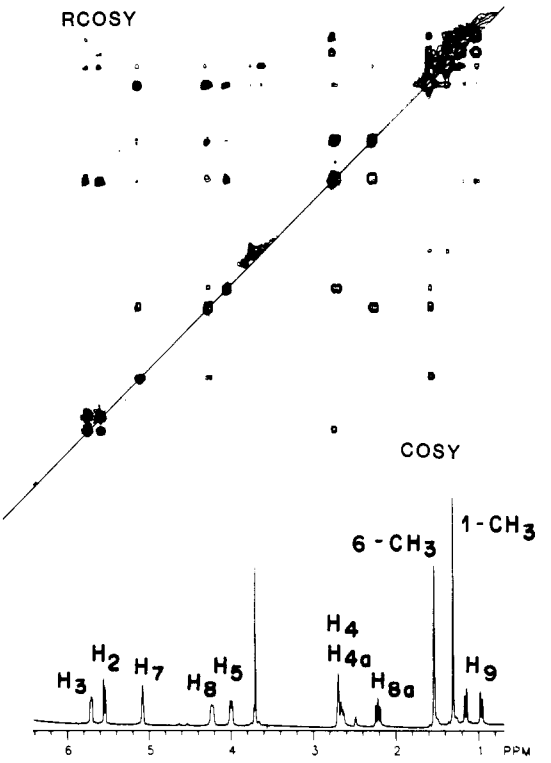



**Figure 1.** Composite 2-D NMR contour plot showing the normal COSY spectrum plotted below the diagonal and the homonuclear relayed coherence transfer spectrum (RELAY or RCOSY) optimized for 4 Hz (62.5 ms) plotted above the diagonal. A conventional high-resolution reference proton spectrum is plotted beneath the contour plot. Both spectra were acquired and processed in the absolute value mode.

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(6) Csicsery, S. M. *J. Org. Chem.* **1960**, *25*, 518.

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**1b**) with sodium borohydride in the presence of cerous chloride.[8]

**Results of 2-D NMR Studies on Diol 3.** Assignment of signals in the proton and carbon-13 NMR spectra of **3** was carried out via analysis of its COSY and homonuclear relayed COSY (i.e., RCOSY[9]) spectra. A composite spectrum which affords connectivity information derived from the COSY spectrum (responses below the diagonal) and from the RCOSY spectrum (responses above the diagonal) is shown in Figure 1. With the COSY responses in the upper half of the matrix as a starting point, a number of initial assignments can be made.

The bridging methyl group protons ($H_{9s}$ and $H_{9a}$) can be assigned readily to the upfield AB pattern. Both of these protons display weak responses that confirm their correlation with the proton that resonates all $\delta$ 2.72. When sufficient contour levels are plotted, it becomes possible to assign the absorption at $\delta$ 2.72 to $H_4$. Proton $H_4$, in turn, is expected to exhibit coupling to two additional protons (i.e., $H_3$ and $H_{4a}$). The connectivity that exists between $H_4$ and the vinyl proton that resonates at $\delta$ 5.75 permits assignment of this vinyl proton to $H_3$.

Off-diagonal responses in the COSY spectrum correlate $H_3$ with $H_2$; the latter proton resonates at $\delta$ 5.55. Similarly, the fact that the signal at $\delta$ 5.75 ($H_3$) is correlated with both $H_2$ and $H_4$ is confirmed by the RCOSY spectrum, which contains a relay response that correlates $H_2$ with $H_4$.[10] There are no additional correlations that involve $H_2$ since the adjacent carbon atom, $C_1$, is quaternary.

Assignment of the remaining correlation that involves $H_4$ (i.e., that between $H_4$ and $H_{4a}$) is not straightforward. The off-diagonal response which normally would be used to correlate $H_4$ with $H_{4a}$ (peaks that appear at $\delta$ 2.72 and 2.70, respectively) resides essentially astride the diagonal. Indeed, it is quite probable that this response could not be discerned even if phase-sensitive processing were to be employed. This leaves a potential discontinuity in the proton–proton connectivity network.

We note that the COSY spectrum does not contain responses that correlate $H_4$ with either $H_5$ or $H_{8a}$ (which resonate at $\delta$ 4.01 and 2.24, respectively). In contrast, the RCOSY spectrum does contain information that establishes these connectivities. It is possible for $H_4$ to exhibit responses that correlate it with $H_5$ and with $H_{8a}$ when an intervening proton is present to which each pair is mutually coupled (viz., $H_{4a}$). Magnetization is relayed from $H_4$ to $H_5$ and $H_{8a}$ via $H_{4a}$. Hence, the connectivity between $H_4$ and $H_{4a}$ is established indirectly, since it must exist in order for the observed magnetization transfer between $H_4$ and $H_{8a}$ to occur.

In addition, proton $H_{8a}$ correlates with $H_8$; the latter proton resonates at $\delta$ 4.25. Finally, an intense response is observed that correlates $H_8$ with the vinyl proton that resonates at $\delta$ 5.1. The foregoing connectivity network thereby permits assignment of the resonance at $\delta$ 5.1 to $H_7$. The linear nature of the $H_{8a}$–$H_8$–$H_7$ spin network is confirmed by the observed off-diagonal response in the RCOSY spectrum that results via correlation of $H_{8a}$ to $H_7$.

We can now make use of the $H_5$ resonance to distinguish between structures **3a** and **3b**. If the correct structure is **3a**, then $H_5$ is vicinally coupled only to $H_{4a}$. However, if instead the correct structure is **3b**, then the $H_5$ proton could be vicinally coupled to vinyl proton $H_6$. From the COSY portion of Figure 1, we note that there is a relatively weak response that correlates $H_5$ with the vinyl proton that resonates at $\delta$ 5.1 (i.e., $H_7$). The fact that this interaction is weak is consistent with structure **3a**, since the indicated $H_5$ is separated from $H_7$ by four intervening bonds (this corresponds to the situation that exists for long-range proton–proton allylic coupling). The assignment of this long-range $H_5$–$H_7$ correlation was confirmed when the data was reprocessed by using a 5-Hz Gaussian multiplication prior to obtaining both Fourier transformations. This operation eliminates responses that are due to long-range couplings.[11] Our assignment of structure **3a** for diol **3** has been confirmed independently by the results of a single-crystal X-ray crystallographic study.[12]

## Experimental Section

Melting points are uncorrected. Proton NMR spectra of **3a** were acquired by using a Nicolet NT-300 wide-bore spectrometer that operates at 300.068 MHz. The spectrometer was controlled by a Model 293-C pulse programmer and was equipped with a 5-mm dual-tuned $^1H/^{13}C$ probe. COSY spectra[13] were obtained as 200 × 1 K complex data points and were zero-filled to 512 × 512 points during processing. Sinusoidal multiplication was used prior to both Fourier transformations. The data also were symmetrized prior to plotting.[14] Relayed COSY spectra were acquired by using the pulse sequence devised by Eich, Bodenhausen, and Ernst[9] and by using the 32-step phase cycle described by Bax and Drobny.[15] Data were obtained as 200 × 1 K complex points and were processed in the manner described above in connection with the COSY data.

**Diels–Alder Addition of Methylcyclopentadienes to Toluquinone.** A solution of toluquinone (4.0 g, 33 mmol) in methanol (10 mL) was cooled to 0 °C via application of an external ice bath. To this cooled solution were added with stirring freshly cracked methylcyclopentadienes (mixture of 1-methyl and 2-methyl isomers,[6] 2.8 g, 35 mmol) in cold methanol (3 mL). After the addition of the methylcyclopentadienes had been completed, the ice bath was removed, and the reaction mixture was allowed to warm gradually to room temperature. The reaction mixture was stirred at room temperature for 24 h and then concentrated in vacuo. The residue, a mixture of isomeric Diels–Alder adducts, was obtained as a light yellow oil (5.4 g, 82%). This oil was purified via flash column chromatography (silica gel stationary phase, 2% ethyl acetate–hexane mixed solvent as eluent). Isomerically pure **1a** (200 mg) was thereby obtained as pale yellow microcrystalline solid: mp 95–96 °C; IR (KBr) 3010 (w), 1720 (vs), 1630 (vs), 1430 (s), 1360 (s), 1310 (s), 1225 (s), 1120 $cm^{-1}$ (s); $^1H$ NMR ($CDCl_3$) $\delta$ 1.40 (m, 2 H), 1.54 (s, 3 H), 1.90 (s, 3 H), 2.82 (m, 1 H), 3.37 (m, 2 H), 5.77 (m, 2 H), 6.32 (s, 1 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 16.07 (q), 17.05 (q), 49.43 (t), 50.86 (d), 53.52 (d), 55.61 (s), 57.69 (d), 134.5 (d), 139.4 (d), 139.8 (d), 151.2 (s), 198.5 (s), 199.6 (s); mass spectrum (70 eV), *m/e* (relative intensity) 202 (molecular ion, 73.2), 174 (40.6), 159 (47.3), 132 (45.4), 131 (100.0), 91 (55.2), 80 (76.6), 77 (40.4), 39 (74.6).

Anal. Calcd for $C_{13}H_{14}O_2$: C, 76.79; H, 6.88. Found: C, 77.02; H, 6.98.

**Intramolecular Photocyclization of 1a.** A solution of **1a** (200 mg, 1.0 mmol) in ethyl acetate (250 mL) was purged with nitrogen. The solution was then irradiated under nitrogen with a 450-W Hanovia medium-pressure mercury lamp (Pyrex filter) for 15 min. The reaction mixture was concentrated in vacuo, thereby affording crude **2** as a pale yellow oil. This material was distilled under reduced pressure [bp 90 °C (0.1 mmHg)], thereby

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(10) Note that no response can be observed in the normal COSY spectrum that indicates that $H_2$ is correlated with $H_4$. The fact that correlation between $H_2$ and $H_4$ can be observed in the RCOSY spectrum establishes the existence of the $H_2$–$H_3$–$H_4$ connectivity in **3**.

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Table I. Proton and Carbon NMR Chemical Shift Assignments for 3a Recorded at 300.068/75.459 MHz for $^1H/^{13}C$ ($CDCl_3$ Solvent)

| position | $\delta$ $^1H$ (ppm) | $\delta$ $^{13}C$ (ppm) | position | $\delta$ $^1H$ (ppm) | $\delta$ $^{13}C$ (ppm) |
|---|---|---|---|---|---|
| 1 | | 53.59 | 7 | 5.08 | 126.66 |
| 2 | 5.55 | 139.40 | 8 | 4.25 | 65.96 |
| 3 | 5.75 | 132.45 | 8a | 2.24 | 48.17 |
| 4 | 2.72 | 44.72 | 9 | 0.98, 1.17 | 56.84 |
| 4a | 2.70 | 46.61 | 1-$CH_3$ | 1.34 | 20.12 |
| 5 | 4.01 | 67.81 | 6-$CH_3$ | 1.55 | 18.51 |
| 6 | | 136.54 | | | |

affording a colorless oil, which soldified upon standing overnight in a refrigerator. Recrystallization of the resulting solid from acetone afforded pure **2** (120 mg, 60%) as a colorless microcrystalline solid: mp 58–59 °C; IR (KBr) 2990 (s), 1720 (vs), 1170 (s), 1010 (s), 850 $cm^{-1}$ (m); $^1H$ NMR ($CDCl_3$) $\delta$ 1.70 (m, 6 H), 1.87 (m, 2 H), 2.42 (m, 2 H), 2.72 (m, 4 H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 15.48 (q), 15.87 (q), 41.88 (d), 43.52 (d), 46.11 (t), 46.37 (s), 47.74 (d), 50.92 (d), 52.22 (s), 55.61 (d), 59.96 (d), 211.3 (s), 212.7 (s); mass spectrum (70 eV), *m/e* (relative intensity) 202 (molecular ion, 71.8), 174 (37.5), 159 (49.2), 121 (100.0), 91 (48.3), 80 (72.9), 77 (41.6), 39 (66.9).

Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 76.95; H, 7.00.

**1,6-Dimethyl-1α,4α,4aα,5α,8β,8aα-hexahydro-1,4-methanonaphthalene-5,8-diol (3a).** Sodium borohydride reduction of **1a** (200 mg, 1.0 mmol) was performed in the presence of cerous chloride by using a previously published procedure.[8] Crude diol **3a** (180 mg, 90%) was thereby obtained. Recrystallization of this material from acetone afforded pure **3a** (180 mg, 90%) as a colorless microcrystalline solid: mp 129–130 °C; IR (KBr) 3500 (vs), 3010 (w), 1610 (s), 1410 (s), 1320 (s), 1110 $cm^{-1}$ (s); mass spectrum (70 eV), *m/e* (relative intensity) (no molecular ion), 109 (17.0), 97 (18.5), 80 (100.0), 79 (43.0), 77 (19.4), 53 (10.2), 39 (19.2); $^1H$ and $^{13}C$ NMR data for **3a** are given in Table I.

Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.77. Found: C, 75.45; H, 9.01.

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## Palladium(0)-Catalyzed Cyclization Followed by Allylation of Allylic Alkynoates and the Related System

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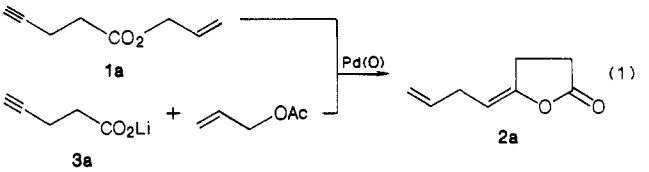
Intramolecular cyclization of alkynoic acids catalyzed by mercury(II)[1] and palladium(II) salts[2] provides a convenient method of preparing synthetically and biologically important unsaturated lactones. The development of the cyclization coupled with a carbon–carbon bond-forming reaction which gives a substituted unsaturated lactone may be expected to enhance remarkably the usefulness of this methodology. Very recently it has been reported that the alkenylpalladium chloride intermediates generated by the $PdCl_2$-catalyzed intramolecular cyclization of lithium alkynoates are trapped by allylic chlorides to give the allyl-substituted unsaturated lactones. Use of a large amount of allylic chlorides (20 equiv), however, is required for the trapping.[3] Here we have studied another approach to the synthesis of substituted unsaturated lactones, i.e., the palladium(0)-catalyzed cyclization followed by allylation of allylic alkynoates and a related system of lithium alkynoates and allylic acetates (for example, eq 1). This approach is featured with the use of an equimolar amount of alkynoate and allylic moieties, respectively.




When allyl 4-pentynoate (**1a**) was heated at 100 °C in acetonitrile in the presence of a palladium(0) complex catalyst (5.0 mol %) generated from $Pd_2(dba)_3{\cdot}CHCl_3$ and trimethylolpropane phosphite, (*E*)-4,7-octadien-4-olide (**2a**) was obtained in a good yield (Table I). Interestingly the formation of the lactone is highly dependent upon the ligand and the solvent. Trimethylolpropane phosphite was the best ligand. Triisopropyl phosphite was similarly effective. On the other hand, trimethyl and triphenyl phosphites were not effective. Triphenylphosphine showed a medium effect. Acetonitrile or a mixed solvent containing acetonitrile was a good solvent for the synthesis of **2a**. No formation of the lactone was observed in benzene or THF although the starting substrate **1a** was consumed.

Various allylic 4-pentynoates could be used for the reaction. Methallyl and cinnamyl esters gave the unsaturated lactones in good yields. In the latter case, diisopropyl phenylphosphonite was an effective ligand. One feature of the reaction is the regio- and stereoselective cyclization of the alkynoate moiety to produce the γ-(*E*)-alkylidene-γ-butyrolactone exclusively. The 4*E* stereochemistry of the products **2a**, **2b**, **2c**, **2c′**, and **2e** was assigned on the basis of the $^1H$ NMR chemical shifts of the C-5 olefinic protons $\delta$ 5.25, 5.29, 5.24, 5.12, and 5.34, respectively. The literature values[3] of the C-5 olefinic protons of (*E*)- and (*Z*)-**2a** are $\delta$ 5.28 and 4.64, respectively, which are compatible with the calculated values.[4] The stereochemistry of the allylic moiety in **2c** and **2e** was predominantly to exclusively *E*. The regioselectivity of the carbon–carbon bond formation toward the allylic moiety depends on its structure. In contrast to the regioselective reaction of the cinnamyl group, the carbon–carbon bond-forming reaction of 2-butenyl 4-pentynoate (**1c**) took place nonregioselectively to give two isomeric γ-(*E*)-alkylidene-γ-butyrolactones, i.e., (4*E*)-7-nonadien-4-olide (**2c**) (7*E* isomer/7*Z* isomer = 9.7) and (*E*)-6-methyl-4,7-octadien-4-olide (**2c′**). It is worth noting that isomeric 1-methyl-2-propenyl 4-pentynoate (**1d**) gave the almost same result as **1c**. This finding suggests the participation of the alkenyl(π-allyl)-palladium complex in the allylation step.

On the basis of two features of the reaction, i.e., the stereoselective cyclization of the alkynoate moiety and the intermediacy of the (π-allyl)palladium complex, the rea-

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(2) Lambert, C.; Utimoto, K.; Nozaki, H. *Tetrahedron Lett.* **1984**, *25*, 5323.
(3) Yanagihara, N.; Lambert, C.; Iritani, K.; Utimoto, K.; Nozaki, H. *J. Am. Chem. Soc.* **1986**, *108*, 2753. Under the ultrasound irradiation, the reaction can be done by the use of 1.5–2.5 equiv of allylic chlorides.
(4) Pascal, C.; Meier, J.; Simon, W. *Helv. Chim. Acta* **1966**, *49*, 164.

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