$C_{44}H_{56}O_8$: C, 74.13; H, 7.92. Found: C, 74.04; H, 7.86.

[3.3.3.3](2,5)-*p*-Benzoquinonophane (2). To a stirred mixture of 152 mg (0.21 mmol) of 1 and 15 mL of CH_2Cl_2 was added 4 mL of 2 M BBr_3 in CH_2Cl_2 and the mixture was stirred overnight at room temperature. Water (10 mL) was added and the mixture was extracted with Et_2O (150 mL) containing small amounts of MeOH. The combined extracts were washed with saturated aqueous NaCl solution, dried over $MgSO_4$, and filtered. Removal of the solvent afforded the crude hydroquinonophane: ^1H NMR (δ, $CDCl_3$–MeOH-d_4) 6.42 (s, 8, aromatic) 1.5–2.7 (m, 24, methylene).

To a mixture of the crude hydroquinonophane, 18 mL of AcOH, and 6 mL of THF was added 650 mg of 90% lead tetraacetate with stirring at room temperature. The solution immediately turned yellow. The flask was covered with aluminum foil to intercept daylight. The mixture was refluxed for 3 h with stirring. A small amount of ethylene glycol was added and the mixture was extracted with $CHCl_3$ (100 mL). The combined $CHCl_3$ solution was washed successively with saturated aqueous $NaHCO_3$ solution and water, dried over $MgSO_4$, and filtered. The filtrate was concentrated to dryness on a rotary evaporator to give brownish yellow solid, which was purified by preparative TLC on silica gel with using $CHCl_3$ and EtOAc (5:1 v/v); 55.6 mg (44% from 1) of the yellow solid was obtained: yellow crystals from benzene; mp 212 °C dec; ^1H NMR (δ, $CDCl_3$) 6.53 (s, 8, olefinic), 2.42 (t, 16, $CH_2CH_2CH_2$), 1.70 (m, 8, $CH_2CH_2CH_2$); IR (KBr) $\nu_{C=O}$ 1656 cm^{-1}, $\nu_{C=C}$ 1610 cm^{-1}; *m/z* (relative intensity) M^+ 592 (11%), $M^+ + 2$ 594 (21%), $M^+ + 4$ 596 (67%), $M^+ + 6$ 598 (100%), and $M^+ + 8$ 600 (45%). Anal. Calcd for $C_{36}H_{32}O_8$: C, 72.96; H, 5.44. Found: C, 73.12; H, 5.54.

Inclusion Behavior of 1 and 2. (1) 1 (5.6 mg, 7.9 μmol) and 8.6 mg (80 μmol) of *p*-benzoquinone were dissolved in 1 mL of THF. The solvent was allowed to evaporate at room temperature and ambient pressure. The resultant crystals were washed with MeOH, air-dried, and characterized by ^1H NMR. But neither *p*-benzoquinone nor THF was detected.

(2) 2 (3.0 mg, 5.0 μmol) and 5.7 mg (52 μmol) of hydroquinone were dissolved in 1 mL of THF. The solution was allowed to evaporate at room temperature and ambient pressure. The resultant precipitate was washed with MeOH, air-dried, and characterized by ^1H NMR. But neither hydroquinone nor THF was detected.

(3) 2 (709 μg, 1.2 mol) was dissolved in 0.25 mL of dioxane (solution A). Hydroquinone (199 μg, 1.8 μmol) was dissolved in 0.25 mL of dioxane (solution B). Solutions A and B were mixed. The color of the mixed solution did not change. The mixed solution was allowed to stand at room temperature for a day. The resultant precipitate was collected by filtration, washed with MeOH, and air-dried. ^1H NMR spectrum of the precipitate showed the presence of dioxane in a 1:1 (host–guest) ratio: ^1H NMR (δ, $CDCl_3$) 6.50 (s, 8, olefinic), 3.67 (s, ca 8, dioxane). The sample for the elemental analysis was recrystallized from dioxane. Anal. Calcd for $C_{36}H_{32}O_8 \cdot 1.1C_4H_8O_2$: C, 70.37; H, 5.96. Found: C, 69.98; H, 5.66.

(4) 2 (3.0 mg, 5.1 μmol) and 7.0 mg (50.7 μmol) of *p*-dimethoxybenzene was dissolved in 1.5 mL of CH_2Cl_2. The resulting crystals were characterized by ^1H NMR. The ^1H NMR spectrum showed the presence of CH_2Cl_2 in a 1:1 host–guest ratio: ^1H NMR (δ, $CDCl_3$) 6.50 (s, 8, olefinic), 5.27 (s, ca 2 H, CH_2Cl_2). The sample for elemental analysis was recrystallized from CH_2Cl_2. Anal. Calcd for $C_{36}H_{32}O_8 \cdot 0.8CH_2Cl_2$: C, 66.91; H, 5.12. Found: C, 67.10; H, 5.41.

Acknowledgment. The present work was partially supported by a Grant-in-Aid for Scientific Research No. 59540291 and a Grant-in-Aid for Encouragement of Young Chemists No. 58740234 from the Ministry of Education in Japan, Science and Culture.

Registry No. 1, 95865-80-8; 2, 95865-81-9; 2 (hydroquinone), 95865-82-0; 2·dioxane, 95865-83-1; 2·CH_2Cl_2, 95865-84-2; 4, 50874-27-6; 5, 13949-89-8; 6, 95865-76-2; 7, 95976-15-1; 8, 95865-77-3; 9, 95892-08-3; 10, 95865-78-4; 11, 95865-79-5; diethyl malonate, 105-53-3.

A Useful Synthon Approach to Bicyclic Enols: Acid-Catalyzed and Base-Catalyzed Rearrangements of Diels–Alder Adducts of 2-Methoxy-5-methyl-1,4-benzoquinone

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Received October 18, 1984

Acid- and base-catalyzed reactions of Diels–Alder adducts of the title compound 1 have been investigated. Bicyclic adducts **6**, **9**, and **11** isomerized to the corresponding enols **8**, **10**, and **13** on treatment with base followed by rapid acidification. However, thermal reactions of 1 with sorbic acid esters afforded the enol products **3** directly. Similar base treatment of tricyclic adducts **15** and **17** resulted in ether cleavage to α-keto enols **16** and **18**. The bicyclic enols suffered facile aerial oxidation to the *cis*- or *trans*-hydroperoxides **31** or **33**, depending on the substituent at the C-5 position. The *trans*-hydroperoxides **33** were reduced to the alcohols **34** on treatment with silica gel; however, the *cis*-hydroperoxides **31** underwent a novel decarbonylation to afford β-keto esters **32**. Acid treatment of adducts **6** gave α-keto enols **35**, but the ester-substituted adducts **4** were stable to acid. These interesting structure–reactivity relationships are summarized in Scheme I.

The successful synthesis of vinyl alcohol, the simplest enol,[1] in the gas phase[2] strikingly indicates that enols are not inherently unstable, although they are usually thermodynamically less stable than their corresponding keto forms.[3,4] Several ways of producing enols, including photoenolization[5] and metal coordination,[6] have been reported.[7–9] However, a systematic study of their chemistry has never been undertaken and might be worthwhile.

Recently, we found that a stable enol was formed as the major product in the Diels–Alder reaction of 2-methoxy-

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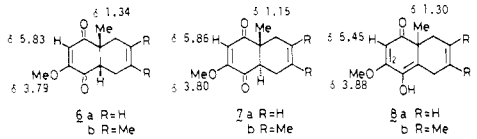
0022-3263/85/1950-1963$01.50/0

Chart I



6 a R=H
b R=Me

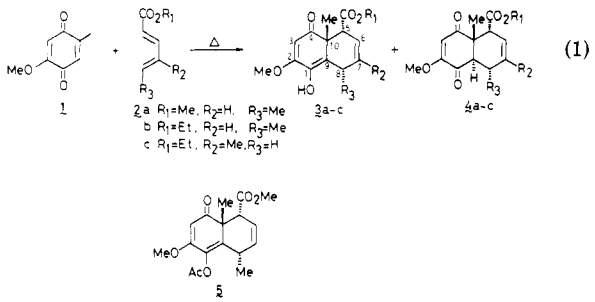
7 a R=H
b R=Me

8 a R=H
b R=Me

5-methyl-1,4-benzoquinone (**1**) with sorbic acid esters.[10] In this paper we report a general preparation of similar bicyclic enols from Diels–Alder adducts of **1** by base treatment followed by rapid acidification. In some cases a novel autooxidative decarbonylation reaction of these enols was observed. Furthermore, acid treatment of these adducts resulted in an interestering rearrangement to α-keto enols. The structure–reactivity relationships in these reactions will be discussed.

Results and Discussion

Thermal Enol Formation.[10] When a mixture of **1** and 8 equiv of methyl sorbate (**2a**) was heated at 100 °C under Ar for 67 h in a sealed tube, a novel crystalline product **3a**, mp 160–161 °C, was obtained in 67% yield together with the known trans Diels–Alder adduct **4a** (5%) and two other minor products (eq 1).[11] No cis adduct was formed. Heating **3a** at 120 °C under Ar resulted in a conversion to **4a** and the dehydrogenated products[11] as well. The enol structure of **3a** was evident in its IR [3310 (OH), 1740 (ester), and 1670 cm^{-1} (enone)] and ^{13}C NMR spectra displaying five singlets in the sp^2 region [δ 203.5 (C-4), 172.5 (CO_2R), 165.7 (C-2), 137.2 (C-9), and 129.0 (C-1)]. The ^1H NMR spectrum (Table I) showed a D_2O-exchangeable singlet at δ 5.41 (OH) and a singlet for H-3 at δ 5.40 which was characteristically shifted upfield. Furthermore, **3a** was readily converted to the acetate **5** (80%), mp 124–125°C, by treatment with Ac_2O/pyridine (0 °C, 30 min), whereas the similar treatment of **4a** required much longer time to give **5**.



(1)

2 a R_1=Me, R_2=H, R_3=Me
b R_1=Et, R_2=H, R_3=Me
c R_1=Et, R_2=Me, R_3=H

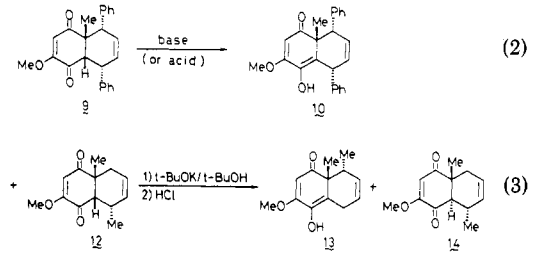
3 a-c

4 a-c

5

The similar reaction of **1** with ethyl sorbate (**2b**) gave the enol adduct **3b**, mp 151–152 °C, as the major product (54%) (eq 1). However, the reaction of **1** with **2c** (80 °C, 9 days), afforded the enol **3c**, mp 141–142 °C, in only 22% yield along with the trans Diels–Alder adduct **4c** as the major product (30%) (eq 1). These enol products were converted into the corresponding trans adducts by heating at the higher temperature (>120 °C) under an inert atmosphere.

Base-Catalyzed Enol Formation. While thermal reaction of **1** with various alkyl-substituted dienes led to a complex mixture of products, the Lewis acid catalyzed reactions proceeded smoothly and gave only cis Diels–Alder adducts such as **6**, **9**, **11**,[12] and **12**.[12] The base-catalyzed enolizations of these cis adducts were then attempted. Treatment of **6** (Chart I) with various bases caused only an isomerization to the trans adducts **7**[13] when the reaction mixture was subjected to the usual aqueous workup. However, it was found that both **6** and **7** could be cleanly converted into the enols **8** (Chart I) by treating with base under the kinetic reaction conditions. Thus, a mixture of **6a,b** and *t*-BuOK in *t*-BuOH (or NaOH in dioxane) was stirred at 25 °C for 20 min and then *rapidly acidified* with aqueous 10% HCl solution followed by ether extraction to give **8a,b** in quantitative yields. When the reaction mixture was extracted after neutralization or extracted directly without acidification, only a mixture of cis and trans adducts was obtained. The cis adduct **9** was similarly converted into the corresponding enol **10** in 60% yield by the base treatment as above (eq 2). The similar base treatment of an inseparable mixture of adducts **11** and **12** (3:1) gave the enol **13** and trans adduct **14** in a 3:1 ratio. This indicated that only **11** underwent the enolization but **12** thoroughly isomerized to trans **14** under these reaction conditions. Recently, Tou and Reusch reported similar results in the Lewis acid catalyzed reaction of **1** and *trans*-piperylene.[12]



(2)

(3)

Also, the trans adducts could be converted into the enols with equal ease. For example, the base treatment of **4c** afforded a quantitative yield of enol **3c** which was the minor product in the thermal reaction (see eq 1).

All these bicyclic enols except for **3a–c** easily isomerized to the corresponding cis and trans adducts by silica gel chromatography. However, crystalline enols like **3**, **8**, and **13** could be isolated in a pure form by recrystallization and their structural determination was made on the basis of the spectroscopic data (Table I) as well as the chemical transformation (vide infra).

This kinetic procedure for enolization was next applied to the tricyclic Diels–Alder adducts **15** and **17** which were prepared by the Lewis acid catalyzed reactions of **1** with the appropriate cyclic dienes. Interestingly, the base treatment of **15a,b** did not give the anticipated enols but instead resulted in the ether cleavage to crystalline products **16a,b** in 98% and 85% yields, respectively (eq 4). Similarly, the anthracene adduct **17** was converted to **18**, mp 163–165 °C, in 75% yield (eq 5). These results indicate that the enol formation at the bridehead position is less favorable in the tricyclic systems, probably due to the increased ring strain.[14] The facile ether cleavage of these nonaromatic compounds is noteworthy.[15] The enol structures of **16** and **18** were confirmed by the IR (OH absorption band) and ^1H NMR spectra (Table I) which showed a new appearance of a D_2O-exchangeable signal (OH) and the loss of a 3-H singlet for the methoxy group.

Structural Requirements for the Enol Formation. In order to clarify the factors facilitating the enolization,

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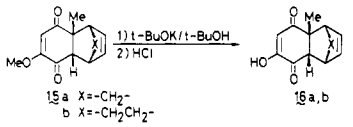
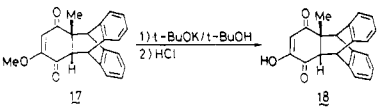
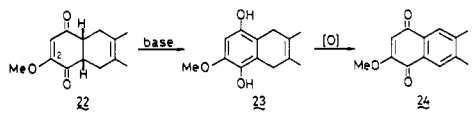


(4)

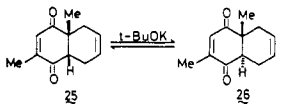


(5)

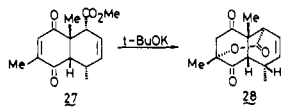
we have investigated the base-catalyzed reactions of Diels–Alder adducts of the structurally related *p*-benzoquinones **19** and **20** (Chart II). When adduct **22** was treated with *t*-BuOK under the same conditions as above, only hydroquinone **23** was obtained as the primary product (40%) which was gradually oxidized to the naphthoquinone **24**, mp 169–171 °C (eq 6). On similar base treatment, adduct **25** gave a mixture of *cis*-**25** and trans adducts **26** (eq 7), and adduct **27** afforded a quantitative yield of tricyclic lactone **28** (eq 8). In contrast, base treatment of **29** gave the enol **30** as a short-lived intermediate (eq 9), which could be fully characterized by ^{1}H NMR spectroscopy (Table I) but only decomposed when its isolation was attempted. These results clearly indicate that the hteroatom substituent at the C-2 position plays an important role in the facile enol formation, i.e., an enol stabilization through intramolecular hydrogen bonding.[8] The apparent stability difference between enols **8a** and **30** may be attributed to the different magnitude of the stabilization by oxygen and sulfur atoms.[16]



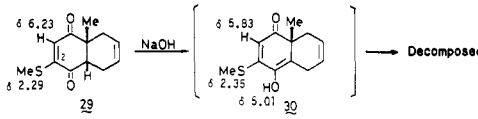
(6)



(7)



(8)



(9)

As a result, the essential factors for the facile enol formation from Diels–Alder adducts may be concluded to be as follows: (a) the presence of a methoxyl group at the C-2 position to stabilize the enol through an intramolecular hydrogen bonding; (b) the presence of an angular methyl group (C-10) to avoid the aromatization to hydroquinone; (c) the method of base treatment to avoid isomerization to the thermodynamically more stable trans adducts. In addition to these, an ester group at the C-5 position also seemed to considerably facilitate the enolization as exemplified by the thermal formation of **3a–c**.

Autoxidation of Enols. Although the above obtained enols were stable in a solid state, they easily suffered an aerial oxidation in solution. Thus, on standing at room temperature (20 h), a concentrated solution of **3a** in ethyl acetate/*n*-hexane (2:1) deposited a crystalline hydroperoxide **31a**, mp 117–118 °C, in 70% yield (eq 10). The structural assignment was based on the spectroscopic data: MS, *m/e* 310 (M^+); IR 3440 (OH) cm^{-1}; ^{13}C NMR δ 91.6

Chart II

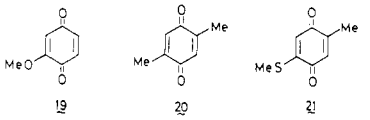
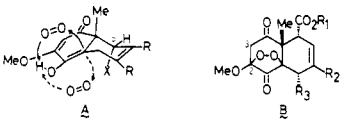
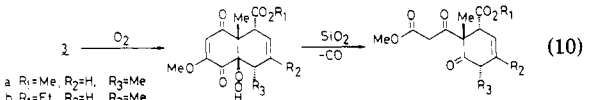


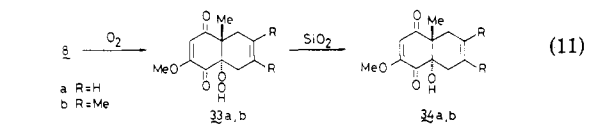
Chart III



(s, C-9), 195.3 and 198.6 (each s, C-1 and C-4). In the ^{1}H NMR spectrum, a D_2O-exchangeable singlet at δ 9.89 was attributed to the hydroperoxy group and the remarkable downfield shift of the angular methyl signal (δ 1.69) was indicative of the cis-fused structure.[11] Percolation of **31a** through a silica gel column resulted in a spontaneous gas evolution to give a crystalline β-keto ester **32a**, mp 120–121 °C, in 90% yield (eq 10). The structure of **32a** (M^+, *m/e* 282) was fully characterized by IR (1750 br and 1720 cm^{-1}), ^{1}H NMR [δ 3.85 (s, 2 H, exchanged by D_2O/NaOD)], and ^{13}C NMR spectra [δ 207.8, 202.5, 172.6, 167.8 (each s)]. Similarly, enols **3b,c** were converted into the corresponding β-keto esters **32b,c** in 76% and 63% yields, respectively, via *cis*-hydroperoxides **31b,c** which were detected by ^{1}H NMR spectroscopy (eq 10).



(10)



(11)

On the other hand, aerial oxidation of enol **8a** afforded *trans*-hydroperoxide **33a**, mp 126–129 °C, in 89% yield (eq 11). The stereochemical assignment was based on the ^{1}H NMR spectrum which showed a 3-H singlet of the angular methyl group at δ 1.14.[11] In sharp contrast to the *cis*-hydroperoxides **31**, **33a** was fairly stable toward silica gel and could be purified by a column chromatography. However, a prolonged treatment of **33a** with silica gel in chloroform at room temperature (3 days) gave an alcohol **34a** in 80% yield, mp 211–214 °C; MS, *m/e* 222 (M^+); ^{1}H NMR δ 1.10 (s, 3 H) and 2.21 (s, 1 H, D_2O exchange). Similarly, **8b** was converted into **34b** in 36% overall yield (eq 11).

The oxidation of enols was remarkably retarded by exclusion of air or by addition of D_2O. This suggested that the hydroperoxide formation occurred via an ene-type reaction between the enol and oxygen.[17–19] The stereochemical dichotomy observed in the reactions of **3** and **8** can be attributed to steric reasons. While the enols with no substituents at C-5 like **8** might be attacked by oxygen preferably from the endo face (trans to the angular methyl group) to give the *trans*-hydroperoxides **33**, the steric hindrance of the endo face by the ester group at C-5 in **3** might favor the exo addition as shown in A (Chart III) to

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Table I. Physical Properties and Spectral Data for Enols

no.	mp, °C	IR ($CHCl_3$), cm^{-1}	^1H NMR,[a] δ ($CDCl_3$)
3a[b,f]	160–161	3555, 1740, 1680, 1640	1.28 (s, 3 H), 1.34 (d, J = 7.0, 3 H), 3.20–3.40 (m, 1 H), 3.60–3.70 (m, 1 H), 3.60 (s, 3 H), 3.88 (s, 3 H), 5.40 (s, 1 H), 5.41 (s, 1 H, D_2O exchangeable), 5.80–5.90 (m, 2 H)
3b	151–152	3540, 1735, 1680, 1640	1.19 (t, J = 7.0, 3 H), 1.29 (s, 3 H), 1.35 (d, J = 7.2, 3 H), 3.10–3.50 (m, 1 H), 3.52–3.73 (m, 1 H), 3.88 (s, 3 H), 4.06 (q, J = 7.0, 2 H), 5.43 (s, 1 H), 5.45 (s, 1 H, D_2O exchangeable), 5.74–5.93 (m, 2 H)
3c[c]	141–142	3560, 1735, 1640	1.17 (t, J = 7.0, 3 H), 1.24 (s, 3 H), 1.77 (br s, 3 H), 2.71 (d, J = 22.0, 1 H), 3.35 (d, J = 22.0, 1 H), 3.61 (br d, J = 7.0, 1 H), 3.88 (s, 3 H), 4.01 (q, J = 7.0, 2 H), 5.39 (s, 1 H, D_2O exchangeable), 5.45 (s, 1 H, 5.40–5.67 (m, 1 H)
8a[f]	110–125	3560, 1630	1.30 (s, 3 H), 2.08–3.36 (m, 4 H), 3.88 (s, 3 H), 5.45 (s, 1 H), 5.58 (br s, 1 H, D_2O exchangeable), 5.63–5.78 (m, 2 H)
8b[d,f]	115–125	3550, 1625	1.26 (s, 3 H), 1.67 (br s, 6 H), 2.18 (br s, 2 H), 2.66 (d, J = 21.0, 1 H), 3.29 (d, J = 21.0, 1 H), 3.87 (s, 3 H), 5.26 (br s, 1 H, D_2O exchangeable), 5.44 (s, 1 H)
10		3500, 1635	1.64 (s, 3 H), 3.64 (s, 3 H), 3.76–4.00 (m, 1 H), 4.41–4.50 (m, 1 H), 4.98 (s, 1 H, D_2O exchangeable), 5.25 (s, 1 H), 5.60 (ddd, J = 9.2, 3.7, 1.0, 1 H), 5.83 (ddd, J = 9.2, 5.0, 2.0, 1 H), 6.93–7.52 (m, 10 H, Ph)
16a[e,f]	140 dec	3400, 1680, 1660	1.49 (s, 3 H), 1.54–1.70 (m, 2 H), 2.95 (d, J = 3.9, 1 H), 3.00–3.19 (m, 1 H), 3.32–3.58 (m, 1 H), 5.93 (dd, J = 5.9, 3.1, 1 H), 6.00 (br s, 1 H, D_2O exchangeable), 6.08 (s, 1 H), 6.20 (dd, J = 5.9, 3.1, 1 H)
16b	200 dec	3400, 1680, 1660	1.36 (s, 3 H), 1.39–2.05 (m, 4 H), 2.62 (d, J = 1.8, 1 H), 2.85–3.20 (m, 2 H), 4.85 (br s, 1 H, D_2O exchangeable), 6.04 (dm, J = 9.2, 1 H), 6.14 (s, 1 H), 6.38 (dm, J = 9.2, 1 H)
18[f]	163–165	3400, 1680, 1660	1.08 (s, 3 H), 2.77 (d, J = 2.3, 1 H), 4.58 (s, 1 H), 4.77 (d, J = 2.3, 1 H), 5.83 (s, 1 H), 6.23 (br s, 1 H, D_2O exchangeable), 6.94–7.55 (m, 8 H, Ph)
30			1.30 (s, 3 H), 2.35 (s, 3 H), 1.85–2.60 (m, 2 H), 2.76 (dm, J = 20.0, 1 H), 3.33 (br d, J = 20.0, 1 H), 5.01 (br s, 1 H, D_2O exchangeable), 5.63–5.80 (m, 2 H), 5.83 (s, 1 H)

[a] J values are given in hertz. [b] ^{13}C NMR ($CDCl_3$) δ 19.1 (q), 28.4 (d), 31.2 (q), 47.7 (q), 51.1 (s), 51.9 (d), 56.5 (q), 97.2 (d), 119.8 (d), 129.0 (s), 134.9 (d), 137.2 (s), 164.7 (s), 172.5 (s), 203.5 (s); MS, m/e 278 (M^+, 100), 203 (46). [c] UV (EtOH) λ_{max} 340 nm (log ε 8.10). [d] UV (EtOH) λ_{max} 340 nm (log ε 8.39). [e] MS, m/e 204 (M^+, 10), 139 (9), 66 (100). [f] Satisfactory C and H analyses were obtained.

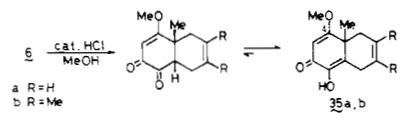
Table II. Physical Properties and Spectral Data for α-Keto Enols

no.	mp, °C	IR,[a] cm^{-1}	^1H NMR,[b] δ (J, Hz)
35a[c]	105–107	3420, 1620	1.36 (s, 3 H), 2.07 (dm, J = 16.5, 1 H), 2.49 (dm, J = 16.5, 1 H), 2.80 (dm, J = 19.5, 1 H), 3.45 (dm, J = 19.5, 1 H), 3.77 (s, 3 H), 5.63 (s, 1 H), 5.67–5.80 (m, 2 H), 6.56 (s, 1 H, D_2O exchangeable)
35b	127–129	3430, 1620	1.31 (s, 3 H), 1.69 (br s, 6 H), 2.09 (br d, J = 17.0, 1 H), 2.50 (br d, J = 17.0, 1 H), 2.80 (br d, J = 20.0, 1 H), 3.29 (br d, J = 20.0, 1 H), 3.77 (s, 3 H), 5.62 (s, 1 H), 6.51 (s, 1 H, D_2O exchangeable)
37[d]	126–128	3400, 1620	1.32 (s, 3 H), 1.41 (t, J = 7.1, 3 H), 1.66 (s, 3 H), 1.72 (s, 3 H), 2.05 (br d, J = 16.6, 1 H), 2.33 (d, J = 16.6, 1 H), 2.76 (br d, J = 20.5, 1 H), 3.30 (d, J = 20.5, 1 H), 3.93 (q, J = 7.1, 2 H), 5.59 (s, 1 H), 6.52 (s, 1 H, D_2O exchangeable)

[a] $CHCl_3$. [b] ^{13}C NMR ($CDCl_3$) δ 23.3 (q), 24.0 (t), 36.6 (t), 40.8 (s), 56.0 (q), 97.8 (d), 123.3 (d), 124.6 (d), 125.3 (s), 140.5 (s), 181.9 (s), 182.9 (s); MS, m/e 206 (M^+, 100), 191 (71), 163 (28), 145 (29). [d] Anal. Calcd for $C_{13}H_{16}O_3$: C, 72.55; H, 8.12. Found: C, 72.33; H, 8.09.

give the *cis*-hydroperoxides **31**. The formation of β-keto esters **32** can be explained by decarbonylation[20] of the *endo*-peroxide **B** (Chart III) initially formed by intramolecular addition of the hydroperoxy group to the C-2,3 double bond in **31**. The remarkable reactivity difference between *cis*-**31** and *trans*-hydroperoxides **33** is noteworthy, and this might stem from their conformational difference due to the *cis*- and *trans*-decalin systems.

Acid-Catalyzed Rearrangements. Finally, acid-catalyzed reactions of the above adducts were also investigated. While the ester-substituted adducts **4** were stable to acid, treatment of cis adducts **6a,b** with a catalytic amount of anhydrous HCl in methanol (25 °C, 20 h) afforded new crystalline products **35a,b** in 85% and 72% yields, respectively (eq 12). Compound **35a** was also obtained in 82% yield by the similar acid treatment of trans adduct **7a**. The enol structures of these products were determined by the spectroscopic data (Table II) as well as the easy transformation of **35a** into the acetate **36** by Ac_2O/pyridine (0 °C, 30 min, 78%) (Chart IV).

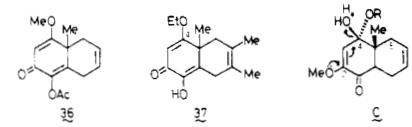


(12)

The methoxy group at the C-4 position in these products apparently came from the solvent since acid treatment of

(20) Bikales, N. M.; Becker, E. I. *J. Org. Chem.* **1956**, *21*, 1405.

Chart IV

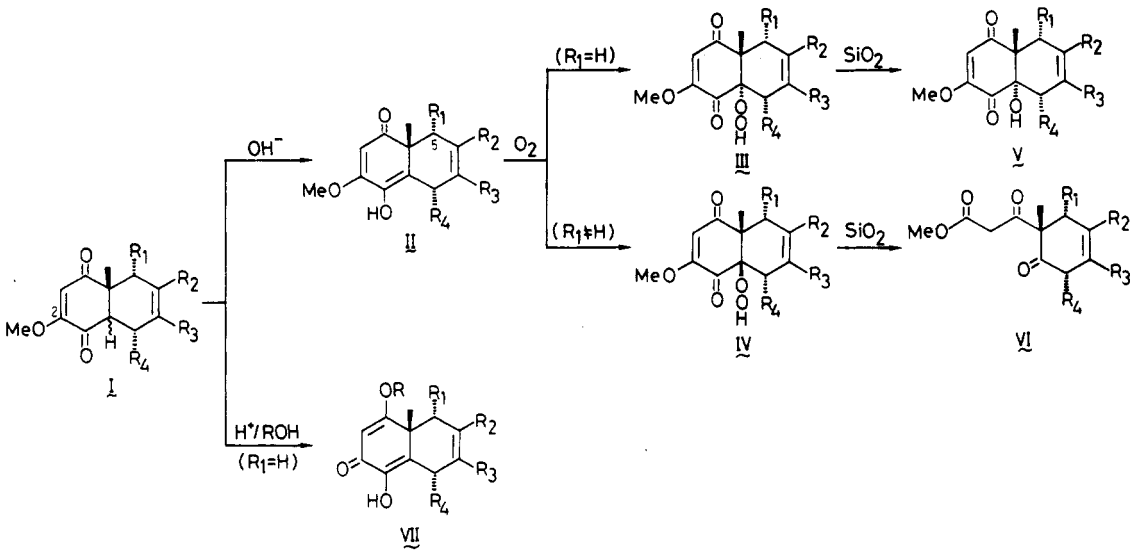


6b in ethanol gave the corresponding ethoxy derivative **37** (Chart IV) in 82% yield. These rearrangements can be reasonably explained by the initial formation of hemiacetal C by acid-catalyzed solvent addition to the C-4 carbonyl group followed by dehydration and hydrolysis of the C-2 vinyl ether to **35** (Chart IV). This was supported by the fact that the similar acid treatment of **25** led to the recovery of unchanged **25** which had no carbonium ion stabilization like **6** as shown in C (Chart IV). The inactivity of **4** could be attributed to the steric effect of the ester group at the C-5 position which might considerably hinder the solvent addition to the C-4 carbonyl group.

Summary

We could have demonstrated a very interesting structure–reactivity relationship in the base- and acid-catalyzed reactions of the Diels-Alder adducts of 2-methoxy-5-methyl-1,4-benzoquinone (**1**) as delineated in Scheme I. The base treatment followed by rapid acidification of adducts I gave the stable enols II which in solution easily suffered the aerial oxidation to give *cis*- or *trans*-hydroperoxides depending on the substituent at C-5 (R_1). While the enols II with no substituent (R_1 = H) exclusively gave

Scheme I



trans-hydroperoxides III, the enols II with the more bulky substituent (R_1 = COOR) afforded *cis*-hydroperoxides IV. These hydroperoxides showed remarkably different reactivities on a silica gel treatment. While III was reduced to the alcohols V, IV underwent to novel decarbonylation reaction to give β-keto esters VI. On the other hand, acid-treatment of adducts I resulted in the α-keto enols VII only when R_1 = H. All these reactions were unique to the adducts of 1. For example, replacement of the C-2 methoxy group with methyl group totally deactivated the molecules and caused none of these interesting rearrangements.

In conclusion, benzoquinone 1 was found to be a very useful reagent for the formation of bicyclic enols, the chemistry of which is now under active investigation in our laboratories.

Experimental Section

The melting points were measured with a Yanagimoto micromelting point apparatus and are uncorrected. The UV spectra were determined with a Hitachi EPS-3T spectrophotometer. The ^{1}H NMR spectra were taken with a JEOL PS-100 spectrometer and a Hitachi R-600 spectrometer with tetramethylsilane as an internal standard, and the chemical shifts are expressed in δ values. The ^{13}C NMR spectra were recorded on a JEOL FX-100 with tetramethylsilane as an iternal standard. The IR spectra were taken with a JASCO IR A-1 infrared spectrometer. Mass spectra were obtained with a JEOL-01SG double-focusing spectrometer operating at an ionization potential of 75 eV. The solid samples were ionized by electron bombardment after sublimation directly into the electron beam at 150–200 °C. Column chromatography was performed by using E. M. Merck Kieselgel 60 (70–200 mesh).

General Procedure for Thermal Cycloadditions of 2-Methoxy-5-methyl-1,4-benzoquinone (1). A mixture of 1 and an excess (5–8 equiv) of the appropriate diene (**2a–c**) was heated under Ar with vigorous stirring in a sealed tube at the following temperatures: for **2a**, 100 °C (67 h, 54% conversion); for **2b**, 100 °C (8 days, 100% conversion); for **2c**, 80 °C (9 days, 78% conversion). The reaction mixture was concentrated under the reduced pressure, and the residue was rapidly chromatographed on a silica gel column with ethyl acetate/*n*-hexane (6:1) as an eluent and recrystallized from ethyl acetate/*n*-hexane to give the corresponding 1:1 enol adducts as colorless crystals in 67% (**3a**), 54% (**3b**), and 22% (**3c**) yields along with several known minor products. The physical properties and spectral data of these enols are summarized in Table I.

3a: Anal. Calcd for $C_{15}H_{18}O_5$: C, 64.74; H, 6.52. Found: C, 64.48; H, 6.39.

4-Acetoxy-3-methoxy-8-(methoxycarbonyl)-5,8a-dimethyl-8,8a-dihydro-1(5*H*)-naphthalenone (5). A solution of **3a** (56 mg, 0.2 mmol) in acetic anhydride–pyridine (1:1, 1 mL) was stirred at 0 °C for 30 min. The reaction mixture was diluted with aqueous 10% HCl solution (5 mL) and extracted with ether. The combined extracts were washed with brine, dried over Na_2SO_4, evaporated, and chromatographed on silica gel with ethyl acetate/*n*-hexane (2:1) to give **5** (48 mg, 75%) as colorless crystals, mp 124–125 °C (*n*-hexane/ether): IR ($CHCl_3$) 1775, 1740, 1670, 1640 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.28 (d, J = 7.0 Hz, 3 H), 1.40 (s, 3 H), 2.26 (s, 3 H), 3.00–3.25 (m, 1 H), 3.65–3.80 (m, 1 H), 3.62 (s, 3 H), 3.77 (s, 3 H), 5.44 (s, 1 H), 5.80–5.90 (m, 2 H); MS, *m/e* 320 (M^+).

General Procedure for Lewis Acid Catalyzed Cycloadditions of 1. To a stirred solution of 1 (152 mg, 1 mmol) in $CHCl_3$ at room temperature was added BF_3·Et_2O (0.123 mL, 1 mmol). After the solution was stirred for 30 min, a slight excess (~1.2 equiv) of the appropriate diene was added at 0 °C and the resulting solution was stirred at this temperature until 1 was completely consumed (2–10 h). After the reaction was quenched by adding water, the product was extracted with $CHCl_3$, dried over Na_2SO_4, and evaporated in vacuo to give a quantitative yield of the adduct which was recrystallized from the given solvent to afford a pure sample. In the case of reactions with cyclic dienes (1.5 equiv), the products were purified by column chromatography on silica gel (ethyl acetate/*n*-hexane).

2-Methoxy-4a-methyl-4a,5,8,8a-tetrahydro-1,4-naphthoquinone (6a): mp 93–95 °C (ethanol); IR ($CHCl_3$) 1720, 1670, 1615 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.34 (s, 3 H), 1.62–3.04 (m, 5 H), 3.79 (s, 3 H), 5.50 –5.72 (m, 2 H), 5.83 (s, 1 H).

2-Methoxy-4a,6,7-trimethyl-4a,5,8,8a-tetrahydro-1,4-naphthoquinone (6b): mp 88–90 °C (ethanol); IR ($CHCl_3$) 1720, 1675, 1620 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.28 (s, 3 H), 1.60 (br s, 3 H), 1.62 (br s, 3 H), 1.71–3.07 (m, 5 H), 3.78 (s, 3 H), 5.82 (s, 1 H).

2-Methoxy-4a-methyl-5,8-diphenyl-4a,5,8,8a-tetrahydro-1,4-naphthoquinone (9): mp 160–162 °C (ethyl acetate/*n*-hexane); IR ($CHCl_3$) 1730, 1660, 1605 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.73 (s, 3 H), 3.15 (s, 3 H), 3.32 (d, J = 5.1 Hz, 1 H), 3.42–3.51 (m, 1 H), 3.84–3.97 (m, 1 H), 5.12 (s, 1 H), 5.95 (dt, J = 10.8, 3.5 Hz, 1 H), 6.62 (dm, J = 10.8 Hz, 1 H), 6.93–7.52 (m, 10 H).

Cyclopentadiene adduct (15a) was obtained without using a Lewis acid catalyst: mp 119–120 °C (ethyl acetate/*n*-hexane); IR ($CHCl_3$) 1695, 1660, 1615 cm^{-1}; ^{1}H NMR δ 1.48 (s, 3 H), 1.54–1.70 (m, 2 H), 2.88 (d, J = 3.0 Hz, 1 H), 2.98–3.16 (m, 1 H), 3.34–3.57 (m, 1 H), 3.73 (s, 3 H), 5.85 (s, 1 H), 5.97 (dd, J = 5.5, 2.4 Hz, 1 H), 6.18 (dd, J = 5.5, 2.4 Hz, 1 H).

Cyclohexadiene adduct (15b): mp 138–139 °C (ethyl acetate/*n*-hexane); IR ($CHCl_3$) 1690, 1650, 1620 cm^{-1}; ^{1}H NMR δ 1.35 (s, 3 H), 1.40–2.03 (m, 4 H), 2.57 (d, J = 1.9 Hz, 1 H), 2.83–3.21 (m, 2 H), 3.74 (s, 3 H), 5.92 (s, 1 H), 6.12 (dd, J = 7.8, 6.6 Hz, 1 H), 6.33 (dd, J = 7.8, 6.6 Hz, 1 H).

Anthracene adduct (17): mp 129–131 °C (ethyl acetate); IR ($CHCl_3$) 1705, 1670, 1630 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.08 (s, 3 H),

2.70 (d, J = 2.7 Hz, 1 H), 3.49 (s, 3 H), 4.53 (s, 1 H), 4.75 (d, J = 2.7 Hz, 1 H), 5.55 (s, 1 H), 6.80–7.73 (m, 8 H).

General Procedure for Base-Catalyzed Enolization of Bicyclic Adducts. Method A. To a stirred suspension of t-BuOK (225 mg, 2 mmol) in t-BuOH (2 mL) was added a solution of the appropriate adduct (1 mmol) in t-BuOH (1 mL) in one portion. The mixture was stirred at room temperature for 20 min and poured into ice water (10 mL). After addition of aqueous 10% HCl solution (2 mL), the mixture was rapidly extracted with ether. The combined extracts were dried over Na_2SO_4, filtered, and evaporated to give a quantitative yield of product as the colorless solid (except for **10**) which was pure enough for the most purposes. A small portion of product was recrystallized from ethyl acetate/n-hexane to give a pure sample. The yields of products obtained by this method were as follows; **3c** (100%), **8a** (92%), **8b** (90%), and **10** (60%).

Method B. To a stirred solution of the appropriate adduct (1 mmol) in dioxane (5 mL) was added aqueous 10% NaOH solution (1 mL) in one portion. After stirring 20 min at room temperature, the reaction mixture was worked-up in the same way as above. The yields of products obtained by this method were as follows: **8a** (95%) and **8b** (98%). The physical properties and spectroscopic data of these products are summarized in Table I.

General Procedure for Ether Cleavage of Tricyclic Adducts. The same procedure as above (method A) was applied to the tricyclic adducts (**15a,b** and **17**) and the products were purified by recrystallization from ether. The yields of the products were as follows: **16a** (98%), **16b** (85%), and **18** (75%).

16a: Anal. Calcd for $C_{12}H_{12}O_3$: C, 70.58; H, 5.92. Found: C, 70.25; H, 5.88.

18: Anal. Calcd for $C_{21}H_{16}O_3$: C, 79.73; H, 5.10. Found: C, 79.55; H, 5.14.

The physical properties and spectroscopic data of these products are summarized in Table I.

2-Methoxy-1,4-benzoquinone (19). Compound **19** was prepared by the modified method of Teuber and Rau.[21] To a stirred solution of guaiacol (1 g, 8 mmol) in $CHCl_3$ (100 mL) at 0 °C was added a solution of sodium acetate (5 g) and freshly prepared Fremy's salt[22] in water (300 mL) dropwise within 2 h. After the mixture was stirred for additional 1 h, the chloroform layer was separated, dried over Na_2SO_4, and evaporated. The residue was chromatographed on silica gel (ethyl acetate/n-hexane) to give **19** (1 g, 90%) as yellow crystals: mp 138–139 °C (lit.[21] mp 139–140 °C); IR (Nujol) 1685, 1652 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.84 (s, 3 H), 5.97 (br s, 1 H), 6.73 (br s, 2 H).

2-Methyl-5-(methylthio)-1,4-benzoquinone (21). To a stirred suspension of m-cresol (2.16 g, 20 mmol) and $AlCl_3$ (1.6 g, 20 mmol) in CH_2Cl_2 (10 mL) at 0 °C was added dimethyl disulfide (1.08 mL, 12 mmol). After heating under reflux for 8 h, the reaction mixture was washed successively with water, aqueous 2% HCl, and 4% NaOH. The organic phase was dried over Na_2SO_4, evaporated, and chromatographed on silica gel to give 5-methyl-2-(methylthio)phenol (600 mg, 32%). To a stirred solution of this phenol (154 mg, 1 mmol) in acetone (10 mL) was added a solution of Fremy's salt (600 mg) in water (30 mL) and phosphate buffer (5 mL). After stirring at room temperature for 2 h, the mixture was extracted with $CHCl_3$, dried over Na_2SO_4, evaporated, and chromatographed on silica gel to give **21** (134 mg, 80%) as orange crystals: mp 137–139 °C; IR ($CHCl_3$) 1650, 1625 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.06 (d, J = 1.6 Hz, 3 H), 2.31 (s, 3 H), 6.33 (s, 1 H), 6.65 (q, J = 1.6 Hz, 1 H).

1,4-Dihydroxy-2-methoxy-6,7-dimethyl-5,8-dihydronaphthalene (23) and 2-Methoxy-6,7-dimethyl-1,4-naphthoquinone (24). Adduct **22** (110 mg, 0.5 mmol) was treated with NaOH as above (method B) and the product was purified by column chromatography on silica gel ($CHCl_3$/MeOH = 200:1) to give **23** (44 mg, 40%) as colorless crystals: mp 130–132 °C; IR (Nujol) 3400 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.78 (br s, 6 H), 2.95–3.41 (m, 4 H), 3.83 (s, 3 H), 4.25 (s, 1 H, D_2O exchange), 5.23 (s, 1 H, D_2O exchange), 6.35 (s, 1 H); MS, m/e 220 (M^+). Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32. Found: C, 70.77; H, 7.26.

A solution of **22** (110 mg, 0.5 mmol) in $CHCl_3$ (2 mL) was absorbed on silica gel (5 g) and allowed to stand for 10 days. The product was eluted out with $CHCl_3$, evaporated, and purified by column chromatography on silica gel ($CHCl_3$) to give **24** (99 mg, 90%) as pale yellow crystals: mp 169–171 °C (n-hexane/ether); IR ($CHCl_3$) 1685, 1650, 1615 cm^{-1}; ^1H NMR δ 2.38 (s, 6 H), 3.88 (s, 3 H), 6.09 (s, 1 H), 7.81 (s, 1 H), 7.86 (s, 1 H); MS, m/e 216 (M^+). The conversion of **23** to **24** in $CDCl_3$ was confirmed by ^1H NMR spectroscopy.

Base-Catalyzed Reaction of 5-(Methoxycarbonyl)-2,4a,8-trimethyl-4a,5,8,8a-tetrahydro-1,4-naphthoquinone (27). Adduct **27** (68 mg, 0.26 mmol) was similarly treated with t-BuOK as above (method A) and the crude mixture was recrystallized from ether to give **28** (64 mg, 98%): mp 247–248 °C (sealed); IR ($CHCl_3$) 1760, 1730, 1720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.20 (d, J = 7.0 Hz, 3 H), 1.25 (s, 3 H), 1.26 (s, 3 H), 2.10 (dd, J = 3.8, 1.2 Hz, 1 H), 2.10 and 2.60 (AB-q, J = 18.6 Hz, 2 H), 2.54–2.85 (m, 2 H), 5.70 (dm, J = 10.0 Hz, 1 H), 6.13 (dd, J = 10.0, 2.3 Hz); MS, m/e 248 (M^+).

4-Hydroxy-8a-methyl-3-(methylthio)-8,8a-dihydro-1-(5*H*)-naphthalenone (30). The adduct **29** was quantitatively obtained by the BF_3–Et_2O catalyzed reaction of **21** and excess of 1,3-butadiene at 0 °C; IR ($CHCl_3$) 1700, 1665 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.33 (s, 3 H), 2.29 (s, 3 H), 1.50–3.08 (m, 5 H), 5.57–5.76 (m, 2 H), 6.23 (s, 1 H).

The similar base treatment (method B) of **29** afforded **30** which could not be purely isolated because of its instability: ^1H NMR ($CDCl_3$) δ 1.30 (s, 3 H), 2.35 (s, 3 H), 1.85–2.60 (m, 2 H), 2.76 (dm, J = 20.0 Hz, 1 H), 3.33 (br d, J = 20.0 Hz, 1 H), 5.01 (br s, 1 H, D_2O exchange), 5.63–5.80 (m, 2 H), 5.83 (s, 1 H).

Autoxidation of Enols. A solution of enol **3a** (70 mg, 0.25 mmol) in a 2:1 mixture of ethyl acetate and n-hexane (0.5 mL) was allowed to stand at room temperature for 1 day in an open beaker. The precipitates were collected by filtration and washed with a small amount of ether to give 8a-hydroperoxy-2-methoxy-5-(methoxycarbonyl)-4a,8-dimethyl-4a,5,8,8a-tetrahydro-1,4-naphthoquinone (**31a**) (54 mg, 70%) as colorless crystals: mp 117–118 °C; IR ($CHCl_3$) 3440, 1740, 1685 cm^{-1}; ^1H NMR δ 1.03 (d, J = 7.6 Hz, 3 H), 1.69 (s, 3 H), 3.15 (dd, J = 2.9, 2.2 Hz, 1 H), 3.40–3.50 (m, 1 H), 3.78 (s, 3 H), 3.83 (s, 3 H), 5.60 (ddd, J = 10.7, 3.7, 2.9 Hz, 1 H), 5.91 (s, 1 H), 6.18 (dt, J = 10.7, 2.2 Hz, 1 H), 9.89 (s, 1 H, D_2O exchange); ^{13}C NMR ($CDCl_3$) δ 19.3 (q), 24.8 (d), 32.6 (q), 44.4 (q), 52.1 (d), 55.2 (s), 57.0 (q), 91.6 (s), 111.2 (d), 123.0 (d), 128.4 (d), 161.8 (s), 172.1 (s), 195.3 (s), 198.6 (s).

A solution of **8a** (206 mg, 1 mmol) in $CHCl_3$ (1 mL) was allowed to stand for 1 week in an open beaker. After evaporation of the solvent, the residue was chromatographed on silica gel with $CHCl_3$/MeOH (50:1) to give **33a** (212 mg, 89%) as colorless crystals: mp 126–129 °C; IR ($CHCl_3$) 3520, 3250, 1730, 1675, 1615 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.14 (s, 3 H), 2.10–2.81 (m, 4 H), 3.83 (s, 3 H), 5.59–5.78 (m, 2 H), 5.85 (s, 1 H), 8.48 (s, 1 H, D_2O exchange); MS, m/e 238 (M^+).

Anal. Calcd for $C_{12}H_{14}O_5 \cdot {}^1/_{10}H_2O$: C, 60.04; H, 5.96. Found: C, 59.91; H, 5.90.

Compounds **3b,c** and **8b** were similarly oxidized in $CHCl_3$ into the corresponding hydroperoxides (**31b,c** and **33b**) which were used for the next reactions without further purification.

Methyl 3-(3-Cyclohexen-1-yl)-3-oxopropionates 32a–c. A solution of **31a** (40 mg, 0.13 mmol) in a 1:1 mixture of ethyl acetate and n-hexane was percolated through a silica gel column (3 g) and the filtrates were concentrated in vacuo to give **32a** (33 mg, 90%) as colorless crystals: mp 120–121 °C; IR ($CHCl_3$) 1750, 1720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.27 (d, J = 7.3 Hz, 3 H), 1.57 (s, 3 H), 3.08 (br q, J = 7.3 Hz, 1 H), 3.46–3.51 (m, 1 H), 3.66 (s, 3 H), 3.72 (s, 3 H), 3.85 (s, 2 H, D_2O/KOD exchange), 5.88–5.92 (m, 2 H); MS, m/e 282 (M^+).

Anal. Calcd for $C_{14}H_{18}O_6$: C, 59.57; H, 6.43. Found: C, 59.40; H, 6.42.

The similar silica gel treatments of crude **31b,c** prepared from **3b,c** afforded **32b,c** in 76% and 63% overall yields.

32b: mp 76–77 °C; IR ($CHCl_3$) 1735 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.21 (t, J = 7.0 Hz, 3 H), 1.27 (d, J = 7.2 Hz, 3 H), 1.56 (s, 3

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H), 3.08 (br q, J = 7.2 Hz, 1 H), 3.34–3.57 (m, 1 H), 3.73 (s, 3 H), 3.85 (s, 2 H, D_2O/KOD exchange), 4.10 (q, J = 7.0 Hz, 2 H), 5.77–5.95 (m, 2 H).

32c: oil; IR ($CHCl_3$) 1730 cm^{-1}; ^1H NMR δ 1.23 (t, J = 7.0 Hz, 3 H), 1.45 (s, 3 H), 1.78 (s, 3 H), 2.99 (br s, 2 H), 3.47 (br d, J = 6.7 Hz, 1 H), 3.72 (s, 3 H), 3.89 (s, 2 H, D_2O/KOD exchange), 4.11 (q, J = 7.0 Hz, 2 H), 5.49–5.83 (m, 1 H).

8a-Hydroxy-2-methoxy-4a-methyl-4a,5,8,8a-tetrahydro-1,4-naphthoquinones (34a,b). A mixture of **33a** (190 mg, 0.8 mmol) and silica gel (3 g) in $CHCl_3$ (10 mL) was allowed to stand at room temperature for 3 days. The mixture was filtered and the silica gel was washed well with $CHCl_3$. The combined filtrates were concentrated and the residue was chromatographed on silica gel with $CHCl_3$ to give **34a** (143 mg, 80%) as colorless crystals: mp 211–214 °C; IR ($CHCl_3$) 3600, 3400, 1725, 1675, 1610 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.10 (s, 3 H), 2.13–2.43 (m, 2 H), 2.21 (s, 1 H, D_2O exchange), 2.71 (d, J = 20.7 Hz, 1 H), 3.81 (s, 3 H), 5.60–5.80 (m, 2 H), 5.86 (s, 1 H); MS, m/e 222 (M^+).

Anal. Calcd for $C_{12}H_{14}O_4 \cdot {}^1/_{10}H_2O$: C, 64.33; H, 6.39. Found: C, 64.09; H, 6.25.

The similar silica gel treatment of **33b** afforded **34b** in 36% yield: mp 175–178 °C; IR ($CHCl_3$) 3570, 3400, 1720, 1665, 1610 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.07 (s, 3 H), 1.70 (br s, 6 H), 2.03–2.98 (m, 4 H), 2.17 (s, 1 H, D_2O exchange), 3.81 (s, 3 H), 5.85 (s, 1 H).

General Procedure for Acid-Catalyzed Reaction of Adducts. To a stirred solution of the appropriate adduct (1 mmol) in anhydrous methanol or ethanol (5 mL) at 0 °C was added one small drop of acetyl chloride. After stirring at room temperature for 20 h, the mixture was concentrated in vacuo and the residue was chromatographed on silica gel with a $CHCl_3$/MeOH solvent system to give the pure product (the yields are given in text). The physical properties and spectroscopic data of these products are summarized in Table II.

1-Acetoxy-4-methoxy-4a-methyl-5,8-dihydro-2(4a*H*)-naphthalenone (36). A solution of **35a** (62 mg, 0.3 mmol) in a 1:1 mixture of acetic anhydride and pyridine (1 mL) was stirred at room temperature for 30 min. The usual workup and chromatography on silica gel afforded **36** (58 mg, 78%) as colorless crystals: mp 91–93 °C (ether/n-hexane); IR ($CHCl_3$) 1775, 1680, 1650, 1620 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.42 (s, 3 H), 2.29 (s, 3 H), 2.18 (dm, J = 16.5 Hz, 1 H), 2.56 (dm, J = 16.5 Hz, 1 H), 2.80 (dm, J = 20.0 Hz, 1 H), 3.22 (dm, J = 20.0 Hz, 1 H), 3.75 (s, 3 H), 5.59 (s, 1 H), 5.64–5.78 (m, 2 H). Anal. Calcd for $C_{14}H_{16}O_4$: C, 67.73; H, 6.50. Found: C, 67.54; H, 6.45.

Acknowledgment. We are grateful to Y. Okamoto (Kyhushu University) for the preparation of 1,4-benzoquinones **19–21**.

Registry No. 1, 614-13-1; **2a**, 689-89-4; **2b**, 2396-84-1; **2c**, 13369-24-9; **3a**, 90454-41-4; **3b**, 90454-42-5; **3c**, 90454-45-8; **5**, 90454-43-6; **6a**, 96040-58-3; **6b**, 96040-59-4; **8a**, 96040-60-7; **8b**, 96040-61-8; **9**, 96040-62-9; **10**, 90454-44-7; **15a**, 92173-45-0; **15b**, 96040-63-0; **16a**, 96040-64-1; **16b**, 96040-65-2; **17**, 96040-66-3; **18**, 96040-67-4; **19**, 2880-58-2; **21**, 90111-21-0; **22**, 96040-68-5; **23**, 96040-69-6; **24**, 52280-68-9; **27**, 58822-93-8; **28**, 96055-50-4; **29**, 96055-51-5; **30**, 96040-70-9; **31a**, 90454-48-1; **31b**, 90454-49-2; **31c**, 96040-71-0; **32a**, 90454-47-0; **32b**, 90454-46-9; **32c**, 96040-72-1; **33a**, 96040-73-2; **33b**, 96040-74-3; **34a**, 96040-75-4; **34b**, 96040-76-5; **35a**, 96040-77-6; **35b**, 96040-78-7; **36**, 96040-79-8; **37**, 96040-80-1; guaiacol, 90-05-1; m-cresol, 108-39-4; 5-methyl-2-(methylthio)-phenol, 23385-54-8; 1,3-butadiene, 106-99-0.

Notes

Organoboranes in Organic Synthesis: Reactions of Homo- and Heterocuprates with 9-Borabicyclo[3.3.1]nonane

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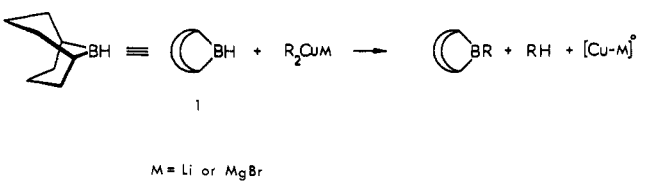
Received August 10, 1983

For sometime we have been investigating the reaction of various lithium and halomagnesium dialkylcuprates with organoboranes[1,2] (Scheme I). The advantage of this method enables the synthesis of certain organoboranes (*B*-methyl, *B*-aryl, *B*-1-ethynyl, *B*-neopentyl, *B*-benzyl) which cannot be prepared via the normal hydroboration of carbon–carbon multiple bonds. The published preparation of such organoboranes involves a two-stage procedure and certain protic reagents or Lewis acids (CH_3SO_3H, CH_3OH, HCl, $BF_3(CH_3CH_2)_2O$.[3-5] Our method overcomes the use of these reagents and allows the new synthesized organoboranes to be used for further proton-sensitive reactions.

Despite this convenience of having the new organoborane generated in situ, a disadvantage is that only one of the alkyl groups of the cuprate is utilized, a problem

Scheme I



if such cuprates are difficult to prepare or involve expensive starting materials.

Certain workers[6-7] have reported the use of homo- and heterocuprates in reactions with various electrophiles where the valuable alkyl group (Rt) is selectively transferred to the electrophile leaving the dispensable residual (Rr) attached to the copper metal. This appears most pronounced when the copper (I) derivative of the residual group [(Rr)Cu] is particularly stable (eq 1).

$$(Rt)(Rr)CuM + E^+ \rightarrow (Rt)E + [(Rr)Cu] + M^+ \quad (1)$$

Rr = n-BuC≡C, n-PrC≡C, t-BuC≡C, t-BuO, PhO, PhS

M = Li, MgBr

We now report the reaction of various homo- and heterocuprates with 9-borabicyclo[3.3.1]nonane (9-BBN, 1).

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