

hydrochloride: mp 288–290 °C (acetone–MeOH). Anal. Calcd for $C_{19}H_{25}ClN_2O_2$: C, 65.40; H, 7.22; Cl, 10.17; N, 8.03. Found: C, 65.34; H, 7.20; Cl, 10.12; N, 8.00.

trans-3-Ethyl-3,4,6,7,12,12b-hexahydroindolo[2,3-a]-quinolizin-2(1H)-one (1). A solution of acetal 21 (0.2 g, 0.6 mmol) in MeOH (20 mL) and 4 N aqueous HCl (20 mL) was refluxed for 24 h. The mixture was basified with Na_2CO_3 and extracted with CH_2Cl_2 . The organic layer was dried, and the solvent was removed to leave an oil, which was purified by flash chromatography (99:1 Et_2O -DEA) to give 1 (160 mg, 86%): mp 208–209 °C (acetone) [lit.^{6a} mp 208 °C (EtOH)]; IR (KBr) 3320, 1690 cm^{-1} ; 1H NMR δ 0.98 (t, $J = 7$ Hz, 3 H, CH_3), 1.2–1.4 (m, 1 H, CH_2CH_3), 1.8–2.0 (m, 1 H, CH_2CH_3), 2.46 (t, $J = 11$ Hz, 1 H, 1- H_a), 2.6–2.8 (m, 1 H, 3- H_a), 2.64 (br t, $J = 11$ Hz, 1 H, 6- H_a), 2.72 (t, $J = 11$ Hz, 1 H, 4- H_a), 2.82 (ddd, $J = 14$, 5, and 2 Hz, 1 H, 7- H_a), 3.0 (dd, $J = 11$ and 2.3 Hz, 1 H, 1- H_b), 3.05 (m, 1 H, 7- H_b), 3.27 (ddd, $J = 11$, 5, and 2 Hz, 1 H, 6- H_b), 3.4 (dd, $J = 11$ and 5 Hz, 1 H, 4- H_b), 3.64 (br d, $J = 11$ Hz, 1 H, 12b- H_a), 7.0–7.2 (m, 2 H, 9-H and 10-H), 7.3 (dt, $J = 7$ and 1.4 Hz, 1 H, 11-H), 7.48 (dd, $J = 7$ and 1.4 Hz, 1 H, 8-H), 7.74 (br s, 1 H, NH); ^{13}C NMR δ 11.7 (CH_3), 19.4 (CH_2CH_3), 21.9 (7-C), 45.9 (1-C), 51.6 (6-C), 51.7 (3-C), 59.4 (12b-C), 60.4 (4-C), 108.6 (7a-C), 111.0 (11-C), 118.3 (C-9), 119.7 (8-C), 121.9 (10-C), 127.0 (7b-C), 133.2 (11a-C), 136.2 (12a-C), 208.9 (2-C); MS (m/e , relative intensity) 268 (M^+ , 60), 267 (79), 225 (18), 213 (8), 184 (20), 169 (40), 129 (33), 97 (42), 69 (100), 60 (86). Anal. Calcd for $C_{17}H_{20}N_2O$: C, 76.09; H, 7.56; N, 10.44. Found: C, 76.35; H, 7.54; N, 10.71.

trans-5-Ethyl-6,6-(ethylenedioxy)-1,2,5,6,7,7a-hexahydro-4H-pyrido[1',2':1,2]pyrazino[4,3-a]indole (22). To a solution of alcohol 16 (160 mg, 0.48 mmol) in anhydrous CH_2Cl_2 (10 mL) were successively added dropwise TFA (0.39 mL, 5.28 mmol) and Et_3SiH (0.27 mL, 1.68 mmol). The mixture was refluxed under N_2 for 24 h, cooled, basified with anhydrous Na_2CO_3 , poured into ice-water, and extracted with CH_2Cl_2 . The extract was washed with aqueous $NaHCO_3$, dried, and evaporated. The residue was purified by flash chromatography (99:1 Et_2O -DEA) to give 22 (70 mg, 47%). This material was identical with that obtained by cyclization of 6.

trans-8-Chloro-5-ethyl-6,6-(ethylenedioxy)-1,2,5,6,7,7a-hexahydro-4H-pyrido[1',2':1,2]pyrazino[4,3-a]indole (23). Operating as above, from alcohol 11 (730 mg, 2 mmol), CH_2Cl_2 (20 mL), TFA (1.82 mL, 24 mmol), and Et_3SiH (1.22 mL, 7.7 mmol) was obtained compound 23 (200 mg, 29%) after flash

chromatography (99:1 Et_2O -DEA): mp 144–146 °C (Et_2O); MS (m/e , relative intensity) 348 ($M^+ + 2$, 4), 346 (M^+ , 13), 301 (40), 285 (3), 259 (15), 231 (13), 204 (33), 178 (13), 149 (29), 127 (26), 97 (37), 69 (96), 55 (100), 43 (84). Anal. Calcd for $C_{19}H_{23}ClN_2O_2$: C, 65.89; H, 6.65; Cl, 10.11; N, 8.09. Found: C, 65.75; H, 6.71; Cl, 9.80; N, 7.89.

X-ray crystal structure analysis of indoloquinolizidin-2-one (1): $C_{17}H_{20}N_2O$, $F_w = 268.36$, monoclinic, $a = 14.855$ (3) Å, $b = 8.217$ (1) Å, $\beta = 114.53$ (2) °, $V = 1469.8$ (7) Å³, $P2_1/a$, $D_x = 1.212$ g cm^{-3} , $Z = 4$, $F(000) = 576$, $\lambda(Mo K\alpha) = 0.71069$ Å, $\mu = 0.82$ cm^{-1} , 188 K.

A prismatic crystal (0.1 × 0.1 × 0.15 mm) was selected and mounted on a Philips PW-1100 four circle diffractometer. Unit-cell parameters were determined from 25 reflections ($4 \leq \theta \leq 12^\circ$) and refined by least-squares method. Intensities were collected with graphite monochromatized Mo $K\alpha$ radiation, using the ω -scan technique, with scan width 0.8° and scan speed 0.03° s^{-1} ; 1156 independent reflections were measured in the range $2 \leq \theta \leq 25^\circ$, 1034 of which were assumed as observed applying the conditions $I \geq 2.5\sigma(I)$. Three reflections were measured every 2 h as orientation and intensity control, significant intensity decay was not observed. Lorentz-polarization, but no absorption, corrections were made.

The structure was solved by direct methods, using the MULTAN84²⁶ system of computer programs and refined by full-matrix least-squares method, using the SHELX76 program.³¹ The function minimized was $\sum w||F_o| - |F_c||^2$, where $w = (\sigma^2(F_o) + 0.0013|F_o|^2)^{-1}$. A total of 19 hydrogen atoms were located from a difference synthesis and refined with an overall isotropic temperature factor and anisotropically the remaining atoms. The final R value was 0.049 ($R_w = 0.052$) for all observed reflections.

Acknowledgment. We wish to thank the Fondo de Investigaciones Sanitarias (projects 87/1252 and 88/1949) and the University of Barcelona for financial support.

Supplementary Material Available: Tables of non-hydrogen atom positional and anisotropic thermal parameters, hydrogen atom positional, interatomic distances, and bond angles (7 pages). Ordering information is given on any current masthead page.

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Successive Michael Reaction–Sigmatropic Rearrangement of Polyquinones with Silyl Ketene Acetals[†]

Mariko Aso, Kenji Hayakawa, and Ken Kanematsu*

Institute of Synthetic Organic Chemistry, Faculty of Pharmaceutical Sciences, Kyushu University 62, Higashi-ku, Fukuoka 812, Japan

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Michael-type additions of polyquinones such as quinizarinquinone (1) and naphthodiquinone (2) with various *O*-silylated ketene acetals followed by successive sigmatropic rearrangements of the adducts are described. The Michael-type additions of the *O*-silylated ketene acetals with the highly electrophilic polyquinones took place exclusively at the internal double bond without any catalysts. Some of the resultant adducts performed interesting rearrangements under thermal or Lewis acid conditions to give external adducts that are obtained formally by the addition to polyquinones at the less reactive external double bond.

Polyquinones such as quinizarinquinone (1, Chart I) and naphthodiquinone (2) are activated *p*-benzoquinone derivatives^{1,2} and are expected to react not only as dienophiles but also as electrophiles. Despite their enhanced electrophilicity due to markedly lowered LUMO energy

levels,^{1,2} little attention has been paid to electrophilic reactions of polyquinones.

Because of their cyclic tetraone structures, polyquinones are utilized in Diels–Alder reactions to construct tetracyclic

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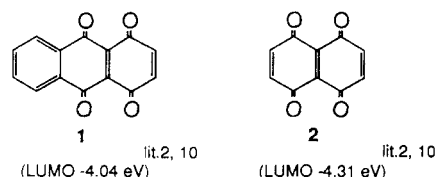
[†]This paper is dedicated to Professor Haruaki Yajima on the occasion of his retirement from Kyoto University in March, 1989.

Table I. Spectral Data of Michael Adducts 4, 10, 11, 18, and 23

compd	mp, °C	IR, ^a cm ⁻¹	¹ H NMR, ^b δ (J, Hz)	MS, m/z
4	131–133	1785, 1755, 1710, 1635	15.13 (s, 1 H), 8.26–8.16, 8.06–7.73 (m, 4 H), 7.12 (d, J = 10.0, 1 H), 7.12 (dd, J = 5.8, 1.6, 1 H), 6.65 (d, J = 10.0, 1 H), 6.05 (dd, J = 5.8, 1.7, 1 H), 5.27 (dd, J = 1.7, 1.6, 1 H)	322 (M ⁺)
10	207–208	1770, 1715, 1635	14.59 (s, 1 H), 8.25–7.69 (m, 4 H), 7.12 (d, J = 10.2, 1 H), 6.66 (d, J = 10.2, 1 H), 4.11 (t, J = 6.6, 2 H), 3.39 (t, J = 9.6, 1 H), 2.09 (m, 2 H)	324 (M ⁺)
11	172–174	1770, 1715, 1635	14.79 (s, 1 H), 8.15–7.71 (m, 4 H), 7.10 (d, J = 10.2, 1 H), 6.58 (d, J = 10.2, 1 H), 4.06 (t, J = 6.0, 2 H), 3.18 (t, J = 9.6, 1 H), 2.06 (m, 2 H)	324 (M ⁺)
14 (15)		1720, 1635	(14, major) 14.87 (s, 1 H), 8.27–7.68 (m, 4 H), 6.97 (d, J = 10.2, 1 H), 6.63 (d, J = 10.2, 1 H), 3.50 (s, 3 H), 3.30 (q, J = 7.2, 1 H), 1.14 (d, J = 7.2, 3 H); (15, minor) 14.62 (s, 1 H), 8.27–7.68 (m, 4 H), 7.08 (d, J = 9.6, 1 H), 6.55 (d, J = 9.6, 1 H), 3.65 (s, 3 H), 3.30 (q, J = 7.2, 1 H), 1.09 (d, J = 7.2, 3 H)	
18	101–102.5	1710, 1635	14.89 (br s, 1 H), 8.27–7.61 (m, 4 H), 7.09 (d, J = 10.2, 1 H), 6.57 (d, J = 10.2, 1 H), 6.55 (dt, J = 15.6, 7.8, 1 H), 5.65 (dd, J = 15.6, 1.5, 1 H), 4.12 (q, J = 7.2, 2 H), 2.96 (ddd, J = 14.0, 7.8, 1.5, 1 H), 2.84 (ddd, J = 14.0, 7.8, 1.5, 1 H)	352 (M ⁺)
23		3400, 1715, 1645, 1570	14.04 (s, 1 H), 6.96 (d, J = 10.2, 2 H), 6.54 (d, J = 10.2, 2 H), 6.53 (dt, J = 15.6, 7.8, 1 H), 5.68 (d, J = 15.6, 1 H), 4.09 (q, J = 7.2, 2 H), 2.89 (d, J = 7.8, 2 H), 1.18 (t, J = 7.2, 3 H)	302 (M ⁺)

^a CHCl₃. ^b CDCl₃.

Chart I. LUMO Energies and Coefficients of Unsymmetrically Substituted Polyquinones by PPP Method



system such as the anthracylines.^{3–7} For such syntheses, the site-selective reaction of the less reactive external double bond is required in preference to the more reactive internal double bond.^{8–12} As a continuation of our systematic studies on the development of the site-selective reactions of polyquinones,^{1,2,13} we report on the reactions of 1 and 2 as electrophiles with a series of *O*-silylated ketene acetals. We find that Michael-type reactions of electron-rich *O*-silylated ketene acetals with 1 and 2 take place exclusively at the more reactive internal double bond, and some of the resultant adducts undergo interesting rearrangements to give products equivalent to *O*-silylated ketene acetals reacting at the less reactive external double bond.¹⁴

Results and Discussion

Reaction of 1 with (Trimethylsilyloxy)furan (3).

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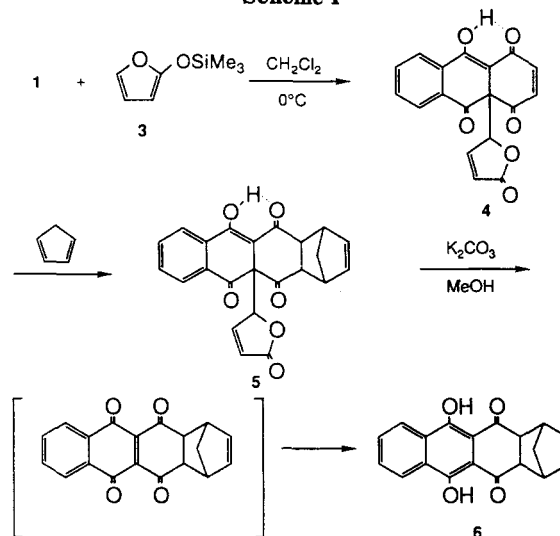
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Scheme I



Generally, *O*-silylated ketene acetals¹⁵ are known to react with various electrophiles, and Michael-type reactions of them with α,β -unsaturated carbonyl compounds proceed in the presence of Lewis acid^{16,17} or in acetonitrile as the solvent.¹⁸ However, there are few examples of reactions of these agents with quinone compounds.¹⁹ We have found that 1 and 2 react with various *O*-silylated ketene acetals without any catalysis. When 1 was reacted with (trimethylsilyloxy)furan (3, Scheme I)²⁰ in dry methylene chloride or dry THF at 0 °C for 30 min and then quenched with an aqueous 5% HCl solution, a yellow crystalline Michael adduct, 4, was obtained in good yield. Even though 3 is also a good diene, no Diels–Alder adduct was observed.

The structural assignment of 4 was based on the spectroscopic data (Table I). The mass spectrum indicated

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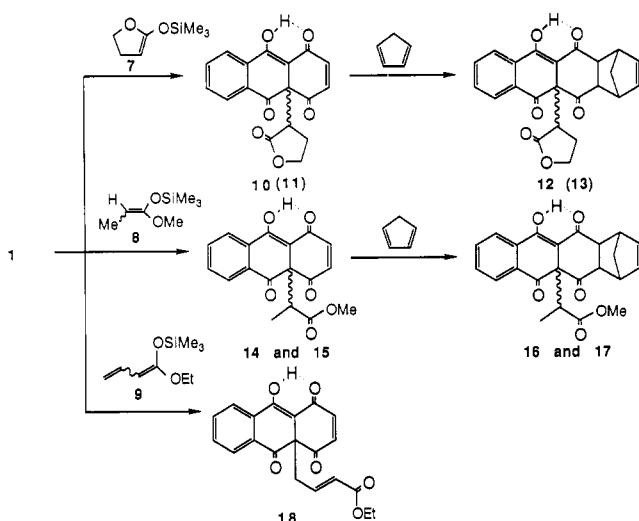
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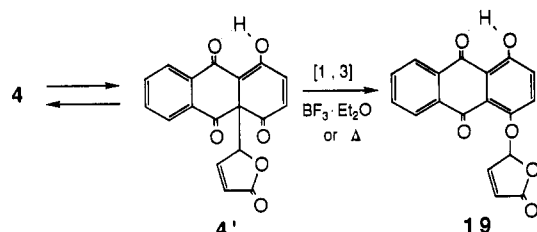
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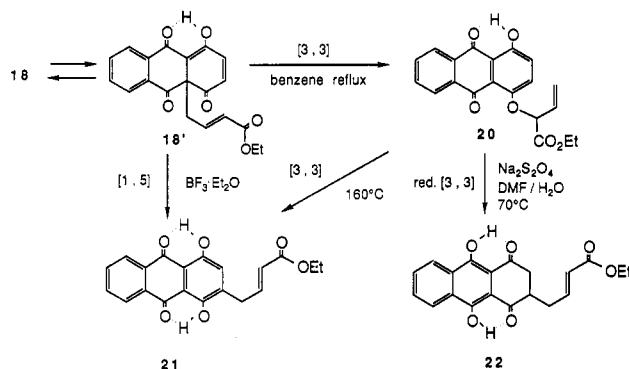
Scheme II



Scheme III



Scheme IV



that **4** was a desilylated 1:1 adduct by the molecular ion peak at m/z 322 (15%) and a characteristic fragmentation peak at m/z 240 (100%) due to the reductive cycloreversion.²¹ The IR spectrum showed characteristic carbonyl bands at 1785, 1755, 1710, and 1635 cm^{-1} . The ^1H NMR showed the characteristic peaks of a hydrogen-bonded phenolic proton at δ 15.13 and olefinic protons of an enedione moiety at δ 7.12 and 6.65 (AB q, $J = 10.0$ Hz) and of an α, β -unsaturated lactone at δ 7.12 (dd, $J = 5.8, 1.6$ Hz) and 6.05 (dd, $J = 5.8, 1.7$ Hz), which indicated the conjugate addition took place at the internal double bond of **1** as shown in Scheme I. As further confirmation of the structure, the remaining external double bond of **4** readily reacted with cyclopentadiene to give the Diels–Alder adduct **5** (84%); whose structure is consistent with ^1H NMR and IR spectral data. Interestingly, treatment of **5** with K_2CO_3 in MeOH resulted in a retro-Michael reaction followed by reduction to quinizarin ring to afford **6**²³ in 76% yield (Scheme I).

Reaction of 1 with Other Silyl Ketene Acetals 7–9. The high reactivity of **1** as a Michael acceptor with **3** promoted us to examine the reaction of **1** with other silyl ketene acetals, **7–9**. Reaction of **1** with **7**,²⁴ prepared from γ -butyrolactone, also proceeded smoothly in methylene chloride at 0 °C to give a separable mixture of diastereomers, **10** (37%) and **11** (19%) (Scheme II; stereochemistry unassigned). Compounds **10** and **11** each underwent the Diels–Alder reactions with cyclopentadiene to give yellow adducts **12** (85%) and **13** (80%), respectively. Attempted retro-Michael reaction by base treatment as above resulted only in isomerization of **12** to **13**.

Reaction of **1** with **8**²⁵ proceeded similarly to give an inseparable diastereomeric mixture of **14** and **15** (2:1) in 70% yield (Scheme II). The Diels–Alder reaction of this

mixture with cyclopentadiene afforded an inseparable mixture of adducts **16** and **17** (2:1) in 62% yield; similar to the above case, base treatment of this mixture resulted in isomerization of the major isomer **16** to **17**.

Conjugate addition of vinyl-substituted silyl ketene acetal **9** to the internal double bond of **1** took place exclusively at the γ -position to give yellow crystalline adduct **18** in 65% yield. The ^1H NMR spectrum showed the presence of a hydrogen-bonded phenolic proton (δ 14.89, 1 H, s), an enedione moiety (δ 7.09 and 6.57, 2 H, AB q, $J = 10.2$ Hz), a crotyl moiety (δ 6.55, 1 H, H β ; δ 5.65, 1 H, H α ; δ 2.96 and 2.84, each 1 H, methylene). A large coupling constant (15.6 Hz) revealed the *E* configuration of the olefinic moiety (Table I).

In summary, we have found that **1** reacts with various *O*-silylated ketene acetals in a reaction requiring no catalysis. In each case, the Michael-type addition took place at the internal double bond, which has the largest LUMO coefficient.²

Sigmatropic Rearrangement of Michael-Type Adducts. Because the Michael-type adducts obtained above have unique π -systems, we subjected to them to conditions that would result in sigmatropic rearrangements. Thus, treatment of **4** with 3 equiv of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ in methylene chloride at 0 °C afforded yellow crystalline **19** in 59% yield. The IR spectrum (1785 and 1755 cm^{-1}) and ^1H NMR spectrum (δ 7.81, 1 H, dd, $J = 5.6, 1.2$ Hz, H β ; δ 6.39, 1 H, dd, $J = 5.6, 1.2$ Hz, H α) indicate the structure of **19** containing α, β -unsaturated lactone moiety rather than β, γ -unsaturated lactone which is the result of a [3,3] sigmatropic rearrangement. The same rearrangement took place by refluxing **4** in benzene or THF. Apparently, **19** is formed through a [1,3] sigmatropic rearrangement via tautomeric isomer **4'** in a symmetry-forbidden transformation²⁶ that is driven to completion by the aromaticity of **19** (Scheme III). Interestingly, the adducts **10**, **11**, and **14** (**15**) failed to undergo this rearrangement under the same conditions.

The adduct **18** also rearranged under Lewis acid or thermal condition, but in a different fashion. Heating **18**

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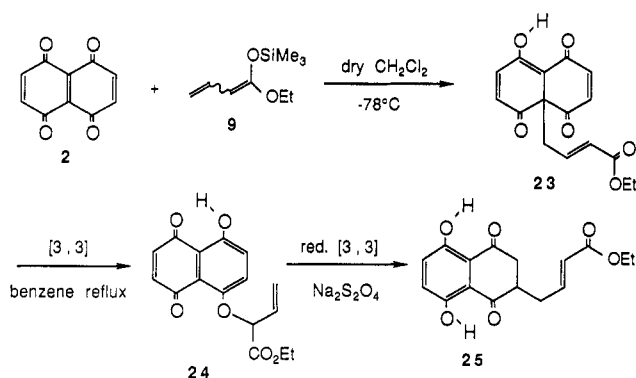
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Scheme V



in refluxing benzene resulted in a [3,3] sigmatropic rearrangement to give orange crystalline **20** in 51% yield. Further rearrangement of a toluene solution of **20** in a sealed tube at 160°C afforded quinizarin derivative **21** in 40% yield. Claisen rearrangement under reductive conditions ($\text{Na}_2\text{S}_2\text{O}_4$, DMF/ H_2O) gave leucoquinizarin derivative **22** in 63% yield. Since adduct **18** was somewhat unstable to silica gel, its purification was not necessary. Direct conversion to **20** followed by reductive rearrangement to **22** in a three-step one-pot sequence proceeded in 51% overall yield. On the other hand, treatment of **18** with 1 equiv of $\text{BF}_3\cdot\text{Et}_2\text{O}$ afforded **21** directly in 45% yield. Since the same treatment did not cause any rearrangement of **20**, **21** must not form via **20** but from two successive [3,3] sigmatropic rearrangements but from tautomeric **18'** via a [1,5] sigmatropic rearrangement (Scheme IV). Compound **21** could be obtained from **1** in 50% overall yield without the isolation of any intermediates.

Reaction of Bicyclic 2 with 9. According to the frontier molecular orbital (FMO) calculations, **2** has a lower LUMO energy level than **1**, and thus **2** is expected to be a more reactive dienophile or electrophile. Indeed, reaction of **2** with **9** proceeded smoothly to give **23** quantitatively (Scheme V). Since **23** was unstable to Lewis acid conditions, treatment with $\text{BF}_3\cdot\text{Et}_2\text{O}$ resulted in only decomposition rather than a [1,5] sigmatropic rearrangement. However, the thermal [3,3] rearrangement of **23** in refluxing benzene gave orange crystalline **24** in quantitative yield. Claisen rearrangement under reductive conditions (saturated aqueous $\text{Na}_2\text{S}_2\text{O}_4$) of **24** afforded **25** as a relatively stable compound which could be purified by column

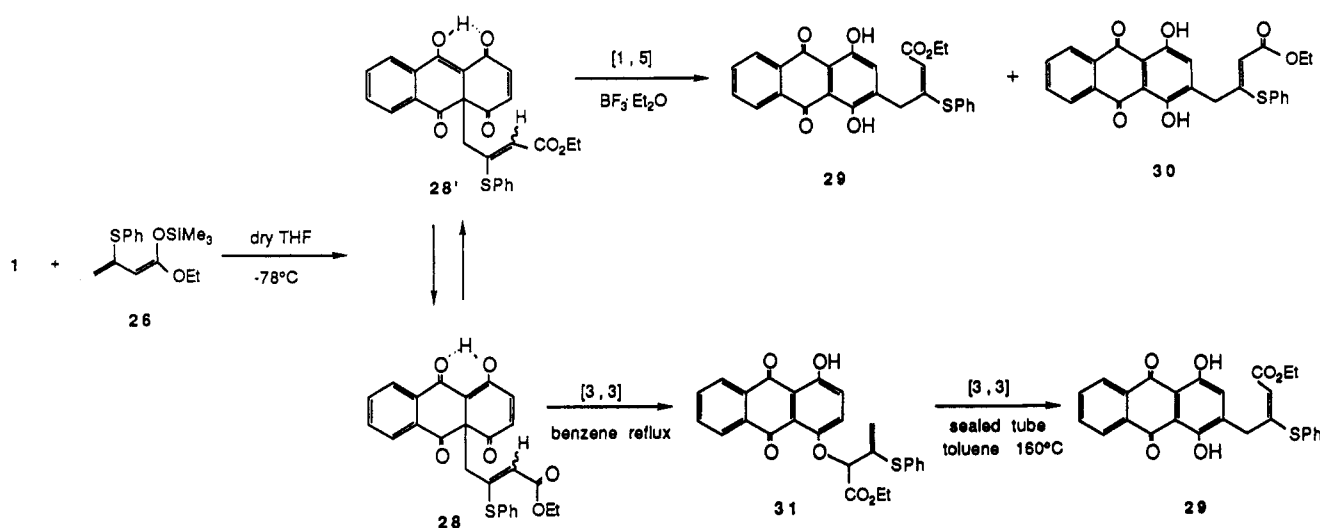
chromatography (Scheme V).

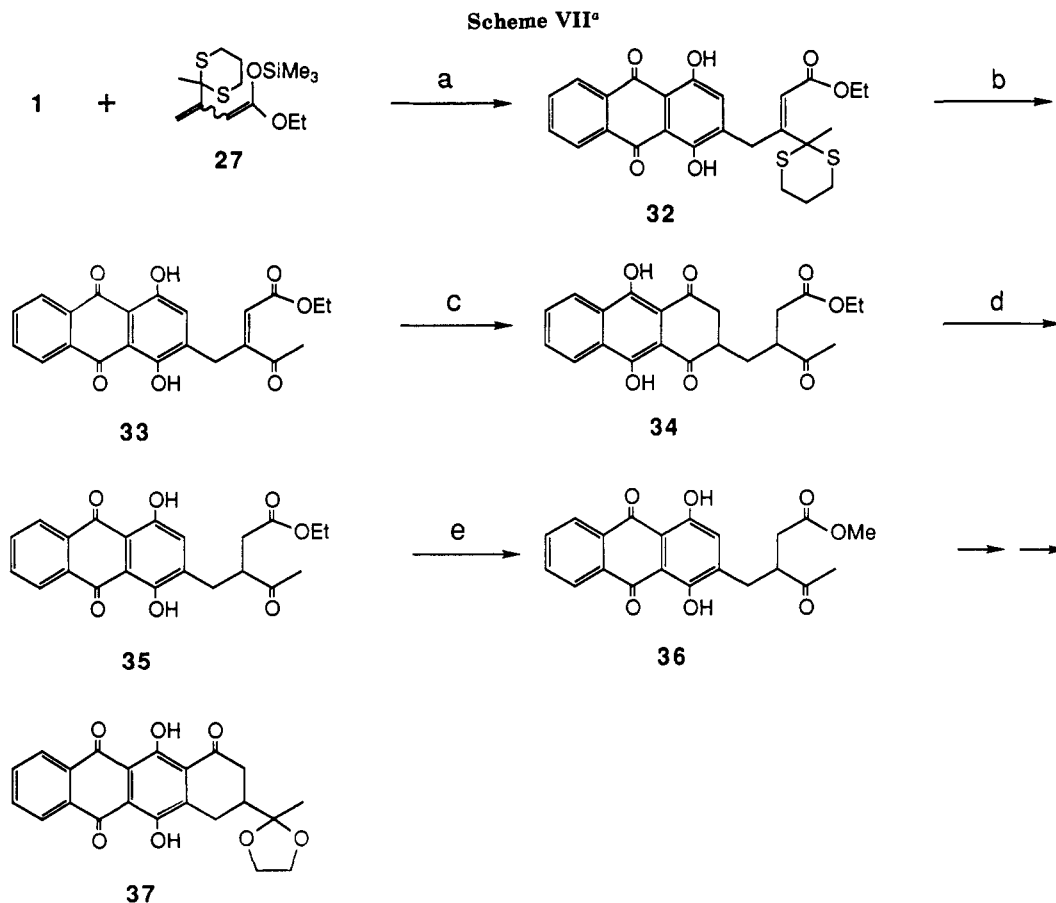
Reaction of 1 with β -Substituted 9, 26, and 27. The quinizarin derivative **21** could be easily transformed to a linear tetracyclic system as we have already reported.¹⁴ Thus, we were interested in examining the reactivity of β -substituted derivatives of **9**, namely, **26** and **27** (Schemes VI and VII). The β -substituents of **26** and **27** correspond to the functional group at the C-9 position in the anthracycline system. The reaction of **26**²¹ with **1** in dry THF at -78°C gave yellow adducts that were unstable to purification by silica gel chromatography. However, the structure of the products could be estimated to be **28** because the treatment of the products with $\text{BF}_3\cdot\text{Et}_2\text{O}$ afforded a [1,5] sigmatropic rearrangement to give a mixture of isomers, **29** (10%) and **30** (20%). The ^1H NMR spectra indicated the stereochemistry of **29** to be *E* and that of **30** to be *Z* by their chemical shifts.

The thermal [3,3] rearrangement of **28** also proceeded smoothly to give **31** in 48% yield. Without isolation of **28**, a two-step one-pot reaction afforded **31** in 48% overall yield. Heating a toluene solution of **31** at 160°C in a sealed tube gave **29** only by a [3,3] sigmatropic rearrangement (Scheme VI).

In contrast to **26**, **27** did not react with **1** in THF at -78°C to room temperature. However, activation of **1** by 1 equiv of $\text{BF}_3\cdot\text{Et}_2\text{O}$ in toluene or methylene chloride at -78°C resulted in the direct formation of the external adduct **32** in 29% yield (Scheme VII). The formation of **32** can be rationalized by two routes. One is the direct reaction of **27** with **1** at the less reactive external double bond, and the other is Michael reaction to the internal double bond followed by Lewis acid catalyzed [1,5] sigmatropic rearrangement. The formation of the Michael adduct as an intermediate could not be detected by TLC. To determine which route is most likely, the reaction of **1** with **9** in the presence and absence of $\text{BF}_3\cdot\text{Et}_2\text{O}$ was studied. In the absence of $\text{BF}_3\cdot\text{Et}_2\text{O}$ the reaction proceeded smoothly in methylene chloride or THF to give **18** in 59% (vide supra). However, in the presence of $\text{BF}_3\cdot\text{Et}_2\text{O}$, the formation of **21** was observed shortly after addition of **9** to a toluene solution of **1** (15%). During the reaction, Michael adduct **18** was not detected by TLC. Furthermore, the [1,5] sigmatropic rearrangement of **18** was evaluated in the -40 to 0°C range and did not occur until near 0°C . These data seem to suggest that both **21** and **32** are formed through a direct reaction of *O*-silylated ketene acetals at the less reactive but sterically favorable external double bond of

Scheme VI





^a Reagents and conditions: (a) $\text{BF}_3 \cdot \text{Et}_2\text{O}$, dry toluene, -78°C (29%). (b) $\text{Hg}(\text{ClO}_4)_2$, THF (75%). (c) Zn, AcOH. (d) TMSCl, Imidazole, DMF/aqueous NaF (60% from 34). (e) MeOH, H_2SO_4 (quantitative).

1. Finally, 32 was transformed easily to the intermediate 36 of Sih's anthracyclinone synthesis.²⁷ Hydrolysis of thioketal 32 ($\text{Hg}(\text{ClO}_4)_2$) gave 33 in 75% yield. Concomitant reduction of the olefin and quinone chromophore of 33 by Zn in AcOH smoothly proceeded to give the leucoquinizarin 34. Oxidation of 34 to the quinizarin 35 was achieved by a silylation-acid hydrolysis procedure. Transesterification of 35 gave the intermediate 36, which was converted to the tetracyclic system 37 by base-catalyzed cyclization (Scheme VII).

In summary, we have demonstrated that polyquinones 1 and 2 serve as Michael acceptors for various *O*-silylated ketene acetals. We emphasize that these addition reactions proceeded without any catalysis and that the regioselectivity is controlled completely by the LUMO coefficients and energy levels. In contrast, catalysis by Lewis acid affected the site selectivity, and the course of reaction was controlled by apparent steric factors to give directly the external adduct.

Experimental Section

The melting points were measured with a Yanagimoto micro-melting-point apparatus and are uncorrected. The ^1H 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 IR spectra were taken with a JASCO A-100 infrared spectrophotometer. Mass spectra were determined on a JEOL-D300 equipped with a JMA 3100/3500 at an ionization voltage of 30–35 eV. Elemental analyses were performed on a Yanagimoto MT2

CHN recorder. Merck precoated TLC plates (Kieselgel 60 F₂₅₄, 0.2 mm) were used for TLC analysis. Column chromatography was performed on Merck Kieselgel 60 (70–200 mesh) silica gel.

Materials. Quinizarinquinone (1) and naphthodiquinone (2) were prepared according to the reported methods.²

General Procedure for Michael Reactions of Quinizarinquinone (1) with *O*-Silylated Ketene Acetals 3, 7, and 8. To a solution of 1 (100 mg, 0.42 mmol) in 10 mL of dry CH_2Cl_2 was added 1 equiv of the *O*-silylated ketene acetals 3, 7, or 8 in 3 mL of dry CH_2Cl_2 at 0°C under Ar. The reactions were monitored by TLC. After 30 min, the reactions were quenched with 10 mL of 5% HCl, and the resulting mixture was extracted with CH_2Cl_2 . The combined organic extracts were washed with saturated NaHCO_3 and brine, dried over Na_2SO_4 , and evaporated under reduced pressure. The residual solids were chromatographed on silica gel eluting with *n*-hexane/AcOEt (1:1–1:4) to give Michael adducts 4 (82%), 10 (37%), 11 (19%), or 14 and 15 (70%). The spectral data of the adducts were summarized in Table I.

Reaction of Quinizarinquinone (1) with *O*-Silylated Ketene Acetals 9 and 26. To a solution of 1 (100 mg, 0.42 mmol) in 10 mL of dry THF or CH_2Cl_2 was added a solution of 9 or 26 in 3 mL of solvent at -78°C under Ar. The reactions were monitored by TLC. After 30 min, 10 mL of 5% HCl was added, and the same workup as described above afforded 18 (96 mg, 65%) or 28. For 18, silica gel chromatography (*n*-hexane/AcOEt = 4:1) and recrystallization from CH_2Cl_2 and *n*-hexane group pure 18 as yellow crystals: mp $101\text{--}102.5^\circ\text{C}$. Anal. Calcd for $\text{C}_{20}\text{H}_{16}\text{O}_6$: C, 68.18; H, 4.58. Found: C, 68.03; H, 4.60.

General Procedure for Cycloaddition Reactions of Michael-Type Adducts 4, 10, 11, and 14 (15). A solution of 4 and an excess of cyclopentadiene (2 equiv) in CH_2Cl_2 was stirred at room temperature. The reactions were monitored by TLC. After consumption of the starting material, the solution was evaporated under reduced pressure, and the residual solid was chromatographed on silica gel eluting with *n*-hexane/AcOEt (4:1–6:1) to give the Diels-Alder adduct 5. Recrystallization from CH_2Cl_2 and

(27) Suzuki, F.; Trenbeath, S.; Gleim, R. D.; Sih, C. J. *J. Org. Chem.* 1978, 43, 4159.

n-hexane gave pure **5**. By the same procedure, Diels–Alder adducts **12**, **13**, and **16** (**17**) were obtained from **10**, **11**, and **14** (**15**), respectively.

5: 84%; mp 154–156 °C; IR (CHCl₃) 1790, 1760, 1725, 1670 cm⁻¹; ¹H NMR (CDCl₃) δ 16.78 (s, 1 H), 8.26–8.16, 7.84–7.67 (m, 4 H), 6.88 (dd, *J* = 5.8, 1.5 Hz, 1 H), 6.14 (dd, *J* = 5.8, 2.0 Hz, 1 H), 6.00 (m, 2 H), 5.59 (dd, *J* = 2.0, 1.5 Hz, 1 H), 3.48 (m, 4 H), 1.58 (m, 2 H).

12: 85%; mp 191–192 °C; IR (CHCl₃) 1765, 1725, 1670 cm⁻¹; ¹H NMR (CDCl₃) δ 16.44 (s, 1 H), 8.28–8.02, 7.79–7.62 (m, 4 H), 6.06 (m, 2 H), 4.12 (t, *J* = 7.2 Hz, 2 H), 3.56–3.10 (m, 5 H), 2.42 (m, 2 H), 1.56 (m, 2 H); MS, *m/z* 390 (M⁺).

13: 80%; mp 188–190 °C; IR (CHCl₃) 1760, 1720, 1670 cm⁻¹; ¹H NMR (CDCl₃) δ 16.10 (s, 1 H), 8.27–8.12, 7.85–7.70 (m, 4 H), 6.05 (m, 2 H), 4.13 (t, *J* = 7.2 Hz, 2 H), 3.80–3.25 (m, 5 H), 2.32 (m, 2 H), 1.51 (m, 2 H); MS, *m/z* 390 (M⁺).

16 and **17**: 62%; IR (CHCl₃) 1725, 1675 cm⁻¹; ¹H NMR (CDCl₃) δ (**16**, major) 16.46 (s, 1 H), 8.28–8.04, 7.84–7.55 (m, 4 H), 6.06 (m, 2 H), 3.82 (s, 3 H), 3.89–3.23 (m, 5 H), 1.52 (m, 2 H), 1.31 (d, *J* = 7.2 Hz, 3 H); (**17**, minor) 16.61 (s, 1 H), 8.28–8.04, 7.84–7.55 (m, 4 H), 6.06 (m, 2 H), 3.33 (s, 3 H), 3.89–3.23 (m, 5 H), 1.52 (m, 2 H), 1.19 (d, *J* = 7.2 Hz, 3 H).

Base-Catalyzed Cycloversion of 5. A mixture of **5** (68 mg, 0.18 mmol) and K₂CO₃ (25 mg, 0.18 mmol) in 3 mL of MeOH was stirred at room temperature. After consumption of the starting material, the mixture was diluted with CH₂Cl₂, washed with 5% HCl, H₂O, and brine, dried over Na₂SO₄, and evaporated under reduced pressure. The residual solids were chromatographed on silica gel eluting with *n*-hexane/AcOEt (2:1) to give **6** (41 mg, 76%) as yellow crystals: mp 143–144 °C (CH₂Cl₂–*n*-hexane); IR (CHCl₃) 1620, 1600 cm⁻¹; ¹H NMR (CDCl₃) δ 14.49 (s, 2 H), 8.55–8.39, 7.82–7.67 (m, 4 H), 6.07 (m, 2 H), 3.70 (m, 2 H), 3.45 (m, 2 H), 1.51 (m, 2 H).

Lewis Acid Catalyzed [1,3] Sigmatropic Rearrangement of 4. To a solution of **4** (111 mg, 0.34 mmol) in 30 mL of dry CH₂Cl₂ was added BF₃·Et₂O (0.13 mL, 1.02 mmol) at –40 °C under Ar, and the reaction mixture was warmed to room temperature. The reaction was monitored by TLC. After consumption of the starting material, the reaction mixture was quenched with 10 mL of H₂O and extracted with CH₂Cl₂, washed with H₂O and brine, dried over Na₂SO₄, and evaporated under reduced pressure. The residual solids were chromatographed on silica gel eluting with *n*-hexane/AcOEt (4:1) to give **19** (65 mg, 59%) as yellow crystals: mp 252–256 °C (CHCl₃–ether); IR (CHCl₃) 1785, 1755, 1665, 1635, 1585 cm⁻¹; ¹H NMR (CDCl₃) δ 13.06 (s, 1 H), 8.37–8.22, 7.88–7.70 (m, 4 H), 7.81 (d, *J* = 5.6, 1.2 Hz, 1 H), 7.64 (d, *J* = 9.3 Hz, 1 H), 7.33 (d, *J* = 9.3 Hz, 1 H), 6.39 (dd, *J* = 5.6, 1.2 Hz, 1 H), 6.30 (t, *J* = 1.2 Hz, 1 H); MS, *m/z* 322 (M⁺).

Thermal [1,3] Sigmatropic Rearrangement of 4. A solution of **4** (100 mg, 0.31 mmol) in 10 mL of benzene was refluxed for 3 h. After the starting material had disappeared, the solvent was evaporated under reduced pressure. The residual solids were chromatographed on silica gel eluting with *n*-hexane/AcOEt (2:1) to give **19** (50 mg, 50%).

[3,3] Sigmatropic Rearrangement of 18 and 28. A solution of **18** or **28** in benzene was refluxed for 3 h. The solvent was evaporated under reduced pressure, and the residual solids were chromatographed on silica gel eluting with *n*-hexane/AcOEt (4:1) to give **20** (51%) or **31** (48%). Recrystallization from CH₂Cl₂ and *n*-hexane afforded samples as follows:

20: mp 121–121.5 °C; IR (CHCl₃) 1730, 1665, 1635, 1590 cm⁻¹; ¹H NMR (CDCl₃) δ 13.03 (s, 1 H), 8.38–8.22, 7.85–7.70 (m, 4 H), 7.34 (d, *J* = 9.3 Hz, 1 H), 7.21 (d, *J* = 9.3 Hz, 1 H), 6.19 (ddd, *J* = 17.2, 10.1, 5.6 Hz, 1 H), 5.80 (ddd, *J* = 17.2, 1.7, 1.2 Hz, 1 H), 5.49 (ddd, *J* = 10.1, 1.7, 1.5 Hz, 1 H), 5.17 (ddd, *J* = 5.6, 1.5, 1.2 Hz, 1 H), 4.28 (q, *J* = 7.2 Hz, 2 H), 1.28 (t, *J* = 7.2 Hz, 3 H); MS, *m/z* 352 (M⁺).

31: mp 84–85 °C; IR (CHCl₃) 1730, 1670, 1635, 1595 cm⁻¹; ¹H NMR (CDCl₃) δ 13.05 (s, 1 H), 8.34–8.13, 7.91–7.69 (m, 4 H), 7.50–7.20 (m, 7 H), 6.06 (d, *J* = 0.6 Hz, 1 H), 5.42 (s, 1 H), 5.16 (d, *J* = 0.6 Hz, 1 H), 4.30 (q, *J* = 7.2 Hz, 2 H), 1.30 (t, *J* = 7.2 Hz, 3 H); MS, *m/z* 460 (M⁺). Anal. Calcd for C₂₆H₂₀O₆S: C, 67.81; H, 4.38. Found: C, 67.55; H, 4.63.

[3,3] Sigmatropic Rearrangement of 20 and 31. A solution of **20** or **31** in toluene was heated at 160 °C in a sealed tube. After consumption of the starting material, the solvent was evaporated

under reduced pressure, and the residual solids were chromatographed on silica gel eluting with *n*-hexane/AcOEt (4:1) to give **21** (40%) or **29** (36%). Recrystallization from CH₂Cl₂ and *n*-hexane afforded pure samples as follows:

21: mp 140–141 °C; IR (CHCl₃) 1710, 1620, 1585 cm⁻¹; ¹H NMR (CDCl₃) δ 13.28 (s, 1 H), 12.83 (s, 1 H), 8.40–8.24, 7.89–7.74 (m, 4 H), 7.12 (dt, *J* = 15.7, 6.9 Hz, 1 H), 7.11 (s, 1 H), 5.91 (dt, *J* = 15.7, 1.4 Hz, 1 H), 4.20 (q, *J* = 7.2 Hz, 2 H), 3.62 (dd, *J* = 6.9, 1.4 Hz, 2 H), 1.28 (t, *J* = 7.2 Hz, 3 H); MS, *m/z* 352 (M⁺). Anal. Calcd for C₂₀H₁₆O₆: C, 68.18; H, 4.58. Found: C, 68.20; H, 4.56.

29: mp 177–178 °C; IR (CHCl₃) 1695, 1620, 1585 cm⁻¹; ¹H NMR (CDCl₃) δ 13.48 (s, 1 H), 12.97 (s, 1 H), 8.43–8.22, 7.89–7.74 (m, 4 H), 7.48–7.35 (m, 6 H), 5.51 (s, 1 H), 4.38 (s, 2 H), 4.07 (q, *J* = 7.2 Hz, 2 H), 1.18 (t, *J* = 7.2 Hz, 3 H); MS, *m/z* 460 (M⁺). Anal. Calcd for C₂₆H₂₀O₆S: C, 67.81; H, 4.38. Found: C, 67.76; H, 4.43.

Reductive [3,3] Sigmatropic Rearrangement of 18. A mixture of **18** (35 mg, 0.1 mmol) and Na₂S₂O₄ (24 mg, 0.14 mmol) in 0.8 mL of DMF–H₂O (3:1) was heated at 70 °C for 2 h under N₂. After cooling, the reaction mixture was diluted with 20 mL of CH₂Cl₂, washed repeatedly with H₂O, dried over Na₂SO₄, and evaporated under reduced pressure. The residual solids were chromatographed on silica gel eluting with *n*-hexane/AcOEt (6:1) to give **22** (22 mg, 63%) as yellow crystals: mp 111–113 °C (CH₂Cl₂–*n*-hexane); IR (CHCl₃) 1710, 1635, 1585 cm⁻¹; ¹H NMR (CDCl₃) δ 13.42 (s, 1 H), 13.40 (s, 1 H), 8.47–8.32, 7.82–7.66 (m, 4 H), 6.97 (dt, *J* = 16.2, 7.2 Hz, 1 H), 5.94 (d, *J* = 16.2 Hz, 1 H), 4.20 (q, *J* = 7.2 Hz, 2 H), 3.68–2.53 (m, 5 H), 1.29 (t, *J* = 7.2 Hz, 3 H); MS, *m/z* 354 (M⁺).

Lewis Acid Catalyzed [1,5] Sigmatropic Rearrangement of 18 and 28. To a solution of **18** or **28** in dry CH₂Cl₂ was added 1 equiv of BF₃·Et₂O under Ar at –40 °C, and the reaction mixture was slowly warmed to room temperature. After the consumption of the starting material, the reaction mixture was quenched with H₂O and extracted with CH₂Cl₂, washed with brine, dried over Na₂SO₄, and evaporated under reduced pressure. The residual solids were chromatographed on silica gel eluting with *n*-hexane/AcOEt (9:1) to give **21** (51%) or **29** (10%) and **30** (20%).

30: mp 175–176 °C; IR (CHCl₃) 1680, 1610, 1575 cm⁻¹; ¹H NMR (CDCl₃) δ 13.03 (s, 1 H), 12.87 (s, 1 H), 8.45–8.22, 7.98–7.77 (m, 4 H), 7.57–7.15 (m, 6 H), 5.83 (s, 1 H), 4.25 (q, *J* = 6.6 Hz, 2 H), 3.56 (s, 2 H), 1.31 (t, *J* = 6.6 Hz, 3 H); MS, *m/z* 460 (M⁺). Anal. Calcd for C₂₆H₂₀O₆S: C, 67.81; H, 4.38. Found: C, 67.75; H, 4.37.

Reaction of Naphthodiquinone (2) with 9. To a solution of **2** (106 mg, 0.56 mmol) in 10 mL of dry CH₂Cl₂ was added a solution of **9** (156 mg, 0.84 mmol) in 3 mL of dry CH₂Cl₂ at –78 °C under Ar, and the reaction mixture was warmed to room temperature. After the starting material had disappeared, the reaction was quenched with 5 mL of 5% HCl, and the resulting mixture was extracted with CH₂Cl₂, washed with H₂O and brine, dried over Na₂SO₄, and evaporated to give **23** as a red oil; IR (CHCl₃) 3400, 1715, 1645, 1570 cm⁻¹; ¹H NMR (CDCl₃) δ 14.04 (s, 1 H), 6.96 (d, *J* = 10.2 Hz, 2 H), 6.54 (d, *J* = 10.2 Hz, 2 H), 6.53 (dt, *J* = 15.6, 7.8 Hz, 1 H), 5.68 (d, *J* = 15.6 Hz, 1 H), 4.09 (q, *J* = 7.2 Hz, 2 H), 2.89 (d, *J* = 7.8 Hz, 2 H), 1.18 (t, *J* = 7.2 Hz, 3 H); MS, *m/z* 302 (M⁺).

[3,3] Sigmatropic Rearrangement of 23. A solution of **23** (110 mg, 0.36 mmol) in 20 mL of benzene was heated at reflux. After the starting material had disappeared, the solution was concentrated under reduced pressure to afford **24** (110 mg, 100%) as red crystals. Recrystallization from benzene and *n*-hexane afforded a pure sample: mp 121–123 °C; IR (CHCl₃) 3400, 1720, 1640, 1605 cm⁻¹; ¹H NMR (CDCl₃) δ 12.43 (s, 1 H), 7.21 (s, 2 H), 6.89 (s, 2 H), 6.18 (ddd, *J* = 15.0, 9.6, 4.8 Hz, 1 H), 5.78 (dm, *J* = 15.0 Hz, 1 H), 5.46 (dm, *J* = 9.6 Hz, 1 H), 5.14 (dm, *J* = 4.8 Hz, 1 H), 4.27 (q, *J* = 7.2 Hz, 2 H), 1.28 (t, *J* = 7.2 Hz, 3 H); MS, *m/z* 302 (M⁺).

Reductive [3,3] Sigmatropic Rearrangement of 24. A solution of **24** (51 mg, 0.17 mmol) in 10 mL of ether was shaken with saturated Na₂S₂O₄ in a separatory funnel until the color of the solution changed from orange to yellow. The organic layer was washed with H₂O and brine, dried over Na₂SO₄, and evaporated under reduced pressure. The residue was chromatographed on silica gel eluting with *n*-hexane/AcOEt (4:1) to give **25** as a red oil: IR (CHCl₃) 3400, 1710, 1640 cm⁻¹; ¹H NMR (CDCl₃) δ 11.86 (s, 1 H), 11.82 (s, 1 H), 7.26 (s, 2 H), 6.93 (dt, *J* = 15.6, 7.2 Hz, 1 H), 5.91 (d, *J* = 15.6 Hz, 1 H), 4.20 (q, *J* = 7.2 Hz, 2 H), 3.00–2.51

(m, 5 H), 1.28 (t, $J = 7.2$ Hz, 3 H); MS, m/z 304 (M^+).

Reaction of 1 with 27. To a stirred solution of 1 (150 mg, 0.64 mmol) in 10 mL of dry toluene at -78 °C was added 1 equiv of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (0.08 mL, 0.64 mmol) under Ar, and the reaction mixture was stirred at -78 °C. After 30 min, 27 (200 mg, 0.64 mmol) was added to the reaction mixture, which was stirred for 30 min. The reaction mixture was quenched with 5 mL of H_2O , extracted with AcOEt, washed with brine, dried over Na_2SO_4 , and evaporated to dryness. The residual solids were chromatographed on silica gel eluting with n -hexane/AcOEt (9:1) to give 32 (89 mg, 29%) as red crystals: mp 180 – 181 °C (CH_2Cl_2 - n -hexane); IR (CHCl_3) 1715, 1620, 1585 cm^{-1} ; ^1H NMR (CDCl_3) δ 13.54 (s, 1 H), 12.94 (s, 1 H), 8.36–8.22, 7.90–7.69 (m, 4 H), 7.05 (s, 1 H), 6.94 (s, 1 H), 4.32 (s, 2 H), 4.14 (q, $J = 7.2$ Hz, 2 H), 2.72–2.65 (m, 4 H), 2.08–1.89 (m, 2 H), 1.66 (s, 3 H), 1.24 (t, $J = 7.2$ Hz, 3 H); MS, m/z 484 (M^+). Anal. Calcd for $\text{C}_{25}\text{H}_{24}\text{O}_6\text{S}_2$: C, 61.97; H, 4.99. Found: C, 61.78; H, 4.97.

Hydrolysis of the Thioketal of 32. To a solution of 32 (20 mg, 0.04 mmol) in 3 mL of THF was added $\text{Hg}(\text{ClO}_4)_2$ (73 mg, 0.16 mmol), and the reaction mixture was stirred at room temperature. After 30 min, the mixture was filtered. The filtrate was diluted with AcOEt, washed with H_2O and brine, dried over Na_2SO_4 , and evaporated to dryness. The residual solids were chromatographed on silica gel eluting with n -hexane/AcOEt (9:1) to give 33 (12 mg, 75%): mp 149 – 150 °C; IR (CHCl_3) 1720, 1685, 1620, 1590 cm^{-1} ; ^1H NMR (CDCl_3) δ 13.44 (s, 1 H), 12.89 (s, 1 H), 8.41–8.20, 7.95–7.73 (m, 4 H), 7.00 (s, 1 H), 6.82 (s, 4 H), 4.26 (s, 2 H), 4.25 (q, $J = 7.2$ Hz, 2 H), 2.43 (s, 3 H), 1.29 (t, $J = 7.2$ Hz, 3 H); MS, m/z 394 (M^+). Anal. Calcd for $\text{C}_{22}\text{H}_{18}\text{O}_7$: C, 67.00; H, 4.60. Found: C, 67.01; H, 4.59.

2-(2'-(Carbomethoxymethyl)-3'-oxobutyl)-1,4-dihydroxy-

anthraquinone (35). A mixture of 50 mg (0.13 mmol) of 33, 51 mg (0.78 mmol) of zinc dust, and 2 mL of acetic acid was stirred at room temperature. After 1 h, the reaction mixture was diluted with 5 mL of CH_2Cl_2 and filtered. The filtrate was washed with saturated NaHCO_3 , H_2O , brine, dried over Na_2SO_4 , and evaporated to dryness. The residual solids were dissolved in 2 mL of DMF and the solution was treated with TMSCl (0.1 mL, 0.78 mmol) and imidazole (70 mg, 1.04 mmol). After this stirred at room temperature under Ar for 1 h, 5 mL of saturated NaF was added. The mixture was stirred for 15 min, extracted with AcOEt, washed with H_2O and brine, dried over Na_2SO_4 , and evaporated under reduced pressure. The residual solids were chromatographed on silica gel eluting with n -hexane/AcOEt (4:1) to give 35 (30 mg, 60%) as red crystals: mp 82 – 84 °C; IR (CHCl_3) 1720, 1620, 1585 cm^{-1} ; ^1H NMR (CDCl_3) δ 13.35 (s, 1 H), 12.80 (s, 1 H), 8.40–8.18, 7.96–7.74 (m, 4 H), 7.10 (s, 1 H), 4.09 (q, $J = 7.2$ Hz, 2 H), 3.64–2.45 (m, 5 H), 2.29 (s, 3 H), 1.21 (t, $J = 7.2$ Hz, 3 H); MS, m/z 396 (M^+). Anal. Calcd for $\text{C}_{22}\text{H}_{20}\text{O}_7$: C, 66.66; H, 5.09. Found: C, 66.49; H, 5.26.

2-(2'-(Carbomethoxymethyl)-3'-oxobutyl)-1,4-dihydroxy-anthraquinone (36). A mixture of 50 mg (0.13 mmol) of 35, 2 drops of H_2SO_4 , and 30 mL of MeOH was stirred for 24 hr. The mixture was diluted with CH_2Cl_2 , washed with saturated NaHCO_3 , H_2O , brine, dried over Na_2SO_4 , and evaporated to dryness. The residual solids were chromatographed on silica gel eluting with n -hexane/AcOEt (4:1) to give 36 as red crystals: mp 182 – 184 °C (lit.²⁷ mp 170 – 180 °C) (CH_2Cl_2 - n -hexane); IR (CHCl_3) 1720, 1620, 1585 cm^{-1} ; ^1H NMR (CDCl_3) δ 13.38 (s, 1 H), 12.83 (s, 1 H), 8.41–8.21, 7.96–7.75 (m, 4 H), 7.10 (s, 1 H), 3.63 (s, 3 H), 3.49–2.45 (m, 5 H), 2.29 (s, 3 H); MS, m/z 382 (M^+). Anal. Calcd for $\text{C}_{21}\text{H}_{18}\text{O}_7$: C, 65.97; H, 4.74. Found: C, 65.78; H, 4.75.

Reaction of Lithium Enolates with Carbon Disulfide: Synthesis of *O*-(1-Alkoxy-2,2-dialkylvinyl) *S*-Alkyl Dithiocarbonates

Syed Mashhood Ali and Shigeo Tanimoto*

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611, Japan

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The reaction of lithium enolates 5, generated from esters 4 having only one α -hydrogen atom, with carbon disulfide at -78 °C followed by alkylation with alkyl halide afforded *O*-(1-alkoxy-2,2-dialkylvinyl) *S*-alkyl dithiocarbonates (7) in excellent yields (84–95%). An unambiguous structural assignment was made with the help of spectral and microanalytical data. A plausible mechanism has been proposed, in light of available literature, that explains the results of the reaction of enolates with carbon disulfide. The transformation is significant from both the synthetic and mechanistic points of view. These products have not previously been reported, and compound 8 was reported to be the primary product of the reaction of lithium enolate with carbon disulfide. This report represents the first example of the formation of a C–O bond between the oxygen of an enolate and the carbon disulfide.

Lithium enolates have played a major role in the development of modern organic chemistry. They are generated by the deprotonation of carbonyl compounds with amide bases, such as lithium diisopropylamide (LDA),¹ lithium tetramethylpiperidide (LTMP),² and lithium hexamethyldisilazane (LHMDS),³ in THF in the presence of a cosolvent or of a complexing agent and preferably at low temperature. The reactions involving enolates were described until recently by drawing a negative charge on the carbon atom, even though it was realized that the negative charge is located on the more electronegative

oxygen, but pragmatically this was done because that is where they react. Recent studies⁴ on the structure and reactivity of enolates, in solution and in the crystalline state, by X-ray, spectroscopic, and physicochemical methods have now established that Li and Na enolates exist as aggregates in nonpolar solvents and that these aggregates,⁵ probably, are the product-forming species. These studies have certainly helped in a better understanding of the reaction of lithium enolates, but there still exist gaps in our knowledge.

The reaction of enolates with carbon disulfide has been well studied.^{6–8} A typical course of the reaction of carbonyl

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