11a (isomer 1), 103367-33-5; **11a** (isomer 2), 103367-45-9; **11b**, 103367-34-6; **12a** (isomer 1), 103367-35-7; **12a** (isomer 2), 103421-23-4; **12b**, 103367-36-8; **13a** (isomer 1), 103367-37-9; **13a** (isomer 2), 103421-24-5; **13b**, 103367-38-0; **14a** (isomer 1), 65451-95-8; **14a** (isomer 2), 65451-94-7; **14b**, 43112-32-9; **15**, 103367-39-1; **16**, 59812-96-3; **17**, 33106-37-5; **18**, 103367-42-6; **19**, 65451-90-3; **20a** (isomer 1), 103367-40-4; **20a** (isomer 2), 103367-46-0; **20b**, 103367-41-5; **21a** (isomer 1), 65451-93-6; **21a** (isomer 2), 65451-92-5; **21b**, 16320-13-1; $H_2C{=}C(CH_3)CO_2CH_3$, 80-62-6; $H_2C{=}CHCO_2CH_3$, 96-33-3; $H_3C(CH_2)_9Li$, 4416-59-5.

High Pressure [4 + 2] Cycloaddition Reactions of 3,4-Dimethoxyfuran with Dichloromaleic Anhydride and with Cyclopropane Derivatives

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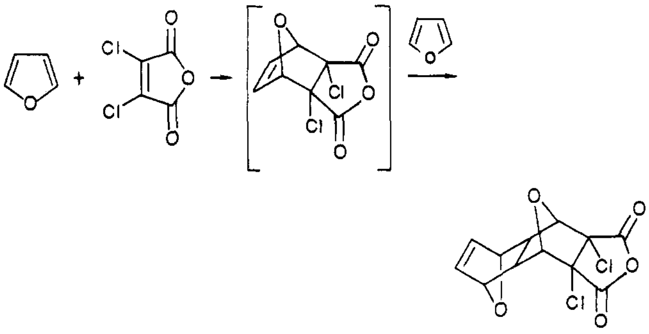
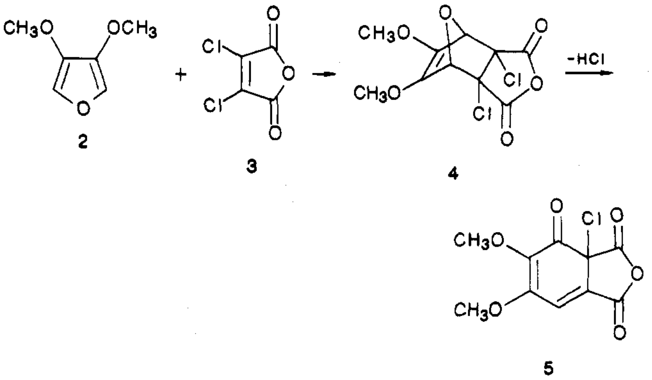
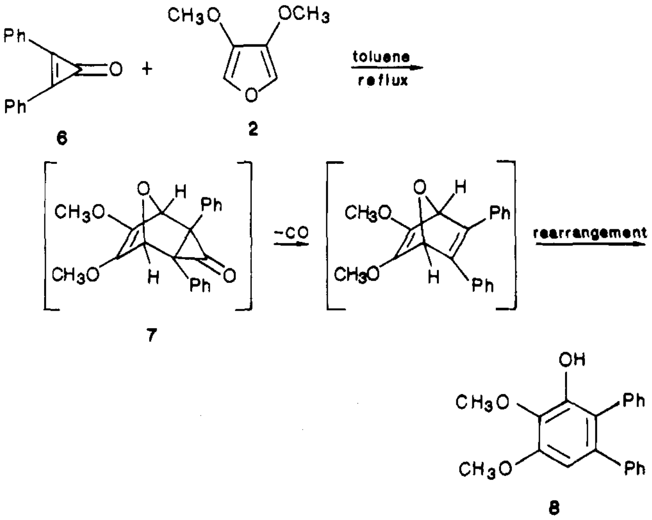
The failure of the [4 + 2] cycloaddition of dimethylmaleic anhydride with furan was a result of both electronic and steric hindrance of the methyl group. Another reason for the failure of the cycloaddition was due to the poor Diels–Alder rectivity of furan.[1]

Recently the more reactive diene isobenzofuran was found to react quantitatively with dimethylmaleic anhydride (**1**) in reluxing xylene to give the cycloaddition product, benzocantharidine.[2] Another reactive furan, 3,4-dimethoxyfuran (**2**), undergoes cycloaddition with **1** under high pressure (22 kbar) at room temperature. The reaction, however, did not proceed at lower pressure, e.g., 10 kbar.[3] We have also demonstrated that when the methyl groups of **1** were replaced by chlorines, it reacted with furan under 5 kbar of pressure to yield a cycloadduct.[4] This result showed that the electron-withdrawing chlorine groups increased its dienophilicity, and the application of high pressure overcomes the steric hindrance. The reaction first yields the 1:1 cycloadduct, which is still reactive as a dienophile, and adds a second molecule of furan giving the 1:2 addition product. Thus, we expect that a reactive diene (**2**) and dichloromaleic anhydride (**3**) may react under more moderate conditions to yield a stable 1:1 cycloaddition product. When **2** and **3** were refluxed in toluene, a polymerization was initiated with the elimination of hydrogen chloride and a black solid was produced. The cycloaddition reaction of **2** and **3** in THF solution was found to proceed under 10 kbar at room temperature. (The reaction failed at lower pressure, 5–6 kbar.) The product **5** was isolated in 67% yield after chromatographic purification. The compound **5** probably arose via 1:1 addition (**4**) followed by dehydrochlorination and rearrangement.

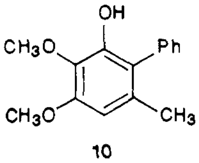




The reaction of furan with diphenylcyclopropenone (**6**) has been reported to be unsuccessful, yielding only the dimer of **6**.[5] We have found that the cycloaddition reaction does not occur even under high pressure (~10 kbar). The more reactive furan **2**, however, underwent the cycloaddition with **6** on refluxing in toluene to give 2,3-dimethoxy-5,6-diphenylphenol (**8**) in 24% yield. The compound **8** may be obtained via the decarbonylation and rearrangement of the initially formed adduct (**7**).



Similarly, methylphenylcyclopropenone (**9**) reacts with **2** in refluxing toluene producing 2,3-dimethoxy-5-methyl-6-phenylphenol (**10**) in 9% yield along with the dimer (**11**)[6] of **9**.



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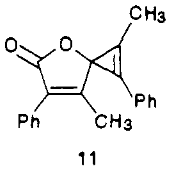

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The yields of these phenols **8** and **10** were greatly improved when the reactions were performed at high pressure, 8–10 kbar. The yields were increased to 51% and

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[†] Kyoto University.

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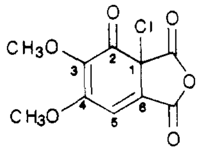
68%, respectively. These results demonstrate also that the use of high pressure is a very valuable tool for synthetic organic chemistry.

Experimental Section

General Aspects. Melting points were taken on a Yanagimoto micro hotstage apparatus and are uncorrected. Infrared spectra on KBr pellets of solids were measured on a JASCO IR-G spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra of $CDCl_3$ solutions with Me_4Si as an internal standard were recorded on a Hitachi R-40 (90 MHz) spectrometer and a JEOL FX-90Q spectrometer, respectively. High pressure experiments were performed in Teflon-brand capsules, reported in our previous paper.[7] Mass spectra were obtained at the Rockefeller University mass spectrometric lab, by using chemical ionization.

Materials. Dichloromaleic anhydride and furan were purchased from Aldrich and purified by sublimation or distillation. Dichloromaleic anhydride melts at 122 °C. 3,4-Dimethoxyfuran and diphenyl- and methylphenylcyclopropenone[8] were prepared according to the literature.

Reaction of Dimethoxyfuran (2) with Dichloromaleic Anhydride (3). A solution of **2** (0.19 g, 1.5 mmol) and **3** (0.25 g, 1.5 mmol) in THF was compressed in a high pressure vessel for 27 h at room temperature. After evaporation of solvent, the residue was chromatographed on silica gel using hexane/ethyl acetate (95/5 and then 50/50 by v/v) as eluent. The yellow fractions gave the crude product **5** (0.26 g, 67%). Recrystallization from dichloromethane gave an analytically pure sample: mp 131–132 °C; IR (KBr) 1765, 1815, 1855 (C=O), 2925, 3120 (CH_3O) cm^{-1}; ^{1}H NMR (90 MHz) 3.81 (s, 3 H, 4.04 (s, 3 H), 7.35 (s, 1 H); ^{13}C NMR (90 MHz) 58.7 (q, CH_3O), 60.7 (q, CH_3O), 125.2 (s, C-1), 128.7 (s, C-6), 130.0 (d, C-5), 145.1 (s, C-3,4), 159.2 (s, C=O), 160.4 (s, C=O). Anal. Calcd. for $C_{10}H_7O_6Cl$: C, 46.44; H, 2.73; Cl, 13.71. Found: C, 46.39, H, 2.67, Cl, 13.87.



Reaction of 2 with Diphenylcyclopropenone (6). A mixture of **1** (0.11 g, 0.86 mmol) and **6** (0.16 g, 0.78 mmol) in toluene (5 mL) was refluxed for 44 h. After evaporation of the solvent, the residue was chromtographed in Florisil successively using hexane–benzene, benzene, and benzene–methyl acetate as the eluents. The product **8** was recrystallized from hexane: yield, 0.058 g (24%); mp 155–156 °C; IR (KBr) 2950, 3000 (OCH_3), 3400 (OH) cm^{-1}; ^{1}H NMR 3.59, 3.87 (s, 3 H × 2, OCH_3), 4.82 (br s, 1 H, OH), 6.87 (s, 1 H, H-4), 7.26–7.63 (m, 10 H, C_6H_5 × 2); ^{13}C NMR 56.6, 60.7 (q, OCH_3), 114.4 (d, C-4), 123–147 (complex, other aromatic carbons). Anal. Calcd for $C_{20}H_{18}O_3$: C, 78.40; H, 5.93. Found: C, 78.38; H, 5.96.

Reaction of 2 with Methylphenylcyclopropenone (9). A mixture of **9** (0.29 g, 2 mmol) and **2** (0.26 g, 2 mmol) in toluene (5 mL) was refluxed for 46 h and worked up as described above, producing 2,3-dimethoxy-5-methyl-6-phenylphenol (**10**) (40 mg, 9%) and the dimer **11** (0.11 g, 10%). **10**: oil; IR (neat) 2940 (OCH_3), 3580 (OH) cm^{-1}; ^{1}H NMR 2.22 (s, 3 H, CH_3), 3.77 and 3.80 (each s, 3 H × 2, OCH_3 × 2), 4.90 (s, 1 H, OH), 6.60 (s, 1 H, 3-H), 7.25–7.45 (m, 5 H, C_6H_5), ^{13}C NMR 9.2 (q, CH_3), 56.4, 60.42 (each q, OCH_3), 111.3 (d, C-4), 119.3 (s, C-5), 122.5 (s, C-6), 127.7, 129.1, 129.2 (each d, CH= of Ph), 137.5 (s, C of 1′Ph), 144.9, 146.6, 147.8 (each s, C-1,2,3). Anal. Calcd for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60. Found: C, 73.69; H, 6.61 **11**: mp 178–179 °C; (lit.[6] mp 169 °C); IR (KBR) 1725 (C=O) cm^{-1}; ^{1}H NMR 2.04 m and 2.25 (each s, 3 H × 2, CH_3), 7.05–7.36 (m, 10 H, C_6H_5 × 2); ^{13}C NMR 9.8 and 10.0 (each q, CH_3 × 2), 73.3 (s, 4a-C), 117–158 (complex, aromatic and olefinic carbons). Anal. Calcd for $C_{20}H_{16}O_2$: C, 83.31; H, 5.59. Found: C, 83.28; H, 5.43.

High Pressure Reaction of 6 (and 9) with 2. A solution of **6** (or **9**) (2 mmol) and **2** (2 mmol) in dichloromethane (8 mL) was reacted at 8 kabr and 55 °C for 48 h. After cooling and release of pressure, the mixture was worked up as described above and **8** and **10** were isolated in 51% and 69% yield, respectively.

Acknowledgment. The support of this work at Kyoto University by Grant-in-Aid for Scientific Research from the Ministry of Education, Science, and Culture (No. 6184007) is gratefully acknowledged.

Registry No. **2**, 58928-51-1; **3**, 1122-17-4; **5**, 103752-32-5; **6**, 886-38-4; **8**, 103752-33-6; **9**, 26307-30-2; **10**, 103752-34-7; **11**, 56764-01-3.

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Communications

Endo-Selective Insertion by Norcaranylidene Carbenoid into the α-C-H Bond of Alkoxides: Evidence of a Hydride Abstraction-Recombination Mechanism

Summary: A hydride abstraction–recombination mechanism in the insertion of the α-C–H bond of alkoxides by norcaranylidene carbenoid is proposed on the basis of the preferential endo stereoselectivity at the carbenic carbon of the insertion products.

Sir: While studies on the stereochemistry of the C–H insertion by carbenes have provided valuable information on the mechanism of the reaction,[1] the major concern has been focused on the stereochemistry of substrates, i.e., whether the insertion proceeds with retention or racemization of configuration. On the other hand, the stereochemistry on the carbenic carbon has received little attention.[2] Herein, we wish to report evidence of the hydride abstraction–recombination mechanism[3] in the insertion by norcaranylidene carbenoid[4] into the α-C–H bond of alkoxides. Our major concern in the present study is the stereochemistry of the carbenic carbon associated with the endo and exo selectivity of the insertion products.

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