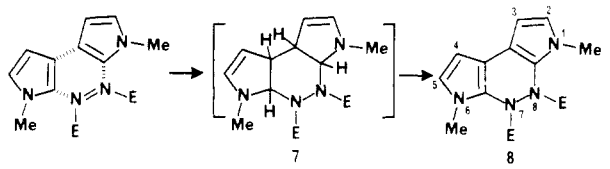
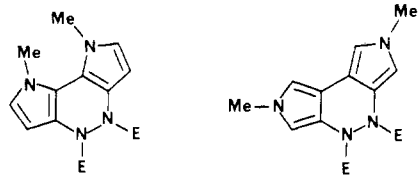
Scheme II



7 8

is inconsistent with structure **10**, which was ruled out at this stage.

Most of the ^{13}C NMR spectrum was assigned in conjunction with DEPT experiments. However, the two peaks at 162.28 and 165.94 ppm provided a clue in distinguishing between the structures **8** and **9**. One of the peaks is due to the carbonyl carbon atom and the other results from a carbon atom in the ring. Such a low field shift of an sp^2 carbon atom may be explained in structure **8** due to bonding to two nitrogen atoms. Similar low field shifts were observed with the pyrrolo[2,3-*d*]pyrimidine system.[12]



9 10

The orientation of the pyrroles and DADC in **8** and the low yield may be explained by a concerted $[_2\pi_s + _2\pi_s + _2\pi_s]$ cycloaddition (Scheme II). DADC has been widely used as a component in various types of addition reactions.[13] However, to our knowledge, a termolecular cycloaddition with DADC has not been reported in the literature. Although the intermediate **7** was not isolated, it seems reasonable to assume that dehydrogenation leading to aromatized pyrrole rings takes place readily. An independent, yet unsuccessful, attempt of preparation of **8** from **3** and **1** in various solvents readily ruled out the possibility of the initial formation of the 1:1 adduct. The yield of **8** from **1b** and DADC in the presence of **3** in ethereal solution did not change appreciably. Similar attempts failed in the presence of either a strong base (*t*-BuOK) or an acid ($AlCl_3$).

The dipyrrolopyridazine **8** can be considered as a carbamate. But unlike to the easy reduction of carbamates to *N*-methyl compounds by $LiAlH_4$,[14] **8** was not reduced under various reaction conditions.

Experimental Section

Melting points were determined on a Fisher Mel-Temp apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 1430 spectrophotometer, and the ultraviolet-visible spectrum was recorded on a Hitachi U-3200 double-beam spectrophotometer. NMR spectra were recorded on a IBM NR/300 NMR spectrometer. Mass spectra were determined on an AEI MS-30 spectrometer at 70 eV and 200 °C. Elemental analyses were performed by M-H-W Laboratories.

Preparation of 2-[*N*,*N*'-Bis(ethoxycarbonyl)hydrazino]-1-methylpyrrole (3), 2,5-Bis[*N*,*N*'-bis(ethoxycarbonyl)hydrazino]-1-methylpyrrole (4), and Diethyl 1,6-Dimethyl-1,6,7,8-tetrahydrodipyrrolo[2,3-*c*:3',2'-*e*]-pyridazine-7,8-dicarboxylate (8). A solution of **1** (dried over molecular sieves and distilled prior to use, 2.00 g, 24.7 mmol) and DADC (8.60 g, 49.4 mmol) in anhydrous ether (dried over $LiAlH_4$ prior to use, 20 mL) was refluxed under N_2 for 10 h. The deep violet precipitate was collected by filteration and was recrystallized from ethanol to give pure **8** (0.36 g, 4%): mp 194 °C dec; IR (KBr) 3180, 2900, 1660 (C=O), 1580, 1235, 1205, 1120, 1090, 1055, 810 cm^{-1}; UV (ethanol) λ_{max} 479 nm infl (ϵ 45 400), 458 (57 500), 326 (6200); ^1H NMR ($CDCl_3$) δ 1.33 (t, 6 H, CH_2CH_3, J = 6.00 Hz), 3.59 (s, 6 H, NCH_3), 4.22 (q, 4 H, OCH_2, J = 6 Hz), an AB pattern centered at 7.33 (2 H, H_3 of pyrrole, J = 6.00 Hz), and 7.50 (2 H, H_2 of pyrrole, J = 6.00 Hz); ^{13}C NMR ($CDCl_3$) ppm 14.46 (CH_3CH_2), 32.39 (NCH_3), 62.13 (OCH_2), 122.65 (C_3), 131.39 (C_2), 131.60 (C_{3a}), 162.28 (C_{8a} or C=O), 165.94 (C=O or C_{8a}); CI-mass spectrum, *m/z* (rel intensity) 333 (8, M + H^+), 287 (9, M^+ - OC_2H_5), 260 (11), 214 (100, M^+ - $COOC_2H_5$, OC_2H_5).

Anal. Calcd for $C_{16}H_{20}N_4O_4$: C, 57.82; H, 6.06; N, 16.85. Found: C, 57.76; H, 6.09; N, 16.70.

The filtrate was evaporated to dryness to give a dark brown residue, which was dissolved in ethanol, decolarized with charcoal, and then left in a refrigerator (4 °C) overnight, giving white precipitate **4** (5.62 g, 53%), mp 170 °C (lit.[8] mp 172-173 °C).

The filtrate after **4** showed three spots on a silica gel TLC plate ($CHCl_3$-MeOH = 4:1, R_f 0.77, **8**; R_f 0.62, **4**; R_f 0.57, **3**). The mixture was chromatographed on a column of silica gel (2.5 cm × 30 cm), collecting ca. 100-mL portion of elutes separately. Each fraction was evaporated and examined by TLC: (1) benzene, 0.5 L; (2) benzene, 0.2 L; (3) benzene-chloroform (9:1), 0.5 L; (4) benzene-chloroform (9:1), 0.5 L; (5) benzene-chloroform (4:1), 0.5 L; (6) benzene-chloroform (1:1), 0.5 L; (7) chloroform, 0.5 L. Fraction 1 gave no organic material. Fractions 2, 3, and 4 gave a trace amount of a mixture of **4** and **8**. Fraction 5 was a trace amount of a mixture of **3** and **4**. Fractions 6 and 7 gave **3** as a gummy solid mass, 2.02 g (32%). It was unsuccessful to obtain crystalline solid from either ethanol or chloroform solution: IR (neat) 3290 (vs, NH), 3100, 2990, 2930, 2850, 1720 (vs, C=O), 1560, 1495, 1400, 1370, 1335, 1230, 1182, 1089, 1050, 980, 910, 760, 715 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.15 (t, 6 H, CH_2CH_3, J = 7.00 Hz), 3.52 (s, 3 H, NCH_3), 4.16 and 4.18 (two overlapping quartets, 4 H, OCH_2, J = 7.00 Hz), 6.05 (m, 2 H, H_3 and H_4 of pyrrole), 6.48 (m, 1 H, H_5 of pyrrole), 7.68 (s, 1 H, NH); EI-mass spectrum, *m/z* (rel intensity) 255 (30, M^+), 196 (82, M^+ - C_2H_5OCO), 150 (100, M^+ - C_2H_5OCO, C_2H_5OH).

Anal. Calcd for $C_{11}H_{17}N_3O_4$: C, 51.76; H, 6.71; N, 16.46. Found: C, 51.66; H, 6.70; N, 16.82.

Reactions of 1b with DADC in Various Solvents. A solution of **1b** (1.00 g, 12.3 mmol) and DADC (4.37 g, 24.7 mmol) in a solvent (15 mL, Table I) was heated in an oil bath at 40 °C (or at 80 °C) for 10 h. The progress of the reaction was examined by TLC and the reaction mixture was chromatographed on a column of silica gel for isolation of **4** and **8**.

Reaction of 1a, 1c, and 1d with DADC in Diethyl Ether. A solution of **1** (10.0 mmol) and DADC (20 mmol) in anhydrous ether (15 mL) was heated at reflux for 10 h. The reaction was monitored by TLC, but only the adduct similar to **4** was isolated as reported previously.[8]

Acknowledgment. Financial support from the Kangweon National University Fund is gratefully acknowledged.

(11) Noland, W. E.; Lee, C. K.; Bae, S. K.; Chung, B. Y.; Hahn, C. S.; Kim, K. J. *J. Org. Chem.* **1983**, *48*, 2488-2490.
(12) Chenon, M.-T.; Pugmire, R. J.; Grant, D. M.; Panzica, R. P.; Townsend, L. B. *J. Am. Chem. Soc.* **1975**, *97*, 4627-4636.
(13) Moody, C. *J. Adv. Heterocycl. Chem.* **1982**, *32*, 1-45.
(14) Piezey, S. S. *Synthetic Reagents*, Vol. 1; Ellis Horwood Ltd.: Chichester, England, 1974; pp 215-216.

An Endo-Selective Ionic Diels-Alder Reaction of α,β-Enone and α,β-Enal Acetals Catalyzed by Electrogenerated Acid

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A variety of modified methods have been proposed for the Diels-Alder cycloaddition to avoid problems such as polymerization and isomerization encountered in these thermal reactions. Lewis acids[1] and certain lanthanide

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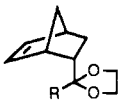
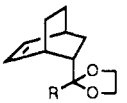
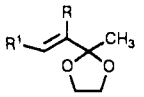
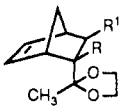
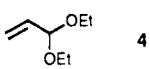
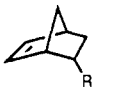
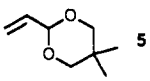
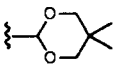
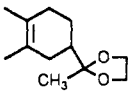
Table I. Results of Ionic Diels–Alder Reactions Catalyzed by Electrogenerated Acid[a]

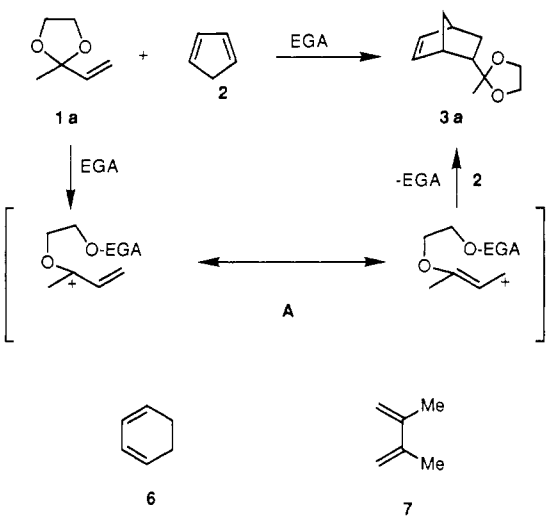
entry	dienophile	diene	product structure	R, R[1]	no.	yield,[b] %	endo/exo ratio[c,d]
1	 **1a**, R = Me	2		Me	**3a**	85	50/1 (3–3.9/1)
2	**1b**, R = Et	2		Et	**3b**	82	8.2/1
3	**1c**, R = H	2		H	**3c**	84	4.8/1 (2.4–2.9/1)
4	**1a**	6		Me	**8a**	85	9.8/1[e]
5	**1b**	6		Et	**8b**	76	7.9/1[e]
6	 **1d**, R = H, R[1] = Me	2		H, Me	**3d**	73	71/1 (1.6–1.8/1)
7	**1e**, R = Me, R[1] = H	2		Me, H	**3e**	30	1/2 (1/1.1–1.2)
8	 **4**	2		$CH(OEt)_2$	**9**	56	4.2/1 (2.4–2.9/1)
9[f]	 **5**	2			**10**	70	4.7/1 (2.4–2.9/1)
10	**1a**	7			**11**	20	

[a] Carried out by electrolysis of dienophile (1 mmol) and diene (2 mmol) at −78 °C in a CH_2Cl_2–$LiClO_4$–Bu_4NClO_4–(Pt) system. [b] Based on isolated products. [c] Unless otherwise noted, endo–exo ratios were determined by GC analyses with column A. [d] Numbers in parentheses are ratios of the corresponding unacetalyzed dienophiles and dienes. These values are taken from ref 10. [e] Determined by GC analyses with column B. [f] Carried out at 0 °C.

complexes[2] are extremely helpful in promoting the reaction of labile dienophiles at low temperature. The high-pressure technique is also useful for unreactive dienes and dienophiles.[3] The Diels–Alder reaction of electron-rich dienophiles are performed through ionization to cation radicals by triarylaminium hexachlorostibnate[4] or 2,4,6-triphenylpyrylium tetrafluoroborate as a sensitizer.[5] However, highly reactive dienophiles such as acrolein and 3-buten-2-one (methyl vinyl ketone) often undergo polymerization even at low temperature. Therefore, employment of acetals or their equivalents as dienophiles is advantageous for both the survival of functionality and the ease of handling.[6] We describe here a convenient procedure for activating the masked dienophiles **1** by catalysis with electrogenerated acid (EG acid)[7] for an ionic [4 + 2]cycloaddition which results in high endo selectivity.[8]

The EG acid catalyzed reactions of enone acetals and dienes were carried out by using platinum electrodes in dichloromethane (CH_2Cl_2) containing lithium perchlorate ($LiClO_4$) and tetrabutylammonium perchlorate (Bu_4NClO_4) as a source of acid catalyst. Thus, the electrolysis of a 1:2 mixture of 3-buten-2-one ethylene acetal (**1a**) and cyclopentadiene (**2**) at −78 °C under a constant applied voltage of 15 V for 0.2 F/mol of electricity (reaction time: about 3.5 h) followed by quenching with triethylamine afforded adducts **3a** in 85% yield (based on **1a**) (Scheme I). Similar electrolysis of a 2:1 mixture of **1a** and **2** as described above gave **3a** in 73% yield (based on **2**). The 50:1 endo/exo ratio of the adducts is based on gas chromatography analyses[9] by comparing with authentic **3a** derived from the Diels–Alder adducts (endo/exo ratio = ca. 4:1) of methyl vinyl ketone and **2** under thermal conditions.[10]

Scheme I



(1) (a) Yates, P.; Eaton, P. *J. Am. Chem. Soc.* **1960**, *82*, 4436. (b) Furuta, K.; Simizu, S.; Miwa, Y.; Yamamoto, H. *J. Org. Chem.* **1989**, *54*, 1481.

(2) (a) Bednarski, M.; Danishefsky, S. *J. Am. Chem. Soc.* **1983**, *105*, 3716. (b) Danishefsky, S.; Bednarski, M. *Tetrahedron Lett.* **1985**, *26*, 2507.

(3) Dauben, W. G.; Krabbenhoft, H. O. *J. Org. Chem.* **1977**, *42*, 282. Reviews: (a) Matsumoto, K.; Sera, A. *Synthesis* **1985**, 999. (b) Uyehara, T.; Yamamoto, Y. *J. Synth. Org. Chem. Jpn.* **1989**, *47*, 321 and references cited therein.

(4) (a) Bauld, N. L. *Tetrahedron* **1989**, *45*, 5307. (b) Bellville, D. J.; Wirth, D. D.; Bauld, N. L. *J. Am. Chem. Soc.* **1981**, *103*, 718.

(5) Mlcoh, J.; Steckhan, E. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 412.

(6) (a) Gassman, P. G.; Singleton, D. A.; Wilwerding, J. J.; Chavan, S. P. *J. Am. Chem. Soc.* **1987**, *109*, 2182. (b) Gassman, P. G.; Chavan, S. P. *Tetrahedron Lett.* **1988**, *29*, 3407. (c) Gassman, P. G.; Riehle, R. J. *Ibid.* **1989**, *30*, 3275.

(7) Torii, S.; Inokuchi, T.; Takagishi, S.; Horike, H.; Kuroda, H.; Uneyama, K. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 2173.

(8) Martin, J. G.; Hiel, R. K. *Chem. Rev.* **1961**, *61*, 537.

(9) Programmed from 80 °C to 270 °C (column A) or 230 °C (column B) with gradient at the rate of 10 °C/min after 10 min at the starting. Endo isomer usually showed longer retention time than the exo isomer.

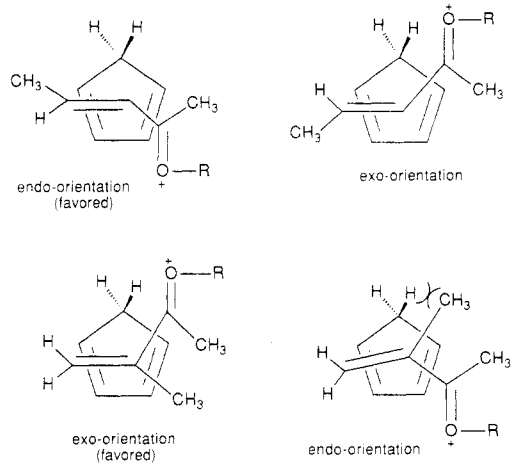


Figure 1. Plausible transition states for an ionic Diels–Alder reaction of enone acetals **1d** and **1e** and cycylopentadiene (**2**).

The [4 + 2] cycloadditions of the β-methyl and α-methyl derivatives **1d** and **1e** proceeded at −78 °C to give the corresponding adducts **3d** and **3e** in 73 and 30% yields, respectively (Table I, entries 6 and 7). In contrast, no appreciable amount of adducts were obtained by reaction of the β,β-dimethyl isomer with **2** at −78 °C to room temperature. Furthermore, the reaction was slightly affected by the kind of acetal protecting moiety. Thus, the ethylene acetal of acrolein **1c** was superior to the diethyl acetal **4** (entries 3 and 8). 2,2-Dimethylpropylene acetal of acrolein **5** was less reactive at −78 °C, and the desired reaction was feasible at 0 °C (entry 9). Other results along with the endo/exo ratio of the adducts are shown in Table I.

As shown in entries 1, 2, 3, 6, 8, and 9, the Diels–Alder reactions of masked dienophiles **1** with cyclopentadiene (**2**) showed generally higher endo selectivities than the thermal ones of the corresponding conjugated enones. These endo/exo ratios of the reactions are strikingly affected by a methyl substituent on olefin function of the masked dienophiles; the *trans*-β-methyl isomer **1d** gave the adducts in the highest endo–exo ratio (71:1), which was 40 times as great as that of the corresponding unacetalized dienophile with **2** under a thermal condition (entry 6). In contrast, the α-methyl isomer **1e** produced the adducts in a 1:2 endo–exo ratio (entry 7).

These dramatic changes in endo–exo ratios can be understood as follows. Cationic species such as A shown in Scheme I is considered to be the reactive intermediate generated from **1** by the action of EG acid.[11] The electron-defficient centers of A act as a strong electron-withdrawing group in the formal [4 + 2] cycloaddition.[12] The interaction of this delocalized cationic species (A) with π-bond system of cyclopentadiene is assumed to occur at first on the β-carbon atom of dienophile.[10,13] Plausible transition states based on these assumptions for the reaction of **1d** and **1e** with cyclopentadiene (**2**) are depicted in Figure 1. The α-methyl group of **1e** would experience a strong steric repulsion from the methylene group of **2** in the endo-oriented transition state, because the steric effect of the α-methyl substituent in the dienophiles is assumed to be greater than that of the acetal protecting group.[10] On the other hand, the β-methyl group of **1d** is less affected by the methylene group of **2** in the endo orientation and the formal [4 + 2] cycloaddition may be favored by the spatial orbital overlap, giving the endo adduct, predominantly.[14]

Since the enone and enal acetals are accessible from the corresponding ketones and aldehydes through (i) acetalization, (ii) bromination, and (iii) the subsequent dehydrobromination with a base,[15] the ionic Diels–Alder reaction of EG acid provides stereoselective access to cyclohexenes bearing acetal substituents, some of which are useful as fragrance compositions.[16]

Experimental Section[18]

***endo*-2-(Bicyclo[2.2.1]hept-5-en-2-yl)-2-methyldioxolane (3a). A Typical Procedure for the Electrochemical Ionic Diels–Alder Reaction.** A mixture of $LiClO_4$ (11 mg, 0.1 mmol) and Bu_4NClO_4 (34 mg, 0.1 mmol) placed in a cylindrical vessel (15-mm diameter and 105-mm height, 10-mL volume) was dried at 100 °C at 0.2 mmHg for 1 h and back flushed with Ar. A CH_2Cl_2 (3 mL) solution containing 3-buten-2-one ethylene acetal[15] (**1a**, 114 mg, 1.0 mmol) and cyclopentadiene (**2**, 132 mg, 2.0 mmol), freshly prepared by cracking of dicyclopentadiene at about 150 °C, was added to the above electrolytes. Two platinum foil electrodes (1.5 × 1.0 cm^2) are immersed in this solution, and the entire mixture was electrolyzed at −78 °C under an applied voltage of 15 V (electric current: 2–3 mA). When 0.2 F/mol of electricity had been passed (about 3.5 h), the reaction was quenched with Et_3N (0.2 mL). The mixture was concentrated under vacuum, and the residue was purified by column chromatography (SiO_2, hexane/AcOEt, 20:1, 50 mL) to give 153 mg (85%) of **3a**, which was analyzed to be a ca. 50:1 endo/exo mixture:[9] bp 71–73 °C (15 mm); IR (neat) 3066, 1574, 1162, 1067, 1038, 874, 727 cm^{-1}; ^1H NMR (500 MHz) δ 0.94 (ddd, 1 H, J = 11.5, 5.6, 2.5 Hz), 1.23 (s, 3 H), 1.25 (d, 1 H, J = 7.9 Hz), 1.36 (dq, 1 H, J = 7.9, 2.1 Hz), 1.81 (ddd, 1 H, J = 11.5, 9.4, 4.0 Hz), 2.42 (ddd, 1 H, J = 9.4, 5.6, 3.1 Hz), 2.78 (br s, 1 H), 2.91 (br s, 1 H), 3.84–3.95 (m, 4 H), 5.93 (dd, 1 H, J = 5.6, 2.9 Hz), 6.11 (dd, 1 H, J = 5.6, 2.9 Hz); ^{13}C NMR (125 MHz) δ 23.90, 28.18, 42.35, 44.16, 47.35, 50.50, 63.96, 64.96, 111.14, 132.54, 135.85. Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.18; H, 9.22.

Physical properties and spectral data of products listed in Table I are as follows.

***endo*-2-(Bicyclo[2.2.1]hept-5-en-2-yl)-2-ethyldioxolane (3b)**: bp 73–75 °C (15 mm); IR (neat) 3066, 1340, 1073, 922, 725 cm^{-1}; ^1H NMR (500 MHz) δ 0.91 (t, 3 H, J = 7.5 Hz), 0.95 (ddd, 1 H, J = 11.4, 5.7, 2.5 Hz), 1.24 (d, 1 H, J = 7.9 Hz), 1.35 (dq, 1 H, J = 7.9, 2.2 Hz), 1.56–1.61 (m, 2 H), 1.80 (ddd, 1 H, J = 11.4, 9.4, 4.0 Hz), 2.47 (ddd, 1 H, J = 9.4, 5.7, 3.2 Hz), 2.76 (br s, 1 H), 2.88 (br s, 1 H), 3.84–3.95 (m, 4 H), 5.93 (dd, 1 H, J = 5.6, 3.0 Hz), 6.10 (dd, 1 H, J = 5.6, 3.0 Hz); ^{13}C NMR (125 MHz) δ 8.12, 28.08, 30.72, 42.20, 43.98, 45.26, 50.36, 64.58, 65.61, 112.92, 132.65, 135.64. Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.47; H, 9.12.

***endo*-2-(Bicyclo[2.2.1]hept-5-en-2-yl)dioxolane (3c)**: bp 61–63 °C (15 mm); IR (neat) 3062, 1932, 1338, 1106, 986, 832 cm^{-1}; ^1H NMR (500 MHz) δ 0.92 (ddd, 1 H J = 12.0, 4.0, 2.5 Hz), 1.24 (d, 1 H, J = 8.5 Hz), 1.40 (dq, 1 H, J = 8.5, 1.5 Hz), 1.87 (ddd, 1 H, J = 12.0, 8.5, 4.0 Hz), 2.19 (ddd, 1 H, J = 8.5, 8.4, 4.0 Hz), 2.82 (br s, 1 H), 2.97 (brs, 1 H), 3.75–3.83 (m, 2 H), 3.92–3.98 (m,

(10) Kobuke, Y.; Fueno, T.; Furukawa, J. *J. Am. Chem. Soc.* **1970**, *92*, 6548.

(11) The Diels–Alder reaction of **1a** and **2**, giving **3a** in 55–80% yields, can be carried out by using the electrochemically prepared triphenylmethyl perchlorate ($TrClO_4$).[17] The EG acid catalyzed Diels–Alder reaction may proceed via a cationic mechanism rather than an electron-transfer chain mechanism.[4,5]

(12) Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 239.

(13) Berson, J. A.; Remanick, A.; Mueller, W. A. *J. Am. Chem. Soc.* **1960**, *82*, 5501.

(14) Berson, J. A.; Remanick, A. *J. Am. Chem. Soc.* **1961**, *83*, 4947.

(15) Byrne, B.; Wengenroth, K. J. *Synthesis* **1986**, 870.

(16) McCloud, D. L.; Schleppnic, A. A. U.S. Patent 3,748,344 (cl. 260-340.7); *Chem. Abstr.* **1973**, *79*, 78225c.

(17) Inokuchi, T.; Kurokawa, Y.; Kusumoto, M.; Tanigawa, S.; Takagishi, S.; Torii, S. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 3739.

(18) All reactions were carried out under an argon atmosphere. Boiling points indicated by an air-bath temperature and melting points are uncorrected. GC analyses were carried out on a "Quadrex" Bond-Fused silica capillary column (column A, methyl silicone; column B, polyethylene glycol 20M: 0.25 mm film thickness, 25 m × 0.25 mm i.d.). ^1H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$. Elemental analyses were performed in our laboratory.

2 H), 4.21 (d, 1 H, J = 8.4 Hz), 5.97 (dd, 1 H, J = 5.7, 2.9 Hz), 6.15 (dd, 1 H, J = 5.7, 3.0 Hz); ^{13}C NMR (125 MHz) δ 28.19, 42.24, 43.09, 44.23, 49.45, 64.72, 64.85, 108.50, 132.43, 137.61.

***endo*-2-(Bicyclo[2.2.2]oct-5-en-2-yl)-2-methyldioxolane (8a)**: bp 81–83 °C (15 mm); IR (neat) 3044, 1149, 1038, 866, 716 cm^{-1}; ^{1}H NMR (500 MHz) δ 1.11–1.16 (m, 1 H), 1.13 (s, 3 H), 1.17–1.25 (m, 2 H), 1.39–1.46 (m, 1 H), 1.48–1.57 (m, 1 H), 1.72 (ddd, 1 H, J = 13.0, 10.0, 3.0 Hz), 1.94 (m, 1 H), 2.52 (br s, 1 H), 2.63 (br s, 1 H), 3.87–3.92 (m, 4 H), 6.16 (t, 1 H, J = 6.8 Hz), 6.21 (t, 1 H, J = 6.8 Hz); ^{13}C NMR (125 MHz) δ 21.93, 27.90, 28.61, 29.94, 30.55, 31.06, 45.68, 63.67, 64.54, 112.20, 132.92, 133.11. Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.26; H, 9.38.

***endo*-2-(Bicyclo[2.2.2]oct-5-en-2-yl)-2-ethyldioxolane (8b)**: bp 86–88 °C (15 mm); IR (neat) 3044, 1156, 1042, 810, 712 cm^{-1}; ^{1}H NMR (500 MHz) δ 0.85 (t, 3 H, J = 7.4 Hz), 1.16 (ddt, 1 H, J = 12.3, 7.4, 2.4 Hz), 1.19–1.26 (m, 2 H), 1.45–1.46 (m, 1 H), 1.47–1.56 (m, 3 H), 1.68 (ddd, 1 H, J = 12.3, 9.5, 3.3 Hz), 2.00 (t, 1 H, J = 8.8 Hz), 2.52 (br s, 1 H), 2.62 (br s, 1 H), 3.89–3.99 (m, 4 H), 6.16 (t, 1 H, J = 6.5 Hz), 6.21 (t, 1 H, J = 6.5 Hz); ^{13}C NMR (125 MHz) δ 7.68, 23.43, 28.01, 28.41, 29.94, 30.18, 30.93, 43.67, 64.99, 65.44, 113.86, 132.88, 133.03. Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 74.67; H, 9.82.

***trans-endo*-2-(3-Methylbicyclo[2.2.1]hept-5-en-2-yl)-2-methyldioxolane (3d)**: bp 76–78 °C (15 mm); IR (neat) 3066, 1152, 1040, 948, 801 cm^{-1}; ^{1}H NMR (500 MHz) δ 1.16 (d, 3 H, J = 7.0 Hz), 1.23 (s, 3 H), 1.36 (dq, 1 H, J = 8.3, 2.7 Hz), 1.43 (m, 1 H), 1.50 (d, 1 H, J = 8.3 Hz), 1.86 (dd, 1 H, J = 5.3, 3.0 Hz), 2.34 (br s, 1 H), 2.85 (br s, 1 H), 3.84–3.95 (m, 4 H), 5.92 (dd, 1 H, J = 5.0, 3.0 Hz), 6.16 (dd, 1 H, J = 5.0, 3.0 Hz); ^{13}C NMR (125 MHz) δ 21.85, 23.85, 36.19, 44.93, 47.24, 49.26, 56.15, 64.07, 64.91, 111.46, 133.67, 136.25. Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.12; H, 9.44.

2-(Methylbicyclo[2.2.1]hept-5-en-2-yl)-2-methyldioxolane (3e): bp 73–75 °C (15 mm); IR (neat) 3064, 1371, 1174, 1044, 951, 710 cm^{-1}; ^{1}H NMR (500 MHz) δ 1.26 (s, 1 H), 1.29 (d, 1 H, J = 3.7 Hz), 1.31 (d, 1 H J = 3.7 Hz), 1.33 (s, 3 H), 1.40 (dd, 1 H, J = 11.6, 2.5 Hz), 1.68 (d, 1 H, J = 8.2 Hz), 2.49 (br s, 1 H), 2.74 (br s, 1 H), 3.80–4.02 (m, 4 H), 6.03 (dd, 1 H, J = 5.4, 2.9 Hz), 6.06 (dd, 1 H, J = 5.4, 2.9 Hz); ^{13}C NMR (125 MHz) δ 21.45, 26.48, 36.32, 36.17, 42.68, 48.42, 51.28, 63.26, 65.13, 113.52, 135.39, 135.69. Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.19; H, 9.34.

***endo*-5-(1,1-Diethoxymethyl)bicyclo[2.2.1]hept-2-ene (9)**: bp 66–68 °C (15 mm); IR (neat) 3062, 1118, 1058, 932, 721 cm^{-1}; ^{1}H NMR (500 MHz) δ 0.80 (ddd, 1 H, J = 11.8, 4.5, 3.0 Hz), 1.16 (t, 3 H, J = 7.5 Hz), 1.23 (q, 3 H, J = 7.5 Hz), 1.32 (d, 1 H, J = 8.0 Hz), 1.39 (d, 1 H, J = 8.0 Hz), 1.83 (ddd, 1 H, J = 11.8, 9.4, 3.8 Hz), 2.42 (ddd, 1 H, J = 9.4, 9.3, 4.5 Hz), 2.78 (br s, 1 H), 2.88 (br s, 1 H), 3.44–3.74 (m, 4 H), 3.87 (d, 1 H, J = 9.3 Hz), 5.96 (dd, 1 H, J = 5.6, 3.0 Hz), 6.15 (dd, 1 H, J = 5.6, 3.0 Hz); ^{13}C NMR (125 MHz) δ 15.38, 15.46, 28.60, 42.22, 42.26, 44.02, 49.37, 60.42, 60.85, 106.31, 132.71, 137.59. Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.48; H, 10.11.

***endo*-2-(Bicyclo[2.2.1]hept-5-yl)-5,5-dimethyl-1,3-dioxane (10)**: mp 71–73 °C; IR (KBr) 3064, 1396, 1112, 1023, 721 cm^{-1}; ^{1}H NMR (500 MHz) δ 0.66 (s, 3 H), 0.84 (ddd, 1 H, J = 11.5, 5.6, 2.5 Hz), 1.16 (s, 3 H), 1.20 (d, 1 H, J = 8.0 Hz), 1.36 (d, 1 H J = 8.0 Hz), 1.81 (ddd, 1 H, J = 11.5, 9.0, 4.0 Hz), 2.30 (ddd, 1 H, J = 9.0, 5.5, 3.2 Hz), 2.77 (br s, 1 H), 2.93 (br s, 1 H), 3.26–3.62 (m, 4 H), 3.71 (d, 1 H, J = 9.0 Hz), 5.90 (dd, 1 H, J = 5.6, 3.0 Hz), 6.11 (dd, 1 H, J = 5.6, 3.0 Hz); ^{13}C NMR (125 MHz) δ 21.86, 23.05, 28.39, 30.10, 42.18, 43.60, 43.62, 49.21, 77.10, 77.28, 106.35, 132.69, 137.51. Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 75.15; H, 9.45.

2-(1,2-Dimethyl-1-cyclohexen-4-yl)-2-methyldioxolane (11): bp 77–79 °C (15 mm); IR (neat) 2984, 2880, 1377, 1151, 1044, 948 cm^{-1}; ^{1}H NMR (500 MHz) δ 1.23–1.33 (m, 2 H), 1.26 (s, 1 H), 1.59 (s, 3 H), 1.61 (s, 3 H), 1.75–2.00 (m, 4 H), 3.87–3.96 (m, 4 H); ^{13}C NMR (125 MHz) δ 18.76, 19.15, 20.90, 24.19, 32.17, 32.98, 43.31, 64.68, 64.72, 111.69, 124.82, 125.34. Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.57; H, 9.98.

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Supplementary Material Available: Spectra and spectral data for compound **3c** (4 pages). Ordering information is given on any current masthead page.

The First Friedel–Crafts Reaction of Nitrobenzene

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It is a widely accepted generalization in chemistry that low selectivity in a reaction implies high reactivity. We were therefore intrigued by the apparent inertness of benzenes with meta-directing substituents, especially the nitro group, toward Friedel–Crafts alkylations, in which the attacking electrophile is R^+.[1-3] Friedel–Crafts alkylations exhibit the lowest selectivity among electrophilic aromatic substitutions,[4] implying an extremely early transition state, and reflecting the power of the alkyl cation as an electrophile. Why then, we wondered, is it possible to, say, nitrate a similarly substituted compound with the weaker electrophile NO_2^+, but not to alkylate it? The mystery is further complicated in light of σ^+ values, which provide a relative measure of the susceptibility of the substrate to electrophilic attack. The higher the σ^+ value, obviously, the lower its reactivity with respect to an attacking electrophile. Yet, some of the polyhalobenzenes, such as pentachlorobenzene, have been alkylated through the Friedel–Crafts reaction, in spite of the fact that their σ^+ values are higher than those of benzenes bearing meta-directing substituents, such as nitrobenzene.[5] The apparent deactivation toward Friedel–Crafts alkylations observed in benzenes with meta-directing substituents therefore stands in direct conflict with expectations based on both the selectivity/reactivity relationship, and σ^+ values. By all indications, these compounds should be inherently reactive toward Friedel–Crafts alkylations.

In fact, a few examples of the Friedel–Crafts alkylation of benzenes with meta-directing groups, including acetophenone, benzonitrile, and benzoic acid and its ester,[6,7] have appeared in the literature, albeit with reportedly very low reactivity. In all of these cases, a large excess of aluminum chloride, rather than the catalytic amount traditionally used, was added. Furthermore, the products obtained were composed almost exclusively of the meta isomer, in stark contrast to the typical selectivity observed in other Friedel–Crafts alkylations. To our knowledge, there are no examples of successful Friedel–Crafts alkylations of benzenes with meta-directing substituents in which only a catalytic amount of $AlCl_3$ was used. We

(1) Olah, G. A. *Friedel-Crafts and Related Reactions*; Interscience Publishers: New York, 1963; Vol. 1, p 34.
(2) March, J. *Advanced Organic Chemistry*, 2 ed.; McGraw-Hill: New York, 1977; p 487.
(3) Morrison, R. T.; Boyd, R. N. *Organic Chemistry*, 4 ed.; Allyn and Bacon: Boston, 1983; p 636.
(4) Stock, L. M.; Brown, H. C. In *Advanced Physical Organic Chemistry*; Academic: London, 1963; Vol. 1, p 50.
(5) Riera, J.; Castaner, J.; Armet, O.; Rovira, C. *An. Quim.* **1986**, *82C*, 268.
(6) Baddeley, G. *J. Chem. Soc.* **1949**, S 229.
(7) Campbell, B. N., Jr.; Spaeth, E. C. *J. Am. Chem. Soc.* **1959**, *81*, 5933–5936.

0022-3263/90/1955-3961$02.50/0