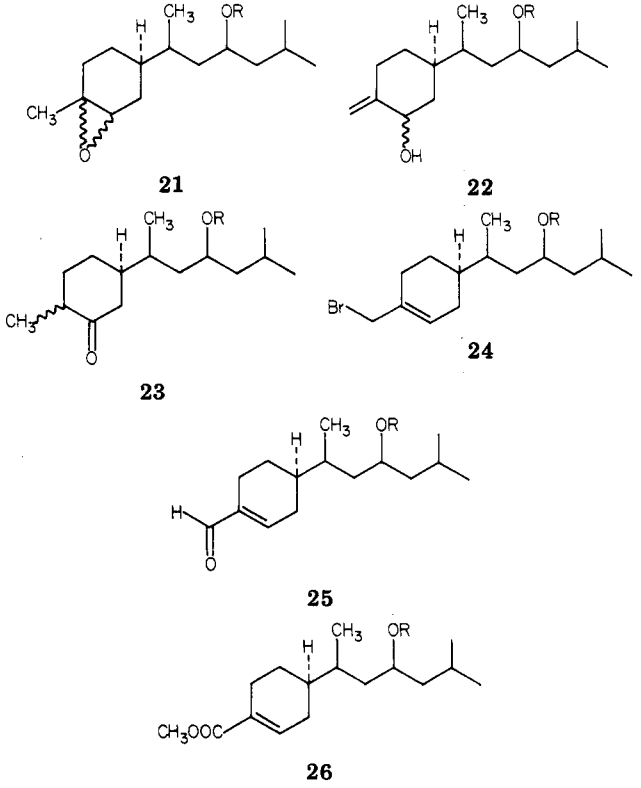
propanol (1:2:2 by volume) by dropwise addition of the bromides in THF at 22 °C followed by warming (40–50 °C, 1 h).[11] Finally oxidation to the methyl esters **26** was achieved with manganese dioxide in the presence of sodium cyanide–acetic acid (22 °C, 12 h, 87%),[12] and desilylation with tetra-*n*-butylammonium fluoride (dry THF at reflux, 7 h, 88%) afforded the natural products.[13]



21 **22** **23** **24** **25** **26**

Thus, the major adducts from condensation of sulfoxides **7** and **8** each display the 1,3-substituents in an anti relationship (as illustrated in the extended conformations). Sulfide **9** led to synthesis of (+)-juvabiol (**1**) and minor adduct **10** gave (+)-isojuvabiol (**2**), whereas (+)-epijuvabiol (**3**) was obtained from sulfoxide **14** and (+)-isoepijuvabiol (**4**) from **13**. We anticipate the feasibility of significant improvement of stereoselectivity in α-sulfinyl carbanion condensations. Further studies are underway.

Acknowledgment. We are most grateful to John F. Manville, Centre de Recherche Forestierte du Pacifique, Victoria, Canada, for samples of (+)-juvabione, (+)-juvabiol, and (+)-isojuvabiol. Acknowledgement is made to donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

(11) Montavon, M.; Lindlar, H.; Marbet, R.; Rüegg, R.; Ryser, G.; Saucy, G.; Zeller, P.; Isler, O. *Helv. Chim. Acta* **1957**, *40*, 1250.

(12) Corey, E. J.; Gilman, N. W.; Ganem, B. E. *J. Am. Chem. Soc.* **1968**, *90*, 5616.

(13) The synthetic substances **1** and **2** were identical in all respects, including ^{13}C NMR, by comparison to samples of (+)-juvabiol and (+)-isojuvabiol. Data for compounds **3** and **4** were identical with spectroscopic information published for (+)-epijuvabiol and (+)-isoepijuvabiol, respectively (see ref 2). Juvabiol (**1**): $[\alpha]^{23}_D$ +50.0° (*c* 0.15, EtOH). Isojuvabiol (**2**): $[\alpha]^{23}_D$ +41.5° (*c* 0.137, EtOH). Epijuvabiol (**3**): $[\alpha]^{23}_D$ +24.0° (*c* 0.25, EtOH). Isoepijuvabiol (**4**): $[\alpha]^{23}_D$ +45.6° (*c* 0.16, EtOH).

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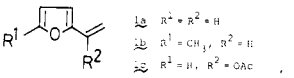
High-Pressure Diels–Alder Reactions of Vinylfurans[1]

Summary: The Diels–Alder reactions of vinylfurans with dimethyl acetylenedicarboxylate and dimethyl maleate very nicely proceed under the conditions of 15 kbar and 30 °C in dichloromethane.

Sir: 2-Vinylfuran has two alternative diene systems, and it is known that the conjugated system involving the exocyclic double bond is more reactive than the furan ring system itself (Scheme I).[2] Under conventional conditions, however, the reported yields of the adducts are extremely poor even after long reaction times.[3,4]

One of the most powerful features of high-pressure reactions is to highly accelerate the rate of reactions having a large negative activation volume under thermally mild conditions (usually at *room temperature*).[5] So we have investigated the Diels–Alder reactions of vinylfurans (**1**)



with dimethyl acetylenedicarboxylate (**2**) and dimethyl maleate (**3**) at 15 kbar and 30 °C in dichloromethane and found that the yields are considerably improved.[6] The results are summarized in Table I.[7]

In all of the reactions with **2**, benzofurans, which would be formed by the aromatization of the intermediate cycloadducts, were obtained as main products without being accompanied by 7-oxabicyclo[2.2.1]hepta-2,5-diene deriv-

(1) High-Pressure Organic Chemistry. 6. Part 4: Kotsuki, H.; Nishizawa, H. *Heterocycles* **1981**, *16*, 1287. Part 5: Kotsuki, H.; Nishizawa, H.; Ochi, M.; Matsuoka, K. *Bull. Chem. Soc. Jpn.*, in press.

(2) Acheson, R. M. "An Introduction to the Chemistry of Heterocyclic Compounds", 3rd ed.; Wiley: New York, 1976; p 136.

(3) Davidson, W. J.; Elix, J. A. *Aust. J. Chem.* **1973**, *26*, 1059 and references cited therein. For instance, the reported yield of the adduct **4** from **1a** and **2** is 5% in the reaction at 80 °C for 24 h or at room temperature for 4 days.

(4) For our intramolecular approach to this chemistry, see: Kotsuki, H.; Kawamura, A.; Ochi, M.; Tokoroyama, T. *Chem. Lett.* **1981**, 917.

(5) For recent reviews, see: Asano, T.; le Noble, W. J. *Chem. Rev.* **1978**, *78*, 407. Osugi, J., et al. *Kagaku Sosetsu* **1979**, *No. 22*, 157. Matsumoto, K.; Uchida, T.; Acheson, R. M. *Heterocycles* **1981**, *16*, 1367. Isaacs, N. S. "Liquid Phase High Pressure Chemistry"; Wiley: New York, 1981.

(6) For a description of our high-pressure apparatus and general procedure for high-pressure reactions, see: Kotsuki, H.; Nishizawa, H.; Kitagawa, S.; Ochi, M.; Yamasaki, N.; Matsuoka, K.; Tokoroyama, T. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 544.

(7) Physical and spectral data are as follows. **4**: mp 66–67 °C (lit.[3] mp 64–66 °C). **5**: mp 71–73 °C; ν_{max} ($CHCl_3$) 1720, 1600 cm^{-1}; λ_{max} (EtOH) 229 nm (ϵ 19600), 252 (5400), 306 (3100). ^1H NMR ($CDCl_3$) δ 2.45, 3.86, 3.90 (each 3 H, s), 6.58 (1 H, br s), 7.41, 7.58 (each 1 H, d, J = 9 Hz). **6**: mp 85–87 °C; ν_{max} ($CHCl_3$) 1775, 1730 (sh), 1630, 1600 cm^{-1}; λ_{max} (EtOH) 224 nm (ϵ 30900), 258 (7500), 296 (3800); ^1H NMR (CCl_4) δ 2.36, 3.84, 3.87 (each 3 H, s), 7.00 (1 H, d, J = 2 Hz), 7.43 (1 H, s), 7.66 (1 H, d, J = 2 Hz). **7**: mp 89–90 °C; ν_{max} ($CHCl_3$) 1720, 1620, 1545 cm^{-1}; λ_{max} (EtOH) 220 nm (ϵ 27000), 238 (21000), 299 (18000); ^1H NMR (CCl_4) δ 3.77, 3.87 (each 3 H, s), 3.89 (6 H, s), 6.91 (1 H, s), 6.95 (1 H, d, J = 2 Hz), 7.65 (1 H, s), 7.75 (1 H, d, J = 2 Hz). **8** (as a tetrahydro derivative): mp 51–52 °C; ν_{max} ($CHCl_3$) 1740 cm^{-1}, ^1H NMR (CCl_4) δ 0.96 (3 H, t, J = 8 Hz), 1.2–1.9 (4 H, m), 1.74 (2 H, q, J = 8 Hz), 2.81, 3.05 (each 1 H, d, J = 10 Hz), 3.54, 3.56 (each 3 H, s), 4.92 (1 H, d, J = 4 Hz). **9** (X = OOH): mp 92–95 °C; ν_{max} ($CHCl_3$) 3400, 1740, 1500 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.44 (1 H, ddd, J = 14, 12.5, 4 Hz), 2.81 (1 H, ddd, J = 14, 3, 2 Hz), 3.17 (1 H, ddd, J = 12.5, 6, 3 Hz), 3.66, 3.72 (each 3 H, s), 4.07 (1 H, d, J = 6 Hz), 5.08 (1 H, dd, J = 4, 2 Hz), 6.40 (1 H, d, J = 2 Hz), 7.37 (1 H, d, J = 2 Hz), 8.26 (1 H, s). **10**: mp 68–72 °C; ν_{max} ($CHCl_3$) 1730, 1665, 1570 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.85 (3 H, dd, J = 3, 1.5 Hz), 2.1–2.9 (4 H, m), 3.51 (1 H, dd, J = 6, 3 Hz), 3.61, 3.69 (each 3 H, s), 4.87 (1 H, m), 5.09 (1 H, ddd, J = 7, 3.5, 1.5 Hz). **12**: oil; ν_{max} (film) 1740, 1440, 1200 cm^{-1}; ^1H NMR(CCl_4) δ 2.08 (3 H, s), 3.26 (1 H, d, J = 10 Hz), 3.7–3.5 (1 H, m), 3.54, 3.56 (each 3 H, s), 5.01 (1 H, m), 5.05, 5.21 (each 1 H, d, J = 2 Hz), 6.41 (1 H, dd, J = 6, 2 Hz), 6.50 (1 H, d, J = 6 Hz). **13**: oil; ν_{max} (film) 1740, 1440, 1200 cm^{-1}; ^1H NMR (CCl_4) δ 2.12 (3 H, s), 2.67, 2.94 (each 1 H, d, J = 9 Hz), 3.52, 3.59 (each 3 H, s), 5.27 (2 H, s), 5.33 (1 H, br s), 6.41 (2 H, s).

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Scheme I

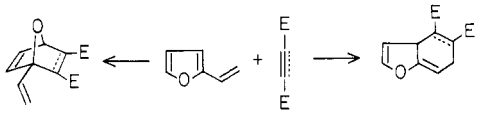


Table I. Diels–Alder Reactions of Vinylfurans (CH_2Cl_2, 15 kbar, 30 °C)[a]

vinylfuran	dienophile	time, h	products (% yield)[b]
1a	2	6[c]	4 (33)
1b	2	6[c]	5 (28)
1c	2	6	6 (20), 7 (25)
1c	2[d]	6	6 (16), 7 (36)
1a	3	24	8[e] (5), 9 (3)
1b	3	8	10 (48)[f]
1c	3	16	12[e] + 13[e] (50)[g]

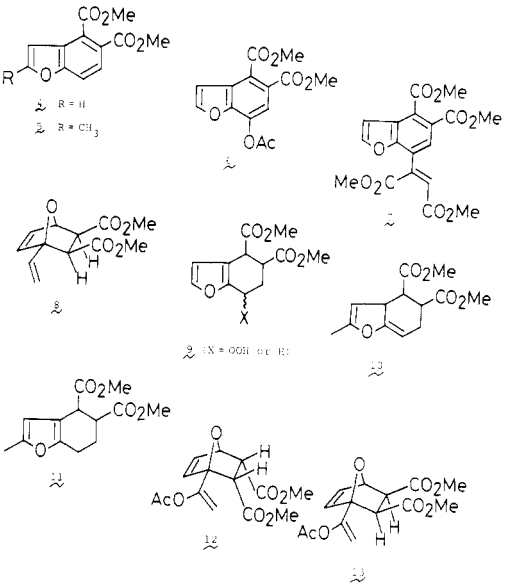
[a] All the reactions were performed at a concentration of 3 M for the reactants. The structures of all adducts were confirmed by elemental analysis and NMR, IR, and UV spectra. [b] Isolated yields after short column chromatography on neutral alumina or rapid preparative TLC on silica gel unless otherwise noted. [c] The yields could not be improved even after reaction for 24 h. [d] The molar ratio of 1c to 2 is 1:2. [e] These adducts were highly unstable at room temperature, so the elemental analyses were performed after hydrogenation with 10% Pd/C in AcOEt. [f] The yield estimated by ^{1}H NMR was 77%; see text. [g] The yield by ^{1}H NMR.

atives derived from the reaction of the furan ring diene with the dienophile.[8] The reaction of **1c** with **2** gave the 1:2 adduct **7** in addition. The formation of a similar product has been reported in the reaction of **1a** with **2** at an elevated temperature[3] and is explained by "ene" addition of a second molecule of **2** to the adduct and subsequent elimination of acetic acid. As expected, the yield of **7** was raised when the molar ratio of **2** to **1c** was increased.

In the case of the reactions with **3**, the adducts were first formed at high pressure.[9] And a remarkable difference of the reactivity between each vinylfuran was recognized. **1a** afforded the adducts **8** and **9** in comparable amounts, which represented two alternative modes of the reaction. The stereochemistry of **8** was determined as having an exo configuration from the ^{1}H NMR analysis.[7] **9** (X = OOH) is probably formed by "ene" addition with atmospheric oxygen to the initially formed adduct. Anal. Calcd for $C_{12}H_{14}O_7$: C, 53.33; H, 5.22. Found: C, 53.47; H, 5.26. **1b** gave almost a single product as revealed by the ^{1}H NMR spectrum of the crude reaction mixture and from which **10** could be successfully crystallized in 48% yield as an ether-insoluble substance.[10] Expectedly, **10** was extremely unstable and spontaneously isomerized to **11** on standing at room temperature. **1c** afforded cleanly the endo and exo adducts **12** and **13** in an approximate ratio of 2:1. No adducts derived from the reaction of the conjugated diene system containing the exocyclic double bond were obtained. Thus, the experiments demonstrated that the diene system involving the exocyclic double bond in **1b** was highly reactive, in contrast to **1c**. These differences may be attributed to the inductive and resonance effects of the substituents; i.e., the methyl group is electron donating ($\mathcal{F}$ = –0.052 and $\mathcal{R}$ = –0.141) and the acetoxy group is electron withdrawing ($\mathcal{F}$ = 0.679 and $\mathcal{R}$ = –0.071).[11]

(8) Unidentified complex byproducts were also formed.
(9) No detectable amounts of the adduct were obtained in the reaction between **1a** and **3** at reflux in toluene for 20 h.
(10) Purification by chromatography resulted in a complete decomposition.

Chart I



All attempted reactions between vinylfurans (**1**) and other dienophiles such as methyl acrylate and α-chloroacrylonitrile under same conditions were unsuccessful due to considerable polymerization. We are continuing our investigation to elucidate the scope of these reactions.

Acknowledgment. We thank Professor T. Tokoroyama, Osaka City University, for his helpful discussion and continuous encouragement.

Registry No. **1a**, 1487-18-9; **1b**, 10504-13-9; **1c**, 41019-60-7; **2**, 762-42-5; **3**, 624-48-6; **4**, 19665-37-3; **5**, 79816-77-6; **6**, 79816-78-7; **7**, 79816-79-8; **8**, 79816-80-1; **8** (tetrahydro), 79816-81-2; **9**, 79816-82-3; **10**, 79816-83-4; **11**, 79816-84-5; **12**, 79816-85-6; **13**, 79816-86-7.

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Electrochemical Reductive Cyclizations to the β-Position of Cyclic α,β-Unsaturated Ketones. Formation of Fused Ring Systems[1]

Summary: The electrochemical reductive cyclization of certain conjugated cyclohexenone sulfonate esters has been shown to be a synthetically useful method for the preparation of bicyclo[4.3.0]nonan-3-ones and bicyclo[4.1.0]-heptan-3-ones.

Sir: The recent report of a mechanistic study of the electrochemical reduction of **1**[2] has prompted us to report our synthetically useful findings on the alkylation of the β-position of α,β-unsaturated ketones by electrochemical methods. In 1965, Stork and co-workers demonstrated[3]

(1) Taken in part from: Rasmy, O. M.S. Thesis, University of Minnesota, 1978.
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0022-3263/81/1946-5455$01.25/0