transform instrument. High-resolution mass spectra (HRMS) were determined on a Kratos mass spectrometer.

General Procedure for the Diels-Alder Reaction. A solution of the diene (1-2 equiv) and quinone sulfoxide (1 equiv) was dissolved in the solvent (1 M with regard to the sulfoxide) and stirred at the temperature specified below until TLC indicated that the sulfoxide was gone. The solvent was removed in vacuo and the crude product was chromatographed on silica gel to afford pure product.

Entries 1-3, 7, and 8: refluxing carbon tetrachloride. Entries 4 and 5: refluxing toluene. Entry 6: carbon tetrachloride at room temperature.

1-Acetoxy-4-methyl-1,4-dihydro-9,10-anthraquinone: NMR ($CDCl_3$) δ 1.28 (d, J = 7 Hz, 3 H), 1.98 (s, 3 H), 3.40-4.04 (m, 2 H), 4.24 (d, J = 4 Hz, 2 H), 5.70-5.92 (m, 2 H), 7.52-7.80 (m, 2 H), 7.84-8.12 (m, 2 H); IR ($CDCl_3$) 1740, 1668, 1231, 1205, 915 cm^{-1}; mass spectrum, m/e 208, 224, 235, 266 ($M^+ - CH_2O$; HRMS for $C_{17}H_{14}O_3$ requires 266.09429, found 266.09398.

Anthracene adduct: NMR ($CDCl_3$) δ 6.03 (s, 2 H), 7.00-7.30 (m, 4 H), 7.35-7.82 (m, 4 H), 7.90-8.30 (m, 4 H); mass spectrum, m/e 334.

Methoxyfuran adduct: 300-MHz NMR ($CDCl_3$) δ 3.96 (s, 3 H), 5.48 (d, J = 2 Hz, 1 H), 7.06 (s, 1 H), 7.62 (d, J = 2 Hz, 1 H), 7.68-7.78 (m, 2 H), 8.03-8.15 (m, 2 H); mass spectrum, m/e 189, 204, 239, 254; HRMS for $C_{15}H_{10}O_4$ requires 254.0579, found 254.0573.

3-Hydroxy-1-methoxy-9,10-anthraquinone: 300-MHz NMR ($CDCl_3$) δ 3.92 (s, 3 H), 6.78 (s, 1 H), 7.25 (s, 1 H), 7.66-7.82 (m, 2 H), 8.03-8.18 (m, 2 H), 10.75 (br s, 1 H); mass spectrum, m/e 139, 152, 168, 197, 208, 225, 237, 254. The ^{13}C NMR spectrum was identical with that reported in ref 10 for the known compound.

Acknowledgment. We thank the National Institutes of Health (GM 34342) for generous support of this work.

Registry No. **A**, 99397-95-2; **B**, 6932-37-2; **C**, 99416-46-3; (E)-$H_2C{=}CHCH{=}CHOAc$, 35694-20-3; (E)-$H_2C{=}C(CH_3)CH{=}CHOAc$, 52062-24-5; (E,E)-$MeCH{=}CHCH{=}CHCH_2OAc$, 57006-69-6; $H_2C{=}C(OSiMe_3)CH{=}C(OMe)_2$, 61539-61-5; $H_2C{=}CHCH{=}CH_2$, 106-99-0; 2-(methylsulfinyl)naphthoquinone, 91136-55-9; 2-(methylsulfinyl)-8-hydroxynaphthoquinone, 99397-94-1; anthracene, 120-12-7; 2-methoxyfuran, 25414-22-6; anthraquinone, 84-65-1; 2-methylanthraquinone, 84-54-8; 3-hydroxy-1-methoxyanthraquinone, 28504-24-7; 1-hydroxyanthraquinone, 129-43-1; 1,4-dihydro-5-hydroxyanthraquinone, 99397-96-3.

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[10] Berger, Y.; Castonguay, A.; Brassard, P. *Org. Magn. Reson.* **1980**, *14*, 103.

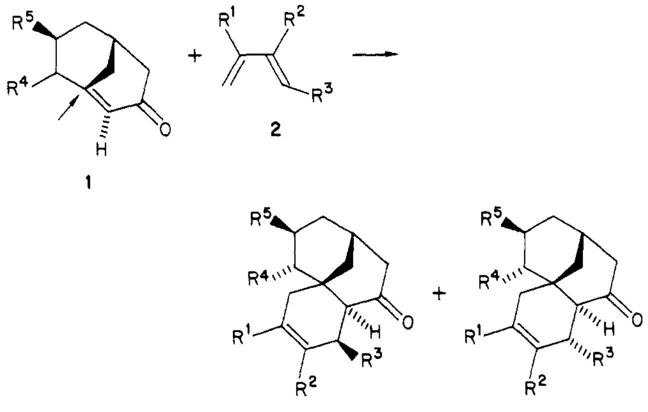
Communications

Diels-Alder Reactions of Bridgehead Enones

Summary: Diels-Alder reactions of bridgehead enone 1 with activated dienes proceed in excellent yields.

Sir: The Diels-Alder reaction and the Michael addition reaction represent two of the most versatile tools of the modern organic chemist. Both reactions employ unsaturated carbonyl compounds.[1] While both cyclic and acyclic unsaturated ketones have been extensively used, the subclass wherein either the α or β carbon of the enone is at a bridgehead has been little explored. House and coworkers, in their classic studies on bridgehead enones of various ring sizes, have identified several significant points.[2] Of interest in synthetic planning is that an enone such as 1 is too reactive to be isolated. Even substitution at the α carbon atom with a methyl group does not permit isolation. Using Allinger's MMP1 molecular mechanics program for conjugated systems, House has calculated probable geometries for 1. He has reported an average twisting deformation of the enone double bond of approximately 25° and an inherent strain energy of approximately 21 kcal/mol: House and co-workers have also investigated some characteristic reactions of the in situ derived bridgehead enones. In the presence of nucleophiles such as malonate anions or alkoxides, Michael addition reactions occur readily. However, in order to obtain good yields in Diels-Alder reactions with furan, it was necessary to use furan as the solvent. Recently Bestmann has generated enones such as 1 in ethanol and examined their chemistry.[3] Magnus has utilized a bridgehead enone in an elegant synthesis of kopsanone.[4] To the best of our knowledge, this represents the first use of bridgehead enones in natural products synthesis. Our research group has recently employed an in situ derived bridgehead enone in two direct syntheses of racemic lycopodine.[5]

Scheme I



Information regarding regio- and stereospecificity of Diels-Alder reactions of 1 with various dienes is essential, since both House and Magnus have examined only symmetrical dienes. Additionally, reaction conditions must be identified such that only a slight excess of diene is required for a successful reaction. Molecular models indicate that the Diels-Alder reaction will occur only from the outer face of the twisted enone system. Since the enone would be expected to be polarized such that the β

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[1] Michael addition: House, H. O. "Modern Synthetic Reactions"; Benjamin: Menlo Park, CA; 1972; pp 595-623. Diels-Alder reaction: Desimoni, G. "Natural Products Synthesis"; American Chemical Society: Washington, DC, 1983; ACS Monograph Series.

[2] House, H. O.; Outcalt, R. J.; Haack, J. L.; VanDerveer, D. *J. Org. Chem.* **1983**, *48*, 1654 and references therein.

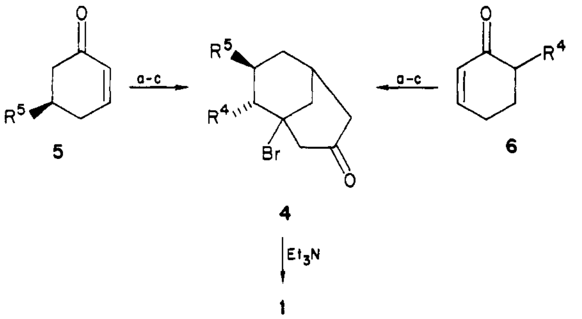
[3] Bestmann, H. J.; Schade, G. *Tetrahedron Lett.* **1982**, *23*, 3543.

[4] Magnus, P.; Gallagher, T.; Brown, P.; Huffman, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 2105.

[5] Kraus, G. A.; Hon, Y. S. *J. Am. Chem. Soc.* **1985**, *107*, 4341.

0022-3263/86/1951-0116$01.50/0

Scheme II[a]



[a] (a) $CH_3COCH_2CO_2Et$, NaOEt; (b) KOH; (c) PBr_3.

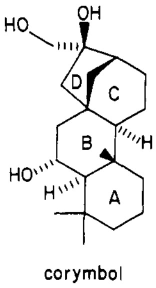
Table I. Diels–Alder Reactions of Bridgehead Enones

$1 + 2 \rightarrow$ 3-exo

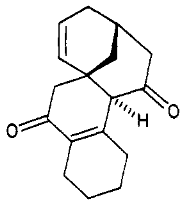
entry	R^1	R^2	R^3	R^4	R^5	% yield	cmpd
1	$OSiMe_3$	$-(CH_3)_4-$		PhS	H	97	**8**
2	$OSiMe_3$	$-(CH_3)_4-$		H	CH_3	52	**9**
3	H	H	H	PhS	H	41	**10**
4	$OSiMe_3$	H	OCH_3	PhS	H	98	**11**
5	H	H	OAc	PhS	H	63	**12**
6	H	H	OAc	H	CH_3	55	**13**

carbon atom would have a partial positive charge, a regioselective reaction should result. It is not clear how the exo/endo ratio will be affected by the nonplanarity of the enone. While House has determined an exo/endo ratio of 2.3 with furan, literature data indicate that furan often exhibits a slight exo preference, even with dienophiles which afford largely endo adducts with other dienes.[6] Adducts may be generated by endo (**3**-endo) or exo (**3**-exo) modes of addition (Scheme I).

The bromo ketone precursors to the bridgehead enones were constructed by using literature procedures.[7] In both cases the substituted cyclohexenones were treated with ethyl acetoacetate and a slight excess of base. Subsequent decarbalkoxylation produced hydroxy ketones by using phosphorus tribromide in benzene. Both bromo ketones were recrystallized and were only one diastereomer as evidenced by ^{13}C NMR. The structure of **4** (R_4 = SPh, R_5 = H) was determined by X-ray crystallography.[8] The bridgehead enones were generated by adding 2 equiv of triethylamine to a solution of **4** (1 equiv) and the diene (1.5 equiv) in methylene chloride at 0 °C (Scheme II). Table I indicates that dienes bearing electron-donating groups afforded high yields of Diels–Alder adducts. The ^{13}C NMR spectrum of each purified adduct showed that the reactions were highly stereoselective. In each case in Table I only a single set of resonances was observed: For adducts **11** and **12**, decoupling experiments gave a coupling constant of 7 Hz for the two adjacent methine protons. This value is consistent with a trans diaxial relationship and therefore an exo adduct. Additional evidence for the exo mode of addition was provided by an X-ray crystal structure of the acid hydrolysis product of **8**.



corymbol



7

Adduct **8** represents an attractive intermediate for the synthesis of members of the kaurane family of diterpenes.[9] One member of this family, corymbol, is shown. The key transformation involves the introduction of the tetrasubstituted enone. As illustrated in eq 1, the requisite enone

$$8 \xrightarrow{\text{a–c}} 7 \tag{1}$$

(a) $Pd(OAc)_2$; (b) $NaIO_4$, MeOH; (c) 180 °C

was constructed from **8** by oxidation of the enol silyl ether with palladium acetate and benzoquinone.[10] Reduction of the ketone prior to silyl ether oxidation afforded mostly the isomeric enone, as evidenced by a vinyl hydrogen absorption at 6.9 ppm in the spectra.[11] Sulfide oxidation with sodium metaperiodate in methanol at ambient temperature followed by sulfoxide elimination at 180 °C produced ketone **7** in approximately 60% overall yield from adduct **8**. Ketone **7** contains the appropriate functionality for eventual conversion to corymbol. Importantly, ketone **7** also permits the introduction, via conjugate addition, of a hydroxymethyl group, which is common to the more biologically active members of this class.[12]

Overall, the dissection A + CD → ABCD constitutes an entirely new approach to the synthesis of diterpenes bearing a bicyclo[3.2.1]octane subunit. The convergent approach plus the flexibility and good overall yields combine to make this synthetic route a significant one.

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(6) House, H. O.; DeTar, M. B.; VanDerveer, D. *J. Org. Chem.* **1979**, *44*, 3793.

(7) For synthesis, see: ref 5 and also House, H. O.; Outcalt, R. J.; Cliffton, M. D. *J. Org. Chem.* **1982**, *47*, 2413.

(8) Ketone 1 (R_4 = PhS, R_5 = H) was produced as a mixture of diastereomers. The major isomer was used in this study.

(9) Corymbol: Perezamador, M. C.; Jimenez, F. G. *Tetrahedron* **1966**, 1937.

(10) Ito, Y.; Hirao, T.; Saegusa, T. *J. Org. Chem.* **1978**, *43*, 1011.

(11) The reduction with sodium borohydride in ethanol afforded largely one diastereomer. It was tentatively assigned the β configuration on the basis of steric hindrance on the top face of the molecule.

(12) For example, the trichorabdals: Node, M.; Sai, M.; Fujita, E.; Fuji, K. *Heterocycles* **1984**, *22*, 1701.

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2 + 3 Dipolar Cycloadditions of a Monomeric Thioaldehyde

Summary: Thiopivaldehyde is a highly reactive dipolarophile toward nitrones, nitrile *N*-oxides, diazo compounds, azomethine *N*-imines, thiomunchnones, and sydnones.

Sir: Thioketones are recognized as highly reactive dipolarophiles[1] and even higher reactivity would be expected for thioaldehydes.[2,3] The recent preparation of reasonably

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(1) For example: (a) Gotthard, H.; Huisgen, R.; Knorr, R. *Chem. Ber.* **1968**, *101*, 1056. (b) Schönberg, A.; Fateen, A. E. K.; Samous, A. E.-M-A. *J. Am. Chem. Soc.* **1957**, *79*, 6020. (c) Middleton, W. J. *J. Org. Chem.* **1969**, *34*, 3201. (d) Black, D. St. C.; Watson, K. G. *Aust. J. Chem.* **1973**, *26*, 2491. (e) Katada, T.; Eguchi, S.; Sasaki, T. *J. Chem. Soc., Perkin Trans. 1* **1984**, 2641.

(2) Diazoalkanes + transient thioaldehyde: Burri, K. F.; Paioni, R.; Woodward, R. B., unpublished results. We thank Dr. Burri for informing us of this work.

(3) Nitronate ester + transient thioaldehyde: Vedejs, E.; Perry, D. A. *J. Org. Chem.* **1984**, *49*, 573.