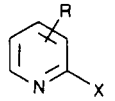
diffuse out of the tight ion pair cage, so that the polarized solvent molecules will be the ones to react with the *N*-fluorocarbocation. It should be noted that while AcOF does not react with the chlorinated or the brominated solvents to produce free or anionic halogen, it oxidizes compounds such as MeI or CH_2I_2 to iodine and therefore no iodination of the pyridine ring could be achieved.[15]



4, R = 4-Me; X = Cl
5, R = 4-Me; X = OAc
6, R = 3-Cl; X = Cl
7, R = 3-Cl; X = Br
8, R = 3-COPh; X = Cl
9, R = H; X = OMe
10, R = H; X = OEt

While routes for direct halogenation, difficult as they might be, do exist, no direct methods for alkoxylation are known. Ethers are usually prepared through already derivatized rings. Acetyl hypofluorite provides an excellent opportunity to close this gap. Replacing the halogenated solvents with primary alcohols such as MeOH or EtOH resulted in an about 70% yield of 2-methoxy- and 2-ethoxypyridine (**9** and **10**), respectively, again accompanied by 15% to 20% of the acetoxylated derivative **2**.

In conclusion this work shows that elemental fluorine, that most neglected of reagents, can perform indirectly some very selective reactions leading to difficult to obtain fluorine-free compounds under incomparably mild conditions.

Acknowledgment. We thank the Fund for Basic Research administrated by the Israel Academy of Science and Humanities for supporting this research.

Registry No. **1**, 109-09-1; **1** (X = H), 110-86-1; **2**, 3847-19-6; **3**, 109-04-6; **4**, 3678-62-4; **4** (X = H), 108-89-4; **5**, 108168-80-5; **6**, 2402-77-9; **6** (X = H), 626-60-8; **7**, 96424-68-9; **8**, 80099-81-6; **8** (X = H), 5424-19-1; **9**, 1628-89-3; **10**, 14529-53-4; AcOF, 78948-09-1; $CH_2(Cl)_2$, 75-09-2; *t*-BuCl, 507-20-0; $CH_2(Br)_2$, 74-95-3; MeBr, 74-83-9; MeOH, 67-56-1; EtOH, 64-17-5.

(15) For similar behavior of F_2 with halogenated compounds, see: Rozen, S.; Brand, M. *J. Org. Chem.* **1981**, *46*, 733.

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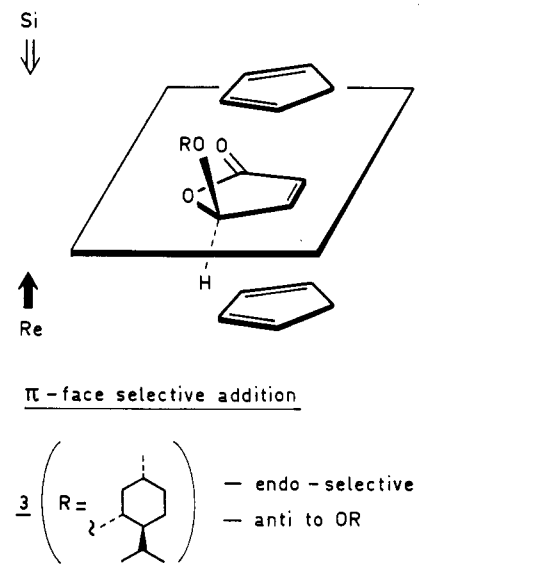
Asymmetric Diels–Alder Reactions with a Chiral Maleic Anhydride Analogue, 5-(1-Menthyloxy)-2(5*H*)-furanone

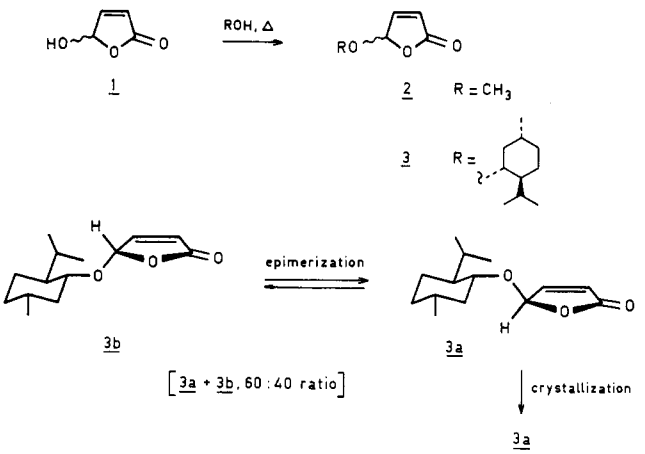
Summary: 5-(1-Menthyloxy)-2(5*H*)-furanone was used as a chiral dienophile in thermal asymmetric Diels–Alder reactions with several cyclic and acyclic dienes to give enantiomerically pure products.

Sir: The challenge of control of the absolute stereochemistry in Diels–Alder reactions[1] is evident from its prominent role in organic synthesis. Excellent diastereoselectivity has been achieved in Lewis acid catalyzed Diels–Alder reactions of chiral acrylates.[2,5] Modest to high asymmetric inductions were the result of cycloadditions using chiral catalysts,[3] chiral dienes,[4] or dienophiles.[1,2,5] However, the synthetic utility has been severely restricted by the scope of the asymmetric Diels–Alder reactions, the necessity of Lewis acid catalysis, or the accessibility of the chiral auxiliary. Only limited success has been reached in thermal asymmetric Diels–Alder reactions.[1,2] We have now developed a versatile synthetic route to enantiomerically pure Diels–Alder products using chiral maleic anhydride analogue synthons.

Scheme I



Scheme II



(1) Paquette, L. A. *Asymmetric Synthesis*; Morrison, J. D., ed.; Academic: New York, 1984, Vol. 3, Chapter 7.
(2) Oppolzer, W. *Angew. Chem.* **1984**, *96*, 840; *Angew Chem., Int. Ed. Engl.* **1984**, *23*, 876.

(3) (a) Hashimoto, S.; Komeshima, N.; Koga, K. *J. Chem. Soc., Chem. Commun.* **1979**, 437. (b) Narasaka, K.; Inoue, M.; Yamada, T. *Chem. Lett.* **1986**, 1967.
(4) (a) Trost, B. M.; Godleski, S. A.; Genêt, J. P. *J. Am. Chem. Soc.* **1978**, *100*, 3930. (b) Trost, B. M.; Krougly, D. O.; Belletire, J. L. *Ibid.* **1980**, *102*, 7595.
(5) (a) Corey, E. J.; Ensley, H. E. *J. Am. Chem. Soc.* **1975**, *97*, 6908. (b) Oppolzer, W.; Kurth, M.; Reichlin, D.; Moffatt, F. *Tetrahedron Lett.* **1981**, 2545. (c) Evans, D. A.; Chapman, K. T.; Bisalia, J. *J. Am. Chem. Soc.* **1984**, *106*, 4261. (d) Oppolzer, W.; Chapuis, C.; Bernadinelli, G. *Helv. Chim. Acta* **1984**, *67*, 1397. (e) Poll, T.; Sobczak, A.; Hartmann, H.; Helmchen, G. *Tetrahedron Lett.* **1985**, *26*, 3095. (f) Helmchen, G.; Karge, R.; Weetman, J. *Modern Synthetic Methods*; Springer: Berlin, 1986; Vol. 4, p 266. (g) Oppolzer, W.; Chapuis, C.; Dao, G. M.; Reichlin, D.; Godel, T. *Tetrahedron Lett.* **1982**, *23*, 4781. (h) Poll, T.; Helmchen, G.; Bauer, B. *Tetrahedron Lett.* **1984**, *25*, 2191. (i) Oppolzer, W.; Chapuis, C.; Bernadinelli, G. *Tetrahedron Lett.* **1984**, *25*, 5885. (j) Furuta, K.; Iwanaga, K.; Yamamoto, N. *Tetrahedron Lett.* **1986**, *27*, 4507. (k) Curran, D. P.; Kim, B. H.; Hiyasena, H. P.; Loncharich, R. L.; Houk, K. N. *J. Org. Chem.* **1987**, *52*, 2137. (l) Kunz, H.; Muller, B.; Schanzenbach, D. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 267.

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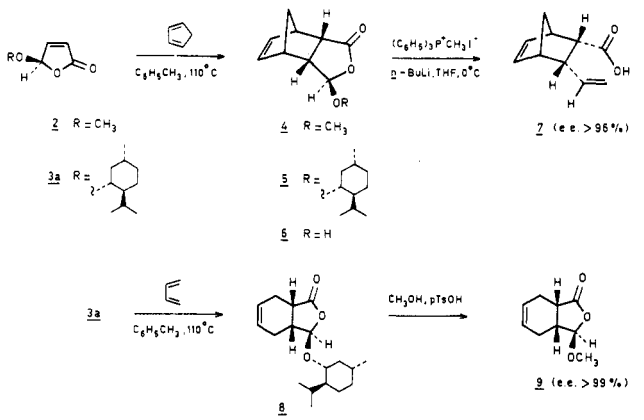
Scheme III



The approach is based on enantiomerically pure 5-(1-menthyloxy)-2(5*H*)-furanone (**3**), which is expected to undergo π-face selective cycloaddition with a variety of dienes, e.g., cyclopentadiene (Scheme I). In contrast to acrylate-based chiral dienophiles, where Lewis acid chelation appears to be essential to reach high ee's,[2] conformational restriction is intrinsic to the chiral lactone structures **2** and **3**.[6] The 5-hydroxy- and 5-alkoxybutenolides were readily prepared by sensitized photooxidation of furan aldehydes.[7] By employing 1-menthol as a chiral auxiliary 5-(1-menthyloxy)-2(5*H*)-furanone (**3**) was formed in 61% yield via esterification at 100 °C for 18 h. It consists of a mixture of two diastereoisomers **3a** + **3b** (60:40 ratio). Crystalline enantiomerically pure **3a**[8,9] was obtained after two crystallizations from light petroleum. A remarkable second-order asymmetric transformation of **3** in solution to a 60:40 ratio of diastereoisomers (**3a** + **3b**) accompanies the crystallization process. The epimerization of **3b** into **3a** was deduced from ^{1}H NMR analyses of the solution of **3** prior to crystallization and the mother liquor just after crystallization of **3a**. This "crystallization-induced epimerization" is essentially driven by the continuous removal of the major crystalline isomer **3a** from the solution[9] (Scheme II). We propose that the epimerization takes place via enolization of **3b** to the unstable 5-(1-menthyloxy)-2-hydroxyfuran intermediate (which is achiral except for the 1-menthyloxy moiety).[10] When enantiomerically pure **3a** was heated at reflux in toluene or petroleum ether for several hours no epimerization took place.[11] This property of **3a** is an essential condition for successful use in enantioselective thermal Diels–Alder reactions.

Table I. Asymmetric Diels–Alder Reactions of 5-(Menthyloxy)-2(5*H*)-furanone (3a) in Toluene

entry	diene	temp, °C	yield[a]	de,[b] %	ee,[b] %
1	cyclopentadiene	110	65	>96	*d*
2	2-methylbutadiene	120	56	>96[c]	>99
3	2,3-dimethylbutadiene	120	44	96[e]	96
4	1,3-cyclohexadiene	120	47	>96	>99
5	anthracene	190[g]	63	>96	*d*
6	sulfolene	120	77	73	72
7	butadiene	120	45	>96	>99
8	cyclopentadiene	110	60	20[f]	*d*

[a] Yields (not optimized) for isolated products.[8] [b] Diastereomeric excess (de) was determined on the basis of ^{1}H NMR and ^{13}C NMR of the menthyloxy derivative of the product (e.g., **5** for entry 1). The enantiomeric excess (ee) was determined on the basis of GC analysis[15] of the methoxy derivative (e.g., **9** for entry 7). [c] Mixture of two regioisomers (50:50 ratio). [d] Not determined. [e] Starting material **3a** + **3b** (98:2 ratio). [f] Starting material **3a** + **3b** (60:40 ratio). [g] Decalin as solvent.

Alkoxybutyrolactones **2** and **3** can be considered as chiral analogues of maleic anhydride although, not unexpected, with decreased reactivity in cycloaddition reactions. When heated at 110 °C in toluene for 4.5 h with a twofold excess of cyclopentadiene **2** and **3** reacted to give adducts **4** and **5**, respectively (>97% endo isomer as determined by ^{1}H NMR[8,12]), in 60–70% isolated yield (Scheme III). Starting with enantiomerically pure **3a** only one isomer of **5** was found, resulting in a diastereoselectivity (de) >96%[9] (Scheme III). When **3** was used as a 60:40 mixture of diastereoisomers the adduct **5** was obtained with a diastereoselectivity of 20%. These results show that complete π-face selective addition takes place and that no epimerization of **3** occurs during the cycloaddition reaction. The chiral auxiliary was readily removed by hydrolysis (SiO_2, H_2O) or methanolysis leading to enantiomerically pure hydroxy- or methoxy-substituted lactones **6** and **4**,[8] respectively.

The synthetic versatility of the above described asymmetric synthesis is illustrated in the methylenation of **6** to afford **7** (55% yield, ee >96% by ^{1}H NMR). Acid **7** constitutes the key intermediate in the synthesis of *d,l*-6,7-dehydroaspidospermidine systems by Magnus and co-workers.[13] Similarly enantiomerically pure cyclohexene derivative **9** was prepared preserving the three consecutive chiral centers. A single isomer with exclusive cis relationship between the methoxy substituent and the bridgehead hydrogens was the result of the solvolysis of **8** (Scheme III). Table I shows the results of the asymmetric Diels–Alder reaction of several dienes with **3a**.[14,15]

(6) For asymmetric Diels–Alder reactions with carbohydrate derived chiral enones and a ribonolactone derived chiral butenolide, see: (a) Primeau, J. L.; Anderson, R. C.; Fraser-Reid, B. *J. Chem. Soc., Chem. Commun.* **1980**, 6. (b) Mann, J.; Thomas, A. *J. Chem Soc., Chem. Commun.* **1985**, 737. (c) Ortuno, R. M.; Corbera, J.; Font, J. *Tetrahedron Lett.* **1986**, *27*, 1081.

(7) (a) Feringa, B. L. *Recl. Trav. Chim. Pays-Bas* **1987**, 106, 469. (b) Feringa, B. L.; Butselaar, R. J. *Tetrahedron Lett.* **1983**, *24*, 1193. (c) Gollnick, K.; Griesbeck, A. *Tetrahedron* **1985**, *41*, 2057.

(8) All new compounds gave satisfactory analytical and ^{1}H NMR, ^{13}C NMR, IR, and MS data.

(9) Although the absolute configuration of **3a** (and consequently also of the Diels–Alder products) has not yet been determined (X-ray analysis in progress), molecular model studies and force-field calculations suggest the *R* configuration at the anomeric center for the more stable diastereoisomer. The program we used for these calculations was Chem-X, developed and distributed by Chemical Design Ltd, Oxford, England.

(10) This epimerization makes diastereoisomer separation unnecessary and allows a theoretical 100% yield of **3a**; for crystallization induced asymmetric transformation, see also: (a) Jacquet, J.; Collet, A.: Wilen, S. H. *Enantiomers, Racemates and Resolutions*; Wiley: New York, 1981; p 369. (b) Reider, P. J.; Davis, P.; Hughes, D. L.; Grabowski, E. J. J. *J. Org. Chem.* **1987**, *52*, 957. It is well possible that traces of acid present during crystallization catalyze enolization of **3b** and consequently the epimerization into **3a**.

(11) It was demonstrated that enantiomerically pure **3a**, when redissolved in petroleum ether or toluene, is not in equilibrium with **3b**. In this case acid-catalyzed epimerization was rigorously excluded.

(12) Single ^{1}H NMR absorptions for the acetal hydrogens are observed for **4** and **5** at 4.71 and 4.99 ppm, respectively, whereas **5** prepared from a mixture of **3a** and **3b** shows absorptions at 4.99 and 4.83 ppm (60:40 ratio), with $J < 1.0$ Hz, characteristic for the endo product.

(13) Magnus, P.; Cairns, P. M.; Kim, C. S. *Tetrahedron Lett.* **1985**, *26*, 1963.

(14) In a typical experiment 5-(1-menthyloxy)-2(5*H*)-furanone (5.16 mmol) and 2.3-dimethyl-1,4-butadiene (10.32 mmol) dissolved in dry toluene (10 mL) were heated in a sealed tube at 120 °C during 24 h. The reaction mixture was cooled, and the solvent was removed under reduced pressure. Acetone was added, and possible polymeric material present was removed by filtration. The solution was evaporated to dryness to yield the adduct (one isomer by ^{1}H NMR), which was crystallized from light petroleum to afford analytically pure[8] product: 0.73 g (44%), mp 72.2–72.3 °C; $[\alpha]^{20}_D$ −124° (*c* 1, *n*-hexane); ^{1}H NMR (60 MHz, $CDCl_3$) δ 0.67–3.20 (m, 32 H), 3.48 (m, J <1 Hz, 1 H), 5.22 (s, 1 H); ^{13}C NMR (50.32 MHz, $CDCl_3$) δ 15.46 (q), 18.74 (q), 19.19 (q), 20.75 (q), 22.08 (q), 22.98 (t), 25.41 (d), 28.27 (t), 30.18 (t), 31.22 (d), 34.21 (t), 36.70 (d), 38.97 (d), 39.68 (t), 47.70 (d), 76.31 (d), 103.60 (d), 123.25 (s), 124.56 (s), 178.61 (s).

Excellent stereochemical control is exerted in all cases, except for 3-sulfolene. Furthermore removal of the chiral auxiliary did not lead to racemization. In fact in all cases studied so far (except for entry 6) only one diastereoisomer of the Diels–Alder product was found when enantiomerically pure **3a** was used as dienophile. With anthracene even at 190 °C in decalin as a solvent the same stereoselectivity was observed. Preliminary experiments showed that the reaction of **3a** and anthracene can also be performed at 20 °C by using $TiCl_4$ as Lewis acid catalyst with a de >96%.

In conclusion, we have demonstrated that preparative easily accessible (menthyloxy)butyrolactones can be effectively used in new asymmetric Diels–Alder reactions with cyclic and acyclic dienes to give virtually enantiomerically pure Diels–Alder products. No Lewis acid catalysis is required, and the chiral auxiliary can be recovered by mild procedures. Furthermore both enantiomers of the chiral auxiliary are readily available. Applications of this methodology in natural product synthesis is currently under investigation.

Acknowledgment. Use of the services and facilities of the Dutch CAOS/CAMM Center, under Grants SON-11-20-700 and STW-NCH-44.0703, is gratefully acknowledged.

(15) The capillary GC column used was a XE-60 (*S*)-valine-(*S*)-α-phenylethylamine (50 m × 0.25 mm, Chrompack). Racemic methoxy adducts gave two well-separated peaks for the enantiomers, whereas a single peak was observed for enantiomerically pure products when using this column.

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A Free Radical Addition–Fragmentation Reaction for the Preparation of Vinyl Sulfones and Phosphine Oxides

Summary: A free radical chain process is reported which gives vinyl sulfones or phosphine oxides in good to moderate yields under nonreducing conditions; the reaction involves irradiation of appropriate precursors to carbon-centered radicals with β-tri-*n*-butylstannyl α,β-unsaturated sulfones or phosphine oxides in the presence of AIBN.

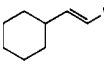
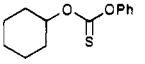
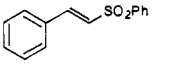
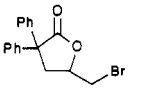
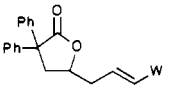
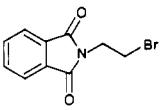
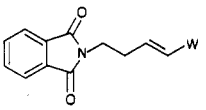
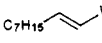
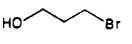
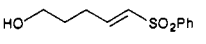
Sir: The development of free radical or "one-electron" chain processes for the formation of C–C bonds has been an area of ongoing interest.[1] While our previous efforts in this area have focused on the general process of free radical allylation, utilizing allylic stannanes[2] and sulfides,[3] we have also been interested in the development of reagents for free radical vinylation reactions. Specifically, we hoped to design simple reagents which could deliver a vinyl synthon to carbon-centered radicals under nonreducing radical conditions.[4]

(1) For a recent and very readable account of radical reactions in organic synthesis, note: Hart, D. J. *Science (Washington, D.C.)* **1984**, *234*, 883. A recent symposium-in-print has been devoted to radical reactions and contains many relevant articles: Giese, B., Ed. *Tetrahedron* **1985**, *41*, 3887.

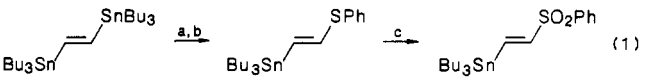
(2) (a) Keck, G. E.; Yates, J. B. *J. Am. Chem. Soc.* **1982**, *104*, 5829. (b) Keck, G. E.; Enholm, E. J.; Yates, J. B.; Wiley, M. W. *Tetrahedron* **1985**, *41*, 4079.

(3) Keck, G. E.; Byers, J. H. *J. Org. Chem.* **1985**, *50*, 5442.

Table I. Isolated Yields for Vinyl Sulfones and Phosphine Oxides

substrate	product	yield (reagent, product *E*/*Z* Ratio)
		79% (W = SO_2Ph) 61% (W = $PO(Ph)_2$)
		83% (W = SO_2Ph) 75% (12:1, W = $PO(Ph)_2$)
		82% (8:1)
		45% (6:1, W = SO_2Ph) 42% (6:1, W = $PO(Ph)_2$)
		73% (W = SO_2Ph) 46% (8:1, W = $PO(Ph)_2$)
		77% (W = SO_2Ph) 58% (10:1, W = $PO(Ph)_2$)
$C_7H_{15}I$		76% (W = SO_2Ph) 78% (8:1, W = $PO(Ph)_2$)
		66%

One such reagent that we have examined is 1-(tri-*n*-butylstannyl)-2-(phenylsulfonyl)ethene (**1**). This reagent is prepared in two operations and 79% overall yield from (*E*)-1,2-bis(tri-*n*-butylstannyl)ethene[5] (**2**) as shown in eq 1.



(a) 1.1 equiv of *n*-BuLi, THF, −78 °C; (b) PhSSPh, −78 to −25 °C; (c) 2.2 equiv of *m*-CPBA, CH_2Cl_2, −45 to −25 °C.

Photolysis[7] of a variety of alkyl and aryl iodides, bromides, and phenylthionocarbonates with an excess of **1** and catalytic AIBN in benzene led to the formation of vinyl sulfones in usually good yields as shown in Table I.[8] The predominant isomer in all cases examined is of the *E*

(4) The term "nonreducing conditions" means that the radical chain is terminated by some means other than hydrogen abstraction by the product.

(5) (a) Corey, E. J.; Wollenberg, R. H. *J. Org. Chem.* **1975**, *40*, 3788. (b) The monolithiation and quenching of **2** with a variety of electrophiles is discussed in: Wollenberg, R. H. Ph.D. Thesis, Harvard University, 1976.

(6) Attempts to prepare **1** more directly, by quenching the vinyllithium prepared from **2** with benzenesulfonyl chloride, led to extensive polymerization.

(7) The light source for photolysis was a 450-W Hanovia lamp equipped with a Pyrex filter.

(8) A general procedure for all reactions is as follows. In a screw-top Pyrex test tube were placed 0.33 mmol of the substrate, 1 mmol of **1** which had been freshly flushed through a pad of alumina, 0.03 mmol of AIBN, and 1 mL of benzene. The solution was degassed by bubbling argon through the reaction mixture for ~15 min, and the tube was secured adjacent to the photolysis lamp. Photolysis for 12 h was usually sufficient for the completion of the reaction, except when aryl halides were employed as substrates, in which case the reaction took a greater length of time. When the reaction was complete, as indicated by the disappearance of the substrate by TLC or GC, the crude mixture was diluted to 25 mL with ether, washed with 10 mL saturated KF solution, and purified by medium-pressure liquid chromatography. The unreacted excess of **1** could usually be recovered during chromatography and reused in subsequent experiments.

0022-3263/88/1953-1127$01.50/0