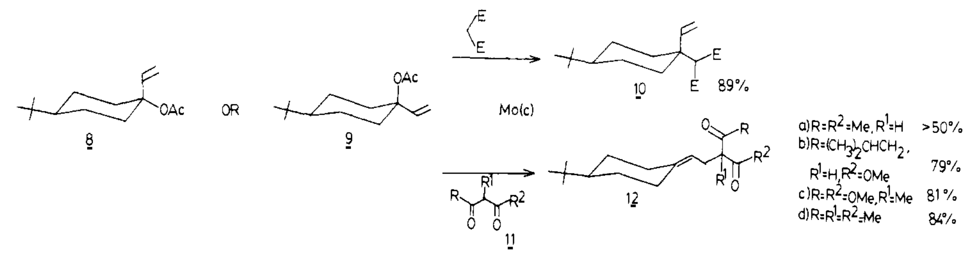
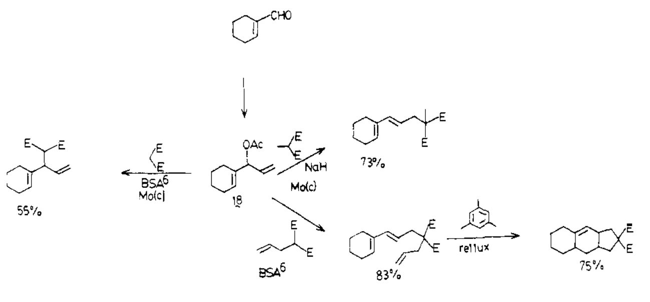
Scheme II

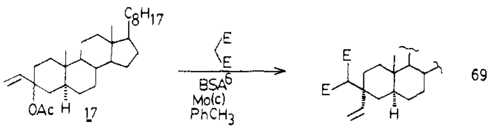


Scheme III



minishes the importance of the charge distribution in **16** and leads to preferential formation of the thermodynamically more stable olefin. Finally, a β-keto ester, intermediate in reactivity, shows intermediate behavior. When steric factors dominate as with the anion of 2-carbomethoxycyclopentanone, only path 3b is observed. On the other hand, the keto ester **11b** prefers attack at the more hindered position (i.e., formation of **5**) unless the steric requirements of the allyl system overwhelms as in the case of allyl acetate **8**.

The complementary regiochemical behavior of malonate and substituted malonates offer interesting applications. As shown in the case of **8** and the steroid substrate **17**, a high preference



for equatorial attack of malonate creates a quaternary center with high stereoselectivity[11,12] and independent of the stereochemistry of the starting allyl acetate[13]—a result that permits a single product to result from a stereoisomeric mixture of starting materials.

The failure of an additional double bond as in diallyl acetate **18**[4] to change the established trends permits a tandem alkylation–cycloaddition as shown in Scheme III.[4] The fact that **18** arises so simply by addition of a vinyl organometallic to an α,β-unsaturated carbonyl system makes this an attractive strategy for making substrates capable of an intramolecular Diels–Alder reaction.[14]

These results demonstrate that by appropriately choosing the nucleophile, great regiochemical control can be exercised in Mo(c)-catalyzed reactions. Combined with the earlier observation[3] that the choice of ligands also affects regiochemistry, molybdenum templates provide a most powerful tool for allylic alkylations.

Acknowledgment. We thank the National Science Foundation for their generous support of our programs, the NSERC of Canada for a graduate fellowship for M.L., and Brian Petersen for preparation of several starting materials. We thank Pressure Chemical Co. and Climax Molybdenum Co. of Michigan for gifts of molybdenum hexacarbonyl.

Registry No. 1, 53723-50-5; **2**, 82352-45-2; **3**, 85390-61-0; **4**, 18424-76-5; **5**, 85390-62-1; **6**, 67428-13-1; **7**, 85390-63-2; **8**, 85390-64-3; **9**, 85390-65-4; **10**, 85390-66-5; **11a**, 123-54-6; **11b**, 30414-55-2; **11c**, 609-02-9; **11d**, 815-57-6; **12a**, 85390-67-6; **12b**, 85405-71-6; **12c**, 85390-68-7; **12d**, 85390-69-8; **13**, 85390-70-1; **14**, 85390-71-2; **15**, 85390-72-3; **17**, 85390-73-4; **18**, 7014-63-3; $Mo(CO)_6$, 13939-06-5; methyl 2-hydroxy-1-cyclopentene-1-carboxylate•Na, 63178-03-0; methyl 1-(10-bromodec-2-enyl)-2-oxo-1-cyclopentanecarboxylate, 85390-74-5; methyl 10-bromo-3-ethenyl-2-methoxycarbonyldecanoate, 85390-75-6; methyl 12-bromo-2-methoxycarbonyldodec-4-enoate, 85390-76-7; methyl 2-oxocyclopentanecarboxylate, 10472-24-9; methyl 5-(cyclohex-3-en-1-yl)-2,4-dimethyl-2-methoxycarbonylpent-4-enoate, 85390-77-8; 3α-ethenyl-3β-[bis(methoxycarbonyl)methyl]-5α-cholestane, 85390-78-9; methyl β-ethenyl-α-methoxycarbonyl-1-cyclohexene-1-propanoate, 85390-79-0; methyl 5-(cyclohex-1-en-1-yl)-2-methyl-2-methoxycarbonyl-4-pentenoate, 85390-80-3; 7-(cyclohex-1-en-1-yl)-4,4-bis(methoxycarbonyl)-1,6-heptadiene, 85390-81-4; 2,2-bis(methoxycarbonyl)-2,3,3a,6,7,8,9,9a,10,10a-decahydro-1*H*-benz[*f*]indene, 85390-82-5.

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[11] For an excellent review see: Martin, S. F.; *Tetrahedron* **1980**, *36*, 419. For a case using Grignard reagents and allyl alcohols with nickel catalysts see: Buckwalter, B. L.; Burfitt, I. R.; Felkin, H.; Joly-Gondket, M.; Naemura, K.; Salomon, M. F.; Wenkert, E.; Wovkulich, P. M. *J. Am. Chem. Soc.* **1978**, *100*, 6445.

[12] The stereochemistry of the alkylation product of **17** is assigned by analogy to **10**.

[13] As in the case of **8**, **10** is by far the major product, but the alternative stereoisomer is also observed.

[14] Cf.: Brieger, G. *J. Am. Chem. Soc.* **1963**, *85*, 3783. Corey, E. J.; Glass, R. S. *J. Am. Chem. Soc.* **1967**, *89*, 260. Frater, G. *Helv. Chim. Acta* **1974**, *57*, 172. Bajorek, J. J. S.; Sutherland, J. K. *J. Chem. Soc., Perkin Trans. 1* **1975**, 1559. Oppolzer, W.; Snowden, R. L. *Tetrahedron Lett.* **1976**, 4187.

Lewis Acid Catalysis of Coumarin Photodimerization

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Lewis acids have been widely employed as catalysts for thermal Diels–Alder and ene reactions, especially those involving α,β-unsaturated esters.[1,2] The enhanced reactivity and stereoselectivity observed in many such reactions have been attributed to changes in frontier orbital energies and C═C double bond polarity upon complexation of the carbonyl oxygen.[2] We recently reported that the spectroscopic properties and unimolecular photoisomerization reactions of several α,β-unsaturated esters are profoundly changed by complexation with Lewis acids such as BF_3, $EtAlCl_2$, and $SnCl_4$.[3] The possibility that Lewis acids might also serve as catalysts for photochemical [2 + 2] cycloaddition reactions was suggested many years ago by reports concerning the photodimerization of dibenzylideneacetone in the presence of UO_2^+ and $SnCl_4$[4] and is borne out by investigations currently in progress in our laboratory. We report here on the pronounced effects of the Lewis acid BF_3 on the efficiency and regiochemistry of coumarin photodimerization.

The photodimerization of coumarin has been the subject of numerous preparative and mechanistic investigations.[5] The

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[1] Flemming, I. "Frontier Orbitals and Organic Chemical Reactions"; Wiley: New York, 1976,; pp 214–223.

[2] Houk, K. N.; Strozier, R. W. *J. Am. Chem. Soc.* **1973**, *95*, 4094–4096.

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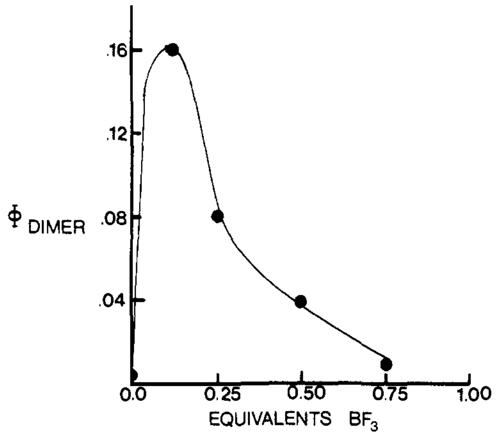
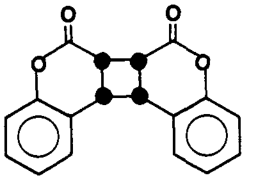


Figure 1. Quantum yields for photodimerization of 0.2 M coumarin in dichloromethane solution vs. BF_3 concentration. Quantum yield measurements employed monochromatic 313-nm irradiation and 0.1 M *trans*-stilbene actinometers.

relevant conclusions of these investigations are (a) the syn head-to-head dimer I and syn heat-to-tail dimer II are the major and minor products, respectively, of a highly inefficient singlet-state reaction ($\Phi \sim 10^{-3}$ for 0.3 M coumarin) and (b) the anti head-to-head dimer III is the major product of a moderately efficient triplet-state dimerization ($\Phi \sim 10^{-1}$, benzophenone sensitization).



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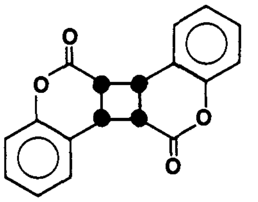
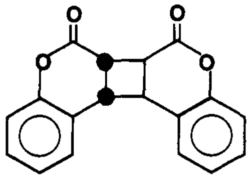


II



III

Irradiation of a 50-mL dichloromethane solution 0.2 M in both coumarin and $BF_3{\cdot}OEt_2$ under dry nitrogen for 28 h with a Pyrex-filtered 450-W Hanovia medium-pressure lamp results in nearly quantitative consumption of coumarin. Recrystallization from benzene/heptane yields >85% of a single product, identified as the head-to-tail syn dimer II on the basis of physical and spectroscopic data.[6] As previously reported by Schenck et al.,[5c] the four cyclobutane protons appear as a singlet in the 60-MHz ^1H NMR spectrum. Addition of 2 equiv of $Eu(fod)_3$ transforms this signal into two triplets with $J = J' = 9$ Hz, a result uniquely consistant with the assigned stereochemistry. The effect of BF_3 concentration on the quantum yield for photodimerization of 0.2 M coumarin is shown in Figure 1. The values increase from 10^{-3} with no BF_3 to 0.16 for 0.125 equiv of BF_3 and decrease at higher BF_3 concentrations. Similar quantum yield enhancement is observed with $BF_3{\cdot}OEt_2$; however, higher concentrations are necessary due to equilibrium complexation of BF_3 with coumarin and ether.

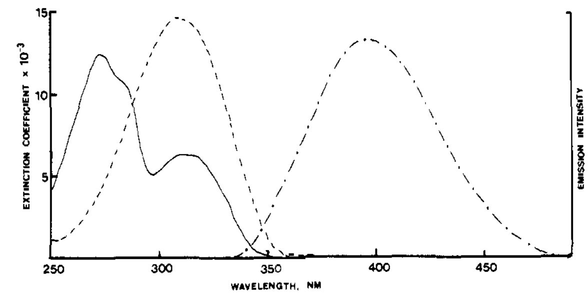


Figure 2. Absorption (- - -) and fluorescence (-•-) spectra of coumarin in the presence of BF_3 and in the absence of BF_3 (—).

Coumarin is known to form 1:1 solid-state adducts with boron and aluminum halides.[7] NMR analysis of a 4:1 molar mixture of coumarin and BF_3 indicates rapid equilibration of BF_3 between coumarin molecules. The absorption and emission spectra of coumarin in the absence and presence of BF_3 (1 equiv) are shown in Figure 2. Spectral changes resulting from complexation of coumarin are similar to those previously observed for protonation. Room-temperature emission from protonated coumarin ($\Phi = 0.5$, $\tau = 5$ ns) is attributed to a $^1\pi,\pi^*$ state.[8] The change in the coumarin absorption spectrum upon addition of BF_3 indicates that the equilibrium constant for complexation is large.

A plausible mechanism for the BF-promoted photodimerization of coumarin (C) is outlined in eq 1–3. Excitation of coumarin–BF_3 solutions at 365 nm, where the complex absorbs more strongly than coumarin (Figure 2), results in efficient dimerization.

$$C + BF_3 \rightleftarrows C{\cdot}BF_3 \qquad (1)$$

$$C{\cdot}BF_3 \xrightarrow{h\nu} C{\cdot}BF_3{}^* \qquad (2)$$

$$C{\cdot}BF_3{}^* + C \rightarrow II + BF_3 \qquad (3)$$

The decrease in Φ_{II} with BF_3 concentration (Figure 1) supports the reaction of excited complex with ground-state coumarin. While we cannot at present distinguish between singlet vs. triplet excited complex, the former seems more likely in view of the observation of strong room-temperature emission (Figure 2) and the highly selective formation of a syn dimer. The kinetics and mechanism of the BF_3-catalyzed reaction are currently under investigation.

Both the singlet-state photodimerization of coumarin and the BF_3-catalyzed photodimerization yield exclusively syn adducts, as expected for processes involving singlet excimers or exciplexes with optimal π-orbital overlap.[9] The formation of the head-to-head dimer I as the major regioisomer of coumarin photodimerization is in accord with the predictions of FMO theory.[1] Unlike Lewis acid catalyzed Diels–Alder reactions, which normally yield the same (but enhanced) regioselectivity as the uncatalyzed reaction, the BF_3-catalyzed photodimerization of coumarin results in a complete reversal of regiochemistry. Complexation, like protonation, should substantially alter the ground- and excited-state energies and charge densities of coumarin and thus account for both the enhanced reactivity and reversal of regiochemistry observed for the BF_3 complex.[10]

Registry No. II, 21453-75-8; coumarin, 91-64-5; boron trifluoride, 7637-07-2; coumarin·BF_3 complex, 85407-50-7.

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(6) Mp 204–206 °C (lit.[5c] mp 204–206 °C); IR ($CHCl_3$) ν_{max} 3020, 1750, 1610, 1580, 1485, 1450, 1360, 1180, 1105 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.23 (s, 4 H), 6.4–6.8 (m, 2 H), 6.9–7.45 (m, 6 H); mass spectrum, *m/e* 292 (M^+). Anal Calcd for $C_{18}H_{12}O_4$: C, 73.96; H, 4.15. Found: C, 73.82; H, 4.11.

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