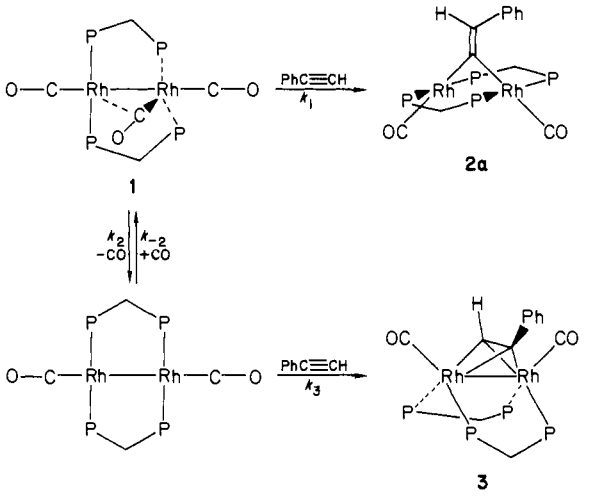
Scheme I



isotope effect. These mechanistic conclusions are summarized in Scheme I and yield a rate expression for the reaction which can be written as

$$\frac{-d[1]}{dt} = k_1[1][PhCCH] + \frac{k_2k_3[1][PhCCH]}{k_{-2}[CO] + k_3[PhCCH]}$$

We conclude that at least two channels exist for the reaction of PhCCH with the binuclear complex $Rh_2(CO)_3(dppm)_2$ leading to distinctly different products and that μ_2-η^2 coordinated acetylene does not lie on the reaction path of the metal complex promoted acetylene-to-vinylidene transformation.

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Registry No. 1, 74507-92-9; **2a**, 94294-59-4; **2b**, 94294-58-3; **3**, 74507-96-3; PhCCH, 536-74-3; *t*-BuCCH, 917-92-0.

Stereochemistry of Cycloadditions of Fluoroallene

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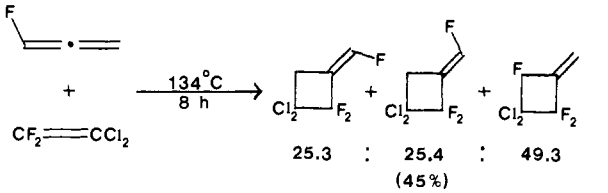
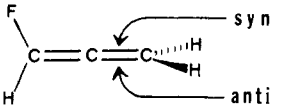
The cycloadditions of fluoroallene (MFA) and 1,1-difluoroallene (DFA) may, on the basis of reaction characteristics, be clearly demarcated into two broad categories, which also seem to be clearly distinguishable mechanistically. First, those reactions that are orbital-symmetry allowed, such as Diels–Alder[1] and 1,3-dipolar cycloadditions,[2] are regiospecific with respect to the allene with reactions occurring exclusively at the C_2–C_3 bond. In contrast the [2 + 2] reactions of MFA and DFA have been shown to be nonregiospecific,[1,3] with an excess of C_2–C_3 cyclization for MFA and an excess of C_1–C_2 cyclization for DFA being observed. These results have been rationalized as characteristic of concerted mechanisms for the Diels–Alder and 1,3-dipolar cycloadditions and of a multistep, diradical mechanism for the [2 + 2] reactions.

In the cycloadditions of MFA there is also a question of stereochemistry. In its [2 + 2] cycloadditions, where initial bond formation is likely to C_2 of the C_1–C_2 π-bond, the net stereochemical outcome of such reactions is determined by whether the fluorine substituent, in rotating into allylic conjugation, prefers to rotate toward or away from the attacking reagent. The reaction of MFA with 1,1-dichloro-2,2-difluoroethylene demonstrates that for a substituent of such small steric demand as fluorine, *no* apparent rotational preference is observed.[1] This is in marked



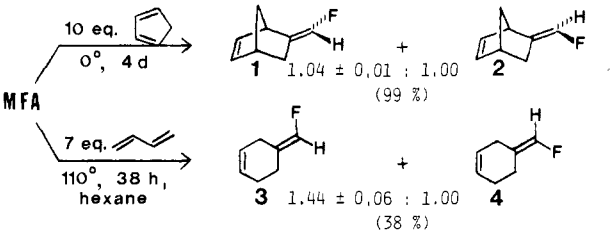
contrast to comparable studies of monoalkyl allenes wherein a definite preference for net anti addition has been reported and a steric rationale proposed.[4]

In concerted cycloadditions, however, addends should add to MFA via either a syn or an anti approach vis-ā-vis the fluorine



substituent. In view of the likely insignificance of a steric influence on the mode of addition, *other* factors should be able to be examined unambiguously. In this paper we would like to report the observation of a modest preference for syn addition of dienes to MFA in Diels–Alder reactions and an even more dramatic syn preference for MFA's 1,3-dipolar cycloadditions with nitrones.

While the cycloaddition of MFA with cyclopentadiene provides only a barely measurable excess of the syn adduct **1** (51:49), its

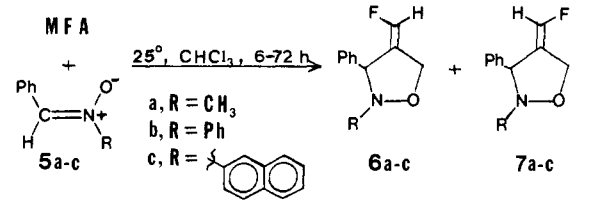


reaction with 1,3-butadiene leads to a much more significant (59:41) preference for the syn adduct **3**.[5]

Even more dramatic was the preference for syn addition shown in the 1,3-dipolar cycloadditions of nitrones to MFA (Table I). The product isoxazolidines, **6** and **7**, were in each case completely

Table I. Cycloadditions of Nitrones to Fluoroallene

nitrone	R	% yield	6:7 (error ±0.3)	*k*(rel)
5a	CH_3	95	4.6:1.0	1.0
5b	Ph	99	6.1:1.0	11.6
5c	2-naphthyl	90	5.2:1.0	12.0



characterized spectroscopically and analytically,[6,7] with the ste-

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(2) (a) Dolbier, W. R., Jr.; Burkholder, C. R.; Winchester, W. R. *J. Org. Chem.* **1984**, *49*, 1518. (b) Dolbier, W. R., Jr.; Burkholder, C. R. *Isr. J. Chem.*, in press.

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(5) The reaction mixtures were probed by ^{19}F NMR at 282 MHz and by GLPC to obtain product ratios and to demonstrate that the only products formed were **1**–**4** along with a 6% yield of 1-ethenyl-3-(fluoromethylene)-cyclobutane in the butadiene reaction. The stereochemical assignments were made by comparison of the allylic proton chemical shifts and C–F coupling constants with those of the nitrone cases.

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reochemical assignments being made on the basis of difference NOE experiments on **6a** and **7a**[8] and a corroborative X-ray structure determination of **6c**.[9]

The nitrone reactions are regiospecific as indicated and proceed in high yield. They are moreover well-behaved, second-order kinetic processes, showing the expected[10] moderate decrease in rate as one increases the polarity of the solvent. (C_6D_6, E_T = 34.5; $CDCl_3$, E_T = 39.1; CD_3OD, E_T = 55.5 kcal/mol; relative rates of 16, 5.4, and 1.0, respectively, for the reaction of MFA with **5a**.)

The observed remarkable preference for syn addition of nitrones to MFA is in dramatic contrast to similar additions to methoxy and phenoxyallene wherein anti products were formed to large excess, likely due to steric effects.[11] Since a fluorine substituent should exert little if any steric effect, the observed stereochemical preferences must derive from other subtle influences. The fluorine substituent of MFA may indeed provide a unique probe of such subtle effects.

The results may be related to the observation of preferential syn addition of 1,3-dipoles to *cis*-3,4-dichlorocyclobutene[12] although it should be noted that its Diels–Alder reactions exhibited no similar syn selectivity.[13] Moreover, the syn selectivity exhibited in the dichlorocyclobutene system is not reflected in similar studies on the *cis*-3,5-dichlorocyclopentene system.[14] The present work indeed constitutes the first example of the stereochemical directing effect of an allylic fluorine substituent on a cycloaddition.[15]

Distinction between a number of possible explanations for these results cannot yet unambiguously be made. It would appear, however, that an explanation involving direct interaction of the 1,3-dipole with fluorine's lone pairs is unlikely, inasmuch as the basicity as reflected by the proton affinity of a carbon-bound fluorine substituent is seemingly low.[16,17] Further studies are under way to clearly distinguish such an explanation involving direct fluorine lone-pair interaction from other potential sources of influence such as transition-state dipole–dipole interactions or orbital distortion of the C_2–C_3 π-bond by its proximate, eclipsed allylic fluorine substituent.[18,19]

Acknowledgment. We acknowledge with thanks the support of this research in part by the National Science Foundation.

Registry No. 1, 75372-17-7; **2**, 75372-20-2; **3**, 75372-19-9; **4**, 75372-22-4; **5a**, 3376-23-6; **5b**, 1137-96-8; **5c**, 31928-56-0; **6a**, 98857-92-2; **6b**, 98857-93-3; **6c**, 98857-94-4; **7a**, 98857-95-5; **7b**, 98857-96-6; **7c**, 98857-97-7; fluoroallene, 51584-22-6; cyclopentadiene, 542-92-7; butadiene, 106-99-0.

Supplementary Material Available: IR, NMR, and mass spectral determinations of **1–4**, **8**, **6a–c**, and **7a–c**, X-ray structure determination of **6c**, and tables of bond lengths and angles of **6c** (9 pages). Ordering information is given on any current masthead page.

(6) The reaction mixtures were probed by ^{19}F NMR and TLC indicating only **6** and **7** to be products along with two unidentified possible products for the R = CH_3 case, each present in 3% yield. The products were fully characterized.[7]

(7) Salient spectroscopic features of stereochemical importance were (for the R = 2-naphthyl case—others analogous): (a) Greater deshielding of cis-allylic protons by F; ^1H NMR (300 MHz) δ **6c** 5.65 (br s, 1 H, CHPh), 4.61 (m, 2 H, CH_2); **7c** 5.22 (br s, 1 H, CHPh), 4.88 (m, 2 H, CH_2). (b) Larger transoid allylic J_{HH}; ^1H NMR δ **6c** 6.49 (ddt, J_{HF} = 81.55, J_{HHcis} = 1.70, $J_{HHtrans}$ = 1.86 Hz by decoupling experiments, 1 H, CHF); **7c** 6.47 (ddt, J_{HF} = 80.68, $J_{HHtrans}$ = 2.19, J_{HHcis} = 1.34 Hz, 1 H, CHF). (c) Larger transoid allylic J_{CF}; ^{13}C NMR (75 MHz) δ **6c** 69.6 (s, CHPh), 65.8 (d, $J_{FCtrans}$ = 5.9 Hz, CH_2); **7c** 69.5 (d, $J_{FCtrans}$ = 4.9 Hz, CHPh), 66.1 (s, CH_2).

(8) For the irradiation of the PhCH and CH_2 in the ^1H NMR, the CHF NOE enhancements were 1.9% and 4.2%, respectively, for **6a**. For the analogous irradiations in **7a**, the enhancements were 1.9% and <1%.

(9) The crystal was grown from slow evaporation of solvent from an ethanolic solution of **6c** in an uncapped NMR tube. Crystal data: monoclinic, $P2_1/c$, a = 5.940 (1) Å, b = 23.685 (3) Å, c = 22.672 (4) Å, β = 91.69 (1)°, V = 3188.4 (8) Å^3, Z = 8. Intensity data: Nicolet R3m diffractometer; Mo Kα radiation, graphite monochromator; ω–2θ scan to 2θ = 50.0°; 5439 unique reflections; 3545 reflections $I \geq 3\sigma(I)$. Structure solution and refinement: SHELXTL programs; direct methods and Fourier synthesis; least-squares refinement; R(usual) = 0.073, R(weighted) = 0.078; goodness of fit = 1.61.

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(15) See however: Franck-Newmann, M.; Sedrati, M. *Tetrahedron Lett.* **1983**, *24*, 1387.

(16) The proton affinities, defined as the enthalpies for the gas-phase reactions $BH^+ \rightarrow B + H^+$, of ethane, CH_3F, CH_3Cl, H_2O, and NH_3 are, for example, 142, approx. 151, 160, 170, and 205 kcal/mol, respectively.[17]

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(18) Burgess, E. M.; Liotta, C. L. *J. Org. Chem.* **1981**, *46*, 1703.

(19) Houk has suggested that "pyramidalization of the alkene carbons" of the 3,4-disubstituted cyclobutenes may contribute to their syn selectivity.[14]

Stereoselective Total Synthesis of (±)-8-Deoxyanisatin

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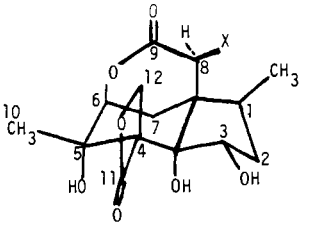
The convulsant principle of the seeds of Japanese star anise (*Illicium anisatum*, L.) was first characterized by Lane et al. in 1952,[1] and the full structure and stereochemistry of this potent $C_{15}H_{20}O_8$ toxin were established in a masterful 1968 paper by Yamada's group at Nagoya.[2] The structure of anisatin was shown to be the highly functionalized dilactone **1** on the basis of extensive



1 X = OH, **2** X = H

degradative and spectroscopic data as well as by elucidation of its facile rearrangement reactions in base or upon heating.[3]

In 1982 Woodward et al.[4] reported model studies to construct the bridging α-hydroxy δ-lactone unit of this challenging synthetic target, and recently Lindner[5] continued this approach in an imaginative yet so far unsuccessful attack on the anisatin system. We now report a stereoselective sequence that comprises the first total synthesis of (±)-8-deoxyanisatin (**2**).

Conjugate addition of $LiMe_2Cu$ to 2-allyl-2-cyclopentenone,[6] with stereoselective trapping of the resulting enolate by 2-(trimethylsilyl)-1-buten-3-one followed by aldol cyclization[7] gave the methylhydrindenone **3**.[8] Stiles carboxylation of **3** followed by

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(5) Lindner, D. L. Ph.D. Thesis, Harvard University, Cambridge, MA, 1982. We are indebted to Dr. Lindner for a copy of his thesis prior to its formal publication.

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(7) Cf.: Boeckman, R. K., Jr. *J. Am. Chem. Soc.* **1973**, *95*, 6867.

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