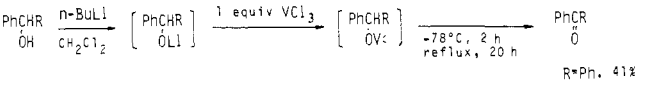
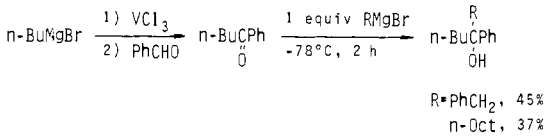
Scheme II

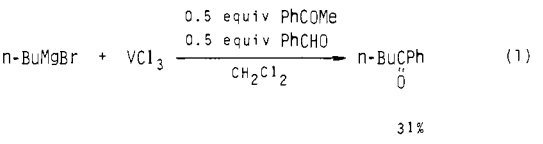


Scheme III



the chloro substituent was inert under the conditions employed here. Starting from alkyl aldehydes and the organovanadium reagent from *n*-BuLi, the oxidation process did not proceed. The successful transformation to ketones was performed by use of the Grignard reagent instead. Various Grignard reagents such as vinyl- or arylmagnesium halides were employed in the ketone synthesis via organovanadium compounds. The reagent from allylmagnesium bromide did not undergo the oxidation reaction with benzaldehyde but only gave the alcohol. Noteworthy is the fact that conjugated aldehydes underwent regioselective 1,2-addition of organovanadium reagents to produce α,β-unsaturated ketones exclusively.

Ketones were also reactive enough toward these organovanadium reagents, but it should be noted that high chemoselectivity was observed in the reaction of *n*-butylvanadium species with a mixture of benzaldehyde and acetophenone (eq 1).



(1)

Acetophenone was recovered and the only product was valerophenone derived from benzaldehyde.

Although an intermediate organovanadium species has not been isolated, ketone synthesis is considered to be characteristic of presumed $RVCl_2$.[4a] Use of more than 2 equiv of *n*-butylmagnesium bromide per vanadium trichloride resulted in alcohol formation.[4b] The present transformation was unsuccessful when VCl_4 or $V(O)Cl_3$ was employed.

Treatment of the reaction mixture under reflux is important since workup at −78 °C gave alcohols exclusively. The intermediacy of the secondary alkoxyvanadium species seems likely. In fact, when lithium alkoxides were treated with vanadium trichloride in dichloromethane, oxidation to the corresponding ketones occurred (Scheme II). This oxidation step might be formally explained by a β-elimination reaction.

An application of this selective ketone synthesis was demonstrated by a facile one-pot synthesis of tertiary alcohols as exemplified in Scheme III.

A useful synthesis of unsymmetrical ketones from aldehydes is now possible by organovanadium chemistry. Vanadium-mediated synthetic reactions have scarcely been studied.[2,4,5] Further investigation is in progress.

Registry No. *n*-BuLi, 109-72-8; *n*-BuMgBr, 693-03-8; MeMgI, 917-64-6; PhMgBr, 100-58-3; $PhCH{=}CHMgBr$, 30094-01-0; $CH_2{=}CHCH_2MgBr$, 13291-18-4; PhCHO, 100-52-7; p-MeC_6H_4CHO, 104-87-0; p-ClC_6H_4CHO, 104-88-1; PhCOMe, 98-86-2; *n*-PrCHO, 123-72-8; $CH_3(CH_2)_6CHO$, 124-13-0; $PhCH{=}CHCHO$, 104-55-2; $CH_3CH{=}CHCHO$, 4170-30-3; $CH_3(CH_2)_3COPh$, 1009-14-9; $CH_3(CH_2)_3CH(OH)Ph$, 583-03-9; $CH_3(CH_2)_3COC_6H_4$-p-OMe, 1671-76-7; 4-*n*-$BuCOC_6H_4Cl$, 25017-08-7; *n*-BuCOPr, 589-63-9; *n*-$BuCO(CH_2)_6CH_3$, 19780-10-0; PhCOPh, 119-61-9; PhCOPr, 495-40-9; $BuCOCH{=}CHPh$, 4071-84-5; $BuCOCH{=}CHCH_3$, 4643-27-0; $PhCOCH{=}CHPh$, 94-41-7; $PhCOCH{=}CHCH_3$, 495-41-0; $PhCH{=}CHCOPr$, 4646-80-4; $CH_2{=}CHCH_2CH(OH)Ph$, 936-58-3; 2-furancarboxaldehyde, 98-01-1; cyclohexanone, 108-94-1; butyl 2-furyl ketone, 3194-17-0; 1-butylcyclohexanol, 5445-30-7; 2-phenyl-2-hexanol, 4396-98-9; vanadium trichloride, 7718-98-1.

(4) (a) Razuvaev, G. A.; Latyaeva, V. N.; Vyshinskaya, L. I.; Drobotenko, V. V. *J. Organomet. Chem.* **1981**, *208*, 169. (b) The reaction of trimesitylvanadium with ketones in ether was reported leading to olefins, alcohols, or a radical: Kreisel, G.; Seidel, W. *Ibid.* **1984**, *260*, 301.

(5) Imwinkelried, R.; Seebach, D. *Helv. Chim. Acta* **1984**, *67*, 1496. Kinney, R. J.; Jones, W. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1978**, *100*, 635. Ho, T.-L.; Olah, G. A. *Synthesis* **1976**, 807 and references cited therein.

Competitive C–H Activation and C≡C Coordination in the Reactions of Acetylenes with a Binuclear Rhodium Complex

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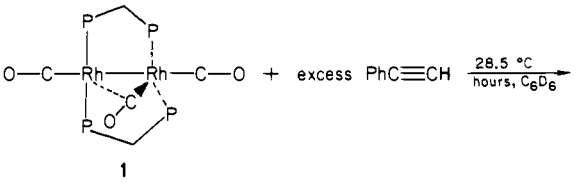
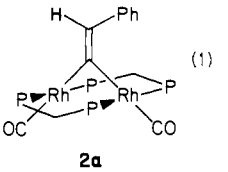
Received June 21, 1985

Terminal alkynes react with transition-metal complexes either by coordination of the C≡C bond as $2e^-$ or $4e^-$ donor[2] or by C–H bond activation to form acetylide complexes, which often undergo subsequent transformations.[3] In this paper, we describe a detailed study of the reaction between phenylacetylene and the binuclear complex $Rh_2(CO)_3(dppm)_2$ (**1**, dppm = bis(diphenylphosphino)methane) which provides insight into the factors influencing modes of acetylene reactivity and shows that in this system η^2 coordination between the two Rh atoms (μ_2-η^2) does not lie on the reaction profile leading to C–H activation.

Complex **1**, which was recently been found to possess an $18e^-/16e^-$ non-A-frame structure,[4] reacts readily with a 10-fold excess of PhCCH in benzene at 28.5 °C to form an intensely purple colored product **2a** cleanly and without observable intermediates, eq 1.[5] This product has been established by a single-crystal X-ray study to be a phenylvinylidene bridged A-frame complex having the structure shown in Figure 1.[6] **2a** possesses approximate mirror symmetry with no formal Rh–Rh bond and



1



(1)

2a

(1) Present address: Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104.

(2) See, for example: (a) Hoffman, D. M.; Hoffmann, R.; Fisel, C. R. *J. Am. Chem. Soc.* **1982**, *104*, 3858 and references therein. (b) Lukehart, C. M. "Fundamental Transition Metal Organometallic Chemistry"; Brooks/Cole Publishers: Monterey, CA, 1985; pp 154–163 and references therein.

(3) Wolf, J.; Werner, H.; Serhaldli, O.; Ziegler, M. L. *Angew. Chem.,Int. Ed. Engl.* **1985**, *22*, 414. Al-Obaidi, Y. N.; Green, M.; White, N. D.; Taylor, G. E. *J. Chem. Soc., Dalton Trans.* **1982**, 319–326.

(4) Woodcock, C.; Eisenberg, R. *Inorg. Chem.* **1985**, *24*, 1285.

(5) Spectroscopic data for **2a**. ^1H NMR (C_6D_6) (CH_2 region) δ 3.85 (m, 2 H), 2.25 (m, 2 H); $^{31}P\{^1H\}$ NMR δ 31.22 (m); IR (Nujol mull) ν(CO) 1934 (s), 1910 (s) cm^{-1}.

(6) Crystal data for **2a**: $P\bar{1}$ with a = 14.684 (4) Å, b = 14.818 (4) Å, c = 13.527 (2) Å, α = 102.56 (2)°, β = 101.56 (2)°, γ = 73.13 (2)°, and V = 2719.3 Å^3; Z = 2, d_{calcd} = 1.377 g cm^{-3}; convergence with R_1 = 0.048, R_w = 0.069, and GOF = 1.93 (631 variables, 4562 reflections with $I > 3\sigma(I)$, all non-hydrogen atoms anisotropic). Full details of the structure solution will be presented in a separated report.

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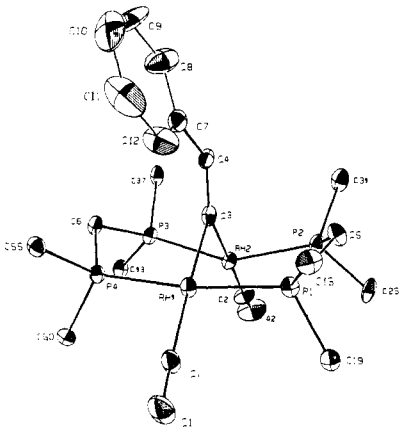
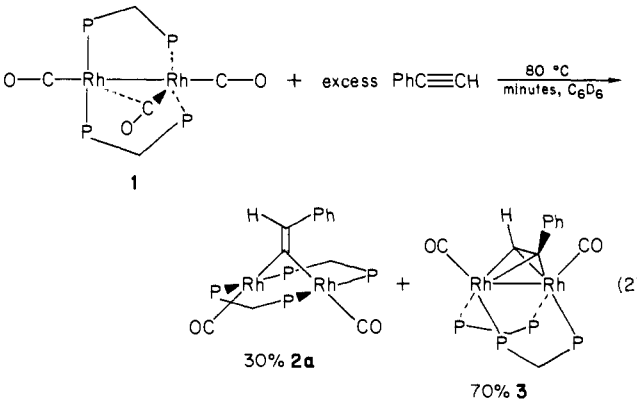


Figure 1. Molecular structure of **2a** (only ipso carbons of dppm phenyl rings included for clarity). Selected bond distances (Å) and angles (deg): Rh1–Rh2 = 3.011 (1); Rh1–C3 = 2.063 (7); Rh2–C3 = 2.051 (7); C3–C4 = 1.329 (9); Rh1–C3–Rh2 = 94.1 (3); C3–C4–C7 = 126.2 (7); C1–Rh1–C3 = 177.3 (3); C2–Rh2–C3 = 178.6 (3); P1–Rh1–P4 = 172.12 (7); P2–Rh2–P3 = 152.44 (8).

square-planar coordination about each Rh (see Figure 1 caption for important distances and angles). A reaction similar to (1) also occurs between *t*-BuCCH and **1** forming the intensely blue vinylidene complex $Rh_2(CO)_2(dppm)_2(C{=}C(H)(t\text{-}Bu))$ (**2b**). Both **2a** and **2b** have recently been reported by Grundy following a different synthetic route.[7]

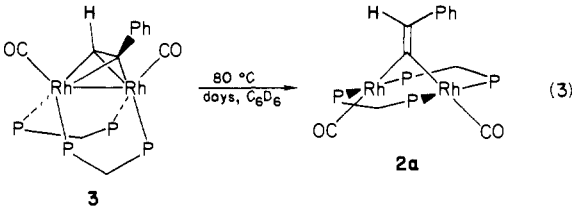
The reaction between **1** and PhCCH when carried out at 80 °C, however, yields a different product distribution as shown in eq 2. Under these conditions, **2a** accounts for only 30% of the



(2)

products, with the remainder being a new compound **3**. This compound, which is the sole initial product if **1** is reacted with PhCCH in acetone, shows a stretch at 1425 cm^{-1} assignable to η^2-coordinated C≡C.[8-10] The ^1H NMR spectrum of **3** exhibits four inequivalent dppm methylene protons and an acetylene proton split into a triplet by two equivalent Rh nuclei. The $^{31}P\{^1H\}$ NMR spectrum shows two multiplets indicative of two inequivalent dppm P donor atoms. We assign an acetylene-bridged structure to **3** on the basis of this spectroscopic data and the fact that the analogous diphenylacetylene complex, $Rh_2(\mu\text{-PhCCPh})(CO)_2(dppm)_2$, with similar spectroscopic properties has been found by X-ray crystallography to have a μ_2-η^2 acetylene bridged structure.[11]

The isolated vinylidene complex **2a** is stable indefinitely at 80 °C in benzene or acetone solution, while the acetylene complex **3** slowly converts to **2a** under the same conditions, eq 3. This



(3)

isomerization takes place with a half-life of ca. 27 h, in contrast with the formation of products in eq 2 which is complete within 15 min. Thus it can be concluded that the formation of **2a** and **3** in eq 2 follows a kinetic distribution of products.

The kinetics of the reaction between **1** and PhCCH have been studied using ^1H NMR spectroscopy.[12] When the reaction is carried out under pseudo-first-order conditions ([**1**], 13.4–15.6 mM; [PhCCH], 0.351–1.52 M; benzene, 28.5 °C), the disappearance of **1** is first order in both [**1**] and [PhCCH], with **2a** representing >95% of the total products formed and **3** corresponding to the remaining ~5%. When approximately equal concentrations of **1** and PhCCH are employed, plots of $[\mathbf{1}]^{-1}$ vs. time are linear yielding a second-order rate constant of 4.28 (5) × 10^{-4} M^{-1} s^{-1} but with a product ratio **2a**:**3** of 2.7:1. Significantly, this ratio remains approximately constant during the course of these runs, showing only minor change from 2.7 to 2.9 reflecting the slow conversion established in eq 3. The constancy of the product ratio under second-order conditions indicates that at low [PhCCH] both **2a** and **3** follow a rate dependence that is proportional to [**1**][PhCCH]. The overall second-order rate constant can therefore be partitioned according to the observed product ratio, yielding individual rate constants for the formation of **2a** and **3** of 3.1 (1) × 10^{-4} M^{-1} s^{-1} and 1.2 (1) × 10^{-4} M^{-1} s^{-1}, respectively.

When PhCCD is employed under approximately equimolar conditions, an overall rate constant of 2.22 (5) × 10^{-4} M^{-1} s^{-1} is obtained with a product ratio **2a**-d_1:**3**-d_1 of 1.1:1. As with PhCCH, this ratio remains nearly constant through >85% completion of the reaction, allowing calculation of k_2 for **2a**-d_1 and **3**-d_1 of 1.2 (1) × 10^{-4} M^{-1} s^{-1} and 1.1 (1) × 10^{-4} M^{-1} s^{-1}, respectively. From these data, a kinetic isotope effect k_H/k_D for the formation of **2a** is determined to be 2.6 while that for the formation of **3** is 1.1. The ratio of **2a**-d_1:**3**-d_1 is greatly influenced by CO, changing from 1.1:1 in the absence of CO to ca. 4:1 under a CO pressure of 100 torr.[13,14]

The kinetics study shows that while the formation of **2a** at both high and low [PhCCH] is first order in phenylacetylene concentration, the kinetic dependence on [PhCCH] for the formation of **3** exhibits a more complicated functional form, being first order in [PhCCH] only a low concentrations of the acetylene and significantly less than first order at high [PhCCH]. This observation together with the inhibition of **3**-d_1 relative to **2a**-d_1 under CO strongly suggests a preequilibrium involving CO dissociation in the formation of **3**. The formation of the vinylidene complex **2a**, on the other hand, proceeds via a bimolecular process between **1** and PhCCH with C–H activation occurring in or before the rate-determining step of the reaction as indicated by the kinetic

(7) Deranylgala, S. P.; Grundy, K. R. *Organometallics* **1985**, *4*, 424–426.

(8) Spectroscopic data for **3** obtained in 52% isolated yield. ^1H NMR (C_6D_6) δ 6.02 (1 H, t, $^2J_{Rh\text{-}H}$ = 6.8 Hz, PhCC*H*), 4.51 (1, H, q, $J_{P\text{-}H} \sim J_{H\text{-}H}$ = 11 Hz, CH_2), 3.76 (1 H, q, $J_{P\text{-}H} \sim J_{H\text{-}H}$ = 11 Hz, CH_2), 3.53 (1 H, q, $J_{P\text{-}H} \sim J_{H\text{-}H}$ = 11 Hz, CH_2), 3.33 (1 H, q, $J_{P\text{-}H} \sim J_{H\text{-}H}$ = 11 Hz, CH_2); $^{31}P\{^1H\}$ NMR δ 22.39 (m), 19.65 (m); IR ν(CO) 1938 (sh), 1923 (s) cm^{-1}; ν(C≡C) 1425 (m) cm^{-1}.

(9) By comparison, ν(C≡C) = 1425 cm^{-1} in the PhC≡CPh analogue[11] and 1402 cm^{-1} in $Co_2(CO)_6(HC{\equiv}CH)$: Iwashita, Y.; Tamura, F.; Nakamura, A. *Inorg. Chem.* **1969**, *8*, 1179–1183.

(10) Compound **3** has been previously reported as a product in the reaction of $Rh_2(CO)_2(dppm)_2(H)_2$ with PhCCH: Kubiak, C. P.; Woodcock, C.; Eisenberg, R. *Inorg. Chem.* **1978**, *21*, 2119.

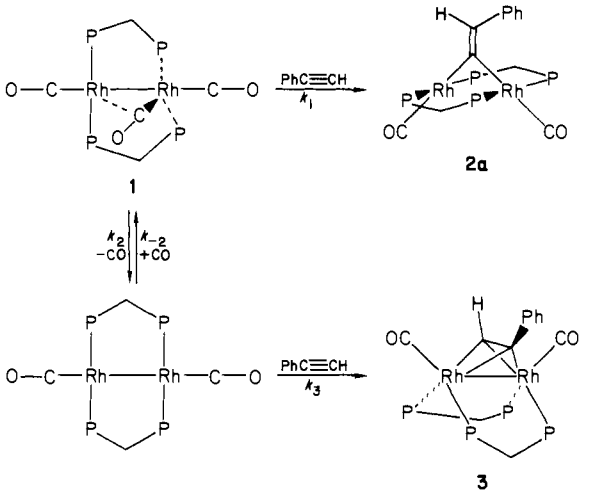
(11) Berry, D. H.; Eisenberg, R., manuscript in preparation.

(12) Phenyl acetylene was twice distilled, freeze–pump–thawed, and stored in a nitrogen atmosphere glovebox. Standard solutions of **1** in benzene-d_6 (0.0161–0.0165 M) were prepared and used under nitrogen. All runs were followed to 75–95% completion. NMR tube samples were flame-sealed under nitrogen. Temperatures were maintained constant within ±0.2 °C.

(13) The inhibition of **3** by CO has been observed qualitatively at 28.5 and 80 °C. In addition, the formation of **2a** appears to be slowed somewhat by CO, probably as the result of reversible coordination of CO to **1** forming the fully saturated complex $Rh_2(CO)_4(dppm)_2$.

(14) Compound **2a** appears to coordinate CO rapidly and reversibly, as evidenced by an upfield shift in the methylene protons in the ^1H NMR spectrum and a change of the intense purple color to yellow. Coming after the slow step, this equilibrium only affects the kinetics in that the CO concentration in solution is diminished.

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.

Acknowledgment. We thank the National Science Foundation (CHE 83-08064) and the Office of Naval Research for support of this work and the Johnson Matthey Co., Inc., for a generous loan of rhodium salts.

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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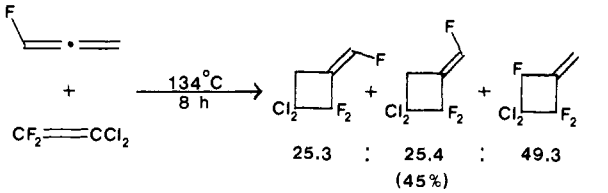
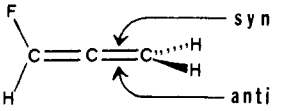
The cycloadditions of fluoroallene (MFA) and 1,1-difluoroallene (DFA) may, on the basis of reaction characteristics, be clearly demarcated into two broad categories, which also seem to be clearly distinguishable mechanistically. First, those reactions that are orbital-symmetry allowed, such as Diels–Alder[1] 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



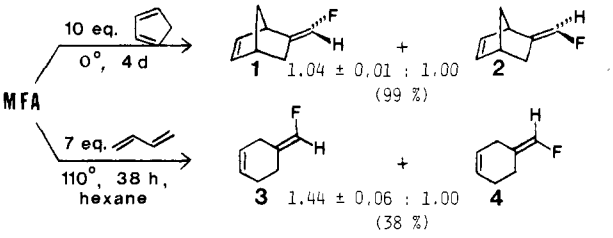
contrast to comparable studies of monoalkyl allenes wherein a definite preference for net anti addition has been reported and a steric rationale proposed.[4]

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

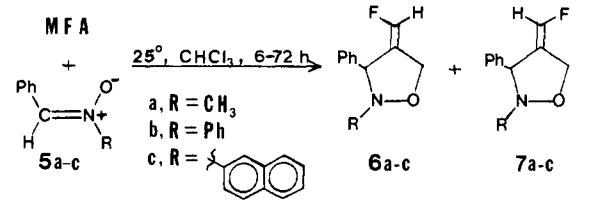


reaction with 1,3-butadiene leads to a much more significant (59:41) preference for the syn adduct **3**.[5]

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-

(1) Dolbier, W. R., Jr.; Burkholder, C. R. *J. Org. Chem.* **1984**, *49*, 2381 and references therein.

(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.

(3) Dolbier, W. R., Jr.; Wicks, G. E. *J. Am. Chem. Soc.* **1985**, *107*, 3626.

(4) (a) Pasto, D. J.; Warren, S. E. *J. Am. Chem. Soc.* **1982**, *104*, 3670. (b) Pasto, D. J.; Yang, S.-H. *J. Am. Chem. Soc.* **1984**, *106*, 152.

(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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