lett-Packard 5381A frequency counter and are shown in δ. Coupling constants were obtained by a first-order analysis of the spectra and are reliable to ±0.2 Hz. Some of the ^1H spectra were also recorded on a Hitachi R-20B spectrometer at 60 MHz so as to aid the spectral assignments.

Materials. Syntheses and characterizations of triptycenes **2**,[16] **3**,[17] **5**,[20] **9**,[6] and **10**[7] are described elsewhere. 9-Methyl-,[25] 9-ethyl-,[25] 9-benzyl-,[26] 9-isopropyl-,[27] and 9-*tert*-butylanthracene[28] were prepared as described in the literature. Preparation of 1,8-dichloro-9-ethylanthracene is described elsewhere.[29]

General Procedure for the Synthesis of Tetrafluorotriptycenes. To a boiling solution of 1.5 mmol of 9-alkylanthracene and 0.5 mL of isopentyl nitrite in 30 mL of dichloromethane was added dropwise a solution of 3.0 mmol of tetrafluoroanthranilic acid[30] in 20 mL of tetrahydrofuran during the course of 1 h, and the mixture was heated under reflux for 1 h. After evaporation of the solvent, the residue was chromatographed through an alumina column with hexane containing 5% of benzene as the eluent. The fractions containing the desired triptycene were usually contaminated with a considerable amount of the corresponding 1,4-adduct, 9-alkyl-1,2,3,4-tetrafluoro-5,12-dihydro-5,12-ethenonaphthacene, which was removed by fractional crystallizations from tetrahydrofuran–hexane. Yields, melting points, and analytical data of the triptycenes are compiled in Table IV.

Registry No. 1, 89657-23-8; 2, 89657-24-9; 3, 73524-75-1; 4, 89657-25-0; 5, 88473-97-6; 6, 89657-26-1; 7, 89657-27-2; 8, 89657-28-3; 9, 86194-40-3; 19, 89657-29-4; 3,4,5,6-tetrafluoroanthranilic acid, 1765-42-0.

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Rearrangements of Ylides Generated from Reactions of Diazo Compounds with Allyl Acetals and Thioketals by Catalytic Methods. Heteroatom Acceleration of the [2,3]-Sigmatropic Rearrangement

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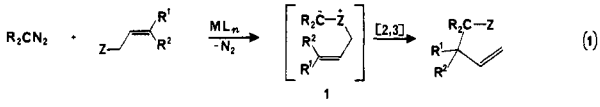
Allyl acetals undergo ylide generation in rhodium(II) acetate catalyzed reactions with diazo esters with subsequent production of 2,5-dialkoxy-4-alkenoates by the [2,3]-sigmatropic rearrangement in moderate to good yields. The synthetic versatility of this class of polyfunctional compounds has been examined with selected transformations. Cyclopropanation and Stevens rearrangement compete with the [2,3]-sigmatropic rearrangement in certain cases, and the influence of reactant structure and reaction conditions on this competition is reported. Comparative results with allyl ethers, which undergo cyclopropanation almost exclusively, demonstrate that heteroatom substitution on the allylic carbon accelerates ylide rearrangement. With dithioketals such as 2-ethenyl-2-methyl-1,3-dithiane, the ylide generated from $Rh_2(OAc)_4$ catalyzed reactions of ethyl diazoacetate undergoes [2,3]-sigmatropic rearrangement in competition with intramolecular elimination but without evidence of either cyclopropanation or Stevens rearrangement. Only when the [2,3]-sigmatropic rearrangement cannot occur competitively does the Stevens rearrangement become important in reactions with dithioketals. In these examples the catalytic methodology for ylide generation is advanced as an attractive alternative to base promoted methodologies.

We have previously reported that $Rh_2(OAc)_4$ and $Rh_6(CO)_{16}$ catalyzed reactions of diazo compounds with a broad selection of allylic substrates result in products of the [2,3]-sigmatropic rearrangement of intermediate allylic ylides (eq 1).[1] Allylamines, sulfides, and iodides give the



(1)

corresponding sigmatropic rearrangement product exclusively, whereas allyl bromides and chlorides undergo catalytic cyclopropanation in competition with ylide formation and rearrangement. In the series of allyl chloride, bromide, and iodide, allyl iodide gave the highest and allyl chloride the lowest yield of ylide-derived product. The extent of ylide generation through reaction of an allyl halide with an electrophilic metal carbene is consistent with the relative nucleophilicities of halides,[2] but C–Z bond strengths may also contribute to the effectiveness of these sigmatropic rearrangements.

Although the catalytic methodology for ylide generation is applicable to the general classification of allylic substrates, its most advantageous use is in the preparation of allylic ylides that are not amenable to generation by the base-promoted methodologies.[3] However, the relative ability of heteroatoms such as oxygen[4] or chloride[1] to stabilize free ylides such as **1** has been disappointing. Cyclopropane formation is the dominant product-forming process with these allylic substrates. To compensate for

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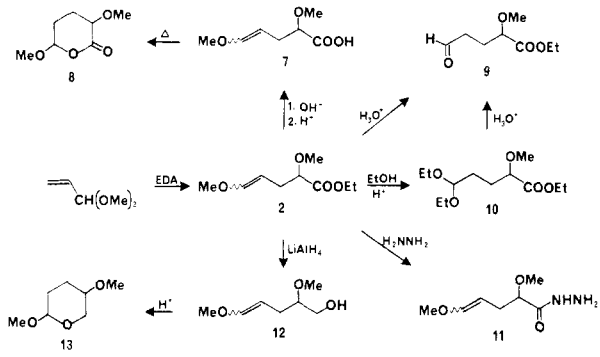
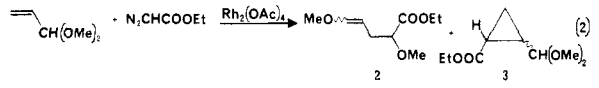
Scheme I



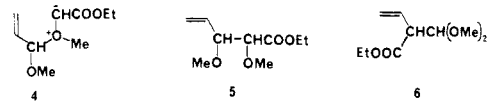
this apparent decreased tendency toward ylide generation, we have positioned substituents on the allylic carbon that can be expected to enhance the reactivity of the catalytically derived ylide intermediate toward formal [2,3]-sigmatropic rearrangement.[5] We now report results of transition metal catalyzed reactions of diazo compounds with allyl acetals and thioketals that provide a simple route to synthetically useful multifunctional organic compounds. These results demonstrate the effectiveness of heteroatom substitution at the allylic carbon in orienting product formation through the formal [2,3]-sigmatropic rearrangement pathway.

Results

Oxygen Ylides. Treatment of the dimethyl acetal of acrolein with ethyl diazoacetate at 25 °C in the presence of 0.5 mol % of $Rh_2(OAc)_4$ results in the formation of **2** and **3** (eq 2) in a molar ratio of 3.3 (**2**/**3**). The production



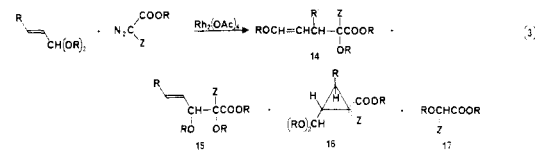
of **2**, formally derived from [2,3]-sigmatropic rearrangement of the oxygen ylide **4**, is surprising in view of our



observation that cyclopropane formation in reactions of ethyl diazoacetate with allyl ethyl ether and allyl methyl ether occurred to the near exclusion of insertion (<5% yield) under identical conditions.[6] Neither the product of direct insertion on acrolein dimethyl acetal (**5**) nor **6**, which is formed in high yield by Lewis acid catalysis,[7] is observed. However, ethyl methoxyacetate is reproducibly formed under these conditions, albeit in low yield (1%).

When prepared on a moderate synthetic scale (0.2 mol) with a [acetal]/[EDA] ratio of only 2.0, **2** could be obtained after distillation in 47% yield and in greater than 90% purity. The synthetic versatility of this polyfunctional compound was briefly examined (Scheme I) and, except for the acid-catalyzed conversion of **12** to **13**, the products described were isolated in greater than 80% yield. Although the sensitivity of **13** to acid resulted in its partial decomposition, the approach to its synthesis outlined in Scheme I is preferable to that previously employed.[8]

In an effort to understand the scope and limitations of oxygen ylide generation and rearrangement similar to that found with acrolein dimethyl acetal, reactions of both ethyl diazoacetate and dimethyl diazomalonate with a series of representative acetals were examined under standard conditions. In addition to the anticipated cyclopropane products and those formally derived from the [2,3]-sigmatropic rearrangement of intermediate oxygen ylides, [1,2]-insertion products were also observed in select cases as was the α-alkoxyacetate or malonate derived from the reactant diazo compound (eq. 3). Diethyl fumarate and



maleate from reactions with ethyl diazoacetate were also evident in many of these reactions, but their yield was dependent on the rate of addition of ethyl diazoacetate. Their presence could be virtually eliminated by proper choice of addition time.[9] Cyclopropanation of the vinyl ether product **14** was competitive with formation of the primary reaction products. This secondary transformation was minimized with the use of excess reactant allyl acetal and was negligible when a 10-fold molar excess of the allyl acetal was employed. Results for reactions catalyzed by $Rh_2(OAc)_4$ are presented in Table I.

A variety of structural influences is evident in the products and product yields from reactions of these acetals with diazo compounds. Acetal modification from methyl to ethyl results in a dramatic reduction of the relative percentage of ylide derived products with a corresponding increase in cyclopropane products, whereas with the ethylene acetal of acrolein cyclopropane production is a minor process and carbon–oxygen insertion is relatively important. Increased selectivity for ylide-derived products is observed with the use of dimethyl diazomalonate rather than ethyl diazoacetate, but in reactions of either the dimethyl or diethyl acetals of acrolein with ethyl diazoacetate the carbon–oxygen insertion product **15** is not produced (<0.2%), even when these reactions were performed at 50 °C. A phenyl substituent at the 3-position of the reactant acetal greatly diminishes competition with cyclopropanation but facilitates occurrence of the [1,2]-insertion process.

The balance of products is further influenced by reaction temperature. Increasing the temperature does not greatly influence the ratio of ylide-derived to cyclopropane products (**14**+**15**/**16**) but, as was previously observed in reactions of crotyl bromide with ethyl diazoacetate,[1] temperatures greater than 25 °C cause a decrease in overall product accountability and an increase in the yield of **17**. The E/Z ratios for **14a** and **14c** are markedly affected by the reaction temperature and by acetal structure. Increasing the reaction temperature also causes a moderate decrease in cyclopropane stereoselectivity and in diastereoselectivity for formation of **14f** and **15e**,**f**.

Alternatives to $Rh_2(OAc)_4$, specifically CuCl·P(O-*i*-Pr)$_3$, Cu bronze, $Cu(OTf)_2$, $Rh_6(CO)_{16}$, and $Rh_2(OOCCF_3)_4$, were also evaluated for their activity in reactions of acrolein dimethyl acetal with ethyl diazoacetate, but only with

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Table I. Rhodium(II) Acetate Catalyzed Reactions of Diazo Esters with Allyl Acetals[a]

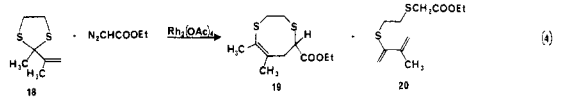
acetal, A	diazo compound, D[b]	temp, °C	addn time, h	[A]/[B]	yield, %[c]	relative yield, % 14 (isomer ratio)[d]	15 (isomer ratio)[e]	16 (isomer ratio)	17	(14 + 15)/16[f]
a H_2C=CHCH(OMe)$_2$	EDA	0	8	10	75	76 (5.7)		23 (2.1)	1	3.3
		25	8	10	60	75 (7.7)		23 (2.0)	2	3.3
		50	8	10	32	62 (12)		19 (1.9)	19	3.2
b	DAM	40	8	10	68	59 (>90)	10	16	15	4.3
		50	8	10	18	55 (50)	8	19	18	3.3
c H_2C=CHCH(OEt)$_2$	EDA	0	8	10	85	44		49 (2.2)	7	0.88
		25	8	10	78	42 (10)		49 (2.1)	9	0.74
		50	8	10	42	23		31 (2.0)	46	0.76
d	DAM	40	8	10	53	18 (>100)	5	49	28	0.47
		50	8	10	25	16 (>100)	7	45	32	0.51
e	EDA	0	50	1.0	34[g]	68	18 (4.8)	14 (1.4)	<1	6.1
		25	16	1.0	44[g]	61	24 (4.0)	15 (1.3)	<1	5.7
f (*E*)-C_6H_5CH=CHCH(OMe)$_2$	EDA	0	16	2.0	43	73 (1.58)	16 (1.12)	11 (2.2)		8.1
		25	16	2.0	62	72 (1.49)	18 (1.05)	10 (2.1)		9.0
		50	16	2.0	59	76 (1.33)	15 (0.98)	9 (1.5)		10
g	DAM	25	16	2.0	84	83	17			>100
		40	20	1.0	69[h]	80	20			>100

[a] Catalyst was employed in 1.0 mol %, based on diazo compound. [b] EDA = ethyl diazoacetate, DAM = dimethyl diazomalonate. [c] Isolated composite yield of **14-17**. [d] Except for **14f**, which is the diastereomer ratio of the *E* isomer, *E*/*Z* isomer ratios are reported. [e] Diastereoisomer ratio. [f] trans/cis ratio of cyclopropanes a, c, and e; **16f** (B/A). [g] Products from cyclopropanation of **14e** were isolated in 8–12% yield. [h] Products were isolated after distillation in 53% yield for the reaction performed on a 0.025 mol scale.

$Rh_2(OOCCF_3)_4$ did product yields approach those reported for $Rh_2(OAc)_4$. Comparative results with $Rh_2(OAc)_4$, $Rh_2(OOCCF_3)_4$, and $Cu(OTf)_2$ catalysts are recorded in Table II. The low activity of $Rh_6(CO)_{16}$ and of the copper catalysts for these transformations is consistent with prior observations from reactions of ethyl diazoacetate with allyl bromides and chlorides.[1]

Sulfur Ylides. Ando and co-workers have thoroughly investigated the formation and rearrangements of ylides derived from reactions of diazo compounds with organic monosulfides in thermal, photochemical, and, in select cases, catalytic processes.[10] Three major pathways for sulfur ylide rearrangement have been identified: intramolecular elimination, [1,2] rearrangement, and [2,3]-sigmatropic rearrangement. With simple allyl sulfides the [2,3]-sigmatropic rearrangement is the major reaction pathway, and recent applications to the synthesis of penicillins[11] have demonstrated its advantages. In view of the catalytic effectiveness of $Rh_2(OAc)_4$ for ylide generation from diazo compounds[1] and the enhanced ability of oxygen ylides formed from allyl acetals to undergo the [2,3]-sigmatropic rearrangement, we have examined the reaction characteristics of analogous thioketals.

Because of their convenience in preparation,[12] 2-vinyl derivatives of 1,3-dithiane and 1,3-dithiolane were chosen for investigation. Treatment of **18** with ethyl diazoacetate at 60 °C in the presence of 1.0 mol % of $Rh_2(OAc)_4$ resulted in the production of only two products (eq 4, **19**/**20** = 0.58) in 92% isolated yield when a 4-fold excess of **18**



(4)

over ethyl diazoacetate was employed. With a reactant ratio of 2.0 these products were formed in only 69% yield (**19**/**20** = 0.82), and at least three additional higher boiling compounds, presumed to be products from cyclopropanation of **19** and **20**, were produced in an estimated 16% yield. The *Z* geometry of **19** was inferred by its complex NMR spectrum which revealed that the coupling constants between the proton at the 5-position, adjacent to the carboethoxy group, and each of the two adjacent protons were identical. Inspection of models for (*E*)-**19** suggests a rigid structure that would eclipse H-5 with one of the protons of the adjacent methylene group. Recovery of excess **18** was greater than 90%.

With the analogous 1,3-dithiane **21**, treatment with ethyl diazoacetate at 60 °C in the presence of 1.0 mol % of $Rh_2(OAc)_4$ yielded both of the [2,3]-sigmatropic rearrangement products **22a,b** and the elimination product **23** (**22**/**23** = 3.4) in 97% isolated yield (eq 5) when a 5-fold

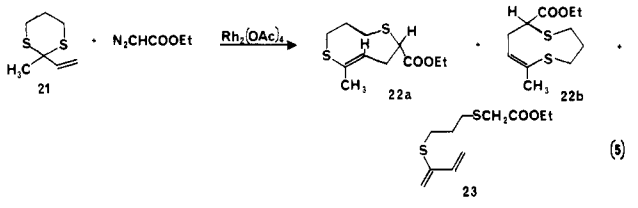


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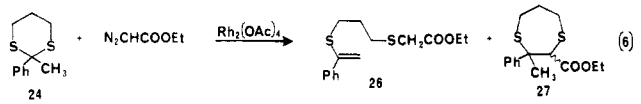
Table II. Influence of Catalyst on Product Yields and Selectivities in Reactions of Ethyl Diazoacetate with Allyl Acetals[a]

acetal	catalyst	addn time, h	[A]/[D][b]	yield, %	rel. yield, % 14 (isomer ratio)[c]	15 (isomer ratio)[c]	16 (isomer ratio)[d]	(14 + 15)/16
a H_2C=CHCH(OMe)$_2$	$Rh_2(OAc)_4$	8	10	60	76		24 (2.0)	3.2
	$Rh_2(OOCCF_3)_4$	8	10	62	69		31 (1.7)	2.2
	$Cu(OTf)_2$	4	10	27	68		32 (2.4)	2.1
f (E)-C_6H_5CH=CHCH(OMe)$_2$	$Rh_2(OAc)_4$	8	2.0	62	72 (1.6)	18 (1.1)	10 (2.2)	9.0
	$Rh_2(OOCCF_3)_4$	8	2.0	10	83 (1.3)	10 (1.1)	7 (1.4)	13
	$Cu(OTf)_2$	4	2.5	35[e]	5 (1.0)	11 (1.2)	21 (2.4)	0.8

[a] Reactions were performed at 25 °C; catalyst was employed in 1.0 mol %, based on ethyl diazoacetate. [b] [acetal]/[EDA]. [c] Diastereoisomer ratio. [d] Trans/cis ratio of cyclopropanes; **16f** (B/A). [e] Reaction mixture included (relative yield) ethyl (E)-2-(dimethoxymethyl)-4-phenyl-3-butenoate (49%) and ethyl (E)-3,3-dimethoxy-5-phenyl-4-pentenoate (14%), both products of Lewis acid promoted homologation (ref 7).

excess of **21** over ethyl diazoacetate was employed. The E and Z olefin isomers were obtained in a ratio (**22a**/**22b**) of 8.3. With a reactant ratio of 2.0 reaction products **22** and **23** were formed in only 73% yield (**22**/**23** = 3.6), and at least three additional higher boiling compounds, consistent with the anticipated reactivity of **22** and **23** toward catalytic cyclopropanation,[9] were produced in an estimated 17% yield. Reactions performed at 40 °C gave similar results. The E geometry of the major isomer of **22** was inferred from the complex NMR spectra of the individual isomers. The olefinic proton of the major isomer is observed at δ 5.69 with unequal coupling constants to the two protons of the adjacent methylene group (10.2 and 6.1 Hz), whereas the olefinic proton of the minor isomer is observed at δ 6.16 with coupling constants to the protons of its adjacent methylene that are nearly equal (7.7 and 7.1 Hz). The large difference in coupling constants from the major isomer is consistent with the anticipated structural rigidity of (*E*)-**22**. The near equivalence of coupling constants from the minor isomer is consistent with the coupling constant pattern of (*Z*)-**19**.

Products of [1,2] rearrangement of intermediate sulfur ylides were not observed (<0.2%) in reactions of ethyl diazoacetate with either **18** or **21**. For comparison, 1,3-dithianes **24** and **25** were treated with ethyl diazoacetate under similar reaction conditions (eq 6,7). With **24** the



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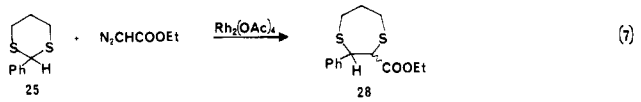
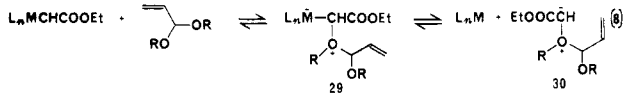


(7)

elimination product **26** was dominant (**26**/**27** = 4.6, 98% isolated yield), and [1,2] rearrangement gave **27** with a diastereoisomer ratio of 15. Chemical shift data from the NMR spectrum of **27** suggests that the major isomer is the one in which the carbethoxy and phenyl groups are oriented trans. With **25**, which cannot undergo elimination, **28** was produced in 73% yield with a diastereoisomer ratio of 1.07.

Discussion

That ylides derived from allyl acetals undergo preferential rearrangement in competition with cyclopropanation, whereas those derived from the corresponding allyl ethers are relatively unresponsive to ylide rearrangement, demonstrates that heteroatom substitution at the allylic carbon accelerates ylide rearrangement. Because of steric congestion and the electron-withdrawing influence of the α-alkoxy substituent, the facility of allyl acetals for [2,3]-sigmatropic rearrangement cannot result from the stability of intermediate ylides or metal-stabilized ylides derived from acetals relative to ethers. Rather, this acceleration of ylide rearrangement must be associated with the electronic influence of the α-alkoxy substituent. Comparison of relative reactivities for ylide rearrangement and cyclopropanation between acetals and ethers further suggests that the electrophilic metal carbene responsible for these competitive transformations exists in dynamic equilibrium with the metal-associated ylide (eq 8). Metal



(8)

dissociation forms the reactive ylide (**30**).[1,13] Dissociation of the nucleophile returns the metal-associated ylide to reactants[14,15] which can subsequently undergo reassociation at oxygen to form **29** or at the carbon–carbon double bond to produce cyclopropane products.[16] However, although reactions with allyl dithioketals and the dimethyl or diethyl acetal of acrolein are adequately explained by this scheme, the formation of [1,2]-rearrangement products (**15**) demands further elaboration.

Products from the Stevens [1,2] rearrangement[17] are produced in reactions of allyl acetals with dimethyl diazomalonate and in reactions of the ethylene acetal of acrolein and the dimethyl acetal of cinnamaldehyde with ethyl diazoacetate (Table I). They are not formed in reactions of allyl dithioketals or of acrolein dialkyl acetals with ethyl diazoacetate (<0.2%). With dithioketals the [1,2] rearrangement process becomes important only when the [2,3]-sigmatropic rearrangement cannot occur competitively. The concerted [2,3]-sigmatropic rearrangement is characteristic of stable ylides, whereas occurrence of the Stevens rearrangement suggests homolytic[3b] or heterolytic[1] cleavage of the intermediate ylide.

Although our results do not conclusively differentiate between homolytic and heterolytic cleavage of ylides, the dramatic influence of structure on the extent of [1,2] rearrangement suggests the pathway described by Scheme

(13) (a) Weber, L. *J. Organomet. Chem.* **1977**, *131*, 49. (b) Casey, C. P.; Burkhardt, T. J.; Bunnell, C. A. Calabrese, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 2127.
(14) (a) Brookhart, M.; Tucker, J. P.; Husk, G. R. *J. Am. Chem. Soc.* **1983**, *105*, 258. (b) Wong, W.-K.; Tam, W.; Gladysz, J. A. *Ibid.* **1979**, *101*, 5441. (c) Brandt, S.; Helquist, P. *Ibid.* **1979**, 6473. (d) Sharp, P. R.; Schrock, R. R. *J. Organomet. Chem.* **1979**, 171.
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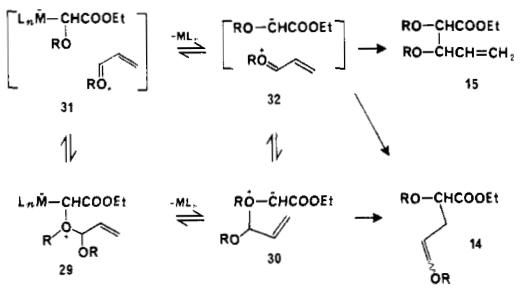
(16) (a) Doyle, M. P.; Dorow, R. L.; Griffin, J. H.; Tamblyn, W. H.; Trudell, M. L. *Organometallics* **1984**, *3*, 44. (b) Doyle, M. P.; Griffin, J. H.; Bagheri, V.; Dorow, R. L. *Organometallics* **1984**, *3*, 53.
(17) Stevens, T. S.; Creighton, E. M.; Gordon, A. B.; MacNicol, M. *J. Chem. Soc.* **1928**, 3193.

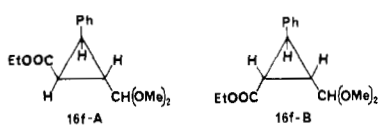
Scheme II



II. Both **29** and **30** are potential precursors of the dissociated species, **31** and **32**, respectively, which can formally recombine to either the [2,3]- or the [1,2]-rearrangement product. That the allyl cation must react with the carbanion $(ROCHCOOEt)^-$ or the corresponding metal stabilized carbanion,[18] rather than the reactant diazo compound, is demanded by results from boron trifluoride catalyzed reactions of these same allyl acetals with ethyl diazoacetate,[7,19] from which a different set of products is formed exclusively. That recombination preferentially occurs to the original acetal carbon, rather than at the 3-position, is inferred by results from reactions of similar cations with nucleophiles,[20] including ethyl diazoacetate,[7] in which combination occurs at the 1-position with a high degree of selectivity. As indicated by results with cinnamaldehyde dimethyl acetal and reactions of allyl acetals with dimethyl diazomalonate, increasing the stability of either or both of the dissociated species in **31** or **32** increases the importance of this pathway for product formation.

Rhodium(II) acetate catalyzed reactions of allyl acetals with diazo compounds also forms products (**17**) that are formally derived from alcohol insertion by the intermediate carbenoid species. These products are most prevalent when the [1,2] rearrangement is operative and also when reactions are performed at temperatures above 25 °C. The dissociative pathway outlined in Scheme II is consistent with these observations. Proton transfer to the enolate or to the metal-associated enolate completes the formation of **17**.

The stereoselectivity observed in the formation of the cyclopropane product derived from the dimethyl acetal of cinnamaldehyde and ethyl diazoacetate provides a unique example for examination of the constraints encountered in catalytic cyclopropanation reactions. The reaction of ethyl diazoacetate with styrene using $Rh_2(OAc)_4$ catalysis forms the trans isomer preferentially (t/c = 1.6). As is evident from Table I, the *trans*-cyclopropane is produced with even greater stereochemical preference using the dimethyl acetal of acrolein (t/c = 2.0). Extrapolation of these selectivities to the cyclopropanation of the dimethyl acetal of cinnamaldehyde would suggest that **16f**-A would



dominate. Instead, **16f**-B is the dominant isomer (B/A = 2.1). The cause of this apparently abnormal selectivity is directly associated with preferential initial bond formation with the intermediate metal carbene at the 2-position, rather than at the 3-position, of (*E*)-1,1-dimethoxy-3-phenyl-2-propene that provides stabilization of the developing electrophilic center by the phenyl substituent, rather than by the dimethoxymethyl group. Application of this contribution to the detailed mechanism of cyclopropane formation from electrophilic metal carbenes[16b] accounts for the observed selectivity.

Bond dissociation that would lead to Stevens rearrangement products is not observed for the sulfur ylides derived from **18** and **21**. In these cases competition between [2.3]-sigmatropic rearrangement and intramolecular elimination of the intermediate ylide provide full accounting of the reaction process (Scheme III). Ring size of the sigmatropic rearrangement product, **19**, and, perhaps, the 2-propenyl group of **18** influence the rate for rearrangement relative to elimination, causing the 2:1 preference for elimination. With **21**, the [2,3]-sigmatropic rearrangement is favored over elimination by nearly 4:1. This 8-fold change in relative reactivity is consistent with Scheme III. Although less stable than **34a**, ylide diastereoisomer **33a** is the source of **19** in reactions of **18** with ethyl diazoacetate. Since sigmatropic rearrangement of **34a** would lead to the unstable *E* isomer, which is not observed, and the alternative elimination pathway is available to this diastereoisomer, formation of **20** as the major reaction product can be explained as a consequence of this competition. With **21**, on the other hand, sigmatropic rearrangement and elimination can occur competitively from **34**.

Ring expansion by the [2,3]-sigmatropic rearrangement has recently received considerable attention.[21] The base-promoted methodology, developed by Vedejs, has been used with noteable success for macrolide synthesis.[22] The catalytic methodology, employed with diazoesters and copper powder, was reported to be inadequate by comparison.[23] However, results with **18** and **21** (eq 4,5) suggest that the use of $Rh_2(OAc)_4$ with diazoesters is an attractive alternative to the base-promoted methodology. This rhodium catalyst is employed at temperatures that are significantly lower than those previously used with copper catalysts (60 °C vs. 100 °C). The higher temperatures that are required for ylide generation with sulfur- or nitrogen-containing substrates compared with oxygen- or halide-containing substrates are the result of coordination of $Rh_2(OAc)_4$ with sulfur- or nitrogen-containing compounds that inhibits catalytic decomposition of diazo compounds.[1] Despite the higher reaction temperatures, however, reactions competing with sigmatropic rearrangement, such as the Stevens rearrangement, that are indicative of homolytic or heterolytic detachment within the ylide are negligible in the examples accumulated thus far.[1,4]

The diastereoselectivity observed in Stevens rearrangements of the ylides derived from **24** and **25** (eq 6,7) is surprising. The 2-methyl substituent has an unexpected influence in ordering the transition state for this intramolecular combination, resulting in a diastereoisomer ratio of 15 as opposed to a ratio of 1.1 when the methyl group is replaced by hydrogen. Just the opposite result would have been expected if diastereoselection was a consequence

(18) Alternate association through enolate oxygen is also consistent with this explanation.

(19) In BF_3-catalyzed reactions the dominant product was that of formal carbene insertion between the vinyl and acetal carbons.

(20) Perst, H. "Oxonium Ions in Organic Chemistry"; Academic Press: New York, 1971; Chapter 5.

(21) (a) Vedejs, E.; Arco, M. J.; Powell, D. W.; Renga, J. M.; Singer, S. P. *J. Org. Chem.* **1978**, *43*, 4831. (b) Vedejs, E.; Arnost, M. J.; Hagen, J. P. *Ibid.* **1979**, *44*, 3230. (c) Vedejs, E.; Hagen, J. P. *J. Am. Chem. Soc.* **1975**, *97*, 6878. (d) Schmid, R.; Schmid, H. *Helv. Chim. Acta* **1977**, *60*, 1361. (e) Cere, V.; Pollicino, S.; Sandri, E.; Fava, A. *J. Am. Chem. Soc.* **1978**, *100*, 1516.

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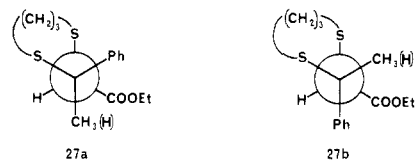
of product stability (e.g., **27a,b**). Although we are not able



27a 27b

at this time to provide definitive structural assignment of the major diastereoisomer derived from **24**, NMR spectra suggest **27b**. This assignment is consistent with steric influences by the methyl group on the orientation of the phenyl substituent in the transition state, for product formation. If allignment of the plane of the phenyl substituent is perpendicular to the C–CH_3 bond in the transition state for formation of **27**, but is parallel to the C–H bond for formation of **28**, the diastereoselectivity of both transformations is understandable.

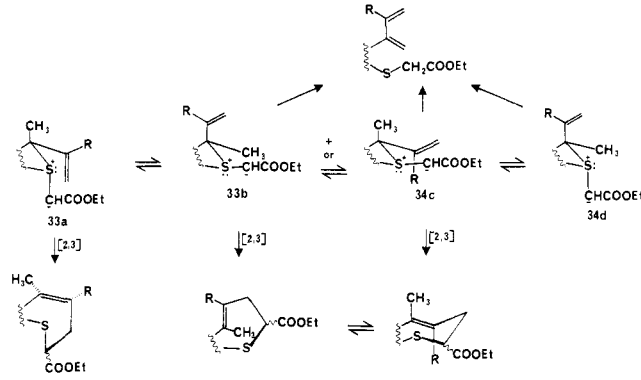
Experimental Section

General Methods. Instrumentation has been previously described.[16] Copper(II) trifluoromethanesulfonate,[24] rhodium(II) trifluoroacetate dimer,[25] copper bronze,[26] and (triisopropyl phosphite)copper (I) chloride[27] were prepared by standard procedures. The dimethyl acetal of cinnamaldehyde was prepared from cinnamaldehyde and trimethyl orthoformate in methanol.[28] The ethylene acetal of acrolein was obtained from the reaction of acrolein with 2-methoxy-1,3-dioxolane[29] in ethylene glycol. Dimethyl diazomalonate was prepared from dimethyl malonate and tosyl azide.[30] 2-Phenyl-1,3-dithiane (**25**) was prepared from 1,3-propanedithiol and benzaldehyde,[31] and the synthesis of 2-methyl-2-phenyl-1,3-dithiane (**24**)[32] employed the same procedure with acetophenone used in place of benzaldehyde.

Ethyl 2,5-Dimethoxy-4-pentenoate (2). Ethyl diazoacetate (25.4 g, 0.200 mol) was added at a rate of 1.5 mL/h to a stirred mixture of acrolein dimethyl acetal (40.8 g, 0.400 mol) and rhodium(II) acetate dimer (440 mg, 0.0010 mol) that was maintained at 20 °C. After addition was complete, the reaction solution was passed through a 2-cm column of neutral alumina with ether washings. Distillation of the resulting solution afforded 19.2 g of a fraction (bp 107–112 °C at 13 torr) which by GC analysis was composed of 93% **2** (47% yield) and 7% **3**. **2**, *E* isomer: ^{1}H NMR ($CDCl_3$) δ 6.34 (d of t, J = 12.6, 0.6 Hz, =C*H*OMe), 4.70 (d of t, J = 12.6, 7.5 Hz, CH_2CH=), 4.21 (q, J = 7.1 Hz, CH_2O), 3.73 (t, J = 5.8 Hz, CH_2CHOMe), 3.50 (s, =CHOCH_3), 3.39 (s, CHOCH_3), 2.36 (d of d of d, J = 7.5, 5.8, 0.6 Hz, CH_2CH=), 1.28 (t, J = 7.1 Hz, CH_3CH_2O). *Z* isomer: ^{1}H NMR ($CDCl_3$) δ 5.96 (d of t, J = 6.1, 1.5 Hz, =C*H*OMe), 4.41 (d of t, J = 7.3, 6.1 Hz, CH_2CH=), 4.21 (q, J = 7.1 Hz, CH_2O), 3.78 (t, J = 6.2 Hz, CH_2CHOMe), 3.57 (s, =CHOCH_3), 3.39 (s, CHOCH_3), 2.53 (d of d of d, J = 7.3, 6.2, 1.5 Hz, CH_2CH=), 1.28 (t, J = 7.1 Hz, CH_3CH_2O). Purification by redistillation (bp 80 °C at 1.5 torr) left only the *E* isomer ($E/Z > 50$). Anal. Calcd for $C_9H_{16}O_4$: C, 57.43; H, 8.57. Found: C, 57.30; H, 8.46.

Ethyl 2-(dimethoxymethyl)-1-cyclopropanecarboxylate (3): ^{1}H NMR ($CDCl_3$) δ 4.38 (d, J = 7.3 Hz, C*H*$(OMe)_2$, trans isomer), 4.33 (d, J = 4.3 Hz, C*H*$(OMe)_2$, cis isomer), 4.16 (q, J = 7.1 Hz, OCH_2, cis isomer), 4.13 (q, J = 7.1 Hz, CH_2O, trans isomer), 3.40 and 3.32 (s, OCH_3, cis isomer), 3.33 (s, 6 H, OCH_3, trans isomer), 1.80–1.55 (m, C*H*COOEt), 1.40–0.85 (m, 3 H), 1.27 (t, J = 7.1 Hz, OCH_2CH_3 of cis isomer), 1.25 (t, J = 7.1 Hz, OCH_2CH_3 of trans isomer).

Scheme III



Continued distillation of the reaction mixture revealed a second fraction, bp 125–133 °C at 13 torr, which was identified as the product of catalytic cyclopropanation of **2** by ethyl diazoacetate (5.3 g, 19 mmol): ^{1}H NMR ($CDCl_3$) δ 4.20 (q, J = 7.1 Hz, CH_2O, minor isomer), 4.12 (q, J = 7.1 Hz, CH_2O, major isomer), 3.95–3.50 (m, 2 H), 3.35 and 3.32 (s, 6 H, OCH_3), 2.5–1.6 (m, 4 H), 1.25 (t, J = 7.1 Hz, CH_3CH_2O, major isomer), 1.23 (t, J = 7.1 Hz, CH_3CH_2O, minor isomer). No other volatile products were obtained.

α,δ-Dimethoxy-δ-valerolactone (8). To 1.01 g of the mixture of ethyl 2,5-dimethoxy-4-pentenoate (93% **2**, $E/Z > 50$, 5.0 mmol) and **3** (7%) was added 10 mL of water containing 0.308 g of sodium hydroxide (5.5 mmol), and the resulting mixture was heated at reflux for 15 min. After cooling the homogeneous solution in an ice bath, 5.5 mL of 1 M hydrochloric acid was added and the resulting mixture was immediately extracted with ether. After drying over anhydrous magnesium sulfate, the ether was removed to yield 0.84 g of an oil whose spectral characteristics were the composite of 90% (*E*)-**7** and 10% of the acid derived from **16a**. Kugelrohr distillation of this oil at 130 °C (1.5 torr) yielded 0.69 g of **8** (89% yield). Anal. Calcd for $C_7H_{12}O_4$: C, 52.49; H, 7.55. Found: C, 52.29; H, 7.69.

Ethyl 2-Methoxy-5-oxopentanoate (9). Treatment of ethyl 2,5-dimethoxy-4-pentenoate (0.63 g of 90% **2**, 3.0 mmol) with concentrated sulfuric acid (1.5 mmol) in 30 mL of 98% aqueous acetone for 1.5 h at room temperature, followed by addition of water, and extraction with ether yielded 0.43 g of a colorless oil after distillation: bp 108–110°C (1.3 torr). 2,4-Dinitrophenylhydrazone of **9**, twice recrystallized from ethanol/water, gave mp 65°C.

Ethyl 5,5-Diethoxy-2-methoxypentanoate (10). Ethyl 2,5-dimethoxy-4-pentenoate (91% **2**, 2.0 mmol) was dissolved in 10 mL of absolute ethanol. After addition of 50 mg of *p*-toluenesulfonic acid, the reaction solution was heated at reflux for 1 h. Product isolation yielded 0.49 g of a colorless liquid composed of 88% **10** (87% yield) and 12% **16c**. Anal. Calcd for $C_{12}H_{24}O_5$: C, 58.04; H, 9.74. Found: C, 57.78; H, 9.92. Acetal **10** was converted into aldehyde **9** in 49% yield following treatment of **10** (0.41 g, 1.6 mmol) with 0.1 mL of concentrated hydrochloric acid in 0.5 mL of water and refluxing for 45 min.

2,5-Dimethoxy-1-oxo-4-pentenohydrazide (11). Ethyl 2,5-dimethoxy-4-pentenoate (91% **2**, 0.41 g, 2.0 mmol) was combined with 0.15 g of 60% aqueous hydrazine (3 mmol), and the resulting mixture was heated at 90 °C for 18 h. Excess hydrazine, water, and ethanol were removed under reduced pressure. Ether was then added to the residue, the mixture was filtered, and the ether was evaporated to leave 0.32 g of colorless oil.

2,5-Dimethoxytetrahydropyran (13). Ethyl 2,5-dimethoxy-4-pentenoate (91% **2**, 19.9 g, 0.106 mol) was added slowly to a stirred suspension of 4.8 g of lithium aluminum hydride in 70 mL of anhydrous ethyl ether. The mixture was stirred for an additional 15 min before careful addition of 5 mL of water, 10 g of anhydrous sodium sulfate, and 50 mL of ether. Following filtration and evaporation of the ether, the residual liquid was distilled (bp 73–75 °C (0.3 torr)) to yield 14.2 g of 90% pure **12** (91% yield). Alcohol **12** (11.7 g, 72 mmol) was added at a controlled rate over an 18-h period to a solution composed of 0.5 mL

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of concentrated sulfuric acid in 350 mL of ether. After 20 h sodium bicarbonate was added to neutralize the acid, and the volume of ether was reduced to 100 mL. The ether solution was then filtered through 2 cm of neutral alumina, and the residual ether was distilled under reduced pressure. Distillation of the remaining liquid yielded 6.8 g of **13**, bp 80 °C (21 torr) [lit.[8] bp 65 °C (10 torr)]. The spectral characteristics of **13** were identical with those previously reported.[8]

Reactions of Diazo Esters with Allyl Acetals. General Procedure. The diazo compound was added at a controlled rate (Sage Model 355 syringe pump) to a stirred mixture of the acetal and transition metal catalyst that was maintained under a nitrogen atmosphere. After gas evolution was complete, reaction solutions were passed through a 2-cm column of neutral alumina with ether washings. With $Cu(OTf)_2$ catalyzed reactions, ether was added to the reaction solution and then washed twice with a 25% aqueous solution of ethylene diamine. Dibenzyl ether was added as the internal standard. Product yields from reactions with the methyl and ethyl acetals of acrolein were determined by GC on Carbowax 20M or SP-2330 capillary columns. Duplicate experiments were minimally performed for each reported reaction. GC results were consistent with those obtained from integration of characteristic NMR absorptions for reaction products relative to those of the internal standard. Reaction products were distilled under reduced pressure: **e**, bp 76–84 °C (0.1 torr); **f**, bp 95–112 °C (1.0 torr); **g**, bp 130–145 °C (1.2 torr).

Methyl 2-carbomethoxy-2,5-dimethoxy-(*E*)-4-pentenoate (14b): ^{1}H NMR ($CDCl_3$) δ 6.35 (d of t, J = 12.7, 1.0 Hz, =C*H*OMe), 4.61 (d of t, J = 12.7, 7.6 Hz, CH_2CH=), 3.79 (s, 6 H, $COOCH_3$), 3.50 (s, OCH_3), 3.40 (s, OCH_3), 2.69 (d of d, J = 7.6, 1.0 Hz, CH_2CH=). Anal. Calcd for $C_{10}H_{16}O_6$: C, 51.71; H, 6.96. Found: C, 51.55; H, 6.89.

Methyl 2-carbomethoxy-2,3-dimethoxy-4-pentenoate (15b): ^{1}H NMR ($CDCl_3$) δ 6.11–5.68 (m, C*H*=CH_2), 5.45–5.20 (m, CH=C*H*$_2$), 4.21 (d, J = 7.4 Hz, C*H*OMe), 3.81 and 3.80 (two s, $COOCH_3$), 3.58 (s, OCH_3), 3.31 (s, OCH_3). Anal. Calcd for $C_{10}H_{16}O_6$: C, 51.71; H, 6.96. Found: C, 51.63; H, 6.88.

Dimethyl 2-(dimethoxymethyl)-1,1-cyclopropanedicarboxylate (16b): ^{1}H NMR ($CDCl_3$) δ 4.41 (d, J = 4.5 Hz, C*H*$(OMe)_2$), 3.75 and 3.73 (two s, $COOCH_3$), 3.31 (s, 6 H, OCH_3), 2.15 (d of d of d, J = 9.3, 7.4, 4.5 Hz, C*H*CH$(OMe)_2$), 1.76 (d of d, J = 7.4, 4.5 Hz, 1 H), 1.43 (d of d, J = 9.3, 4.5 Hz, 1 H). Anal. Calcd for $C_{10}H_{16}O_6$: C, 51.71; H, 6.96. Found: C, 51.50; H, 7.08.

Ethyl 2,5-diethoxy-4-pentenoate (14c): ^{1}H NMR ($CDCl_3$) δ 6.28 (d, J = 12.7 Hz, =C*H*OEt), 4.75 (d of t, J = 12.7, 7.5 Hz, CH_2CH=), 4.20 (q, J = 7.1 Hz, $COOCH_2$), 3.70 (q, J = 7.0 Hz, C*H*$_2$OCH=), 3.90–3.40 (m, CH_2O and C*H*OEt), 2.34 (d of d of d, J = 7.5, 6.6, 0.8 Hz, C*H*$_2$CH=), 1.27 (t, J = 7.1 Hz, $COOCH_2CH_3$), 1.22 (t, J = 7.0 Hz, CH_3CH_2O). Anal. Calcd for $C_{11}H_{20}O_4$: C, 61.07; H, 9.34. Found: C, 61.06; H, 9.48.

Ethyl 2-(diethoxymethyl)-1-cyclopropanecarboxylate (16c): ^{1}H NMR ($CDCl_3$) δ 4.49 (d, J = 7.1 Hz, C*H*$(OEt)_2$, trans isomer), 4.44 (d, J = 4.2 Hz, C*H*$(OEt)_2$, cis isomer), 4.14 (q, J = 7.1 Hz, $COOCH_2$, cis isomer), 4.12 (q, J = 7.1 Hz, $COOCH_2$, trans isomer), 3.9–3.3 (m, OCH_2), 1.85–1.50 (m, C*H*COOEt), 1.40–0.85 (m, 3 H), 1.25 (t, J = 7.1 Hz, $COOCH_2CH_3$), 1.18 (t, J = 7.1 Hz, OCH_2CH_3), 1.16 (t, J = 7.0 Hz, OCH_2CH_3). Anal. Calcd for $C_{11}H_{20}O_4$: C, 61.07; H, 9.34. Found: C, 60.96; H, 9.33.

Methyl 2-carbomethoxy-2,5-diethoxy-(*E*)-4-pentenoate (14d): ^{1}H NMR ($CDCl_3$) δ 6.27 (d of t, J = 12.8, 1.0 Hz, =C*H*Et), 4.66 (d of t, J = 12.8, 7.5 Hz, CH_2CH=), 3.77 (s, 6 H, $COOCH_3$), 3.70 (q, J = 7.0 Hz, CH_2O), 3.56 (q, J = 7.0 Hz, CH_2O), 2.66 (d of d, J = 7.5, 1.0 Hz, CH_2CH=), 1.24 (t, J = 7.0 Hz, 6 H, CH_3CH_2O). Anal. Calcd for $C_{12}H_{20}O_6$: C, 55.36; H, 7.76. Found: C, 55.18; H, 7.65.

Methyl 2-carbomethoxy-2,3-diethoxy-4-pentenoate (15d): ^{1}H NMR ($CDCl_3$) δ 6.15–5.72 (m, C*H*=CH_2), 5.40–5.16 (m, CH=C*H*$_2$), 4.35 (d, J = 7.0 Hz, C*H*OEt), 3.84 and 3.78 (two s, $COOCH_3$), 3.76 (q, J = 6.9 Hz, CH_2O), 3.56 (q, J = 7.0 Hz, CH_2O), 1.24 (t, J = 6.9 Hz, CH_3CH_2O), 1.14 (t, J = 7.0 Hz, CH_3CH_2O). Anal. Calcd for $C_{12}H_{20}O_6$: C, 55.36; H, 7.76. Found: C, 55.35; H, 7.82.

Dimethyl 2-(diethoxymethyl)-1,1-cyclopropanedicarboxylate (16d): ^{1}H NMR ($CDCl_3$) δ 4.52 (d, J = 4.4 Hz, C*H*$(OEt)_2$), 3.75 and 3.72 (s, 6 H $COOCH_3$), 3.70–3.30 (m, 4 H, CH_2O), 2.19 (d of d of d, J = 9.2, 7.4, 4.4 Hz, C*H*CH$(OEt)_2$), 1.78 (d of d, J = 7.4, 4.4 Hz, 1 H), 1.41 (d of d, J = 9.2, 4.4 Hz, 1 H), 1.18 (t, J = 7.1 Hz, CH_3CH_2O), 1.15 (t, J = 7.0 Hz, CH_3CH_2O). Anal. Calcd for $C_{12}H_{20}O_6$: C, 55.36; H, 7.76. Found: C, 55.29; H, 7.74

5-Carbethoxy-2*H*,3*H*,5*H*,6*H*-1,4-dioxocin (14e): ^{1}H NMR ($CDCl_3$) δ 6.41 (d of t, J = 5.8, 1.0 Hz, =C*H*OCH_2), 5.07 (d of t, J = 7.5, 5.8 Hz, CH_2CH=), 4.22 (q, J = 7.1 Hz, CH_3CH_2O), 4.10–3.75 (m, OCH_2CH_2O and C*H*COOEt), 2.63 and 2.61 (two d of d of d, J = 7.7, 7.5, 1.0 Hz and J = 7.5, 7.4, 1.0 Hz, CH_2CH=), 1.29 (t, J = 7.1 Hz, CH_3CH_2O). Anal. Calcd for $C_9H_{14}O_4$: C, 58.05; H, 7.58. Found: C, 58.05; H, 7.63.

2-Carbethoxy-3-vinyl-1,4-dioxane (15e). Major isomer: ^{1}H NMR ($CDCl_3$) δ 5.83 (d of d of d, J = 17.3, 9.8, 5.5 Hz, C*H*=CH_2), 5.33 (d of d, J = 17.3, 0.3 Hz, CH=C*H*H), 5.25 (d of d, J = 9.8, 0.3 Hz, CH=CH*H*), 4.20 (q, J = 7.1 Hz, CH_3CH_2O), 4.25–3.40 (m, 6 H), 1.27 (t, J = 7.1 Hz, CH_3CH_2O). Minor isomer: ^{1}H NMR ($CDCl_3$) δ 5.83 (d of d of d, J = 17.2, 10.0, 5.5 Hz, C*H*=CH_2), 5.35 (d of d, J = 17.2, 0.9 Hz, CH=C*H*H), 5.27 (d of d, J = 10.0, 0.9 Hz, CH=CH*H*), 4.24 (q, J = 7.1 Hz, CH_3CH_2O), 4.25–3.40 (m, 6 H), 1.25 (t, J = 7.1 Hz, CH_3CH_2O).

2-Carbethoxy-1-cyclopropanecarboxaldehyde Ethylene Acetal (16e). Major isomer: ^{1}H NMR ($CDCl_3$) δ 4.85 (d, J = 7.1 Hz, C*H*$(OCH_2)_2$), 4.12 (q, J = 7.1 Hz, CH_3CH_2O), 4.10–3.60 (m, OCH_2CH_2O), 2.05–0.90 (m, 4 H), 1.26 (t, J = 7.1 Hz, CH_3CH_2O). Minor isomer: ^{1}H NMR ($CDCl_3$) δ 4.73 (d of d, J = 4.1, 0.6 Hz; C*H*$(OCH_2)_2$), 4.16 (q, J = 7.1 Hz, CH_3CH_2O), 4.10–3.60 (m, OCH_2CH_2O), 2.05–0.90 (m, 4 H), 1.27 (t, J = 7.1 Hz, CH_3CH_2O).

Ethyl 2,5-Dimethoxy-3-phenyl-(*E*)-4-pentenoate (14f). Major diastereoisomer: ^{1}H NMR ($CDCl_3$) δ 7.26 (s, Ph), 6.36 (d, J = 12.7 Hz, =C*H*OMe), 5.10 (d of d, J = 12.7, 9.4 Hz, CHC*H*=), 4.12 (q, J = 7.1 Hz, CH_2O), 3.96 (d, J = 5.0 Hz, PhCHC*H*OMe), 3.64 (d of d, J = 9.4, 5.0 Hz, PhC*H*CHOMe), 3.53 (s, CH_3O), 3.34 (s, CH_3O), 1.16 (t, J = 7.1 Hz, CH_3CH_2O). Minor diastereoisomer: ^{1}H NMR ($CDCl_3$) δ 7.28 (s, Ph), 6.40 (d, J = 12.5 Hz, =C*H*OMe), 4.94 (d of d, J = 12.5, 9.7 Hz, CHC*H*=), 4.16 (q, J = 7.1 Hz, CH_2O), 3.94 (d, J = 8.0 Hz, PhCHC*H*OMe), 3.56 (d of d, J = 9.7, 8.0 Hz, PhC*H*CHOMe), 3.50 (s, CH_3O), 3.29 (s, CH_3O), 1.22 (t, J = 7.1 Hz, CH_3CH_2O). Anal. Calcd for $C_{15}H_{20}O_4$: C, 68.16; H, 7.63. Found: C, 67.98; H, 7.73.

Ethyl 2,3-Dimethoxy-5-phenyl-(*E*)-4-pentenoate (15f). Major diastereoisomer: ^{1}H NMR ($CDCl_3$) δ 7.55–7.10 (m, Ph), 6.62 (d, J = 16.1 Hz, =CHPh), 6.17 (d of d, J = 16.1, 7.9 Hz, CHC*H*=), 4.25 (q, J = 7.1 Hz, CH_2O), 4.08 (d of d, J = 7.9, 4.7 Hz, C*H*CH=), 3.85 (d, J = 4.7 Hz, C*H*COOEt), 3.46 (s, CH_3O), 3.35 (s, CH_3O), 1.28 (t, J = 7.1 Hz, CH_3CH_2O). Minor diastereoisomer: ^{1}H NMR ($CDCl_3$) δ 7.55–7.10 (m, Ph), 6.65 (d, J = 16.1 Hz, =CHPh), 6.17 (d of d, J = 16.1, 7.2 Hz, CHC*H*=), 4.21 (q, J = 7.1 Hz, CH_2O), 4.18 (d of d, J = 7.2, 1.5 Hz, C*H*CH=), 3.97 (d, J = 1.5 Hz, C*H*COOEt), 3.46 (s, CH_3O), 3.32 (s, CH_3O), 1.25 (t, J = 7.1 Hz, CH_3CH_2O).

Ethyl 2-(Dimethoxymethyl)-3-phenyl-1-cyclopropanecarboxylate (16f). Major isomer: ^{1}H NMR ($CDCl_3$) δ 7.4–7.0 (m, Ph), 4.60 (d of d of d, J = 6.3, 0.5, 0.3 Hz, C*H*$(OMe)_2$), 4.18 (q, J = 7.1 Hz, CH_2O), 3.39 and 3.36 (two s, CH_3O), 2.77 (d of d, J = 6.2, 5.7 Hz, C*H*Ph), 2.05 (d of d, J = 12.8, 6.2 Hz, C*H*COOEt), 1.28 (t, J = 7.1 Hz, CH_3CH_2O), 1.21 (d of d of d, J = 12.8, 6.3, 5.7 Hz, C*H*CH$(OMe)_2$). Minor isomer: ^{1}H NMR ($CDCl_3$) δ 7.4–7.0 (m, Ph), 4.48 (d, J = 3.1 Hz, C*H*$(OMe)_2$), 3.94 (q, J = 7.1 Hz, CH_2O), 3.37 and 3.34 (two s, CH_3O), 2.20–1.95 (m, 2 H), 1.35–1.10 (m, 1 H) 0.97 (t, J = 7.1 Hz, CH_3CH_2O).

Methyl 2-carbomethoxy-2,5-dimethoxy-3-phenyl-(*E*)-4-pentenoate (14g): ^{1}H NMR ($CDCl_3$) δ 7.35–7.15 (m, Ph), 6.41 (d, J = 12.6 Hz, =C*H*OMe), 5.25 (d of d, J = 12.6, 10.2 Hz, CHC*H*=), 3.94 (d, J = 10.2 Hz, C*H*CH=), 3.74 (s, OCH_3), 3.62 (s, OCH_3), 3.54 (s, OCH_3), 3.52 (s, OCH_3). Anal. Calcd for $C_{14}H_{20}O_6$: C, 62.32; H, 6.54. Found: C, 62.12; H, 6.68.

Methyl 2-carbomethoxy-2,3-dimethoxy-5-phenyl-(*E*)-4-pentenoate (15g): ^{1}H NMR ($CDCl_3$) δ 7.50–7.20 (m, Ph), 6.67 (d, J = 16.1 Hz, =C*H*Ph), 6.21 (d of d, J = 16.1, 7.7 Hz, CHC*H*=), 4.38 (d, J = 7.7 Hz, C*H*CH=), 3.81 and 3.79 (two s, $COOCH_3$), 3.61 (s, OCH_3), 3.35 (s, $CHOCH_3$).

2-Methyl-2-(2-propenyl)-1,3-dithiolane (18). *n*-Butyllithium (1.6 M in hexane, 43 mmol) was added via syringe to a rapidly stirred solution of methyltriphenylphosphonium bromide (15.4 g, 43 mmol) in 100 mL of tetrahydrofuran, freshly distilled from

sodium/benzophenone, that was maintained at −78 °C under nitrogen. Warming the resultant mixture to room temperature produced a clear, deep-red solution that was again cooled to −78 °C. 2-Acetyl-2-methyl-1,3-dithiolane (7.0 g, 43 mmol), prepared from 1,2-ethanedithiol and 2,3-butanedione,[33] in 5.0 mL of tetrahydrofuran was added to the phosphorus ylide, and stirring was continued for an additional 30 min at −78 °C. The resulting mixture was stored in a freezer under positive nitrogen pressure overnight. After warming to room temperature, the tetrahydrofuran solution was poured into 100 mL of ice water and extracted with hexane. The hexane solution was washed with 100 mL of water and dried over anhydrous magnesium sulfate, and the solvent was removed under reduced pressure. Distillation of the oil residue yielded 4.7 g of **18** (68% yield, bp 40–42 °C (0.4 torr)): ^{1}H NMR ($CDCl_3$) δ 5.25 (d of q, J = 1.3, 0.4 Hz, =CH trans to Me), 4.89 (d of q, J = 1.3, 1.2 Hz, =CH cis to Me), 3.50–3.30 (m, CH_2CH_2), 2.02 (d of d, J = 1.2, 0.4, CH_3), 1.95 (s, CH_3). Anal. Calcd for $C_7H_{12}S_2$: C, 52.45; H, 7.55; S, 40.00. Found: C, 52.51; H, 7.49; S, 40.17.

Reaction of 2-Methyl-2-(2-propenyl)-1,3-dithiolane with Ethyl Diazoacetate. Ethyl diazoacetate (0.127 g, 1.00 mmol) was added at a controlled rate over 8 h to a stirred purple solution of $Rh_2(OAc)_4$ (0.0044 g, 0.01 mmol) in 2-methyl-2-(2-propenyl)-1,3-dithiolane that was maintained at 60 °C under nitrogen. After addition was complete, the reaction mixture was passed through a 1-cm column of neutral alumina, diphenylmethane was added as an internal standard, and the reaction mixture was subjected to GC and GC/mass spectral analyses. For preparative-scale reactions, the reaction solution was passed through neutral alumina with ether washings, and the resultant solution was distilled under reduced pressure. Bulb-to-bulb distillation provided recovery of reactant olefin. GC analyses exhibited only two products, **19** and **20**, in yields greater than 2%.

5-Carbethoxy-7,8-dimethyl-2,3,5,6-tetrahydro-1,4-dithiocin (19): ^{1}H NMR ($CDCl_3$) δ 4.20 (q, J = 7.1 Hz, CH_2O), 3.89 (t, J = 12.5 Hz, C*H*COOEt), 3.42 (d of d, J = 12.5, 3.8 Hz, =CCH), 3.46–2.75 (m, SCH_2CH_2S), 2.52 (d of d, J = 12.5, 3.8 Hz with further coupling to CH_3, =CCH), 2.11 (t, J = 1.0 Hz, $SCCH_3$), 1.75 (s, $=CCH_3$), 1.30 (t, J = 7.1 Hz, CH_3CH_2O). Anal. Calcd for $C_{11}H_{18}O_2S_2$: C, 53.62; H, 7.36; S, 26.03. Found: C, 53.45; H, 7.20; S, 26.14.

20: ^{1}H NMR ($CDCl_3$) δ 5.44 (s, H_2C=CS), 5.20–5.15 (m, 1 H), 5.12–5.04 (m, 1 H), 4.20 (q, J = 7.1 Hz, CH_2O), 3.24 (s, CH_2COOEt), 3.15–2.80 (m, SCH_2CH_2S), 1.97 (q, J = 0.7 Hz, $=CCH_3$), 1.29 (t, J = 7.1 Hz, CH_3CH_2O).

2-Ethenyl-2-methyl-1,3-dithiane (21). 2-Formyl-2-methyl-1,3-dithiane (14.8 g, 91 mmol), prepared in 75% yield by reaction of the 2-lithio derivative of 2-methyl-1,3-dithiane[34] with dimethylformamide,[35] in 10 mL tetrahydrofuran was added to Ph_3P=CH_2 (91 mmol) at −78 °C. The reaction mixture was allowed to warm to room temperature, then poured into 150 mL of ice and extracted with three 150-mL portions of hexane. The combined hexane solution was washed with 100 mL of water and dried over anhydrous magnesium sulfate, and the solvent was removed under reduced pressure. Distillation yielded 8.0 g of **21**[36] (55% yield, bp 40–42 °C (0.3 torr)): ^{1}H NMR ($CDCl_3$) δ 5.97 (d of d, J = 16.8, 9.8 Hz, C*H*=CH_2), 5.42 (d of d, J = 16.8, 1.6 Hz, CH=C*H*H), 5.24 (d of d, J = 9.8, 1.6 Hz, CH=CH*H*), 3.15–2.50 (m, 4 H), 2.15–1.70 (m, 2 H), 1.59 (s, CH_3).

Reaction of 2-Ethenyl-2-methyl-1,3-dithiane with Ethyl Diazoacetate. Reactions were performed as previously described. Even on a 2.0-mmol scale, excess **21** could be recovered in 90% yield. GC analysis on a 15-m SP-2330 capillary column revealed three distinct products in a ratio of 2.8:1.0:8.3. GC collection from a 2-m SE-30 column gave two fractions identified as **22** and **23**.

6-Carbethoxy-9-methyl-3,4,6,7-tetrahydro-2*H*-1,5-dithionin (22). *E* isomer: ^{1}H NMR ($CDCl_3$) δ 5.69 (d of d of q, J = 10.2, 6.1, 1.3 Hz, =C*H*CH_2), 4.20 (q, J = 7.1 Hz, CH_2O), 3.65–1.50 (m, 9 H), 2.10 (t, J = 1.3 Hz, $C(CH_3)$=CH), 1.29 (t, J = 7.1 Hz, CH_3CH_2O). *Z* isomer: ^{1}H NMR ($CDCl_3$) δ 6.16 (d of d of q, J = 7.7, 7.1, 1.4 Hz, =C*H*CH_2), 4.18 (q, J = 7.1 Hz, CH_2O), 3.65–1.50 (m, 9 H), 2.09 (d, J = 1.4 Hz, $C(CH_3)$=CH), 1.28 (t, J = 7.1 Hz, CH_3CH_2O). Anal. Calcd for $C_{11}H_{18}O_2S_2$: C, 53.62; H, 7.36; S, 26.03. Found: C, 53.45; H, 7.20; S, 26.14.

23: ^{1}H NMR ($CDCl_3$) δ 6.44 (d of d of d, J = 17.3, 10.2, 0.6 Hz, C*H*=CH_2), 5.53 (d of d of d, J = 17.3, 0.9, 0.5 Hz, CH=C*H*H), 5.36 (d of d, J = 1.2, 0.6 Hz, SC=C*H*H), 5.17 (d of d, J = 10.2, 0.5 Hz, CH=C*H*H), 5.11 (d of d, J = 1.2, 0.9 Hz, SC=CH*H*), 4.20 (q, J = 7.1 Hz, CH_2O), 3.21 (s, CH_2COOEt), 2.77 (t, J = 7.0 Hz, CH_2S), 1.94 (quin, J = 7.0 Hz, $SCH_2CH_2CH_2S$), 1.29 (t, J = 7.1 Hz, CH_3CH_2O).

Reaction of 2-Methyl-2-phenyl-1,3-dithiane (24) with Ethyl Diazoacetate. Reactions between **24** and ethyl diazoacetate were performed as previously described. GC analysis on a 15-m SP-2330 capillary column revealed three distinct products in a ratio of 1.0:15:69. GC collection from a 2-m SE-30 column afforded **26** and **27**.

2-Carbethoxy-3-methyl-3-phenyl-1,4-dithiepane (27). Major diastereoisomer: ^{1}H NMR ($CDCl_3$) δ 7.55–7.20 (m, Ph), 4.21 (s, C*H*COOEt), 3.82 (q, J = 7.1 Hz, CH_2O), 3.20–2.60 (m, CH_2S), 2.15–1.75 (m, $SCH_2CH_2CH_2S$), 2.08 (s, CH_3), 0.86 (t, J = 7.1 Hz, CH_3CH_2O). Minor diastereoisomer: ^{1}H NMR ($CDCl_3$) δ 7.60–7.20 (m, Ph), 4.50 (s, C*H*COOEt), 3.83 (q, J = 7.1 Hz, CH_2O), 3.20–2.60 (m, CH_2S), 2.15–1.75 (m, $SCH_2CH_2CH_2S$), 1.79 (s, CH_3), 0.93 (t, J = 7.1 Hz, CH_3CH_2O).

26: ^{1}H NMR ($CDCl_3$) δ 7.7–7.2 (m, Ph), 5.47 (s, =C*H*H), 5.23 (s, =CH*H*), 4.18 (q, J = 7.1 Hz, CH_2O), 3.18 (s, CH_2COOEt), 2.77 (t, J = 6.8 Hz, CH_2S), 2.74 (t, J = 6.8 Hz, CH_2S), 1.98 (quin, J = 6.8 Hz, $SCH_2CH_2CH_2S$), 1.28 (t, J = 7.1 Hz, CH_3CH_2O).

Reaction of 2-Phenyl-1,3-dithiane (25) with Ethyl Diazoacetate. Reactions between **25** and ethyl diazoacetate were performed as previously described. GC analysis on a 15-m SP-2330 capillary column revealed two distinct products in a ratio of 1.00:1.07. GC collection from a 2-m SE-30 column afforded the isomeric composite of **2-carbethoxy-3-phenyl-1,4-dithiepane (28).** Major diastereoisomer: ^{1}H NMR ($CDCl_3$) δ 7.55–7.10 (m, Ph), 4.28 (d, J = 10.7 Hz, C*H*COOEt), 3.92 (q, J = 7.1 Hz, CH_2O), 3.84 (d, J = 10.7 Hz, C*H*Ph), 3.60–2.85 (m, CH_2S), 2.11 (quin, J = 6.0 Hz, $SCH_2CH_2CH_2S$), 0.96 (t, J = 7.1 Hz, CH_3CH_2O). Minor diastereoisomer: ^{1}H NMR ($CDCl_3$) δ 7.55–7.10 (m, Ph), 4.51 (d, J = 4.4 Hz, C*H*COOEt), 3.94 (q, J = 7.1 Hz, CH_2O), 3.92 (d, J = 4.4 Hz, C*H*Ph), 3.60–2.85 (m, CH_2S), 2.10 (quin, J = 6.0 Hz, $SCH_2CH_2CH_2S$), 0.99 (t, J = 7.1 Hz, CH_3CH_2O). Anal. Calcd for $C_{14}H_{18}O_2S_2$: C, 59.54; H, 6.42; S, 22.71. Found: C, 59.53; H, 6.44; S, 22.50.

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Registry No. (*E*)-**2**, 89709-82-0; (*Z*)-**2**, 89709-83-1; *trans*-**3**, 87986-36-5; *cis*-**3**, 87986-35-4; (*E*)-**7**, 89709-85-3; **8**, 89709-84-2; **9**, 89709-87-5; **9** (2,4-dinitrophenylhydrazone), 89709-88-6; **10**, 89709-89-7; **11**, 89709-90-0; **12**, 89709-91-1; **13**, 87125-73-3; **14b**, 89709-92-2; **14c**, 89709-95-5; **14d**, 89709-96-6; **14e**, 89709-99-9; **14f** (isomer 1), 89710-01-0; **14f** (isomer 2), 89710-03-2; **14g**, 89710-07-6; **15b**, 89709-93-3; **15d**, 89709-97-7; **15e** (isomer 1), 89710-00-9; **15e** (isomer 2), 89710-02-1; **15f** (isomer 1), 89710-04-3; **15f** (isomer 2), 89710-05-4; **15g**, 89710-08-7; **16a** (acid), 89709-86-4; **16b**, 89709-94-4; *cis*-**16c**, 87986-38-7; *trans*-**16c**, 87986-39-8; **16d**, 89709-98-8; **16e** (isomer 1), 87986-40-1; **16e** (isomer 2), 72184-71-5; **16f-A**, 89710-06-5; **16f-B**, 89772-15-6; **18**, 89710-09-8; **19**, 89710-10-1; **20**, 89710-11-2; **21**, 64087-39-4; **22a**, 89710-12-3; **22b**, 89710-13-4; **23**, 89710-14-5; **24**, 6331-22-2; **25**, 5425-44-5; **26**, 89710-17-8; **27** (isomer 1), 89710-15-6; **27** (isomer 2), 89710-16-7; **28** (isomer 1), 89710-18-9; **28** (isomer 2), 89710-19-0; $(Ph)_3P$=CH_2, 3487-44-3; H_2C=CHCH$(OEt)_2$, 3054-95-3; (*E*)-C_6H_5CH=CHCH$(OMe)_2$, 4364-06-1; $Rh_2(OAc)_4$, 15956-28-2; 2-acetyl-2-methyl-1,3-dithiolane, 33266-07-8; 2-formyl-2-methyl-1,3-dithiane, 4882-97-7; 2-methyl-1,3-

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dithiane, 6007-26-7; 2-vinyl-1,3-dioxolane, 3984-22-3; copper(II) trifluoromethanesulfonate, 34946-82-2; rhodium(II) trifluoroacetate, 72654-51-4; ethyl diazoacetate, 623-73-4; dimethyl diazomalonate, 6773-29-1; acrolein dimethyl acetal, 6044-68-4; methyltriphenylphosphonium bromide, 1779-49-3; 1,2-ethanedithiol, 540-63-6; 2,3-butanedione, 431-03-8; dimethylformamide, 68-12-2.

Supplementary Material Available: Mass spectral data for reaction products and ^{1}H NMR spectral data for 8–12 (6 pages). Ordering information is given on any current masthead page.

Photolysis of Tri-1-naphthylboron Does Not Give Naphthylborene

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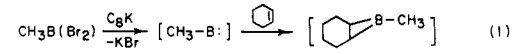
Irradiation of tri-1-naphthylboron in cyclohexene does not give evidence for formation of naphthylborene. No *cis*-1,2-cyclohexanediol is observed after oxidative workup, and only a low yield of 1,1′-binaphthyl is obtained. These findings are in contrast to the results of Ramsey and Anjo, which were used to support naphthylborene formation.

In recent years there has been a resurgence of interest in the chemical and physical properties of reactive intermediates. In part this renewal has been driven by the development of new spectroscopic techniques that permit the direct monitoring of formerly elusive transient species. In particular, our understanding of hypovalent intermediates such as carbenes, nitrenes, and silylenes has benefited from EPR and laser spectrophotometric investigation.[1] In contrast, the corresponding boron-centered hypovalent species (R–B), alternately called either a borylene,[2] boryne[3] or a borene,[4] remains much less studied and is incompletely understood. Indeed, there is some doubt that an authentic example of this intermediate has ever been prepared (vide infra).

There have been two general routes explored for the preparation of borenes. The first is based upon the α-elimination of two groups from a boron atom and is illustrated in eq 1 by the results of van der Kerk and co-

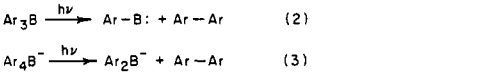


(1)

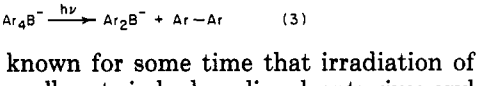
workers[5] who examined the reaction of methylboron dibromide with potassium on graphite in the presence of cyclohexene. A related reaction of phenylboron dibromide in the presence of diphenylacetylene also was used to support the intermediacy of a borene[6] but proved to be unreliable.[4] In neither case was the key boracyclopropane actually isolated or characterized as such.

Using a similar approach, Eisch investigated the reaction of phenylboron dichloride with bis(trimethylsilyl)mercury.[4] In the absence of a trapping olefin, the presumed intermediate phenylborene underwent polymerization in competition with its eventual insertion into carbon–hydrogen bonds. Attempts to intercept the borene with diphenylacetylene failed due to reaction of the acetylene with presumed intermediates formed before the borene is generated. This observation, and others, led Eisch to warn that "...detection of borenes, generated from organoboron dibromides....and reducing agents, by acetylenes cannot give reliable evidence." However, van der Kerk and coworkers[7] argue that these complications do not compromise their findings with cyclohexene.

The second general route for the preparation of hypovalent boron compounds is based on the photochemical elimination of a biaryl from a triarylboron or a tetraarylborate anion. This approach is illustrated in eq 2 and 3.



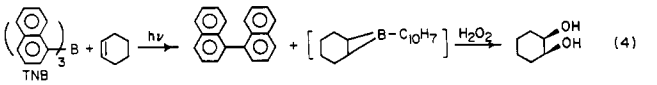
(2)



(3)

It has been known for some time that irradiation of sodium tetraphenylborate in hydroxylic solvents gives aryl coupling products.[8] More recently, Eisch[9] has shown that in ether solvents the diphenylborate can be trapped with diphenylacetylene to give eventually products analogous to the carbene reaction products.

Similarly, early investigation of the photochemistry of triphenylboron in methanol solution revealed the formation of biphenyl in low yield.[10] More recently, Ramsey and Anjo[3] reported on the photochemistry of tri-1-naphthylboron (TNB) in hydrocarbon solvents. They claim that the photolysis of TNB in cyclohexene solution followed by oxidation of the reaction mixture gives *cis*-1,2-cyclohexanediol in 40% yield and 1,1′-binaphthyl, eq 4. These observations led them to suggest that relatively



(4)

efficient formation of 1-naphthylborene (1-NB) occurs on photolysis of TNB. This conclusion encouraged us to begin an investigation of the properties of 1-NB by pulsed laser

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