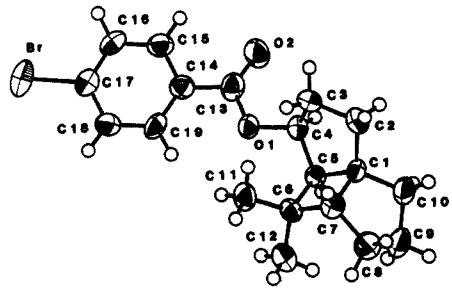


Figure 1. ORTEP drawing of 37 showing 50% probability ellipsoids.

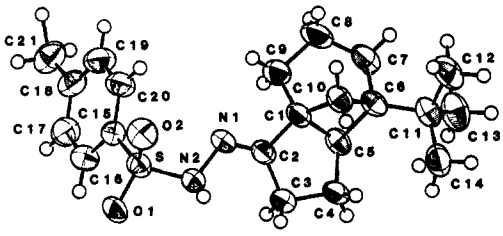


Figure 2. ORTEP drawing of 19bT showing 50% probability ellipsoids.

2 are shown ORTEP drawings for 37 and 19bT, respectively.

Acknowledgment. We thank the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We are indebted to Phyllis Wilson for technical assistance and to Francis Picart for 300-MHz NMR spectra. The 300-MHz spectrometer was purchased with assistance from the National Science Foundation and the Camille and Henry Dreyfus Foundation.

Registry No. 13, 22627-71-0; **13a**, 39865-63-9; **14**, 101761-44-8; **14a**, 101761-45-9; **15**, 101761-46-0; **15a**, 101761-47-1; **16**, 101761-48-2; **16a**, 101761-49-3; **16b** (isomer 1), 101761-50-6; **16b** (isomer 2), 101761-51-7; **17**, 99261-30-0; **17a**, 101761-52-8; **18**, 101761-53-9; **18a**, 101761-54-0; **18b**, 101761-55-1; **19**, 101761-56-2; **19a**, 101761-57-3; **19b**, 101761-58-4; **19bT**, 101761-61-9; **20**, 101761-59-5; **20a**, 101761-60-8; **21**, 43011-53-6; **21b**, 101761-62-0; **22**, 101761-63-1; **22a**, 101761-64-2; **22b**, 101761-65-3; **23**, 101761-66-4; **23b**, 101761-67-5; **23c**, 101761-68-6; **24**, 43011-51-4; **24b**, 101761-69-7; **25**, 101761-70-0; **25a**, 101761-71-1; **25b**, 101761-72-2; **25c**, 101761-73-3; **27**, 52190-40-6; **28** (R = 1-penten-5-yl), 101761-74-4; **28** (R = 2-methyl-1-penten-5-yl), 101761-75-5; **28** (R = 2-methyl-2-hexen-6-yl), 101761-76-6; **29**, 68241-78-1; **30**, 6140-65-4; **31**, 81328-61-2; **33**, 101761-77-7; **34**, 101761-78-8; **34** tosylate, 101761-61-9; **35**, 594-56-9; **36**, 101761-81-3; **37**, 101761-80-2; **38**, 101761-79-9; **39**, 101761-83-5; **40**, 101761-84-6; **41**, 101761-82-4; **42**, 101761-85-7; **45**, 101761-86-8; **46**, 101761-87-9; cyclopentenone, 930-30-3; 5-bromo-1-pentene, 1119-51-3; 5-bromo-2-methyl-1-pentene, 41182-50-7; 6-bromo-2-methyl-2-hexene, 30316-02-0; *p*-bromobenzoyl chloride, 586-75-4; 6,7-dihydro-6-(5,5-dimethyl-4-methylenehexyl)-1,4-dioxaspiro[4.4]nonane, 101761-88-0; 4-bromo-1-butene, 5162-44-7; 2-(3-buten-1-yl)cyclopent-1-enemethanol, 101761-89-1; 4-bromo-2-methyl-1-butene, 20038-12-4; 2-(3-methyl-3-buten-1-yl)cyclopent-1-enemethanol, 101761-90-4; 5-bromo-2-methyl-2-pentene, 2270-59-9; 2-(4-methyl-3-penten-1-yl)cyclopent-1-enemethanol, 101761-91-5; ethylene oxide, 75-21-8.

Supplementary Material Available: Tables of atomic coordinates, bond angles, thermal parameters, and observed and calculated structure factors for **37** and **19bT** (35 pages). Ordering information is given on any current masthead page.

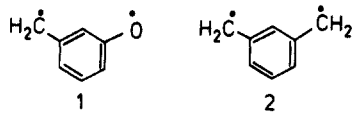
Stereochemistry of Additions of *m*-Quinomethane to Olefins and Acyclic Dienes

Thomas A. Inglin and Jerome A. Berson*

Contribution from the Department of Chemistry, Yale University, New Haven, Connecticut 06511. *Received November 18, 1985*

Abstract: The *m*-quinomethane biradical has a triplet ground state, as judged by the temperature dependence of the intensity of its EPR signal. When generated by pyrolysis or photolysis of 6-methylenebicyclo[3.1.0]hex-3-en-2-one, it adds to olefinic trapping agents to give phenolic indans. Retention of configuration dominates by a factor of 13–17 with *cis*-1,2-dimethoxyethene and by a factor of >100 with *trans*-1,2-dimethoxyethene. With the 2,4-hexadienes, which undergo addition to give phenolic 1-propenylindans, retention again is the favored pathway, but the preference is lower (up to 6-fold). The propenyl stereochemistry in the product is completely retained. A comparison with known results of cycloadditions of trimethylenemethane (singlet) biradical and of *m*-quinodimethane shows that *m*-quinomethane additions are intermediate between the other two in cis stereospecificity. A mechanistic rationale for this ordering is discussed.

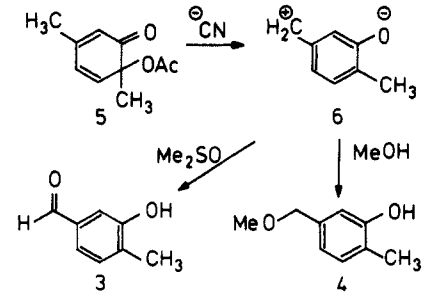
The moment is propitious for a comparison of the stereochemistry of the cycloadditions of the polar non-Kekulé molecule *m*-quinomethane **1**, MQM,[1,2] with that recently reported[3] for the



1 2

parent hydrocarbon *m*-quinodimethane **2**, MQDM. Understanding of the structure, spin state, and reaction mechanisms of non-Kekulé molecules could emerge from such studies, which form the subject matter of the present paper.

Scheme I



Substituted variants of **1** were invoked as reactive intermediates as long ago as 1964, when Leitich and Wessely[4] explained the

(1) Rule, M.; Matlin, A. R.; Hilinski, E. F.; Dougherty, D. A.; Berson, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 5098.
(2) Rule, M.; Matlin, A. R.; Seeger, D. E.; Hilinski, E. F.; Dougherty, D. A.; Berson, J. A. *Tetrahedron* **1982**, *38*, 787.
(3) (a) Goodman, J. L.; Berson, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 1867. (b) Goodman, J. L.; Berson, J. A. *Ibid.* **1985**, *107*, 5409. (c) Goodman, J. L.; Berson, J. A. *Ibid.* **1985**, *107*, 5424.

0002-7863/86/1508-3394$01.50/0 © 1986 American Chemical Society

Scheme II

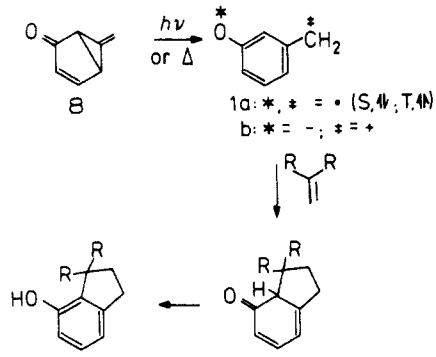
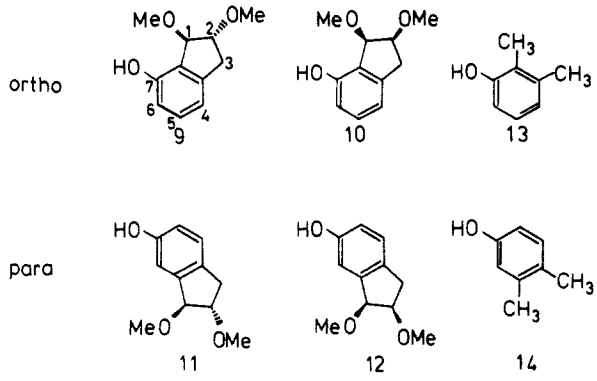
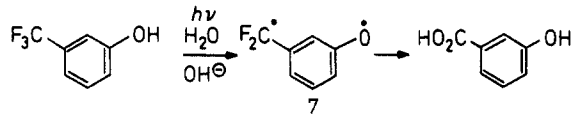


Chart I



formation of the products **3** and **4** in the reactions of the acetoxydiene **5** as arising from the zwitterionic form of a *m*-quinomethane, **6** (Scheme I). Subsequently, Seiler and Wirz[5] proposed the *m*-(difluoromethylene)phenoxyl biradical **7** as the key intermediate in the photohydrolysis of *m*-(trifluoromethyl)phenol to *m*-hydroxybenzoic acid.



Our synthetic approach to *m*-quinomethane (MQM)[1,2,6] has been the thermal or photochemical ring opening of the bicyclic dienone **8**. Previous work[6] showed that the rate-determining step of the thermal cycloaddition is spin-allowed and unimolecular, suggesting a singlet species **1a-S** isomeric with **8** as the *first-formed* intermediate. Moreover, a biradical (or zwitterion), **1a** (or **1b**), generated along this pathway could be intercepted by dienes or electron-rich olefins to give 5- (not shown) or 7-hydroxyindans (Scheme II). The same reactive entity could be generated[6] by photolysis of **8** and gave products indistinguishable from those observed in the thermal reaction. Incompletely resolved were the questions of whether the first-formed intermediate and the reactive entity are one and the same and whether any role in the cycloadditions should be assigned to the triplet species **1a-T**, which previously had been observed[1,2] by electron paramagnetic resonance (EPR) spectroscopy.

The investigation now has been augmented by new experiments which reveal the stereochemistry of these reactions using stereospecifically substituted trapping agents.

Results

Cycloadditions of *m*-Quinomethane to *cis*- and *trans*-1,2-Dimethoxyethene. Reaction of the dienone **8** with a 30-fold excess of 0.112 M *cis*-dimethoxyethene (*cis*-DME) in benzene at 115 °C gave 66% yield (NMR vs. internal standard) of a mixture of the four 1:1 adducts **9–12**, as determined by gas chromatography/mass spectroscopy (GC/MS) (Chart I). Two of these adducts also were formed in the corresponding reaction of **8** with *trans*-DME. The assignments of structure and stereochemistry, which rest upon mutually consistent NMR arguments and upon a stereospecific independent synthesis of a derivative of the cis-ortho cycloadduct, are described in the supplementary material. Analyses of the products were achieved by a combination of NMR spectroscopy (using as models the known xylenols **13** and **14**) and GC and are described in the Experimental Section. The results are given in Table I.

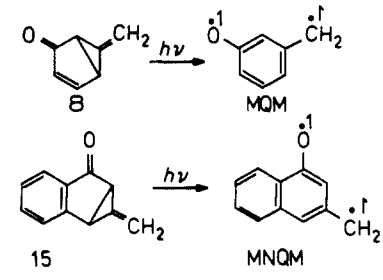
Table I. Relative Yields of Cycloadducts from *cis*- and *trans*-1,2-Dimethoxyethene (DME) with **8** in Benzene at 115 °C

product	reactant: *trans*-DME	reactant: *cis*-DME
9 (trans-ortho)	62	4
10 (cis-ortho)	0	69
11 (trans-para)	38	2
12 (cis-para)	0	25
ret/inv, ortho	>100	17 ± 0.6
ret/inv, para	>100	13 ± 3
ortho/para	1.6	2.8

The adducts from **8** and 99.96% stereochemically pure *trans*-DME consisted exclusively of the trans-ortho and trans-para compounds **9** and **11** resulting from complete retention of configuration, whereas the reaction mixture from 99.88% pure *cis*-DME, although also dominated by retention products (**10** and **12**), gave detectable amounts of adducts in which stereochemical inversion had occurred (**9** and **11**, 4% and 2%, respectively).

That the small amount of crossover product from *cis*-DME did not result from preferential reaction of the small amount of *trans*-DME present was demonstrated by a control experiment. After a 1:1 mixture of *cis*- and *trans*-DME was heated with 0.5 equiv of **8** in benzene-d_6 for 30 min, NMR spectroscopic examination of the crude reaction mixture showed the presence of characteristic cycloadduct peaks along with vinyl and methoxyl resonances of the remaining DME. The stereoisomeric DME ratio was still 1:1, which indicates that under these conditions, no significant preference exists for reaction of *trans*-DME.

Tests for Two Sequentially Formed Intermediates. Previous studies[1,2,8] have identified the triplet states of MQM and its close relative *m*-naphthoquinomethane (MNQM) by EPR spectroscopy of irradiated frozen samples of the enone **8** and the benzo analogue



15. In the case of the naphtho species MNQM, the EPR signal was stable over a sufficiently large temperature range to permit a demonstration of adherence to the Curie law, but the signal of the frozen preparations of the monocyclic MQM triplet in 2-methyltetrahydrofuran (2-MTHF) previously available was unstable above ~40 K. However, Goodman[9] recently has found that the MQM triplet signal is stable up to 77 K in a 1:1 decalin–cyclohexane matrix, and we now have carried out a Curie law study in this medium. The relationship of EPR signal intensity vs. $1/T$ is linear between 65 and 18.5 K, but points at lower temperature are unreliable because signal saturation becomes severe. In a "worst-case" analysis (Figure 1), one can fit the data to a curved plot in which the singlet lies below the triplet by no

(4) Leitich, J.; Wessely, F. *Monatsh. Chem.* **1964**, *95*, 129.
(5) Seiler, P.; Wirz, J. *Helv. Chim. Acta* **1972**, *55*, 2693.
(6) Matlin, A. R.; Inglin, T. A.; Berson, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 4954.
(7) Matlin, A. R. Ph.D. Dissertation, Yale University, 1982.
(8) Seeger, D. E.; Hilinski, E. F.; Berson, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 720.
(9) Goodman, J. L., personal communication.

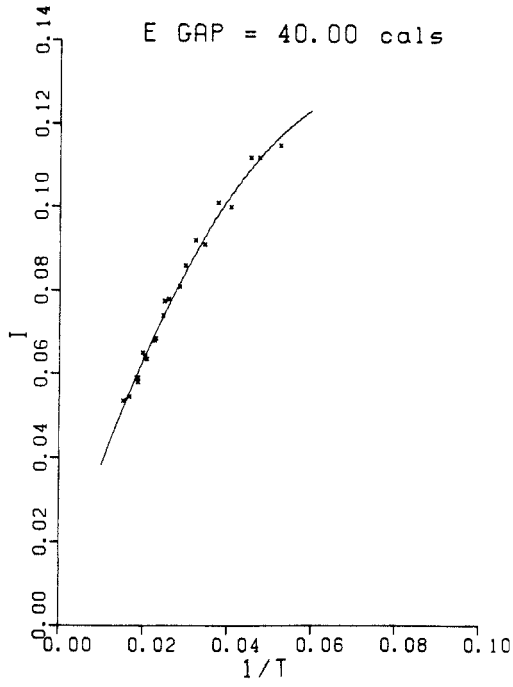


Figure 1. Curie law plot of EPR signal intensity vs. reciprocal temperature for the triplet state of MQM biradical (**1**) in 2-methyltetrahydrofuran glass. The curve shown is drawn based on the assumption that $E_T - E_S = 0.04$ kcal/mol.

more than 0.04 kcal/mol. Unless one accepts the nearly exact degeneracy implied by this result, the alternative (and we believe more plausible) interpretation is that the triplet is the ground state of the monocyclic biradical MQM.

The normal Arrhenius preexponential term (10^{14} s^{-1}) observed[6] in the thermolysis of the enone **8** suggests that the first-formed intermediate is a singlet MQM. Intersystem crossing (ISC) to the more stable triplet might be expected to compete with capture of the singlet. This consequence of a pathway with two successive intermediates (cascade mechanism) has been demonstrated by picosecond flash photolysis studies[10] in the analogous case of the naphtho derivative MNQM in benzene solution with time-resolved absorptive spectroscopic detection at wavelengths of >525 nm. The dynamics are characterized by rate constants for ISC and for capture of the singlet by methanol of 8.5×10^8 s^{-1} and 3.6×10^8 s^{-1} M^{-1}, respectively. However, the MQM absorption spectrum is hypsochromically shifted relative to that of MNQM,[11] and instrumental limitations so far have prevented a picosecond dynamic study of MQM.

We have attempted to observe a dilution effect or a selective trapping of the triplet by oxygen, two chemical tests for a cascade mechanism which have been effective in dissecting the singlet and triplet chemistry of trimethylenemethanes (TMMs).[12,13] The results of the dilution test under thermal conditions (115 °C, benzene solution) were negative, the ratio of retention/inversion products, **10/9**, in the ortho series remaining essentially unchanged (15.3 ± 0.1, 15.5 ± 0.1, and 15.8 ± 0.4) as the concentration of *cis*-DME changed from 0.15 to 0.0375 to 0.0015 M. Similarly, the **10/9** product ratio remained essentially constant when the reaction was carried out under photochemical conditions (0 °C, diethyl ether solution) regardless of whether O_2 was present or absent.

By analogy to trimethylenemethane chemistry,[12] the addition of a triplet *m*-quinomethane (MQM) might have been expected

(10) Goodman, J. L.; Peters, K. S.; Lahti, P. M.; Berson, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 276.
(11) Seeger, D. E.; Lahti, P. M.; Rossi, A. R.; Berson, J. A. *J. Am. Chem. Soc.* **1986**, *108*, 1251.
(12) Berson, J. A. In *Diradicals*; Borden, W. T., Ed.; Academic: New York, 1982; p 152 and references cited therein.
(13) Berson, J. A. *Acc. Chem. Res.* **1978**, *11*, 446 and references cited therein.

Scheme III

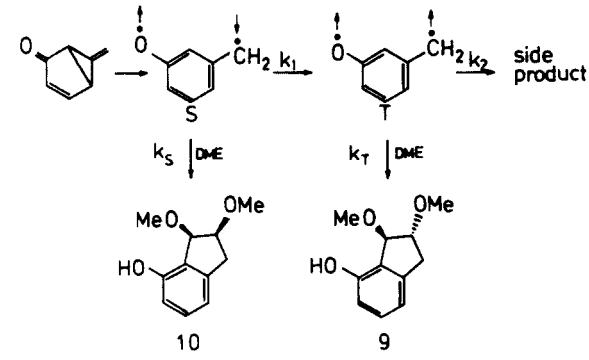


Table II. Product Ratios in the Reaction of **8** with *cis*-1,2-Dimethoxyethene (DME) at 115 °C

product ratio	solvent: benzene	solvent: CH_3CN
cis-ortho/trans-ortho (**10/9**)	17.0 ± 0.6	17.1 ± 0.1
cis-para/trans-para	13 ± 3	14.7 ± 1
ortho/para (**9** + **10**)/(**11** + **12**)	3.2 ± 0.2	1.5 ± 0.1

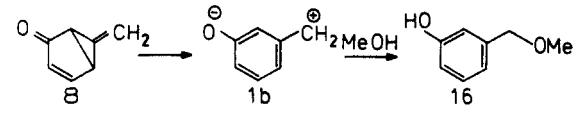
to be less stereospecific than that of the singlet. Hence a cascade mechanism, **8** → singlet MQM → triplet MQM, from which both intermediates could be trapped (Scheme III) should have led to a declining **10/9** product ratio with decreasing *cis*-DME concentration. The absence of such an effect, however, need not necessarily signify the absence of the cascade but might instead be attributable to a slow rate of reaction of triplet MQM with the trapping agent. In terms of Scheme III, if the S → T reaction is assumed to be irreversible, the cycloadduct ratio from singlet and triplet is given by eq 1 (where the rate constant k_2 may contain

$$P_S/P_T = \frac{k_S[\mathrm{DME}]}{k_1} + \frac{k_S k_2}{k_1 k_T} \qquad (1)$$

a term in concentration of another reactant). Equation 1 dissects the product ratio into two terms, only one of which is a function of [DME]. Thus if the rate constant (k_T) for capture of the triplet is small relative to that leading to side products (k_2), the product ratio always will be dominated by the concentration-independent term.

An alternative way to account for the absence of a dilution effect is by postulating a rapid equilibrium between singlet and triplet *m*-quinomethane (MQM). Product then would be formed from a pool of intermediates of invariable composition. This explanation cannot be ruled out, but it requires that the energy of the triplet MQM be barely lower than that of the singlet, a property that conflicts with the theoretically predicted[14] energy gap of 12 kcal/mol in favor of the triplet.

Polarity of the Intermediate. A previous study[6] showed that the value of the rate constant for the thermal methanolysis of enone **8** in CH_3CN is about two-thirds that in benzene. This response

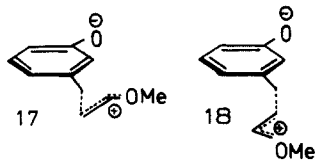


to the polarity of the solvent is weak and in the direction opposite to that expected if charge separation were far advanced in the transition state. Nevertheless, the nature of the product, the *m*-hydroxybenzyl ether **16**, is in accord with a zwitterionic reactive intermediate, **1b**. A plausible reconciliation of these findings is given by the hypothesis of an "early" transition state in the ring-opening step, **8** → **1b**, for which independent support is available.[6]

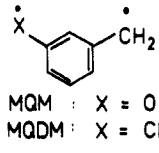
Although a mechanistic rationalization is deferred to the Discussion section, we note here that solvent polarity has little

(14) Lahti, P. M.; Rossi, A. R.; Berson, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 2273.

effect on the cis/trans product ratios (Table II) in the reaction of **8** (via zwitterion **1b**) with *cis*-DME. On the other hand, the ortho/para ratio responds noticeably, with the relative amount of para product increasing in the more polar solvent, CH_3CN. Again pending a subsequent discussion, we ascribe the latter regiospecificity effect to a selective stabilization of the more polar "extended" transition state **18** relative to the less polar "coiled" transition state **17** in a polar solvent.[15]



Reactions of MQM with 2,4-Hexadienes. To elucidate the effect of biradical polarity on the mechanism of cycloaddition, it would be desirable to compare the polar system MQM to the nonpolar



one *m*-quinodimethane (MQDM) in reactions with a *common* olefinic trap. The reactivities of the two species do not offer much breadth in the choice of olefins, since most of the characteristic traps for *m*-quinodimethane (MQM) are electron-rich,[6] whereas those for *m*-quinodimethane (MQDM) are electron-poor.[3] However, the olefin reactivity profiles of the two biradicals intersect at the hydrocarbon conjugated diene structure, and accordingly, we have examined the reactions of MQM with *cis,cis*- and *trans,trans*-2,4-hexadiene, traps whose reactions with MQDM also have been studied recently.[3]

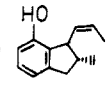
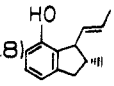
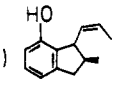
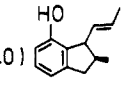
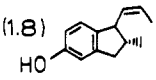
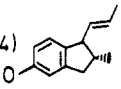
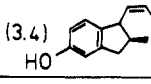
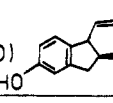
Thermal reaction of MQM (from precursor **8**) with *cis,cis*-2,4-hexadiene in benzene at 116 °C gave four 1:1 adducts, as expected (see Table III). Three of these were isolated by preparative GC and identified by ^{1}H NMR spectroscopy. The two first-emergent adducts had the ortho regiochemistry (**19** and **20**), as could be recognized by the characteristic[6,7] splitting pattern of the aromatic protons: triplet, doublet, doublet (see supplementary material). The fourth-emergent adduct showed a typical para NMR pattern: doublet, doublet, doublet of doublets. That the third-emergent adduct was a cycloadduct was established from its mass spectroscopic cracking pattern. It was not obtained in sufficient quantity for NMR characterization, and its regiochemical and stereochemical assignments were made by exclusionary arguments (supplementary material).

The corresponding reaction with *trans,trans*-2,4-hexadiene again gave four cycloadducts, of which three could be isolated and characterized directly by NMR spectroscopy. Again, assignments to the fourth were made by exclusion. Details of all the assignments are given in the supplementary material. The results are summarized in Table III.

A feature of major mechanistic significance is the clear presistence of the starting diene configuration in the double bond that survives in the adduct (*cis,cis*-diene → only *cis*-olefin; *trans,trans*-diene → only *trans*-olefin), which is evident from the absence of crossover products (Table III). By an argument which is given elsewhere[16] and is analogous to that put forward[3c] in the interpretation of the MQDM cycloadditions, this finding renders highly improbable a conceivable pathway to the indan cycloadducts of Table III via an initial 1,4-addition of MQM to the diene followed by Claisen rearrangement of the intermediate *m*-oxacyclophane. This sequence should have given mixed stereochemistry in the products' propenyl side chain.

(15) For a similar rationalization of solvent effects on the endo vs. exo stereochemistry of the Diels–Alder reaction, see: Berson, J. A.; Hamlet, Z.; Mueller, W. A. *J. Am. Chem. Soc.* **1962**, *84*, 297.
(16) Inglin, T. A. Ph.D. Dissertation, Yale University, 1984.

Table III. Relative Yields of Cycloadducts from the Reaction of **8** (vis MQM) with *cis,cis*- and *trans,trans*-2,4-Hexadiene in Benzene at 116 °C.

from *cis,cis*-	from *trans,trans*-
19 (1.0) 	23 (4.8) 
20 (6.2) 	24 (1.0) 
21 (1.8) 	25 (3.4) 
22 (3.4) 	26 (1.0) 

It is also evident that the diene configuration is predominantly retained at the cycloaddition site. Thus, the cis configuration of the substituents in the ortho and para adducts from *cis,cis*-diene is preferred by factors of 6.2 and 1.9, respectively, whereas the indan trans configuration dominates in the adducts from *trans,trans*-diene by factors of 4.8 and 3.4, respectively. Qualitatively, the results are similar to the preference for retention observed in the dimethoxyethene reactions (Table I), although the stereospecificity is significantly lower with the dienes.

Discussion

Stereospecificities. The stereospecificities of biradical cycloadditions vary greatly. Although no studies of stereospecificities of trimethylenemethane (TMM) additions to conjugated hydrocarbon dienes are available, the reactions of TMM *singlet* biradicals of the 2-alkylidenecyclopentane-1,3-diyl series with other conjugated olefins are highly stereospecific (>100:1),[12] and there is reason to expect this pattern would presist with dienes. MQM additions to dienes are shown by the present studies to be stereospecific (~2.1–~6.1) but much less so than those of TMM singlets, whereas MQDM additions to dienes are nearly stereorandom.[3] Moreover, the present studies also show that MQM additions to the 1,2-dimethoxyethenes (DME) are significantly more stereospecific (Table I) than those to the 2,4-hexadienes (Table III). To summarize the trends which call for explanation, we may write the inequalities 2 and 3.

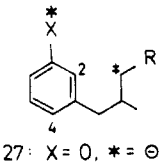
stereospecificity to dienes:

$$\text{TMM (singlet)} > \text{MQM} > \text{MQDM} \quad (2)$$

stereospecificity to MQM: $\text{DME} > \text{2,4-hexadienes} \quad (3)$

That the stereospecificities of the cycloadditions of MQM and MQDM are insensitive to both dilution and the presence of O_2 suggests that, in each case, only one reactive intermediate is being captured by the trapping agent. As before,[3b] we assume for the sake of argument that the intermediate is singlet and develop the consequences of that assumption.

In the diene cycloadditions, the oxygenated (MQM) and hydrocarbon (MQDM) biradicals both give significant amounts of inversion products, but the retention stereospecificity is markedly greater with MQM. It seems clear that a stepwise mechanism is present in both reactions. However, difficulties arise if it is assumed that this is the only pathway. In that hypothesis, the differences in behavior would be attributed to a larger ratio of the rate constants for ring closure/internal rotation in the hypothetical intermediate **27** from MQM than in the corresponding



27: X = O, * = ⊖, ‡ = ⊕
28: X = CH_2, *, ‡ = •

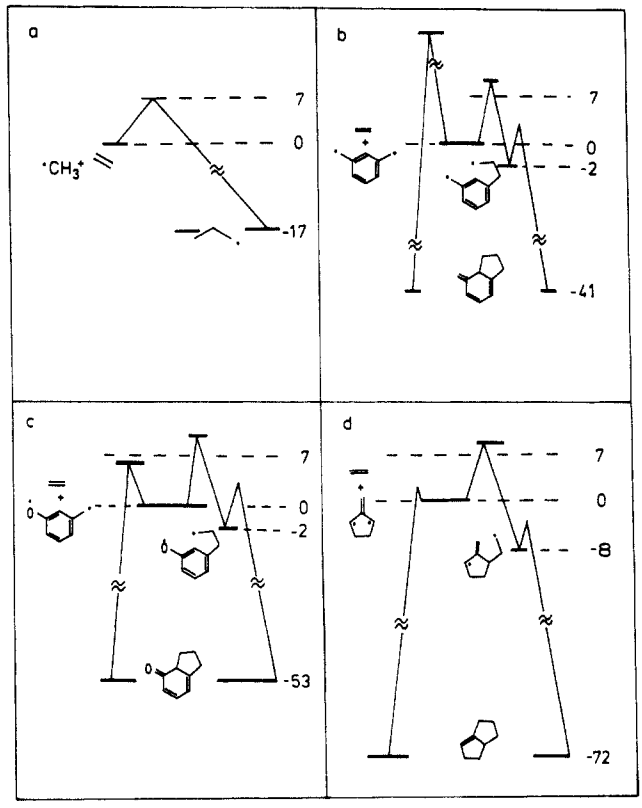


Figure 2. Energy vs. reaction coordinate diagrams for hypothetical competing stepwise and concerted cycloadditions of biradicals (b–d). Part a describes the addition of methyl radical to ethylene.

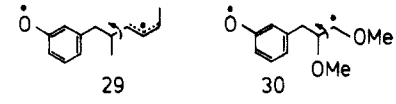
intermediate **28**, derived from MQDM. Why should this be so? We entertained the notion that the apparent relative preference for ring closure in **27** was associated with electrostatic attraction between the charged centers, but as Table II shows, the stereospecificity of MQM addition to DME is not significantly lowered by the large increase of solvent polarity when the reaction medium is changed from benzene to acetonitrile. Similarly, the stereospecificity, especially in nonpolar solvent, might have been expected to be higher in the para adducts, which hypothetically are formed via the electrostatically destabilized "extended" intermediate, compared to that in the ortho adducts, which are formed via the more stable "coiled" intermediate. In the latter, internal rotation should compete better with charge–charge annihilation by ring closure, but this expectation also is not realized (Table III). The absence of these anticipated stereochemical effects suggests that although electrostatic factors at least partially control the *regiospecificities* (ortho vs. para), as indicated above, they probably play a minor role in the control of the *stereospecificities*.

It is more useful to rationalize the facts with the hypothesis[17] that cycloadditions of singlet biradicals can occur by *competing* completely stereospecific concerted and less stereospecific stepwise pathways, as shown in Figure 2b–d. As a reference reaction, Figure 2a also shows a generalized addition of an alkyl radical to an alkene. The basic postulates used in constructing Figure 2b–d are (i) that in each of the stepwise pathways (right side of each graph), the bimolecular step leading to the adduct biradical is rate-determining, (ii) that for reasons already given,[17] the responses of the rates of both the concerted and stepwise pathways to variation in structure are dominated by the corresponding variations in $\Delta H^{\ddagger}$, and (iii) that $\Delta H^{\ddagger}$ decreases as the reaction becomes more exothermic. The reaction enthalpies are estimated by the method of group equivalents.[18a] The data for Figure 2a are taken from the literature.[18b]

In the stepwise mechanisms (right side of Figure 2b–d), the enthalpies of reaction for formation of the adduct biradical intermediates are −2, −2, and −8 kcal/mol, respectively. This should result in rather small differences in the rates of the rate-determining step across the series. However, in the concerted mechanisms (left side of Figure 2b–d), the full exothermicity of cycloadduct formation is released, and since the variation in these reaction enthalpies is much greater (−41, [18c] −53, and −72 kcal/mol), the rates of the concerted reactions should vary more with structure than those of the stepwise reactions. It would not be surprising, therefore, if mechanistic dominance switched from stepwise to concerted somewhere in the series. With reference to Figure 2, we suggest that the crossover point in the sequence occurs at MQM (Figure 2c), where the barrier for the completely stereospecific concerted mechanism is shown as slightly lower than that for the less stereospecific stepwise mechanism. This would lead to predominant but not quite complete retention of configuration in the MQM addition, as is observed.

In the case of MQDM, where the overall reaction exothermicity is less, the barrier for the concerted pathway is raised enough for the stepwise pathway to dominate (Figure 2b), whereas in the case of the TMM derivative (Figure 2d), the exothermicity is large, and the barrier for concerted cycloaddition is lowered enough for that pathway to dominate. Although not uniquely compatible with the data, the competition hypothesis does seem to offer the most economical rationalization of the whole range of reactivity phenomena summarized in inequality 2.

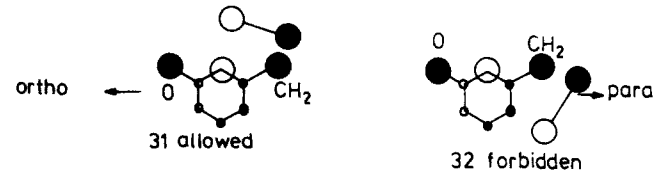
With respect to inequality 3, which expresses the observation that DME captures MQM with higher stereospecificity than does 2,4-hexadiene, we note that the intermediate adduct biradical in the diene addition (**29**) is an allylically stabilized species, whereas



that from the DME addition (**30**) is an α-methoxy radical. Since the stabilization energy of **29** should be about 11–13 kcal/mol,[18a] whereas that of **30** should be about 3 kcal/mol,[19] the competition should favor the stepwise mechanism more in the case of the diene addition. Moreover, the stereospecificity of the stepwise pathway itself also might well be lower in the diene case because the additional stability of the intermediate may retard the cyclization rate, thereby permitting the stereorandomizing internal rotation to become more consequential.

Regiospecificities. The known cycloadditions of TMM singlets are highly regiospecific, and the observed orientations are consistently rationalizable as orbital symmetry phenomena in which the reactive entity is treated as a closed-shell species. Phase matching of the TMM HOMO and the olefin or diene LUMO seems to control the orientational preference.[20]

This reasoning can be extended qualitatively to the case of *m*-quinomethane (MQM) with the aid of an orbital-phase picture of the closed-shell HOMO, shown here with an approaching olefin LUMO in an allowed orientation **31** leading to ortho product. The



out-of-phase forbidden orientation **32** would lead to para product. If these factors were determinative, the ortho adduct would be formed concertedly and stereospecifically, whereas the para adduct

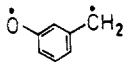
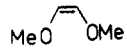
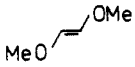
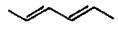
(17) The present argument expands one given in ref 3b.

(18) (a) Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976 and references cited therein. (b) Kerr, J. A. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. I, Chapter 1. (c) We prefer this value to the one used earlier,[3b] −31 kcal/mol, although the argument is not qualitatively affected by the choice.

(19) (a) Timberlake, J. W.; Hodges, M. L. *Tetrahedron Lett.* **1970**, 4147. (b) Berson, J. A.; Walsh, E. J., Jr. *J. Am. Chem. Soc.* **1968**, *90*, 4730. (c) Ohno, A.; Ohnishi, Y. *Tetrahedron Lett.* **1969**, 4405.

(20) (a) Siemionko, R.; Shaw, A.; O'Connell, G.; Little, R. D.; Carpenter, B. K.; Shen, L.; Berson, J. *Tetrahedron Lett.* **1978**, 3529. (b) Siemionko, R. K.; Berson, J. A. *J. Am. Chem. Soc.* **1980**, *102*, 3870.

Table IV. Regiospecificities of 1,2-Cycloadditions of MQDM and MQM to Olefins

diyl	olefin	ortho/para[a]
MQDM		13[b]
MQDM		4.3[b]
MQDM		2.2[b]
MQDM		3.9[b]
MQDM		2.7[b]
 MQM		3.0[c,d,e]
MQM		1.6[c,e], 1.5[c,f]
MQM		1.0[c,e]
MQM		1.4[c,e]
MQM		1.3[c,e]

[a] Estimated experimental error in the ratio ~ 10%. [b] Ratio independent of solvent from the group pentane, tetrahydrofuran, and MeOH. Reference 3b. [c] This work. [d] Average of two separate runs (2.8 and 3.2). [e] Solvent, benzene. [f] Solvent, CH_3CN.

would be formed in a stepwise manner and could suffer some loss of stereochemistry. The anticipated switch in stereospecificity would clearly signal a change in mechanism. However, as Tables II and III show, the ortho additions of MQM to *cis,cis*-2,4-hexadiene and DME do not differ significantly from the para additions in stereospecificity. Orbital symmetry therefore seems to play at most a minor role in the regiochemical outcome of MQM cycloadditions.

Table IV summarizes the regiospecificities observed in cycloadditions of *m*-quinodimethane (MQDM) and *m*-quinomethane (MQM). Except for the MQDM–butadiene addition, which shows an ortho/para product ratio of 13, the other reactions of MQDM are only weakly regiospecific for the ortho product. The stereochemistry of MQDM additions leaves little doubt that these processes are largely stepwise and pass through adduct intermediates of the general structure **28**. Conceivably, the preference for ortho cyclization of **28** may be related to the slightly higher Hückel free valence index at the ortho ring position ($F_2 = 0.504$) compared to that at the para position ($F_4 = 0.462$), although the difference is so small that its influence might be outweighed by steric factors. If the corresponding intermediate (**27**) from *m*-quinomethane (MQM) is modeled as a biradical rather than a zwitterion, the F values are slightly parameter dependent but barely differ from each other: coefficients[21] derived from heteroatom parameters $h = 0.0$ and $k = 0.5$ give $F_2 = 0.432$ and $F_4 = 0.440$, whereas those derived from $h = 0.5$ and $k = 1.0$ give $F_2 = 0.476$ and $F_4 = 0.512$. Modeled as a zwitterion, **27** shows electron densities $q_2 = 0.940$ and $q_4 = 1.040$ for the first parameter set and $q_2 = 1.097$ and $q_4 = 1.095$ for the second. These values do not offer strong reasons to expect large regiospecificities and hence are compatible with the observations.

Conclusions. The *m*-quinomethane (MQM) triplet biradical is the ground state (or at worst a very low-lying excited state). Nevertheless, there is no evidence that more than one intermediate is involved in cycloadduct formation between MQM and olefins. At present, the simplest rationalization invokes a singlet state of MQM as the reactive entity. This species gives largely, but not entirely, stereospecific products with *cis*- or *trans*-1,2-dimethoxyethene and with *cis,cis*-2,4-hexadiene. Although a single pathway passing over an adduct biradical cannot presently be ruled out, mechanistic parsimony is best preserved by the concept of competing concerted and stepwise mechanisms. This places the cycloaddition chemistry of *m*-quinomethane (MQM) in a mechanistic continuum with that of *m*-quinodimethane (MQDM) and trimethylenemethane (TMM).

Experimental Section

Instruments. Proton nuclear magnetic resonance (^{1}H NMR) spectra were taken on a Varian EM-360A spectrometer (60 MHz), JEOL FX-90Q spectrometer (90 MHz), Bruker HX-270 spectrometer (270 MHz), or a Bruker WM-500 spectrometer (500 MHz). Chemical shifts are reported relative to tetramethylsilane (Me_4Si) and were measured relative to the residual solvent signal ($CDCl_3$, 7.27 ppm; acetone-d_6, 2.04 ppm; benzene-d_6, 7.15 ppm; toluene-d_8, 2.09 ppm). The NMR absorptions are reported as follows: chemical shift (parts per million downfield from Me_4Si), multiplicity, number of protons, coupling constant (when measured), and assignment. Variable temperature proton NMR spectra were collected on the HX-270 spectrometer using a Bruker Model B-ST 100/700 variable temperature controller. The temperatures reported correspond to the nominal settings of the controller. ^{13}C NMR spectra were recorded on a JEOL FX-90Q spectrometer (22.5 MHz), and the absorptions are reported relative to Me_4Si.

Infrared (IR) spectra were taken on a Nicolet 7199 FT-IR spectrometer at 4-cm^{-1} digital resolution or a Nicolet 5SX FT-IR spectrometer at 2-cm^{-1} digital resolution. Ultraviolet–visible (UV–vis) spectra were obtained on a Cary 219 spectrophotometer.

Low-resolution mass spectra (MS) were recorded on a Hewlett-Packard 5985A gas chromatograph/mass spectrometer (GC/MS) system. The gas chromatograph (GC) employed either a 3 or 6 ft × 0.125 in. (o.d.) glass column packed with 2% OV-101 Anakrom ABS 110/210. The GC/MS data, *m/e* (relative intensity), are reported with the following conditions in brackets: initial column temperature (°C), time at initial temperature (min), temperature program rate (°C/min), final temperature (°C), and retention time (min). Isothermal runs are indicated by a single temperature. High-resolution mass spectra were performed by Dr. Timothy Wachs of Cornell University or by Dr. Frank W. Crow of the Midwest Center for Mass Spectrometry at the University of Nebraska—Lincoln.

Preparative GC was carried out on a Varian Aerograph 90-P using helium as a carrier gas (60 mL/min) with 0.25-in. columns (see Table V for columns used). Analytical GC was carried out on a Perkin-Elmer 900 gas chromatograph or a Varian 1200 gas chromatograph. Both instruments utilize flame ionization detectors and nitrogen as a carrier gas with 0.125-in. columns (see Table V for columns used). Peaks were quantified by digital integration using a Hewlett-Packard 3390 electronic integrator. Detector response factors (mol/area) were determined by injection of known amounts of the compound of interest. Isomers were assumed to have the same response factor.

Electron paramagnetic resonance (EPR) spectra were recorded on a Varian E-9 spectrometer. For experiments conducted above the boiling point of liquid nitrogen, a Varian Model V-4540 variable temperature accessory was used. An Air Products Model APD-E temperature controller and an Air Products Model LTD-3-110 liquid-transfer helitran refrigerator were used for experiments below 77 K. The sample temperature was monitored by using a gold (0.07%) chromel thermocouple. The thermocouple used for reading the temperature of the sample was located a few centimeters below the sample so that the actual sample temperature may be slightly different. The EPR samples were irradiated in the cavity of the EPR spectrometer with an Oriel Model 6137 mercury arc lamp through a Pyrex filter.

Melting points were taken on a Thomas-Hoover capillary melting-point apparatus and are uncorrected. Computer programs were run on a Digital Equipment 11/750 VAX computer.

Reagents. Chemicals used were of reagent grade or better. When necessary, chemicals were purified by following the procedures recommended in *Purification of Laboratory Chemicals*.[22] All dried solvents were stored over 4-Å molecular sieves. Benzene and tetrahydrofuran (THF) were distilled from benzophenone sodium ketyl (under nitrogen). Methanol was distilled from sodium. Acetonitrile was stirred overnight over calcium hydride and then fractionally distilled under nitrogen. Decalin was stirred against concentrated sulfuric acid for 2 h, washed with water, sodium bicarbonate, and water, respectively, and then dried with calcium chloride. It was further dried overnight with calcium hydride, filtered, and distilled. Methylcyclohexane was passed through

(21) Taken from: Coulson, C. A.; Streitwieser, A., Jr. *Dictionary of π-Electron Calculations*; W. H. Freeman: San Francisco, 1965.

(22) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*; Pergamon: New York, 1966.

Table V. GC Columns

A, 0.25 in. × 5 ft	5% OV-101 Chromosorb W DMCS 60/80
B, 0.25 in. × 3 ft	5% Carbowax 20 M on Chromosorb P AW/DMCS 60/80
C, 0.25 in. × 10 ft	20% Carbowax 20 M on Chromosorb A AW/DMCS 45/60
D, 0.25 in. × 5 ft	15% OV-101 on Chromosorb W DMCS 60/80
E, 0.25 in. × 6 ft	10% OV-101 on Chromosorb W DMCS 60/80
F, 0.25 in. × 5 ft	25% Carbowax 20 M on Chromosorb P AW/DMCS 60/80
G, 0.125 in. × 6 ft	5% Carbowax 20 M on Chromosorv P AW/DMCS 100/120
H, 0.125 in. × 5 ft	5% OV-101 on Anakrom ABS 100/120

basic alumina, which had been activated at 230 °C for 1 h, and then fractionally distilled from sodium.

6-Methylenebicyclo[3.1.0]hex-3-en-2-one (8). This compound was prepared according to Matlin.[2,7] The pure material was obtained by preparative GC (column E, injector 150 °C, detector 100 °C, column 70 °C; column B, injector 130 °C, detector 80 °C, column 80 °C). The spectral properties obtained are in accordance with the literature values.[2,7]

EPR Spectroscopy. For EPR spectroscopy, the sample of **8**[2] was prepared by dissolving 6–12 mg in a methylcyclohexane/decalin (1:1, v/v) mixture and placing the sample in an EPR tube composed of a 30-mm-long quartz tube (4-mm o.d.) connected to a length of Pyrex tubing of the same diameter. The sample was subjected to three freeze–pump–thaw cycles after which it was sealed while under vacuum. The sample was then placed in the cavity of the EPR spectrometer and photolyzed.

Curie Study. The photolysis was carried out at 40.5 K, where the signal was stable. The temperature was then lowered at regular intervals, spectra being recorded, with a microwave power of 0.04 mW, at each temperature until the lowest temperature was reached. The temperature was then raised in the same manner while spectra were recorded until the high-temperature limit was reached. This process was repeated until a sufficient number of spectra had been recorded. The peak height measured from the upper and lower limits of the low- and high-field absorptions, respectively, was taken as proportional to the concentration of absorbing species.

A saturation plot was obtained at the lowest temperature (18.5 K) by recording spectra at various power levels from 0.007 to 0.20 mW. The peak height of the low-field absorption was measured.

***cis*- and *trans*-1,2-Dimethoxyethene.**[23] The flow tube of a horizontal flow pyrolysis apparatus packed with activated alumina (Matheson, Coleman and Bell, 8–14 mesh) was heated to 300 °C, and the inlet flask was kept at 190 °C with nitrogen flowing for 3 h before the collection assembly was cooled. The collection assembly, consisting of water condenser, dry ice acetone condenser, and dry ice–acetone bath, was cooled, and 1,1,2-trimethoxyethane[24,25] (39.1 g, 0.33 mol) was added dropwise to the heated inlet flask from the pressure equalizing funnel over a period of 4.5 h with nitrogen flowing. A yellow liquid condensed in the receiving flask. The crude product mixture can be separated by preparative GC (column C, injector 150 °C, detector 130 °C, column 105 °C) and the stereochemistry assigned by comparison of the spectral parameters to literature values.[23]

***trans*-1,2-Dimethoxyethene**: retention time 13 min; ^{1}H NMR (90 MHz, acetone-d_6) 6.28 (s, 2 H, vinyl), 3.40 (s, 6 H, $-OCH_3$). Purity by analytical GC (column G, 50 °C): once purified 99.44%; twice purified 99.96%.

***cis*-1,2-Dimethoxyethene**: retention time 16 min; ^{1}H NMR (90 MHz, acetone-d_6) 5.25 (s, 2 H, vinyl), 3.49 (s, 6 H, $-OCH_3$). Purity by analytical GC (column G, 50 °C): once purified 98.85%; twice purified 99.88%.

General Procedure for the Reaction of 8 with Olefins. The reactions were carried out in sealed tubes; 6-mm-o.d. Pyrex tubing was washed with concentrated ammonium hydroxide, water, and then acetone, then sealed at one end, and oven dried at 120 °C for several hours. Quartz tubing (10 mm), sealed to Pyrex tubing and prepared as for the Pyrex tubing, was used for photolysis at wavelengths shorter than 300 nm. In a typical experiment, the trapping agent of interest was added to a tube via a syringe, and then a 6-15-mg sample of GC-purified **8** in the solvent of interest (0.25–0.5 mL) was added. The tube was then either sealed under vacuum, freeze–pump–thaw degassed (<0.01 torr, 3×), and sealed under vacuum or fitted with a septum and purged with the desired gas. For the pyrolytic runs the tubes were submerged in a thermostated oil bath at 115 °C for 1 h, unless otherwise noted. For the photolytic runs the tubes were placed in a clear Pyrex Dewar filled with ice water or dry ice–isopropyl alcohol and photolyzed in a Rayonet reactor with 16 bulbs, of the proper wavelength, for 90 min. The quartz tubes were suspended directly in the Rayonet reactor at ambient temperature for photolysis at wavelengths shorter than 300 nm.

(23) Waldron, J. T.; Snyder, W. H. *J. Chem. Eng. Data* **1973**, *18*, 441.
(24) von Rufenacht, K. *Helv. Chim. Acta* **1975**, *57*, 1671.
(25) McElvain, S. M.; Stammer, C. H. *J. Am. Chem. Soc.* **1951**, *73*, 915.

Table VI. Product Ratios from Reaction of **8** with *cis*-1,2-Dimethoxyethene

solvent	reaction conditions	10/9	12/11
benzene	thermal, 115 °C[a]	17.0 ± 0.6[e]	13 ± 3[e]
CH_3CN	thermal, 115 °C[a]	17.1 ± 0.2	14.7
diethyl ether	300 nm, 0 °C[a]	25.0 ± 2.4[e]	
	300 nm, 0 °C[b]	24.3 ± 3.1[e]	
	300 nm, 0 °C[c]	20.0 ± 0.7	
	300 nm, 0 °C[d]	23.4 ± 0.6	
	300 nm, −78 °C[a]	29.2 ± 0.9	
	300 nm, −78 °C[b]	29.0 ± 0.7[e]	
	300 nm, −78 °C[d]	31.3 ± 0.7	
	254 nm, 35 °C[c]	24.2 ± 0.4[b]	

[a] Freeze–pump–thaw degassed and then sealed under vacuum. [b] Sealed under vacuum. [c] Purged with N_2. [d] Purged with O_2. [e] Average of two separate experiments.

Samples from the photochemical or thermal reactions were analyzed in the same manner. The tubes were opened, and the sample was concentrated by a gentle stream of dry nitrogen. The residue was taken up in a small quantity of dry diethyl ether, and the resulting solution was subjected to GC analysis.

Reaction of 8 with *cis*-1,2-Dimethoxyethene. A benzene solution of GC-purified **8** (5.09 mg, 0.048 mmol) and GC-purified *cis*-1,2-dimethoxyethene (112.31 mg, 1.275 mmol) was pyrolyzed. GC analysis of the product mixture (column H, 100 °C isothermal) shows four components. The first two could be isolated by preparative GC (column A, injector 150 °C, detector 125 °C, column 110 °C). The third and fourth compounds did not survive the GC conditions, but some of their spectral characteristics could be ascertained by comparison of the spectra of the crude sample before and after fractionation. The assigned structures were based on the spectral characteristics shown here and on conversion to the products of independent synthesis described and characterized in the supplementary material.

***trans*-1,2-Dimethoxy-7-hydroxyindan (9)**: retention time 3.77 min (column H); ^{1}H NMR partial (90 MHz, acetone-d_6) 7.34 (s, 1 H, aromatic), 7.10 (m, 1 H, aromatic), 6.72 (m, 1 H, aromatic), 4.86 (d, 1 H, J = 3.30 Hz, ArCHOMe); GC/MS [100, 1, 10, 200, 3.8] 194 (49, M^+), 162 (100, $-HOCH_3$), 147 (89), 133 (6), 121 (8), 119 (55), 91 (17).

***cis*-1,2-Dimethoxy-7-hydroxyindan (10)**: retention time 4.92 min (column H); ^{1}H NMR (270 MHz, acetone-d_6) 7.08 (t, 1 H, J = 7.77 Hz, aromatic), 6.68 (br t, 2 H, J = 8.73 Hz, aromatic), 4.86 (d, 1 H, J = 4.84 Hz, ArCHOMe), 3.95 (m, 1 H, CHOMe), 3.40 (s, 3 H, $-OCH_3$), 3.39 (s, 3 H, $-OCH_3$), 2.92 (d, 1 H, J = 7.21 Hz, $^1/_2ArCH_2$), 2.84 (d, 1 H, J = 8.77 Hz, $^1/_2ArCH_2$); GC/MS [100, 1, 10, 200, 4.8] 194 (91, M^+), 193 (19, −H), 179 (23, $-CH_3$), 163 (100, $-OCH_3$), 162 (80, $-HOCH_3$), 147 (98), 119 (59), 91 (22).

***trans*-1,2-Dimethoxy-5-hydroxyindan (11)**: retention time 9.57 min (column H); GC/MS [100, 1, 10, 200, 6.1] 194 (91, M^+), 193 (19, −H), 179 (23, $-CH_3$), 163 (100, $-OCH_3$), 162 (80, $-HOCH_3$), 147 (98), 119 (59), 121 (44), 133 (42), 91 (22).

***cis*-1,2-Dimethoxy-5-hydroxyindan (12)**: retention time 10.69 min (column H); ^{1}H NMR (90 MHz, acetone-d_6) 4.53 (d, 1 H, J = 4.83 Hz, ArCHOMe); GC/MS [100, 1, 10, 200, 6.7] 194 (83, M^+), 193 (19, −H), 179 (23, $-CH_3$), 163 (100, $-OCH_3$), 162 (65, $-HOCH_3$), 147 (85), 133 (43), 121 (45), 119 (52), 91 (21).

Table VI shows the ratios of products under varying reaction conditions. Two samples of *cis*-DME (98.85 % and 99.88% homogeneous) gave indistinguishable product ratios.

The yield of the reaction was determined by NMR analysis. The known amount of starting **8** was compared to the calculated amount of products by use of an added internal standard. The product mixture was concentrated, 5.0 μL of methylene chloride was added, and the mixture was taken up in $CDCl_3$. The ^{1}H NMR spectrum (90 MHz, 20 pulses, 10-s pulse rate, 36-μs 90° pulse) of the mixture was taken, and the integral of the added methylene chloride peak (δ 5.32, s) and the two

Table VII. Ratio of *cis*-DME to *trans*-DME before and after Pyrolysis at 115 °C for 35 min

	δ 5.04/6.26	δ 3.09/3.22
before	1.21 ± 0.02	0.97 ± 0.06
after	1.20 ± 0.15	0.99 ± 0.04

Table VIII. Product Ratios Obtained from a Dilution Study of the Reaction of **8** with *cis*-1,2-Dimethoxyethene (*cis*-DME)

[*cis*-DME], M	[**8**], M	**10**/**9**
3.71	0.150	15.3 ± 0.1
0.928	0.0375	15.5 ± 0.1
0.0371	0.0015	15.8 ± 0.1

doublets at δ 4.58 and 4.98 was measured. The amount of product was calculated as follows:

$$\text{moles of product} = \frac{(\text{moles of } CH_2Cl_2)(\text{area of product})}{\text{area of } CH_2Cl_2}$$

The yield was shown to be 66 ± 1%. The ratio of the δ 4.58 to 4.98 absorbances was 2.77 ± 0.12 (≡ortho/para).

Reaction of 8 with *trans*-1,2-Dimethoxyethene. A benzene solution of **8** (11.30 mg, 0.011 mmol) and GC-purified *trans*-1,2-dimethoxyethene (165 μL, 157 mg, 1.78 mmol) was pyrolyzed. GC analysis of the product mixture (column H, 100 °C isothermal) shows two components, with retention times 4.64 and 11.63 min in the ratio of 2.3/1, respectively. It can be determined that these two compounds are the trans isomers **9** and **11** by inspection of the ^1H NMR spectrum of the crude product, in particular, the coupling constants of the δ 4.87 and 4.56 doublets of the ^1H signals. The ratio of the two compounds determined by the integration of the δ 4.87 and 4.56 resonances is 1.6/1: ^1H NMR (90 MHz, acetone-d_6) 7.34 (s, aromatic), 7.10 (s, aromatic), 7.00 (s, aromatic), 6.68 (m, aromatic), 4.87 (d, J = 2.64 Hz), 4.56 (d, J = 3.30 Hz), 4.02 (m), 3.46 (s, $-OCH_3$), 3.37 (s, $-OCH_3$) (the benzyl CH_2 resonances were partialy obscured by the unreacted olefin); GC/MS [100, 1, 10, 200, 3.9] 194 (46, M^+), 163 (12, $-OCH_3$), 162 (88, $-HOCH_3$), 147 (100), 119 (79) [retention time 6.5 min] 194 (74, M^+), 179 (26, $-CH_3$), 163 (100, $-OCH_3$), 162 (61, $-HOCH_3$), 162 (61, $-HOCH_3$), 147 (91), 119 (56).

Determination of the Relative Reactivities of *cis*- and *trans*-1,2-Dimethoxyethene. In a 1-mL volumetric flask, **8** (10.12 mg, 0.095 mmol), *cis*-1,2-dimethoxyethene (8.7 μL, 8.23 mg, 0.094 mmol), and *trans*-1,2-dimethoxyethene (8.7 μL, 8.27 mg, 0.094 mmol) were dissolved in benzene-d_6 with a small amount of Me_4Si added as an internal reference. A portion of this solution was sealed under vacuum into an NMR tube. NMR spectra (90 MHz, 15 pulses, 15-s pulse repetition rate, 35-μs 90° pulse) were taken of the sample both before and after pyrolysis at 115 °C for 35 min ($t_{1/2}$ = 1043 s, 2.5 half-lives). The resonances of the vinyl and methyl protons of the two olefin isomers were integrated against one another. The phasing of the integral was changed and the integral measured again to give an estimate of the reproducibility of the measurements. Table VII reports the data.

Dilution Studies. In a 1-mL volumetric flask, GC-purified *cis*-1,2-dimethoxyethene (0.326 91 g, 3.175 mmol) and GC-purified **8** (0.015 88 g, 0.1497 mmol) were dissolved in dry benzene. This solution was diluted 4-fold by taking 0.500 mL of the solution and dissolving it in 2 mL of dry benzene in a volumetric flask. The resulting solution was further diluted 5-fold by dissolving 1.00 mL of that solution in 5 mL of dry benzene in another volumetric flask. This process was repeated twice more for further 5- and 10-fold dilutions. The solutions were then pyrolyzed, and the resulting product mixtures were concentrated with a gentle stream of nitrogen and analyzed by GC (column H, 100 °C isothermal). The results are shown in Table VIII. The error limits are the standard deviations of two or more injections.

Reaction of 8 with *cis,cis*-2,4-Hexadiene. In 0.5 mL of dry solvent, GC-purified **8** (15 mg, 0.14 mmol) and *cis,cis*-2,4-hexadiene (75 mg, 0.91 mmol, ICN Pharmaceuticals) were dissolved and placed in a 6-mm-o.d. Pyrex tube. The tube was sealed under vacuum and pyrolyzed at 116 °C for 45 min. The tube was cooled and the solution decanted away from the solid after centrifugation. GC analysis (column H, 100, 1, 2; column G, 100, 1, 8, 200) showed the presence of four 1:1 adducts whose structures and stereochemistries were assigned by their spectral characteristics and by comparison with model compounds.

***trans*-1-((*Z*)-1-Propenyl)-2-methyl-7-hydroxyindan (19)**: retention time (column H) 6.54 min, (column G) 12.23 min; ^1H NMR (500 MHz, $CDCl_3$) 7.07 (t, 1 H, J = 7.49 Hz, aromatic), 6.76 (d, 1 H, J = 7.29 Hz, aromatic), 6.65 (d, 1 H, J = 7.92 Hz, aromatic), 5.92 (m, 1 H, vinyl), 5.65 (s, 1 H, ArOH), 5.61 (m, 1 H, vinyl), 3.76 (t, 1 H, J = 9.96 Hz, ArCH–propenyl), 3.05 (dd, 1 H, J = 15.12, 7.85 Hz, $^1/_2ArCH_2$), 2.60 (dd, 1 H, J = 15.12, 11.19 Hz, $^1/_2ArCH_2$), 2.25 (m, 1 H, CHMe), 1.87 (dd, 3 H, J = 6.88, 1.80 Hz, vinyl CH_3), 1.18 (d, 3 H, J = 6.64 Hz, CH_3); GC/MS [100, 1, 10, 200, 3.9] 188 (90, M^+), 173 (96), 159 (44), 146 (39), 145 (100), 144 (40), 131 (61), 115 (56).

***cis*-1-((*Z*)-1-Propenyl)-2-methyl-7-hydroxyindan (20)**: retention time (column H) 7.66 min, (column G) 13.53 min; ^1H NMR (500 MHz, $CDCl_3$) 7.07 (t, 1 H, J = 7.67 Hz, aromatic), 6.80 (d, 1 H, J = 7.34 Hz, aromatic), 6.65 (d, 1 H, J = 8.02 Hz, aromatic), 5.83 (m, 1 H, vinyl), 5.58 (t, d, 1 H, J = 10.91, 1.56 Hz, vinyl), 5.18 (s, 1 H, ArOH), 4.22 (dd, 1 H, J = 10.86, 7.45 Hz, ArCH–propenyl), 3.06 (dd, 1 H, J = 15.15, 7.13 Hz, $^1/_2ArCH_2$), 2.67 (m, 1 H, CHMe), 2.62 (dd, 1 H, J = 15.21, 5.47 Hz, $^1/_2ArCH_2$), 1.86 (dd, 3 H, J = 6.85, 1.55 Hz, vinyl CH_3), 1.00 (d, 3 H, J = 6.96 Hz, CH_3); GC/MS [100, 1, 10, 200, 4.3] 188 (76, M^+), 173 (82), 159 (38), 146 (33), 145 (100), 144 (38), 131 (59), 115 (52); exact mass calcd for $C_{13}H_{16}O$ 188.1201, obsd 188.1199.

***trans*-1-((*Z*)-Propenyl)-2-methyl-5-hydroxyindan (21)**: retention time (column H) 13.18 min, (column G) 17.05 min; GC/MS [100, 1, 10, 200, 5.3] 188 (76, M^+), 173 (82, $-CH_3$), 159 (22), 146 (18), 145 (68), 144 (31), 131 (35), 115 (36).

***cis*-1-((*Z*)-1-Propenyl)-2-methyl-5-hydroxyindan (22)**: retention time (column H) 14.36 min, (column G) 17.64 min; ^1H NMR (500 MHz, $CDCl_3$) 6.94 (d, 1 H, J = 8.00 Hz, aromatic), 6.70 (d, 1 H, J = 2.09 Hz, aromatic), 6.62 (dd, 1 H, J = 8.08, 2.48 Hz, aromatic), 5.66 (m, 1 H, vinyl), 5.40 (t, d, 1 H, J = 10.4, 1.72 Hz, vinyl), 4.50 (s, 1 H, ArOH), 4.02 (dd, 1 H, J = 9.76, 7.54 Hz, ArCH–propenyl), 3.00 (dd, 1 H, J = 15.62, 7.22 Hz, $^1/_2ArCH_2$), 2.67 (m, 1 H, CHMe), 2.55 (dd, 1 H, J = 15.47, 5.3 Hz, $^1/_2ArCH_2$), 1.76 (dd, 3 H, J = 6.81, 1.72 Hz, vinyl CH_3), 0.94 (d, 3 H, J = 7.08 Hz, CH_3); GC/MS [100, 1, 10, 200, 5.6] 188 (66, M^+), 173 (100, $-CH_3$), 159 (22), 146 (20), 145 (87), 144 (38), 131 (42), 115 (47).

Table IX shows the product ratios.

Reaction of 8 with *trans,trans*-2,4-Hexadiene. In 0.5 mL of dry solvent, GC-purified **8** (15 mg, 0.14 mmol) and *trans,trans*-2,4-hexadiene (100 mg, 1.22 mol, Aldrich) were dissolved and placed in a 6-mm-o.d. Pyrex tube which was sealed under vacuum. The sample was pyrolyzed at 105 °C for 70 min and cooled, and the solution was analyzed by GC (column H, 100, 1, 2; column C, 100, 1, 8, 200), which showed the presence of six 1:1 adducts. Two of these (X and Y) were formed in quantities too small for complete identification.

Compound X: retention time (column H) 5.43 min, (column G) 5.76 min; GC/MS [100, 1, 10, 200, 3.5] 188 (20, M^+), 173 (83, $-CH_3$), 159 (87), 146 (21), 145 (79), 144 (15), 115 (41), 107 (41), 105 (57), 91 (100).

Compound Y: retention time (column H) 5.82 min, (column G) 5.06 min; GC/MS [100, 1, 10, 200, 3.8] 188 (17, M^+), 173 (75, $-CH_3$), 159 (73), 146 (26), 145 (82), 131 (36), 115 (45), 107 (43), 105 (68), 91 (100).

***trans*-1-((*E*)-1-Propenyl)-2-methyl-7-hydroxyindan (23)**: retention time (column H) 6.20 min, (column G) 11.91 min; ^1H NMR (500 MHz, $CDCl_3$) 7.07 (t, 1 H, J = 7.65 Hz, aromatic), 6.75 (d, 1 H, J = 7.30 Hz, aromatic), 6.64 (d, 1 H, J = 8.06 Hz, aromatic), 5.93 (d, q, 1 H, J = 15.29, 6.45 Hz, vinyl), 5.66 (s, 1 H, ArOH), 5.65 (m, 1 H, vinyl), 3.33 (t, 1 H, J = 9.18 Hz, vinyl), 3.05 (dd, 1 H, J = 15.54, 7.83 Hz, $^1/_2ArCH_2$), 2.52 (dd, 1 H, J = 14.96, 9.98 Hz, $^1/_2ArCH_2$), 2.21 (m, 1 H, CHMe), 1.81 (dd, 3 H, J = 6.45, 1.60 Hz, vinyl CH_3), 1.16 (d, 3 H, J = 6.70 Hz, CH_3); GC/MS [100, 1, 10, 200, 4.1] 188 (68, M^+), 173 (70, $-CH_3$), 159 (36), 146 (35), 145 (100), 131 (60), 115 (58), 107 (7), 105 (6).

***trans*-1-((*E*)-1-Propenyl)-2-methyl-5-hydroxyindan (25)**: retention time (column H) 8.64 min, (column G) 26.18 min; ^1H NMR (500 MHz, $CDCl_3$) 6.92 (d, 1 H, J = 7.94 Hz, aromatic), 6.67 (d, 1 H, J = 2.13 Hz, aromatic), 6.62 (dd, 1 H, J = 8.02, 2.35 Hz, aromatic), 5.60 (d, q, d, 1 H, J = 15.09, 6.49, 0.49 Hz, vinyl), 5.37 (ddd, 1 H, J = 15.10, 8.81, 1.60 Hz, vinyl), 4.51 (s, 1 H, ArOH), 3.10 (t, 1 H, J = 8.85 Hz, ArCH–propenyl), 2.96 (dd, 1 H, J = 15.53, 7.63 Hz, $^1/_2ArCH_2$), 2.47 (ddd, 1 H, J = 15.47, 9.84, 0.75 Hz, $^1/_2ArCH_2$), 2.15 (m, 1 H, CHMe), 1.76 (dd, 3 H, J = 6.41, 1.59 Hz, vinyl CH_3), 1.16 (d, 3 H, J = 6.69 Hz, CH_3); GC/MS [100, 1, 10, 200, 5.5] 188 (62, M^+), 173 (100, $-CH_3$), 159 (36), 146 (25), 145 (90), 131 (56), 115 (65), 107 (24), 105 (7).

***cis*-1-((*E*)-1-Propenyl)-2-methyl-7-hydroxyindan (24)**: retention time (column G) 16.73 min. The GC/MS peak corresponding to this com-

Table IX. Product Ratios from Reaction of **8** with *cis,cis*-2,4-Hexadiene

run	solvent	GC column	**19**	**20**	**21**	**22**
1	benzene	G	1.0	6.2	1.8	3.4
		H	1.0	6.5	0.96	3.3
2	benzene	G	1.0	6.0	1.1	2.2
3	bromobenzene	G	1.0	4.7	1.1	2.3

Table X. Product Ratios from Reaction of **8** with *trans,trans*-2,4-Hexadiene

solvent	GC column	X	Y	23	25	24	26
benzene	G	1.0	2.9	12.5	8.9	2.6	2.6
	H	1.0	7.0	29.8	28.2		6.2

pound is not sufficiently separated from the other components of the mixture to allow inspection of its fragmentation pattern.

***cis*-1-((*E*)-1-Propenyl)-2-methyl-5-hydroxyindan (26)**: retention time (column H) 10.0 min, (column G) 18.32 min; ^{1}H NMR (500 MHz, $CDCl_3$) 6.98 (d, 1 H, J = 8.00 Hz, aromatic), 6.62 (s, 1 H, aromatic), 6.60 (br, s, 1 H, aromatic), 5.50 (m, 1 H, vinyl), 5.32 (d, 1 H, J = 11.44 Hz, vinyl), 4.48 (s, 1 H, ArOH), 3.73 (m, 1 H, ArCH–propenyl), 3.17 (dd, 1 H, J = 13.44, 3.78 Hz, $^1/_2$ArCH$_2$), 2.69 (dd, 1 H, J = 13.41, 6.77 Hz, $^1/_2$ArCH$_2$), 2.51 (m, 1 H, CHMe), 1.39 (d, 3 H, J = 7.33 Hz, vinyl CH$_3$), 0.95 (d, 3 H, J = 7.18 Hz, CH$_3$); GC/MS [100, 1, 10, 200, 6.2] 188 (39, M), 173 (100, –CH$_3$), 159 (21), 146 (18), 145 (73), 131 (31), 155 (42), 107 (7), 105 (6).

Table X shows the product ratios.

Hydrogenation of *cis*-1-((*Z*)-1-Propenyl)-2-methyl-7-hydroxyindan (20) and *trans*-1-((*E*)-1-Propenyl)-2-methyl-7-hydroxyindan (23). Several milligrams of GC-purified **20** (column A, 100 °C isothermal) were dissolved in 5 mL of methylene chloride and stirred magnetically at room temperature. Potassium azodicarboxylate (650 mg, 3.5 mmol) was added to the solution. Glacial acetic acid (200 μL, 3.5 mmol) was added over a period of 20 min via a syringe and syringe pump. The mixture was stirred for 20 min after the addition was complete. This cycle was repeated twice by adding additional portions of potassium azodicarboxylate and glacial acetic acid. After three cycles the solid was filtered and the filter cake washed with copious amounts of methylene chloride. The filtrate and the washings were combined, the solvent was removed in vacuo, and the entire process was repeated.

In this same manner **23** was also reduced by using potassium azodicarboxylate and glacial acetic acid. These two samples of hydrogenated major products along with unreacted starting material were shown to be different by GC (column G, 165 °C isothermal). This shows that the major adducts from *cis,cis*- and *trans,trans*-2,4-hexadiene differ in the relative configurations of the indan ring substituents.

***cis*-1-(1-Propyl)-2-methyl-7-hydroxyindan (from 20)**: retention time 10.58 ± 0.03 min; GC/MS [100, 1, 20, 200, 6.1] 190 (14, M$^+$), 147 (100); exact mass calcd for $C_{13}H_{18}O$ 190.1358, obsd 190.1360.

***trans*-1-(1-Propyl)-2-methyl-7-hydroxyindan (from 23)**: retention time 8.34 ± 0.03 min; GC/MS [100, 1, 20, 200, 5.8] 190 (14, M$^+$), 147 (100).

Acknowledgment. We thank the National Science Foundation and the National Institutes of Health for support of this work.

Supplementary Material Available: Details of structural assignments to the dimethoxyethene adducts, Table S-I, and Scheme S-I (7 pages). Ordering information is given on any current masthead page.

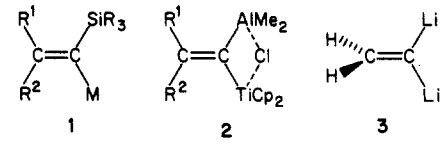
On the Origin of the Configurational Instability of (1-Silyl-1-alkenyl)lithiums and Related Alkenylmetals

Ei-ichi Negishi* and Tamotsu Takahashi

Contribution from the Department of Chemistry, Purdue University, West Lafayette, Indiana 47907. *Received August 30, 1985*

Abstract: The origin of the remarkably facile configurational isomerization of 1-silyl-1-metalloalkenes was investigated by using 1-(trimethylsilyl)-1-lithio-1-octene (**5**) as a representative example. Of seven mechanisms considered, those involving disproportionation via metal–metal exchange (mechanism I), addition–elimination (mechanism II), simple ionization of the Li–C bond (mechanism III), and polarization of the C=C bond (mechanisms IV and VI) have been firmly or tentatively ruled out. Two most plausible mechanisms (mechanisms V and VII) involve a synergistic or "push–pull" interaction of the Li–C σ bond and an empty orbital of Si, the main difference between the two lying in the extent to which the Li–C bond ionizes. The rates of configurational isomerization of (*Z*)-1-lithio-1-(trimethylsilyl)-1-octene (**5a**), generated by treating (*E*)-1-iodo-1-(trimethylsilyl)-1-octene (**6a**) with 2 equiv of *t*-BuLi in ether–pentane at −78 °C, were determined by ^{1}H NMR spectroscopy over the temperature range −40–0 °C. The first-order rate constants (min^{-1}) were 2.9×10^{-2} (−40 °C), 1.5×10^{-1} (−20 °C), 2.2×10^{-1} (−10 °C), and 5.0×10^{-1} (0 °C). The enthalpy and entropy of activation calculated from these data were $\Delta H^{\ddagger}$ = 8.4 ± 1.0 kcal/mol and $\Delta S^{\ddagger}$ = −37 ± 3 cal/(mol·K). The rate of isomerization of (1-(trimethylsilyl)-1-octenyl)metals is dependent on the metals and appears to be roughly proportional to the electropositivity of the metals. Four (*Z*)-β-lithio-β-(trimethylsilyl)styrenes with the *p*-H, *p*-MeO, *p*-Me, and *p*-Cl substituents were synthesized. The first-order rate constants (min^{-1}) for their configurational isomerization in ether–pentane at −20 °C were MeO 0.220 ± 0.010, Me 0.205 ± 0.015, H 0.200 ± 0.010, and Cl 0.185 ± 0.015. The ρ value calculated from these data is −0.1. Although **5** is configurationally much less stable than 1-lithio-1-ethoxyethylene (**14**), ethyl vinyl ether is considerably more acidic than 1-(trimethylsilyl)-1-octene (**7**), indicating that the configurational instability of alkenyllithiums does not necessarily correlate with the acidity of their conjugate acids. The configurational isomerization of **5** is facile ($t_{1/2}$ < 4 min at 0 °C) even in hydrocarbon solvents, although Li–I exchange requires 6–9 h for ≥90% completion. In sharp contrast with the results obtained in ether–pentane, the major product (ca. 90%) was the *Z* isomer (**5a**), suggesting that aggregation plays an important role in hydrocarbons. If the mechanism of isomerization does not significantly change in going from ether to hydrocarbons, mechanism VII would be strongly favored over mechanism V. However, the validity of assumption is unclear at present.

An increasing number of 1,1-dimetalloalkenes, such as 1-silyl-1-metalloalkenes (**1**) containing Li,[1] Mg,[2] Zn,[3] or Al,[4] as well as 1-alumino-1-titanoalkenes[5] (**2**), have been shown to be configurationally unstable. Furthermore, theoretical studies predict



(1) (a) Zweifel, G.; Murray, R. E.; On, H. P. *J. Org. Chem.* **1981**, *46*, 1292. (b) Knorr, R.; Roman, T. v. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 366.

(2) Sato, F.; Watanabe, H.; Tanaka, Y.; Sato, M. *J. Chem. Soc., Chem. Commun.* **1982**, 1126.

0002-7863/86/1508-3402$01.50/0 © 1986 American Chemical Society