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THE DI-π-METHANE REARRANGEMENT

THE EFFECT OF 1,4-DIENE STRUCTURE AND CONFORMATION ON THE REACTION EFFICIENCY AND STEREOCHEMISTRY[†]

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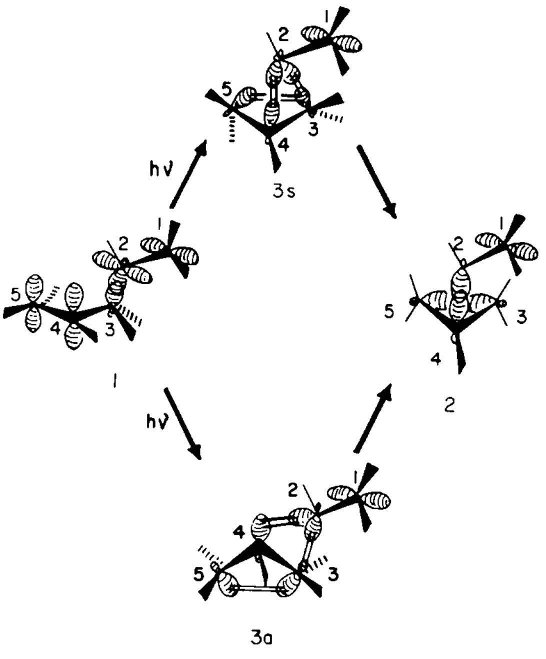
Abstract—The photochemistry of the stereoisomeric 1,3-dimethyl-3(2-phenylethenyl)cyclohexenes has been explored. Direct irradiation of the *cis*- and *trans*-β-styrylcyclohexenes leads to di-π-methane rearrangement, producing the *endo*- and *exo*-3,7-dimethyl-8-phenybicyclo[5.1.0]oct-2-enes, and *cis-trans* isomerization, interconverting the 1,4-diene containing substrates. Triplet sensitized photolysis of both substituted cyclohexenes leads exclusively to *cis-trans* isomerization. Results from low conversion direct irradiations of the *cis*- and *trans*-β-styrylcyclohexenes indicate that the singlet rearrangements are stereospecific, and lead to formation of the 8-*exo* and 8-*endo*-phenylbicyclic octenes, respectively. The relationship between di-π-methane structure and triplet reaction efficiency, and the effect of conformation on the rearrangement stereochemistry are discussed.

In our more recent studies of the di-π-methane rearrangement,[¶] we have continued to explore the questions of how structure of 1,4-dienes influence both the efficiencies of rearrangements from the triplet excited substrates and the stereochemistry of the singlet reaction. With regard to the first question we have attempted to gain further information which would aid in determining whether or not mechanisms for triplet free-rotor deactivation[3] involve the intermediacy of cyclopropyldicarbinyl diradicals. In addition, we have continued to explore the consequences of earlier results from our laboratory which provided an insight into the stereochemical preferences for singlet and triplet di-π-methane rearrangements,[4,5] and have now demonstrated how structure can control reaction stereochemistry.[6]

Earlier observations have indicated that the excited state rearrangements of 1,4-diene (**1**) to vinylcyclopropanes (**2**) follow concerted mechanistic pathways and possess two, low-energy transition states having the anti- (**3a**) and syn-disrotatory (**3s**) orbital geometries. Thus the stereochemistries about the migrating π-bond (C-1 C-2) and at the methane carbon (C-3) for singlet di-π-methane rearrangements are controlled by preferences for transition state orbital topologies which are of a Möbius nature.[7] However, the stereochemical outcome of this process could be subject to control by the additional factor of conformational preference about the σ-bond (C-3 C-4) between the methane carbon and π-moiety serving as the migration terminus. Stereochemical consequences of concerted transformations controlled in this fashion are rendered schematically in Fig. 1. Inspection of this schematic leads one to the conclusion that reactions of the s-*cis* (**1c**) and s-*trans* (**1t**) conformers of a stereospecifically substituted 1,4-diene via either *anti*- or *syn*-disrotatory transition state orbital topologies leads to vinylcyclopropanes which are diastereomerically related.



According to these arguments, the stereochemical course of singlet di-π-methane transformations could be influenced by structural features in the 1,4-diene reactants which control conformational preferences about the methane-vinyl moiety σ-bond.

In order to gain further insight into these questions, we have investigated the photochemistry of the stereoisomeric 1,3 - dimethyl - 3 - (2 - phenylethenyl) - cyclohexenes (**4** and **5**). The results obtained relate directly to the influence of di-π-methane conformation on the singlet rearrangement stereochemistry and to the relative energies of competing mechanistic pathways for the conversion of singlet 1,4-dienes to vinylcyclopropanes. In addition, comparison of the triplet photochemistry of **4** and **5** with that of a close analog, 1 - phenyl - 3 - methyl - 3 - (1 - *cis* - propenyl)cyclohexene (**6**), studied previously,[4] has yielded further information about

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[†] A preliminary report of these studies has appeared.[1]

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[§] Petroleum Research Fund Undergraduate Scholar.

[¶] For a general review of the di-π-methane rearrangement see Ref. 2a and for one on the related oxa-di-π-methane rearrangement see Ref. 2b.

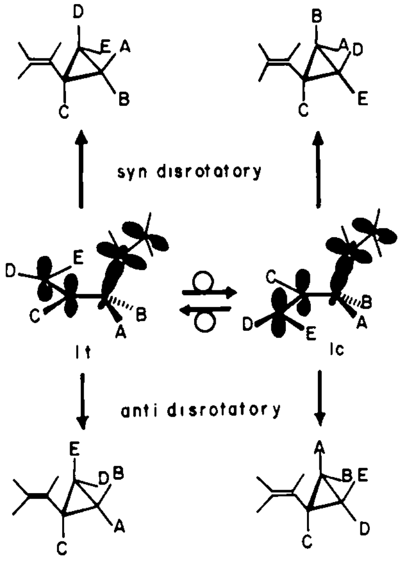

Fig. 1. Diastereomerically related vinylcyclopropanes resulting from concerted di-π-methane rearrangements of s-*cis* and s-*trans* 1,4-diene conformers through anti- and syn-disrotatory reaction pathways.

the mechanistic details responsible for the structure-excited state multiplicity -triplet di-π-methane reaction efficiency relationship discussed earlier.[8]

RESULTS

Synthesis of cis- *and* trans - 1,3 - *dimethyl* - 3 - (2 - *phenylethylenyl*) - *cyclohexene* (4 *and* 5). Preparation of the required styrylcyclohexenes **4** and **5** was easily accomplished using the synthetic sequence delineated in Fig. 2 starting with the known[9] 3 - methylcyclohexenyl - 1 - carboxaldehyde (**7**). Methylation of **7** with potassium t-butoxide and methyl iodide in t-butyl alcohol furnished the β,γ-unsaturated aldehyde **8**, which was converted to a mixture (2.3:1) of **4** and **5** using benzylidene triphenylphosphorane. Isomerically pure (>98%) dienes, having characteristic spectral properties were obtained by chromatography on silica gel.

Triplet sensitized photochemistry of 4 *and* 5. Triplet photosensitized irradiations of the styrylcyclohexenes **4** and **5** were conducted under conditions which insured selective light absorption by the sensitizers and efficient energy transfer from the triplet states of the sensitizers to the 1,4-dienes. Irradiations of acetonitrile solutions of **4** and **5** using 2-acetonaphthone ($E_T = 57$ kcal/mol) and acetophenone ($E_T = 74$ kcal/mol) led exclusively to *cis trans* isomerization of the starting olefins producing the photostationary state mixtures recorded in Table 1. Importantly, no products of di-π-methane or other molecular rearrangements were detected in the photolysates even after long irradiation periods.

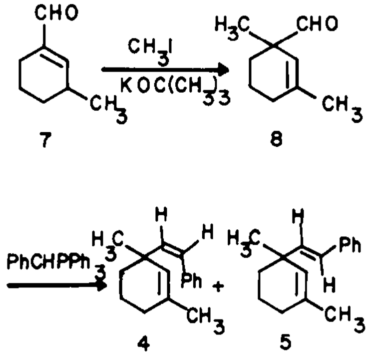

Fig. 2. Synthetic sequence utilized for preparation of the stereoisomeric 1,3 - dimethyl - 3 - (2 - phenylethenyl)cyclohexenes.

Direct irradiation photochemistry of cis- *and* trans - 1,3 - *dimethyl* - 3 - (2 - *phenylethenyl*)*cyclohexene*. Acetonitrile solutions of **4** and **5** were irradiated independently in preparative apparatii using Corex glass-filtered light. In each case the photolysate was found by analytical GLC to contain a mixture of the stereoisomeric dienes together with two major photoproducts **9** and **10**, whose composition varied with both irradiation time and the stereochemistry of the starting styrylcyclohexene. Separation and purification of **9** and **10** were accomplished by preparative GLC (see below for characteristic yields of these reactions).† The structures and stereochemistries of the direct irradiation photoproducts were assigned as 3,7 - dimethyl - 3 - exo - bicyclo[5.1.0oct - 2 - ene (**9**) and its 8-*endo*-phenyl isomer **10** on the basis of spectral and independent synthetic data.

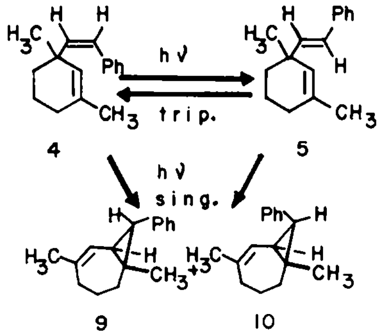

Table 1. Triplet sensitized photochemistry of the styrylcyclohexenes 4 and 5

Starting Diene	Diene Concentration, μM	Sensitizer	Sensitizer Concentration, μM	Photostationary State Compositions[a] 4	5
4	0.14	2-acetonaphthone	1.15	87.8	12.2
5	0.48	2-acetonaphthone	1.15	85.9	14.1
4	1.40	acetophenone	14.60	81.9	18.1
5	1.10	acetophenone	14.60	82.4	17.6

[a] 1,4-Diene compositions of the photolysates were obtained by GLC analysis.

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† That the conditions for purification of the photoproducts did not cause isomerization was established by comparison of NMR spectra of the photomixture before purification with those of the individual components.

The proton and C-NMR spectra of **9** and **10** are characteristically similar and, along with the UV-spectra of both which indicated the absence of strongly absorbing styryl chromophores and the presence of mono-alkyl substituted benzene groupings, are consistent with the structural assignments made. In order to remove any ambiguity from these structural designations the independent synthetic sequence outlined in Fig. 3 was designed.

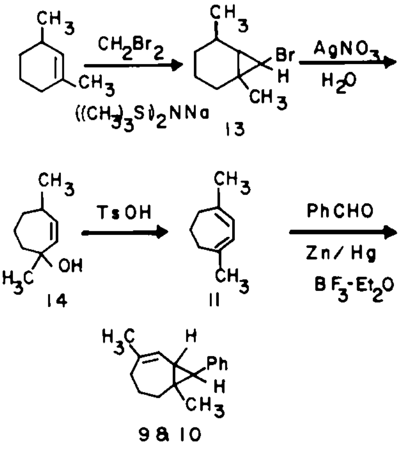
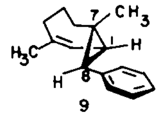


Fig. 3. Independent synthetic sequence for the preparation of 3,7-dimethyl-8-exo- and endo-bicyclo[5.1.0]oct-2-ene.

The strategy chosen for this purpose employed 1,4 - dimethylcyclohepta - 1,3 - diene (**11**) as the synthon, since mono-addition of phenylcarbene across either π-bond would generate the desired bicyclic structure with the correct substitution patterns. Mono-bromocarbene[10] underwent smooth cycloaddition to the available 1,3-dimethylcyclohexene (**12**) to yield a mixture of the *exo*- and *endo*-7-bromobicycloheptanes **13**.[†] Silver catalyzed hydrolytic ring opening of **13** was accomplished in refluxing aqueous tetrahydrofuran and furnished 3,7-dimethylcyclohepten-3-ol (**14**).[‡] Treatment of **14** under acid catalyzed dehydration conditions caused smooth conversion to the diene **11**. The Elphimoff–Felkin[11] procedure for phenylcyclopropanation was used to convert **14** to a mixture of **9** and **10** having identical physical and spectral properties to those for the two direct irradiation photoproducts.

The stereochemistries at C-8 in the photoproducts remained to be assigned. Useful in this regard were the informative NMR studies by Closs and Moss[12] of a series of 1 - methyl - 2 - phenyl - cyclopropanes. In the 8-*exo*-phenyl epimer **9**, the phenyl substituent should reside predominantly in a conformation with the plane of the aromatic ring tilted toward the C-1 proton side of the bisected geometry in order to minimize the nonbonding interactions between the *cis* phenyl and C-7 Me groups. As a result, the C-1 methine proton of **9** is located in the deshielding region of the aromatic ring and, thus, should resonate downfield from C_1–H in the 8-*endo*-phenyl isomer **10**. For similar reasons, the C-7 Me protons of **9** are located in the shielding region of the aromatic ring and should display an upfield shifted resonance when compared to the C_7-Me of **10**. Indeed, inspection of the PMR spectra of both epimers (Fig. 4) shows that both expectations are born out; the C_1-methine and C_7-methyl of **9** resonate at 3.47 and 0.79 ppm while the analogous resonances of **10** appear at the quite normal positions of < 2.0 and 1.33 ppm. Importantly these spectral parameters are in accord with those obtained earlier for model methyl phenyl cyclopropanes.[12]



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Varying conversion direct irradiations. We had noted that in preparative direct irradiations of the 1,4-dienes, **4** and **5**, the ratio of photoproducts **9** and **10** varied depending upon which stereoisomer was irradiated and the extent of conversion to products. Thus, in order to determine if the photoproduct mixture obtained in these cases results from non-stereoselective reaction of each diene, from photointerconversion of the products under the reaction conditions, or from competitive *cis–trans* isomerization of the starting dienes, low, varying conversion direct irradiations were conducted. Acetonitrile solutions of **4** and **5** were independently irradiated for a 30 hr period using Flint-glass filtered light[§] and analyzed periodically by GLC. Analysis of the photoproduct mixtures during irradiation and after completion (irradiation of **4** gave 74.9% recovered **4**, 0.6% **10**, 2.3% **9**, and 22.2% **5**, whereas irradiation of **5** gave 71.1% recovered **5**, 1.9% **10**, 0.0% **9** and 27.4% **4**) indicated that *cis–trans* isomerization is the more efficient direct irradiation process. Additionally independent irradiations of **9** and **10** using either Corex or Flint glass filters failed to bring about any detectable changes. Importantly, these observations appear to also demonstrate that di-π-methane rearrangements of **4** and **5** are stereoselective and result in the predominant formation of **9** and **10**, respectively. The accuracy and sensitivity of our analytical methods coupled with the fact that *cis–trans* isomerization is rapid, however, limits our ability to state quantitatively the exact magnitude of the kinetic product ratios from rearrangement of each of the styrylcyclohexenes.

DISCUSSION

Conformational control of singlet reaction stereochemistry. The first aspect of the observations presented above requiring discussion is the stereochemistry of singlet di-π-methane rearrangements from the isomeric styrylcyclohexenes and its relationship to conformational preferences within the 1,4-diene chromophore and reaction mechanism. The combined results of the triplet sensitized and direct irradiations of **4** and **5** appear to clearly demonstrate that reactions to generate the bicyclooctenes occur in the singlet excited state manifold. Thus, using precedent, gathered from earlier studies[4,5] which have shown that singlet 1,4-dienes rearrange via concerted mechanistic pathways, we can conclude that the conversions of the *cis*- and *trans*-styrylcyclohexenes to predominantly the *exo*- and *endo*-phenylbicyclooctenes, respectively, are most probably one-step processes. In theory, four diastereomeric bicyclooctene products are possible from concerted di-π-

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[†] The stereochemistry at C-5 in **13** was not determined but is assumed to be *exo* on the basis of least hindered approach of the carbene. Both C-7 epimers were obtained but not separated.

[‡] The relative stereochemistries at C-3 and C-7 were not established.

[§] Flint-glass has a UV cut-off at *ca.* 310 nm. Under these irradiation conditions both styrylcyclohexenes are absorbing small amounts of light and, thus, reaction is slow.

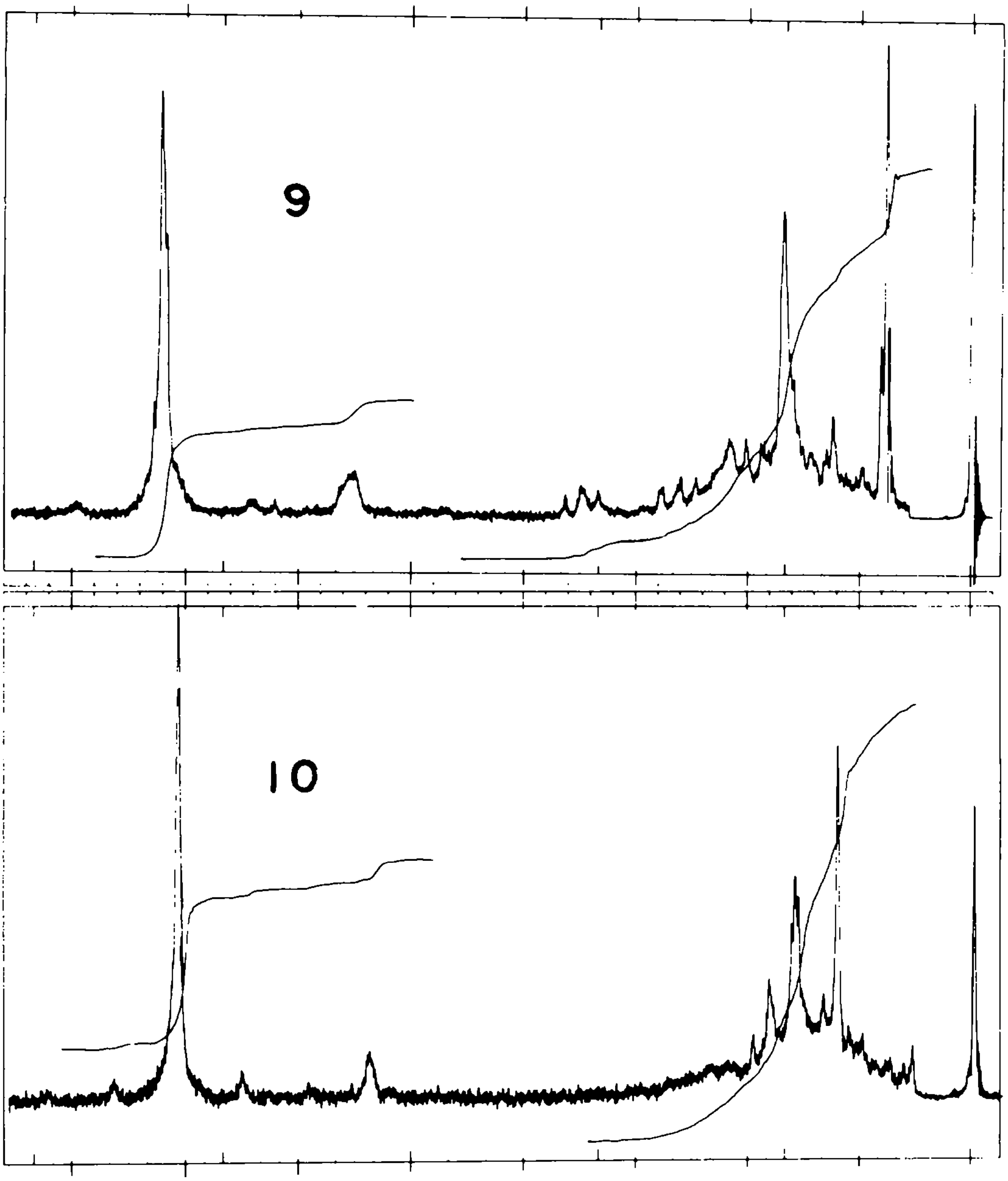

Fig. 4. Proton-NMR spectra of the *exo*- and *endo*-bicyclooctenes 9 and 10.

methane rearrangement of both **4** and **5**, in which migration of the less conjugated, endocyclic π-moiety occurs.† In **4** for example, two low energy conformations, s-*cis* **4c** and s-*trans* **4t**, which place the styryl grouping in correct orientation for maximum overlap of the orbitals at C-3 and C-7, are possible. Reaction of each conformer via the two low energy transition states, having the *anti*- and *syn*-disrotatory orbital topologies, would lead to production of **9**, **10** and two *trans*-fused cyclopropane containing bicyclic compounds, **15** and **16** (Fig. 5). Clearly, the lower energy reactive conformer in this case is **4c** due to minimization of the repulsive interactions between the C-4-axial hydrogen and the *cis*-styryl moiety. It appears likely that this ground state conformational preference in the 1,4-diene, **4**, might play an important role in determining the preferred stereochemical mode chosen for rearrangement.‡ For example, concerted di-π-methane rearrangement of **4c** via an anti-disrotatory mode should be inefficient due to the high energy content of *trans*-fused cyclopropane containing product, **15**, produced. Reaction of the higher energy s-*trans* conformer **4t** by an anti-disrotatory mode leading to the 8-*endo*-phenylbicyclic octene **10** should also pass through a high energy transition state due to unfavorable phenyl-

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†Earlier regiochemical observations[13] lead to the expectation that migration of the less phenyl-substituted endocyclic π-moieties will predominate.

‡Arguments presented to evaluate the relative ground state energies of **4c** and **4t** should also be valid for the excited species and for points early in the reaction progress. In addition if reaction from the singlet excited states of **4c** and **4t** is faster than conformational interconversion, then ground state populations, relative UV absorption characteristics, and reaction quantum yields will be important in determining the product ratios.

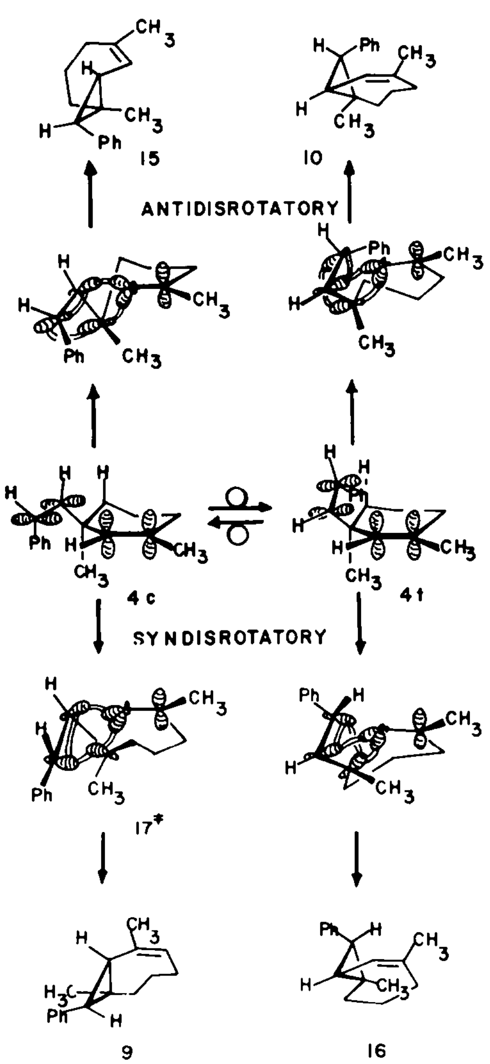
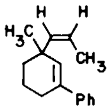


Fig. 5. Possible stereochemical modes for concerted di-π-methane rearrangements of the styrylcyclohexene 4.

hydrogen non-bonded interactions or should be non-competitive due to the low concentration of **4t** in the irradiated solution.† These energy assignments which mix conformational and ring strain considerations, would lead to the prediction that the lowest energy reaction pathway followed by the *cis*-diene **4** would be that producing the 8-*exo*-phenylbicyclooctene **9**. A similar analysis of the reaction of **5** indicates that **10**, resulting from *syn*-disrotatory rearrangement of the s-*cis* diene conformer, should be the predominant product.‡

The agreement between these predictions and the experimental results presented above are noteworthy. Although much is known about the effect of conformation on the stereochemistry of cyclohexadiene-hexatriene photointerconversions,[14] little attention has been given to conformational control of the di-π-methane reaction stereochemistry.[15] Earlier studies[4,5] have demonstrated that rearrangements of structurally and conformationally free di-π-methanes in the singlet manifold occur through concerted pathways and display remarkable stereoselectivities. These have been explained on the basis of an energetic preference for anti-disrotatory motion of the orbitals involved in cyclopropane ring formation. Additional investigations[6] pointed out, however, that structural constraints which block reaction by this mode do not prevent di-π-methane rearrangement; instead, the alternate *syn*-disrotatory route is followed with only slightly lower efficiency. The observations and interpretations presented above demonstrate that 1,4-diene conformations are also very important in determining the stereochemical course of di-π-methane reactions by their influence on the relative energies of competing disrotatory reaction pathways.

Mechanism for triplet di-π-methane energy dissipation. The comparative triplet photochemistry of **4**, **5** and a close structural analog, 1 - phenyl - 3 - methyl - 3 - (1 - *cis* - propenyl)cyclohexene (**6**), which undergoes di-π-methane rearrangement from its triplet, appears to shed light on the mechanism for triplet free-rotor deactivation of 1,4-dienes. Earlier, Zimmerman[8] had noted an interesting interrelationship between di-π-methane structure and the efficiency of triplet di-π-methane rearrangement. Two systems which exemplify this behavior are barrelene (**18**), which undergoes smooth rearrangement to semibullvalene (**19**) upon acetone sensitized photolysis,[16] and the tetraphenyldiene **20**, which is unreactive in the triplet manifold.[8] In light of these results and the observation that the diphenyldiene **21** undergoes triplet *cis–trans* isomerization about the π-bond of higher triplet energy, Zimmerman[3] suggest that triplet energy dissipation in 1,4-dienes occurs at the cyclopropyldicarbinyl diradical stage (e.g. **22**) by a free-rotor effect. According to this rationale, structural constraints placed on the 1,4-diene chromophores that prevent free rotation in the triplet state block this mode of energy dissipation and, as a result, increase the quantum efficiency for rearrangement to vinylcyclopropanes. An interesting question about this postulate is whether or not the ability to produce cyclopropyldicarbinyl diradical intermediates would render 1,4-dienes, which have only one π-moiety contained within a small ring system, unreactive from their triplets. Since the triplet states of **4**, **5** and **6** appear equally capable of forming their corresponding bridged cyclopropyldicarbinyl diradicals **24** and **25**, yet display differing reactivities, free-rotor deactivation from intermediates of this nature is perhaps not necessary in controlling the triplet di-π-methane reactivity of 1,4-dienes. Another important



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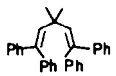

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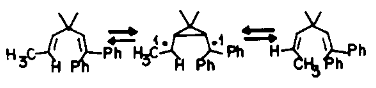
†See footnote ‡ in previous page.

‡Qualitative conformational analyses of **4** and **5** indicate a larger preference for the s-*cis* conformer in the former. Yet, low conversion results appear to indicate that reaction of **5** is more stereoselective. This could very well be due to the fact that the *trans*-diene is more strongly absorbing in the wavelength region utilized. Accordingly, selective reaction of this isomer during early stages of irradiation can occur even though small amounts of the *cis*-isomer are being produced. This would not be the case for irradiations using the *cis*-diene in which competitive light absorption by **5** can occur at a much earlier stage.



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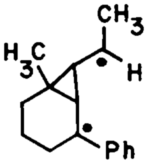
feature might be structural constraints placed on the π-chromophore of lowest triplet energy. This alternative factor appears to prescribe the triplet chemistry of **4**, **5** and **6** and analogs discussed previously by Hixson[17] and Swenton.[18]



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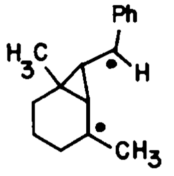

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EXPERIMENTAL

General. Analyses were performed by Galbraith Laboratories, Knoxville, Tennessee. NMR spectra were recorded on Varian T-60 or HA-100 (proton) and Jeol PS-100 (carbon) spectrometers with TMS as the internal standard. IR spectra were taken with a Perkin-Elmer 237 spectrophotometer and UV spectra were measured using a Beckman Acta-III spectrophotometer. Gas chromatographic separations were conducted using a Varian Model-2700 chromatograph and analyses made using a Varian Model-940 chromagograph. Mass spectra were obtained using a Varian MAT CH-7 with a GC inlet and a CEC-21-110 mass spectrometer.

1,3-*Dimethylcyclohexene*-3-*carboxaldehyde* (**8**). To a soln of t-BuOK (44.3 g; 0.43 mol) in 575 ml of t-BuOH was added 3 - methylcyclohexene - 1 - carboxaldehyde[9] (30.0 g; 0.16 mol) and MeI (27.0 g; 0.19 mol) in 50 ml of t-BuOH at 50°. The resulting mixture was stirred for 4 hr and additional MeI (27.0 g; 0.19 mol) was added. The resulting mixture was stirred at room temp. overnight and quenched with water. The aqueous layer was separated and extracted with ether. The combined ethereal extracts were washed with water, dried, concentrated *in vacuo*, and distilled yielding 7.7 g (35%) of a colorless oil, b.p. 29° (0.3 mm), characterized as 1,3 - dimethylcyclohexene - 3 - carboxaldehyde.

Spectral data for this compound are as follows: NMR (CCl_4) δ 1.05 (s, 3H, $-CH_3$), 1.30–3.00 (m, 6H, $-CH_2-$), 1.75 (s, 3H, allylic CH_3), 5.10 (br s, 1H, olefinic), 9.25 (s, 1H, CHO); IR (liq film) 3.40, 3.49, 3.70, 5.82, 6.91 and 7.30 μ, *high resolution mass spectrum* (70 ev): Calcd. for $C_9H_{14}O$ (*m/e*) 138.1045. Found (*m/e*) (rel. intensity) 138.1049 (P, 33.3%) and 109 (P-29, 100.0%).

cis- *and* trans - 1,3 - *Dimethyl* - 3 - (2 - *phenylethenyl*)*cyclohexene* (**4** *and* **5**). To a suspension of triphenylbenzylphosphonium chloride (32.0 g; 0.082 mol) in 100 ml of anhyd ether, was added dropwise 63 ml of a 1.3 M soln of n-BuLi under N_2. The resulting dark orange soln was refluxed for 2 hr before an ethereal soln of 1,3 - dimethylcyclohexene - 3 - carboxaldehyde (7.7 g; 0.056 mol) was added dropwise with concurrent disappearance of the orange color and precipitation of inorganic salts. The resulting suspension was refluxed overnight, cooled to room temp., and quenched with water. The aqueous layer was separated and extracted with ether. The combined ethereal extracts were washed with water, dried, and concentrated *in vacuo*. The residue obtained was stirred with hexane and filtered to remove insoluble triphenylphosphine oxide. The hexane soln was then concentrated *in vacuo* yielding 7.5 g of a yellow oil which was analyzed by GLC (5 ft × 1/8 in, 1.5% OV101 on 100/20 Varaport-30, 153°, 23 ml/min). Two major product (retention times—6.2 and 12.1 min) were detected in the ratio of 7:3 and later characterized as *cis*- and *trans* - 1,3 - dimethyl - 3 - (2 - phenylethenyl)cyclohexene, respectively. The oil was then chromatographed on a 120 × 4 cm column packed with silica gel (Davison, grade 923, 100–200 mesh). Elution was with 8.5 1. of 1% ether in hexane: 500 ml fractions were collected. Fractions 2–5 gave 3.5 g (29.5%) of a colorless oil characterized as 1,3 - dimethyl - 3 - (*cis* - 2 - phenylethenyl)cyclohexene. Fractions 11–17 gave 1.0 g (8.5%) of a colorless oil characterized as the *trans*-isomer. Fractions 6–10 yielded 1.0 g (8.5%) of a mixture of both isomers.

Spectral data for the *cis*-isomer are as follows: NMR (CCl_4) δ 1.05 (s, 3H, $-CH_3$), 1.30 (br s, 3H, allylic CH_3), 1.50–1.90 (m, 6H, $-CH_2-$), 4.90 (br s, 1H, olefinic), 5.50 (d, 1H, J = 12 Hz, vinyl), 6.45 (d, 1H, J = 12 Hz, vinyl), 7.13 (s, 5H, aromatic); IR (liq film) 3.30, 3.45, 3.50, 6.24, 6.70, 6.90, 7.30, 9.41, 9.71, 11.52, 13.32 and 14.35 μ; UV (acetonitrile) λ_{max} 231 nm ($\epsilon = 7400$). Spectral data for the *trans*-isomer are as follows: NMR (CCl_4) δ 1.15 (s, 3H, $-CH_3$), 1.40–2.00 (m, 6H, $-CH_2-$), 1.75 (br s, 3H, allylic CH_3), 5.25 (br s, 1H, olefinic), 6.10 (d, 1H, J = 16 Hz, vinyl), 6.35 (d, 1H, J = 16 Hz, vinyl), 7.30 (br s, 5H, aromatic) IR (liq film) 3.30, 3.40, 3.49, 6.24, 6.76, 6.90, 7.28, 10.33, 13.41 and 14.47 μ; UV (acetonitrile) λ_{max} 255 nm ($\epsilon = 20{,}000$). *cis*-Isomer. Found: C, 90.50; H, 9.45. Calc. for $C_{16}H_{20}$: C, 90.57; H, 9.43%. *trans*-Isomer. Found: C, 90.36; H, 9.54. Calcd. for $C_{16}H_{20}$: C, 90.57; H, 9.43%.

Triplet sensitized photolyses of the 1,3 - *dimethyl* - 3 - (2 - *phenylethenyl*)*cyclohexenes*. Two acetonitrile solns (1.10×10^{-3} M 1.3 - dimethyl - 3 - (2 - *trans* - phenylethenyl)cyclohexene and 1.46×10^{-2} M acetophenone) in 24.5 × 1.5 cm Pyrex tubes were purged with and sealed under N_2. These solns were irradiated using a merry-go-round apparatus consisting of a rotating train at the center of which was a 450-watt Hanovia medium pressure lamp housed within a water-cooled quartz immersion well. Analyses of the photolysates after 12 hr of irradiation were made by GLC (5 × 1/8 in, 1.5% OV101 on 100/20 Varaport-30, 153°, 23 ml/min) and the results are recorded in Table 1.

Two acetonitrile solns (4.78×10^{-4} M 1,3 - dimethyl - 3 - (2 - *cis* - phenylethenyl)cyclohexene and 1.15×10^{-3} M 2-acetonaphthone, and 1.40×10^{-4} M *cis*-diene and 1.15×10^{-3} M 1-acetonaphthone) in 24.5 × 1.5 cm pyrex tubes were purged with and sealed under N_2. These solns were irradiated using the merry-go-round apparatus described above. Analyses of the photolysates after 28 hr of irradiation were made by GLC (same conditions as described above) and the results were recorded in Table 1.

Direct irradiation of the 1,3 - *dimethyl* - 3 - (2 - *phenylethenyl*)*cyclohexenes* (4 *and* 5)

Preparative irradiation of the cis-*diene*. A soln of 1,3 - dimethyl - 3 - (2 - *cis* - phenylethenyl)cyclohexene (1.40 g; 6.61 mmol) in 750 ml acetonitrile was purged with N_2 45 min before and then during the irradiation, which was carried out using a preparative apparatus consisting of a 450-watt Hanovia medium pressure lamp in a water-cooled quartz immersion well and a Corex glass filter, for 45 min. The photolysate was concentrated *in vacuo* and subjected to GLC analysis (5 ft × 1/8 in, 1.5% OV101 on 100/20 Varaport-30, 153°, 23 ml/min) which indicated the presence of both isomers of the starting material and two major photoproducts, **10** (89%) and **9** (10%). Preparative GLC (9 ft × 1/4 in, 4% SE-30 on ABS anakromb, 190°, 60 ml/min) was used to separate these photoproducts, later identified by spectroscopic methods and independent synthesis as *endo*- and *exo* - 3,7 - dimethyl - 8 - phenylbicyclo[5.1.0]oct - 2 - ene, respectively.

Spectral data for **10** are as follows: PMR (CCl_4) δ 1.30 (s, 3H, $-CH_3$), 1.00–2.00 (m, 8H, $-CH_2-$ and CH), 1.38 (br s, 3H, allylic CH_3), 5.30 (m, 1H, olefinic) and 7.00 (s, 5H, aromatic) (Fig. 4); ^{13}C NMR ($CDCl_3$) 18.8, 21.3, 24.3, 24.8, 27.4, 27.9, 30.3, 33.3, 120.5, 125.4, 127.7, 130.8, 137.9 and 138.6 ppm; IR (liq film) 3.32, 3.43, 3.50, 6.24, 6.70, 6.91, 7.38, 9.71, 12.37, 12.51, 13.72 and 14.32 μ; UV (acetonitrile) λ_{max} 220 nm ($\epsilon = 6{,}500$); Mass spec. (*m/e*) (rel. intensity) 212 (p, 17.5), 121 (p-91, 100.0). Spectral data for **9** are as follows: PMR (CCl_4) δ 0.79 (s, 3H, $-CH_3$), 1.20–2.80 (m, 7H, $-CH_2-$ and CH), 1.63 (br s, 3H, allylic CH_3), 3.43 (t, 1H, cyclopropyl and allylic), 5.50 (m, 1H, olefinic) and 7.19 (s, 5H, aromatic) (Fig. 4); ^{13}C NMR ($CDCl_3$) 21.5, 22.8, 23.8, 27.8, 28.4, 31.1, 40.8, 120.6, 125.5, 127.5, 127.8, 128.7, 136.8 and 142.2 ppm; IR (liq film) 3.30, 3.42, 5.22, 6.68, 6.90, 7.26, 8.90, 9.05, 9.36, 9.68, 11.00, 12.21, 12.71, 13.10, 13.61 and 14.45 μ; UV (acetonitrile) λ_{max} 223 nm ($\epsilon = 7{,}800$); Mass spec. (*m/e*) (rel. intensity) 212 (P, 9.8) and 121 (P-91, 100.0). (Found: C, 90–35; H, 9.46. Calcd for **10** $C_{16}H_{20}$: C, 90.57; H, 9.43%; Found: C, 90.47; H, 9.60. Calcd for **9** $C_{16}H_{20}$: C, 90.57; H, 9.43%).

Preparative irradiation of the trans-*diene*. A soln of *trans*-diene **5** (0.17 g; 0.802 mmol) in 300 ml acetonitrile was purged with N_2 and irradiated with the preparative apparatus described above for 45 min. Two photoproducts were obtained, purified by preparative GLC (same conditions as above) and identified on the basis of their spectral properties as photoproducts **10** and **9**, identical to the two obtained from irradiation of the *cis*-diene.

Low conversion irradiation of the 1,3 - *dimethyl* - 3 - (2 - *phenylethylenyl*)*cyclohexenes*

Two acetonitrile solns, one containing 9.44×10^{-3} M 1,3 - dimethyl - 3 - (2 - *cis* - phenylethenyl)cyclohexene and the other 9.44×10^{-3} M *trans*-diene, in two Pyrex tubes, 25 × 0.5 cm, were purged with and sealed under N_2, placed next to the quartz immersion well, containing a 450-watt Hanovia medium pressure lamp surrounded by a Flint glass filter and irradiated for 30 hr. Both solns were then analyzed by GLC (5 ft × 1/8 in, 1.5% OV101 on 100/20 Varaport-30, 139°, 23 ml/min flow). The following compositions of the photolysates were obtained: starting with **4**, 74.9% recovered **4**, 0.6% **10**, 2.3% **9**, and 22.2% **5**; starting with **5**, 71.1% recovered **5**, 1.9% **10**, 0.0% **9** and 27.0% **4**.

Independent synthesis of endo *and* exo - 3,7 - *dimethyl* - 3 - *phenylbicyclo*[5.1.0]*oct* - 2 - *ene* (**10** *and* **9**)

endo *and* exo - 1,5 - *Dimethyl* - 7 - *bromobicyclo*[4.1.0] *heptane* (**13**). To a suspension of sodium hexamethyldisilazide (111.6 g; 0.61 mol) and 1,3-dimethylcyclohexene (11.5 g; 0.095 mol) in 100 ml pentane under N_2 at 0°, was added dropwise dibromomethane (140 g; 0.80 mol). After addition was complete, the resulting brown suspension was warmed to room temp. and stirred overnight. The aqueous layer, after addition of water, was separated and extracted with pentane. The pentane extracts were combined with the original pentane layer, washed with 5% HCl, water, and NaCl aq, then dried and concentrated *in vacuo* giving a residue which distilled, b.p. 61°C (6 mm), yielding 13.3 g (66%) of a colorless oil characterized as a mixture of *endo*- and *exo* - 1,5 - dimethyl - 7 - bromobicyclo[4.1.0]heptane in the ratio of 6 : 4, respectively.

Spectral data for this mixture as as follows: NMR (CCl_4) δ 2.68 (d, J = 4 Hz, BrCH in *exo*-isomer), 2.92 (d, J = 9 Hz, BrCH in *endo*-isomer), the remaining parts of the spectrum were characteristic of the 1,5 - dimethyl - 7 - bromobicyclo[4.1.0]heptane; IR (liq film) 3.41, 3.49, 6.88, 7.25, 8.95, 10.25, 11.00 and 11.88 μ; Mass spec. (*m*/*e*) (rel. intensities) 202 (P, 1.4) and 123 (P-79, 100.0).

All attempts to obtain elemental composition by both microanalysis and high resolution mass spectroscopy failed due to the lability of this compound.

3,7-*Dimethyl*-3-*hydroxycycloheptene* (**14**). To a soln of the mixture of the *endo*- and *exo* - 1,5 - dimethyl - 7 - bromobicyclo[4.1.0]heptane (4.5 g; 0.022 mol) in 25 ml THF, $AgNO_3$ (16.0 g; 0.095 mol) in 25 ml water was added. The resulting mixture was stirred at 50° overnight. Water was added, and the mixture was extracted with pentane. The pentane extracts were washed with water, dried, and carefully distilled to remove the pentane to yield 3.4 g of a slightly yellow oil. No attempt was made to purify this residue, which was characterized as a mixture of unreacted starting material (28%), 3,7 - dimethyl-3-hydroxycycloheptene (43%) and 1,4 - dimethylcyclohepta - 1,3 - diene (29%) on the basis of the NMR spectrum, due to the slow conversion of the alcohol to the diene.

Spectral properties characteristic of the allylic alcohol are as follows: NMR (CCl_4) δ 1.05 (d, 3H, CH_3), 1.73 (s, 3H, vinyl CH_3), and 5.50 (br s, 1H, olefinic).

1,4-*Dimethylcyclohepta*-1,3-*diene* (**11**). To a soln of 3.2 g of the mixture obtained above in 25 ml of pentane under N_2 was added 1.2 g (7.0×10^{-3} mol) of *p*-toluenesulfonic acid. The mixture was stirred at reflux overnight, cooled, and washed with saturated $NaHCO_3$ aq and water, dried, and concentrated by careful distillation, yielding 2.8 g of a yellow oil characterized as a mixture of 1,4 - dimethyl - cyclohepta - 1,3 - diene (63%) and unreacted *exo* - 1,5 - dimethyl - 7 - bromobicyclo[4.1.0]heptane (37%). Attempts at purification of this oil by vacuum distillation resulted in extensive polymerization. However, pure 1,4 - dimethylcyclohepta - 1,3 - diene (51%) can be obtained by preparative GLC (12 ft × 1/4 in, 15% SE-30 on ABS anakromb, 110°, 50 ml/min).

Spectral data for this compound are as follows: NMR (CCl_4) δ 1.73 (s, 6H, allylic CH_3), 2.00–2.40 (m, 6H, $-CH_2-$), 5.38 (s, 2H, olefinic); IR (liq film) 3.36, 3.40, 3.45, 6.90, 8.65, 9.91 and 12.18 μ; UV (acetonitrile) λ_{max} 257 nm ($\epsilon = 9{,}800$); *high resolution mass spectrum* (70 ev): Calcd. for C_9H_{14} (*m*/*e*) 122.1096. Found (*m*/*e*) (rel. intensities) 122.1099 (P, 14.4) and P-15 (100.0).

endo *and* exo - 3,7 - *Dimethyl* - 8 - *phenylbicyclo*[5.1.0]*oct* - 2 - *ene* (**10** *and* **9**). To a mixture of amalgamated Zn dust (0.95 g), 1,4 - dimethylcyclohepta - 1,3 - diene (0.21 g; 1.72×10^{-3} mol), benzaldehyde (0.18 g; 1.7×10^{-3} mol), and 1 ml of anhydrous ether under N_2, BF_3-etherate (0.127 g; 1.9×10^{-3} mol) was added dropwise. The resulting suspension was stirred at room temp. for 22 hr. Additional ether was added and the mixture was washed with $NaHCO_3$ aq and water. The ethereal soln was dried and concentrated *in vacuo* giving a residue which was shown by GLC (5 ft × 1/8 in, 1.5% OV101 on 100/20 Varaport-30, 139°, 23 ml/min) to contain two major product in a 1 : 1 ratio having identical GLC retention times to the *endo*- and *exo* - 3,7 - dimethyl - 8 - phenylbicyclo[5.1.0]oct - 2 - ene. The yield was determined by GLC to be 42%. The residue was chromatographed on a 15 × 1 cm column, packed with alumina (Alco F-20, 100–200 mesh) in hexane. Elution was with hexane; two 50 ml fractions were collected. Concentration of the first fraction *in vacuo* yielded 35 mg (9.6%) of a slightly yellow oil which had an NMR spectrum identical to that of a mixture of *endo* and *exo* - 3,7 - dimethyl - 8 - phenylbicyclo[5.1.0]oct - 2 - ene obtained from the irradiations described above. GC-mass spectral analyses of the two products gave retention times and mass spectral fragmentation patterns identical to those of the *endo*- and *exo*-photoproducts from direct irradiations of *cis*- and *trans* - 1,3 - dimethyl - 3 - (2 - phenylethenyl)cyclohexene.

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REFERENCES

[1] P. S. Mariano and D. G. Watson, *Tetrahedron Letters* 3439 (1975).

[2a] S. S. Hixson, P. S. Mariano and H. E. Zimmerman, *Chem. Rev.* **73**, 531 (1973); [b] K. Schaffner, *Tetrahedron* Rep. No. 3, **32**, 641 (1976).

[3] H. E. Zimmerman and A. C. Pratt, *J. Am. Chem. Soc.* **92**, 6267 (1970).

[4] P. S. Mariano and J. K. Ko, *Ibid.* **94**, 1766 (1972); *Ibid.* **95**, 8670 (1973).

[5] H. E. Zimmerman, J. D. Robbins, R. D. McKelvey, C. J. Samuel and L. R. Sousa, *Ibid.* **96**, 4630 (1974); and Refs cited.

[6] P. S. Mariano and R. B. Steitle, *Ibid.* **95**, 6114 (1973); *Ibid.* **98**, 5899 (1976).

[7] H. E. Zimmerman, *Accounts Chem. Res.* **4**, 272 (1971).

[8] H. E. Zimmerman and P. S. Mariano, *J. Am. Chem. Soc.* **91**, 1718 (1969).

[9] P. Seifert and H. Schinz, *Helv. Chim. Acta* **34**, 728 (1951).

[10] B. Martel and J. M. Hiriat, *Synthesis* 210 (1972).

[11] I. Elphimoff-Felkin and P. Sarda, *Chem. Commun.* 1065 (1967).

[12] G. L. Closs and R. A. Moss, *J. Am. Chem. Soc.* **86**, 4042 (1964).

[13] H. E. Zimmerman and A. C. Pratt, *Ibid.* **92**, 1407 (1970).

[14] W. G. Dauben, M. S. Kellog, J. I. Seeman, N. D. Vietmeyer and P. H. Wendschuh, *Pure Appl. Chem.* **33**, 197 (1973); J. E. Baldwin and S. M. Krueger, *J. Am. Chem. Soc.* **91**, 6444 (1969); C. W. Spangler and R. P. Hennis, *Chem. Commun.* **24** (1972).

[15] J. I. Seeman and H. Ziffer, *Tetrahedron Letters* 4413 (1973).

[16] H. E. Zimmerman and G. Grunewald, *J. Am. Chem. Soc.* **88**, 183 (1966).

[17] S. S. Hixson and J. C. Tausta, *Tetrahedron Letters* 2007 (1974).

[18] J. S. Swenton, R. M. Blankenship and R. Sinitra, *J. Am. Chem. Soc.* **97**, 4941 (1975).