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Stereochemical and Mechanistic Aspects of the Di-π-methane Rearrangement. Effect of Structural Constraints Which Preclude Preferred Modes

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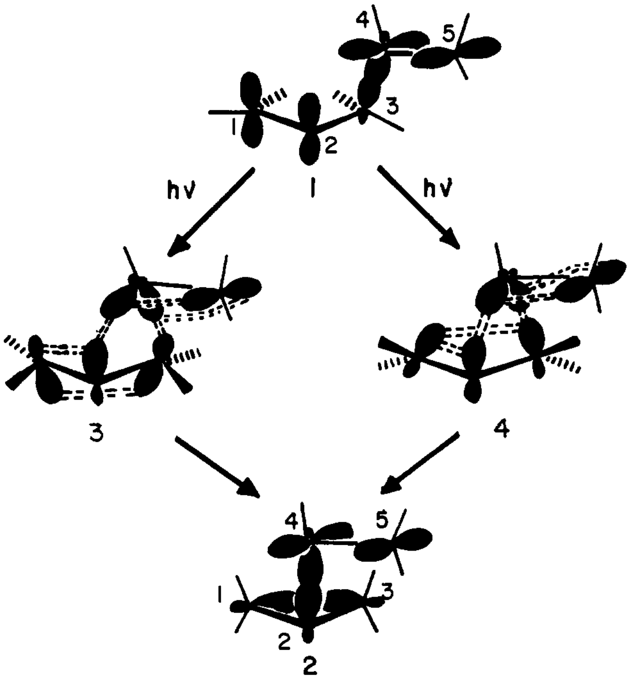
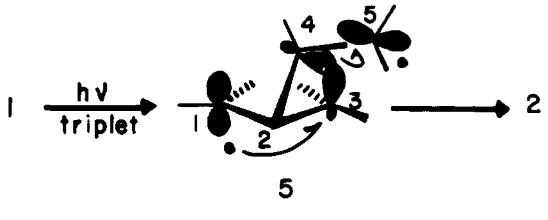
Abstract: A study of stereochemical and mechanistic aspects of the di-π-methane rearrangement using 2-phenylspiro[5.5]undeca-1,7-diene (**6**) is reported. The sole product of direct irradiation of **6** is 11-phenyltricyclo[5.4.0.0^{7,11}]undec-2-ene (**7**). The spirodi-π-methane **6** was unreactive under triplet-sensitized irradiation conditions which employed both benzophenone and acetophenone. This inertness is due to an unreactive triplet-excited **6** rather than inefficient energy transfer from the triplet sensitizers, since **6** serves as an effective quencher of the well-known benzophenone–benzhydrol photoreduction to benzpinacol. The singlet and triplet photochemistry of **6** in comparison to that of the close structural analogue, 1-phenyl-3-methyl-3-(1-*cis*-propenyl)cyclohexene (**23**), is interpreted in terms of preferred di-π-methane reaction modes and how structure controls the relative energies of competing singlet and triplet reaction transition states.

Our recent studies[1] in the area of di-π-methane photochemistry have concentrated on stereochemical aspects of this quite general[2] excited-state conversion of 1,4-dienes (**1**) to vinylcyclopropanes (**2**). Results from our previous investigations[1] and those of Zimmerman and co-workers[3] have indicated that transformations of singlet-excited di-π-methanes follow concerted mechanisms and the configurational integrity at the centers of stereochemistry, i.e., the migrating C-4–C-5 π bond, C-3, and C-1, appear to be controlled by a remarkable energetic preference for transition states having what we have termed[1b] anti-disrotatory orbital geometries (**3**) over their syn-disrotatory (**4**) competitors. The existence and magnitude of this energetic preference seems to derive from factors other than orbital topology[4] or orbital symmetry,[6] since both transition states or concerted reaction pathways are predicted to be equally energetic or allowed on the basis of first-order orbital control methodologies.



Investigations of the stereochemistry of the triplet di-π-methane rearrangement are less abundant than of its singlet counterpart.[8] Thus, information from which to draw conclusions about mechanistic details and factors that control stereochemistry remain absent. In an early report,[1b] we presented mechanistic arguments to temporarily rationalize the stereospecificity of the triplet rearrangements.[9] Our conclusion was that triplet-reactive di-π-methanes reorganize to π-substituted cyclopropanes using a nonconcerted, two-step pathway via an intermediate cyclopropyldicarbinyl diradical (**5**), from



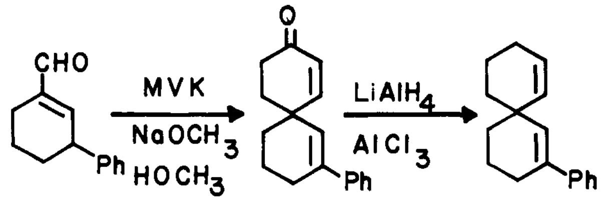
which conversion to product results from attack by C-1 on C-3 with net inversion at C-3.

We have continued our studies of this ubiquitous excited-state reaction with the hope of obtaining more information about the nature of its stereochemical control. This report contains the complete results of our recent investigations designed to determine the effect of structural constraints, which prevent both the singlet and triplet rearrangement by preferred stereochemical modes, on the excited-state chemistry of 1,4-diene systems. We have found that 2-phenylspiro[5.5]-undeca-1,7-diene (**6**), a constrained spirodi-π-methane, undergoes smooth transformation to 11-phenyltricyclo-[5.4.0.0^{7,11}]undec-2-ene (**7**) upon direct irradiation, but that it is unreactive under triplet-sensitized photolytic conditions.

Results

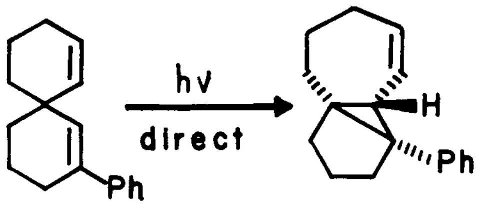
Preparation of 2-Phenylspiro[5.5]undeca-1,7-diene (6). The preparation of this spirodiene was easily accomplished starting with the known[1c] 3-phenylcyclohexene-1-carboxaldehyde (**8**) using the sequence outline in Scheme I. The spectral and analytical properties of this material, obtained as a clear liquid after silica gel chromatographic purification, matched nicely those expected on the basis of the assigned structure.[11]

Scheme I. Synthesis of 2-Phenylspiro[5.5]undeca-1,7-diene

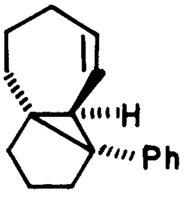


8 9 6

Photochemistry of 2-Phenylspiro[5.5]undeca-1,7-diene. Direct Irradiation. Direct irradiation of the spirodiene **6** in acetonitrile led to the production of only one volatile product in a reasonably good yield, which depended upon the irradiation time (maximally 73.7%).[13] The photoproduct, after GLC purification, possessed analytical and spectral properties consistent with its structural assignment as 11-phenyltricyclo[5.4.0.0^{7,11}]undec-2-ene (**7**).



6 7



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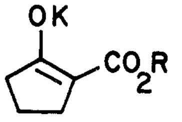
Photoproduct Structure Proof. An unambiguous synthetic and degradative sequence was utilized to more conclusively establish both the structure and stereochemistry of the obtained photoproduct. We felt that this was required, since the spectral and analytical data were not sufficient to rule out the trans-fused tricyclic isomer **10**, albeit predicted to be of high energy,[14] as the material obtained from direct irradiation of **6**. At the fulcrum of this sequence were the isomeric 1-phenyl-5-(4′-hydroxybutyl)-*endo*- and *exo*-6-hydroxymethylbicyclo[3.1.0]hexanes (**11** and **12**), which were independently prepared starting with the potassium enolates (**13**) of the ethyl and methyl esters of cyclopentanone-2-carboxylic acid. Accordingly, alkylation of **13** with 1,4-dibromobutane followed by aqueous acid hydrolysis and decarboxylation of the intermediate β-keto ester **14** furnished the bromobutyl cyclopentanone (**15**). Acetolysis of **15** gave the acetate **16**, which reacted smoothly with excess phenyllithium followed by *p*-toluenesulfonic acid catalyzed dehydration in refluxing benzene to yield the phenylcyclopentenylbutyl alcohol **17**. Introduction of the acetate blocking group was accomplished by treatment of **17** with acetyl chloride and powdered magnesium. The derived olefinic acetate **18** was then carboxycyclopropanated under the standard conditions with ethyl diazoacetate, producing a mixture of esters which were not purified, but saponified in aqueous sodium hydroxide to a mixture of exo- and endo-carboxylic acids **19** and **20**, respectively. Chromatographic separation and purification of these hydroxy acids were performed on silica gel and gave crystalline compounds, which were reduced independently to the respective diols **12** and **11** using lithium aluminum hydride.



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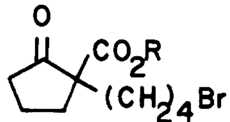

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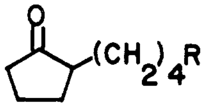
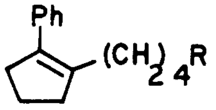
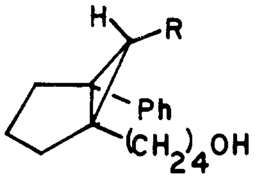


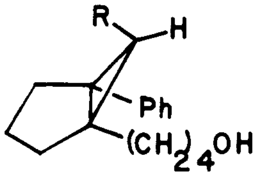
15 R=Br
16 R=OAc



17 R=OH
18 R=OAc

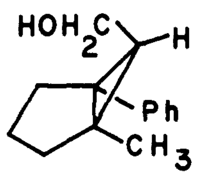


19 R=CO$_2$H
12 R=CH$_2$OH



20 R=CO$_2$H
11 R=CH$_2$OH

The stereochemistries at C-6 in **11** and **12** were determined spectroscopically. The proton NMR spectrum of **12** contained a complex multiplet centered at δ 3.65, consisting of a superposition of resonances for the C-6 and side-chain hydroxymethylene protons. Its endo isomer **11**, however, possesses an NMR spectrum in which the corresponding protons have nearly equivalent chemical shifts and, thus, appear as a superposition of two clean triplets (see Figure 1). Stereochemical conclusions can be drawn from this data when comparisons are made with patterns displayed by the analogous protons in the NMR of two model alcohols, *endo*- and *exo*-1-phenyl-5-methyl-6-hydroxymethylbicyclo[3.1.0]hexane (**21** and **22**), of known stereochemistries[1b] assigned using lanthanide-NMR



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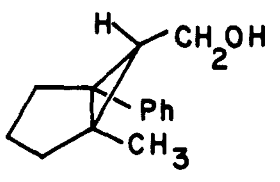


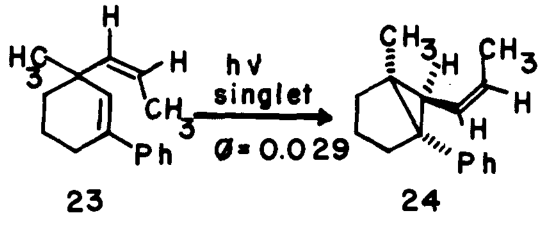
22

data. The diastereotopic hydroxymethylene proton resonances of the model alcohols **21** and **22** appear as characteristically different patterns. In the exo isomer **22** these protons are magnetically nonequivalent, as is expected due to their proximity relative to the substituents responsible for the asymmetry, and thus, their corresponding resonances appear as the AB portion of an ABM pattern. The hydroxymethylene protons in **21**, on the other hand, are magnetically equivalent and appear as a simple doublet. We conclude from these observations that the broad and complex nature of the hydroxymethylene region in the NMR of **12** must be due to the eight-line multiplet for the magnetically nonequivalent exo-hydroxymethylene protons and the triplet for the side-chain hydroxymethylene protons.

With the structures and stereochemistries of the isomeric diols **11** and **12** firmly established on the basis of the synthetic route utilized and their spectral properties, degradation of the direct irradiation photoproduct was commenced. Ozonolysis of **7** was carried out in ethyl ether at −80 °C. The ethereal solution containing the crude ozonide was then treated with lithium aluminum hydride. A single diol product was formed, identical in all respects with 1-phenyl-5-(4′-hydroxybutyl)-*exo*-6-hydroxymethylbicyclo[3.1.0]hexane (**12**) obtained from the synthetic sequence discussed above. The identity gives definitive proof that both the structure and stereochemistry of the sole photoproduct from direct irradiation of **6** is that of the tricyclic diene **7**.

Reaction Multiplicity. Triplet-sensitized irradiations of the spirodiene **6** were conducted in acetonitrile, using both benzophenone and acetophenone as sensitizers, and reaction conditions which insured selective light absorption by sensitizer and efficient energy transfer from the sensitizer triplet only. Under all conditions used, no detectable quantities of **7** or other photoproducts were observed and in each case the spirodiene was recovered quantitatively. To insure that the lack of reactivity of **6** under these conditions was due to its inert triplet state and not to an inefficiency of energy transfer from the expected higher triplet-energy sensitizers,[15] experiments were conducted which demonstrated that the spirodiene effectively quenches the known[17] triplet photoreduction of benzophenone to benzpinacol in the presence of benzhydrol.

$$6 \xrightarrow[\text{Ø} = 0.013]{h\nu,\ \text{singlet}} 7$$



23 24

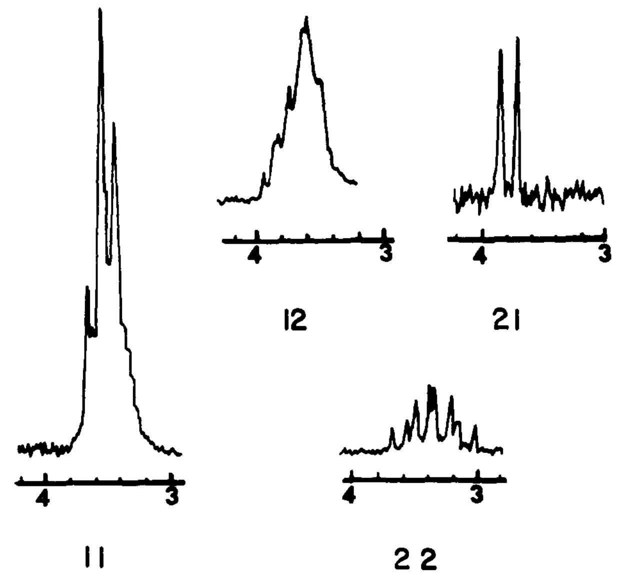


Figure 1. The hydroxymethylene proton regions in the NMR of the diols **11** and **12** and model bicyclic alcohols **21** and **22**, which demonstrate the effect of environment of the diastereotopic methylene protons on their magnetic nonequivalence.

Quantum Efficiencies of the Singlet Reaction of the Spirodiene 6 and the Model Di-π-methane Substrate 1-Phenyl-3-methyl-3-(1-*cis*-propenyl)cyclohexene (23). Quantum yields for the singlet rearrangements of the spirodiene **6** and the close structural analogue 1-phenyl-3-methyl-3-(1-*cis*-propenyl)-cyclohexene (**23**)[1b] were determined using a "linear optical bench" system and potassium ferrioxalate actinometry. Necessary precautions were taken to ensure the absence of singlet self-quenching and secondary reactions of the products, that all light was captured by actinometer or photochemical substrate, and that the filter solutions used to isolate the desired wavelength regions remained transparent throughout the duration of the irradiation.

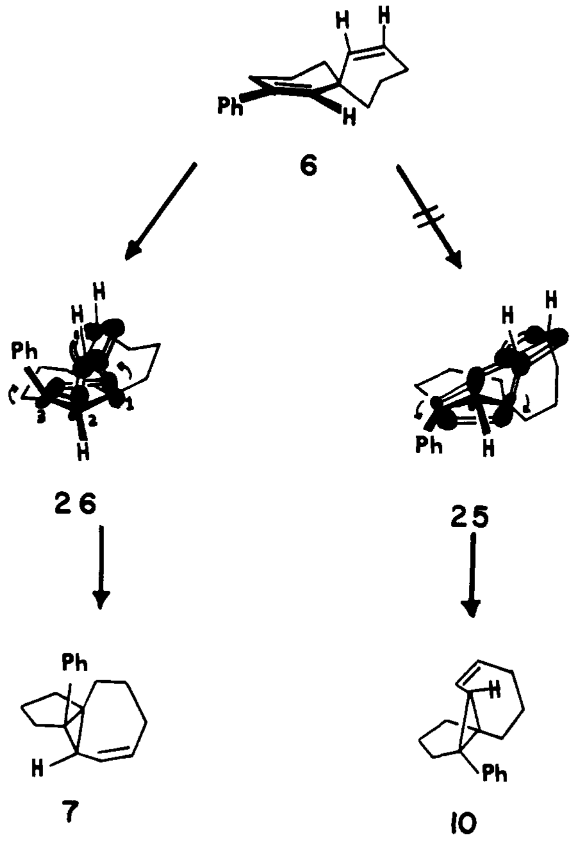
The direct irradiation quantum efficiency for the conversion of spirodiene **6** to the tricyclic undecene **7** was found to be 0.013 ± 0.001 at 8.6% conversion. The quantum yield for rearrangement of the propenylcyclohexene **23** to the bicyclohexane **24** was 0.029 ± 0.002 at 24.5% conversion.[18]

Discussion

The results detailed above appear pertinent in relation to several aspects of the general di-π-methane rearrangement which have received less attention in previous investigations. Specifically, the photochemistry of the highly constrained spirodiene **6** has yielded conclusions directly related to the influence of structure on di-π-methane reactivity and, indirectly, about the relative energies of the two allowed pathways for the concerted singlet reaction and the mechanistic detail of the nonconcerted triplet reaction.

Anti- vs. Syn-Disrotatory Singlet Di-π-methane Reaction Stereochemistry. The "tightly structured" spirodiene **6** contains features that block concerted singlet di-π-methane rearrangement via the transition state **25**, having the anti-disrotatory orbital topology.

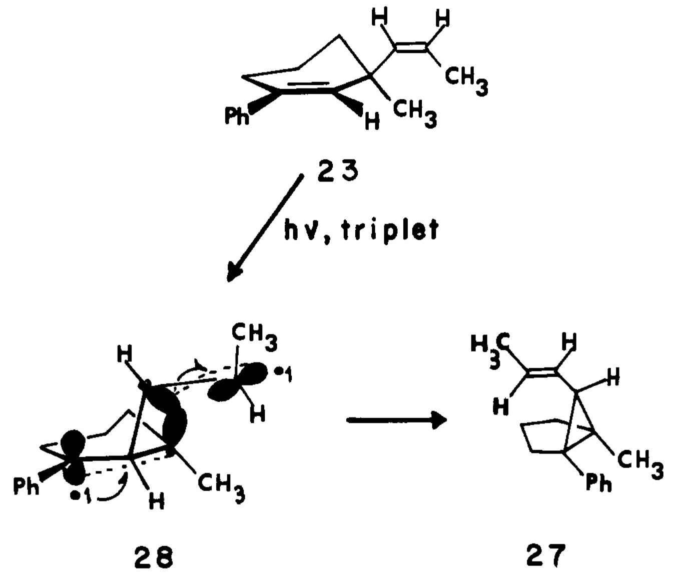
Reaction of **6** through this mode would lead to the highly strained, transfused, tricyclic olefin **10**, which is estimated[14] to have an excessively high energy content. It should be noted that transition states of this orbital topology are known to be of low energy in singlet rearrangements of less constrained 1,4-dienes.[1b,3] Thus, it is informative that despite this structural limitation the direct irradiation, singlet di-π-methane rearrangement of **6** proceeds with modest efficiency to produce exclusively the cis-fused tricycloundecene **7**.[19] The structural and stereochemical outcome of this transformation appears to be most simply interpreted in terms of an alternate concerted mechanism in which the allowed[4,6] transition-state orbital topology (**26**) results from disrotatory motion of the orbitals at C-1 and C-3 syn to the migrating vinyl moiety.[20] In a general



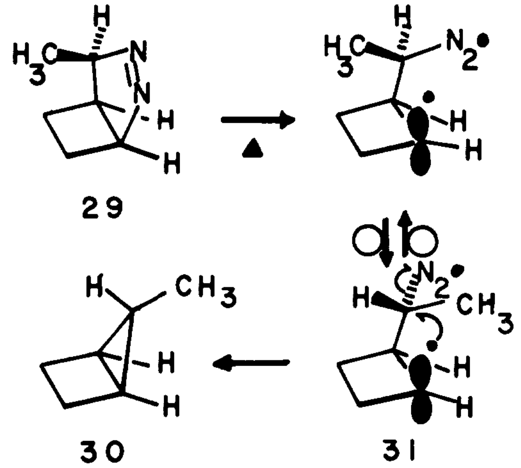
sense, it does not appear that structural constraints placed on the 1,4-diene moiety that prohibit reaction by the preferred antidisrotatory mode serve as limitations for singlet di-π-methane rearrangement.

This qualitative evaluation is supported by the comparative quantum efficiencies for reaction of the *cis*-propenylcyclohexene **23** and spirodiene **6**, found to be 0.029 and 0.013, respectively. Our earlier efforts have demonstrated that **23** undergoes singlet reaction to produce the *endo-cis*-propenylbicyclo[3.1.0]hexane (**24**) exclusively, exemplifying a di-π-methane reactive system which rearranges through the anti-disrotatory pathway. Thus, if the quantum yield differences for the reaction of **6** and **23** are reflective of the relative rate constants for reaction,[21] the energy differences between the anti- and syn-disrotatory transition states must be small.

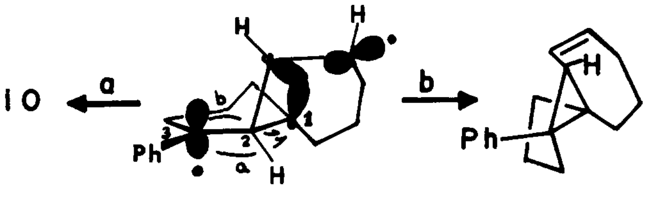
Triplet Di-π-methane Reaction Mechanism. Perhaps of greater significance is the observation that the spirodiene **6** is unreactive from its triplet-excited state, since it represents a rather interesting exception to the general postulates previously suggested about how structure influences triplet di-π-methane reactivity.[2,22] According to these, the spirodiene **6**, having both π moieties contained within small ring systems and, therefore, incapable of free rotation, would represent a classical example of a triplet-reactive di-π-methane system, since competitive, free-rotor, triplet-energy dissipation is blocked.[3a,9b,c] Consequently, the current results seem to suggest that structure can influence triplet di-π-methane reactivity of 1,4-dienes in another fashion. We feel that this derives from mechanistic and stereochemical preferences for the triplet reaction.



Earlier we had presented evidence which combined with a variety of similar observations in the literature to support a nonconcerted, two-step mechanism for the triplet conversion of 1,4-dienes to vinylcyclopropanes. The stereospecificity for the triplet-sensitized transformation of 1-phenyl-3-methyl-3-(1-*cis*-propenyl)cyclohexene (**23**) to solely the endo-trans-bicyclic hexane **27** could best be explained in terms of preferential collapse of the cyclopropyldicarbinyl diradical intermediate **28** by attack of the anti lobe at C-3 on C-1 with inversion of configuration at C-1, as shown below. It is interesting that the stereochemical course of the conversion of **23** to **27**, having cyclopropane formation occurring by radical substitution on carbon with departure of a π bond, is similar to that for analogous reactions noted in decompositions of bicyclic azo compounds.[23] One of the several examples of the latter reaction type and the requirement for inversion of configuration at the reactive carbon center is the sequential conversion of *endo*-4-methyl-2,3-diazabicyclo[3.2.0]hept-2-ene (**29**) to *exo*-5-methylbicyclo[2.1.0]pentane (**30**), having backside displacement of nitrogen in the intermediate **31**.[23b]



Thus, if it is assumed that the mechanism[24] and complementary stereochemistry proposed earlier are required for triplet di-π-methane reactions, the inertness of the triplet-excited state of **6** can be understood. The transition states for collapse of the cyclopropyldicarbinyl diradical intermediate **32** to the tricyclic undecenes **10** and **33**, involving backside displacement on C-1 by either the anti (pathway a) or syn (pathway b) lobe of the orbital at C-3, would have energy



contents which reflect the highly strained, trans-fused products that are forming. It appears then that structural constraints placed on di-π-methane systems, which prevent inversion of configuration at the methane carbon, have a pronounced effect on the triplet reactivity of these systems. In light of this result and its mechanistic conclusion an amendment to the general structure–multiplicity relationship presented earlier[22] is in order.[25] Accordingly, the triplet reactivity of di-π-methanes is governed not only by structural features which influence "free-rotor" energy dissipation about the one of the two π moieties of lowest triplet energy,[25] but also by structural constraints which control collapse of intermediate cyclopropyldicarbinyl diradicals by the preferred stereochemical route involving inversion at the methane carbon.[27]

Experimental Section

General. All melting and boiling points are recorded uncorrected. Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn. Infrared spectra were recorded using a Perkin-Elmer Model 237 spectrometer. Proton NMR spectra were obtained using Varian HA-100 and T-60 spectrometers. Ultraviolet spectra were recorded using a Beckmann Acta-III spectrometer. Carbon-13 NMR spectra were obtained using a Jeol PS-100 spectrometer with a Nicolet data system. Preparative and analytical gas chromatography was performed using Varian Model 2700 and 910 chromatographs, respectively. Mass spectra were obtained using a CEC-21-110 spectrometer.

8-Phenylspiro[5.5]undeca-1,7-dien-3-one (9). To 3.88 g (0.07 mol) of sodium methoxide in 150 ml of methanol at 0 °C and under a nitrogen atmosphere, 12.00 g (0.06 mol) of 3-phenylcyclohexene-1-carboxaldehyde was added with stirring. To this mixture, 6.00 g (0.09 mol) of methyl vinyl ketone in 150 ml of methanol was added dropwise and the resulting mixture was stirred at room temperature for 71 h. Water (500 ml) was added and the separated aqueous layer was extracted with ether. The ethereal extracts were combined with the original ethereal layer, washed with water, dried, and concentrated in vacuo to give 13.35 g of an oil, which was chromatographed on an alumina column (Alcoa, F-20, 80–200 mesh). Elution was with 28% ether in hexane (1.6 l.) and 30% ether in hexane (1.7 l.). The eluent was monitored at 254 nm and 20-ml fractions were collected. Fractions 46–216, upon concentration, gave 6.42 g (41.8%) of pure 8-phenylspiro[5.5]undeca-1,7-dien-3-one.

Spectral data are as follows: NMR (CCl_4) δ 1.4–2.6 (m, 10 H, $-CH_2$), 5.65–5.83 (d, J = 10.5 Hz, 1 H, C=CHC=O), 5.83 (s, 1 H, PhC=CH), 6.45–6.64 (d, J = 10.5 Hz, 1 H, CH=CC=O), and 6.9–7.4 (m, 5 H, aromatic); ir (liquid film) 3.30, 3.32, 3.43, 3.53, 6.30, 6.74, 6.95, 7.26, 8.00, 8.26, 8.72, 9.20, 9.30, 11.70, 11.90, 13.30, and 14.40 μm.

Anal. Calcd for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found: C, 85.78; H, 7.77.

2-Phenylspiro[5.5]undeca-1,7-diene (6). The general procedure of Broome and co-workers[10] was used. To 1.78 g (0.05 mol) of lithium aluminum hydride in 200 ml of anhydrous ether at 0 °C and under a nitrogen atmosphere was added cautiously 12.48 g (0.09 mol) of anhydrous aluminum chloride with good stirring. After all visible reaction had subsided, 6.40 g (0.03 mol) of 8-phenylspiro[5.5]undeca-1,7-dien-3-one in 200 ml of anhydrous ether was added dropwise. The resulting mixture was stirred at room temperature for 48 h, then cooled to 0 °C and a saturated sodium sulfate solution was added dropwise until the appearance of a white precipitate. After filtration to remove this white precipitate, the ethereal layer was separated, washed with water, dried, and concentrated in vacuo to give the crude 2-phenylspiro[5.5]undeca-1,7-diene as a yellow oil. This oil was subjected to column chromatography on a silica gel (Davison, grade 923, 100–200 mesh) column (740 × 50 mm). Elution was with 2.2 l. of 3% ether–hexane and the eluent was monitored at 254 nm. Fractions (20 ml) were collected. Fractions 28–104, upon concentration, gave 3.07 g (51.0%) of the wanted diene. Ultimately, pure diene for analysis was obtained by GLC on a 7 ft × ⅛ in., 4% SE-30 on Anakrom ABS, 60–70 mesh, column at 195 °C and a flow rate of 84 ml/min (R_f 14 min). This material, although possessing correct analytical and spectral properties, was found by C-13 NMR spectroscopy to contain small quantities of an isomeric impurity which is most probably 2-phenylspiro[5.5]undeca-1,8-diene.

Spectral data for the diene are as follows: uv (acetonitrile) λ_{max} at 249 nm (ϵ 10 700); ^1H NMR (CCl_4) δ 1.0–2.6 (m, 12 H, $-CH_2-$), 5.5–6.0 (m, 2 H, olefinic), 5.65 (s, 1 H, PhC=CH), and 7.1–7.5 (m, 5 H, aromatic); ir (liq film) 3.23, 3.26, 3.40, 3.48, 3.50, 5.17, 5.35, 5.60, 6.28, 6.70, 6.92, 6.98, 7.33, 7.45, 8.50, 8.17, 9.30, 9.58, 9.70, 10.60, 10.74, 11.00, 11.34, 11.61, 13.35, and 14.43 μm; high resolution mass spectrum (70 eV), expected molecular ion for $C_{17}H_{20}$ is m/e 224.156500; obtained m/e (relative intensity) 224.156667 (27.9), 209 (1.9), 196 (10.7), 182 (74.1), 181 (22.5), 170 (100.0), 155 (15.8), 141 (13.8), 77 (40.0), and 65 (16.3); ^{13}C NMR ($CDCl_3$), parts per million relative to Me_4Si, 142 (s, C-2), 135 (d, C-1), 133 (d, C-11 and C-10), 128, 126, 125 (d, aromatic), 37, 34, 33, 28, 22, and 19 (d, C-9, C-8, C-7, C-5, C-4, C-3).

Anal. Calcd for $C_{17}H_{20}$: C, 91.01; H, 8.99: Found: C, 90.95; H, 8.77.

Photolysis of 2-Phenylspiro[5.5]undeca-1,7-diene (6). Preparation of 11-Phenyltricyclo[5.4.0.0^{7,11}]undec-2-ene (7). A nitrogen-purged solution containing 1.06 g (4.73 mol) of 2-phenylspiro[5.5]undeca-1,7-diene in 750 ml of spectrograde acetonitrile was irradiated for 4.0 h in a preparative photolysis apparatus consisting of a water-cooled quartz immersion well containing a 450-W Hanovia medium-pressure lamp and Vycor filter. The photolysate was concentrated in vacuo, giving 0.99 g of a yellow oil which was analyzed by GLC on a 7 ft × ⅛ in., 4% SE-30 on 60–70 mesh Anakrom ABS column at 195 °C with a flow rate of 84 ml/min. In addition to the starting diene only one other compound was detected at R_f 10 min in a ca. 1:1 ratio. The photoproduct was separated by preparative GLC, using these conditions, as a clear liquid and was characterized on the basis of the spectral and analytical data given below and by degradative and independent synthetic pathways as 11-phenyltricyclo[5.4.0.0^{7,11}]undec-2-ene.

Spectral data for the photolysis product are as follows: uv (acetonitrile) λ_{max} 257 nm (ϵ 2600); ^1H NMR (CCl_4) δ 0.5–2.5 (m, 13 H, $-CH_2-$ and $-CH-$), 5.2–5.8 (m, 2 H, olefinic), and 6.7–7.6 (m, 5 H, aromatic); ir (liq film) 3.33, 3.40, 3.45, 3.49, 3.51, 6.24, 6.75, 6.96, 8.35, 12.5, 13.4, 13.9, and 14.3 μm; ^{13}C NMR ($CDCl_3$), ppm rel to Me_4Si, 144 (d, C-3), 131 (d, C-2), and 45 (s, C-11).

Anal. Calcd. for $C_{17}H_{20}$: C, 91.01; H, 8.99. Found: C, 90.89; H, 9.08.

Varying Conversion Irradiation. A nitrogen-purged solution of the spirodiene (1.08×10^{-2} M) in acetonitrile was irradiated for a total of 5 h in a preparative apparatus as described above. Aliquots were removed at 1, 2, 3, and 5 h, diluted with a standardized solution of benzophenone, and analyzed by GLC on a 5 ft × ⅛ in. OV-101 on Anakrom ABS column at 159 °C with a flow rate of 23 ml/min. Integration of the peaks for recovered diene and the photoproduct and comparison of these areas to those of the benzophenone standard gave the following absolute yields of recovered diene and tricyclic photoproduct, respectively; 1 h, 57.3 and 27.6%; 2 h, 49.4 and 37.3%; 3 h, 41.2 and 41.8%; 5 h, 25.0 and 44.6%.

Sensitized Photolyses. A nitrogen-purged solution containing 1.01 g (4.51 mmol) of 2-phenylspiro[5.5]undeca-1,7-diene and 1.00 g (5.48 mmol) of benzophenone in 750 ml of spectrograde acetonitrile was irradiated for 4.0 h using the same apparatus for the direct irradiations and a flint glass filter (λ > 310 mm). The photolysate was concentrated in vacuo and chromatographed on an alumina (Alcoa, F-20, 80–200 mesh) column (740 × 50 mm) using 8000 ml of hexane as eluent. GLC analysis of the 0.99 g of recovered material showed it to be solely unreacted starting material.

A nitrogen-purged solution containing 1.03 g (4.60 mmol) of 2-phenylspiro[5.5]undeca-1,7-diene and 0.494 g (4.12 mmol) of acetophenone in 750 ml of spectrograde acetonitrile was irradiated under the same conditions as for the benzophenone-sensitized run. The crude photolysate was short-path distilled under reduced pressure (0.01 mm) to remove acetophenone. GLC analysis showed that the only compound remaining after fractional distillation was 2-phenylspiro[5.5]undeca-1,7-diene.

Test for Energy Transfer Using the Benzophenone Photoreduction in the Presence of Benzhydrol. Absence of 2-Phenylspiro[5.5]undeca-1,7-diene. A nitrogen-purged solution containing 2.00 g (10.99 mmol) of benzophenone and 2.79 g (11.25 mmol) of benzhydrol in 750 ml of spectrograde acetonitrile was irradiated for 0.5 h using the same apparatus and filter as used above for the benzophenone- and acetophenone-sensitized photolyses. The photolysis mixture was concentrated and the resulting white solid was chromatographed on a silica gel (Davison, grade 923, 100–200 mesh) column (750 × 50

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mm) using 5.9 l. of 5% ether–hexane and 3.9 l. of 7% ether–hexane as eluents. The eluent was monitored at 280 nm and 20-ml fractions were collected; fractions 45–75, upon concentration, gave 37.5 mg of a mixture of benzophenone and benzhydrol. Fractions 133–492, upon concentration, gave 3.07 g of benzpinacol. Identity of the compounds obtained after chromatography was accomplished by NMR and ir.

Presence of 2-Phenylspiro[5.5]undeca-1,7-diene. A nitrogen-purged solution containing 2.00 g (10.99 mmol) of benzophenone, 2.79 g (11.25 mmol) of benzhydrol, and 1.00 g (4.66 mmol) of 2-phenylspiro[5.5]undeca-1,7-diene in 750 ml of spectrograde acetonitrile was irradiated for 0.5 h under the same conditions as described above. The photolysis mixture was concentrated and then chromatographed on a silica gel (Davison, grade 923, 100–200 mesh) column (740 × 50 mm) using as eluent 3.2 l. of 1% ether–hexane and 2.0 l. of 5% ether–hexane. The eluent was monitored at 254 nm and 20-ml fractions were collected; fractions 113–159, upon concentration, gave 0.88 g of 2-phenylspiro[5.5]undeca-1,7-diene. Fractions 169–194 gave 1.85 g of benzophenone, fractions 195–227 gave 2.17 g of benzhydrol, and fractions 228–259 gave 0.32 of benzpinacol. The identity of all compounds obtained after chromatography was accomplished by GLC, NMR, and ir.

Degradation of 11-Phenyltricyclo[5.4.0.0^{7,11}]undec-2-ene. Preparation of 1-Phenyl-5-(4′-hydroxybutyl)-6-*exo*-hydroxymethylbicyclo[3.1.0]hexane (12). Ozone in an oxygen stream (from a Welsback T-408 ozonator) at a rate of 2.56 g/h was passed through 90.1 mg (0.4 mmol) of 11-phenyltricyclo[5.4.0.0^{7,11}]undeca-2-ene in 50 ml of anhydrous ether at −80 °C for 30 min. After the ozonide-containing solution was warmed to room temperature, 45.7 mg (1.21 mmol) of lithium aluminum hydride was added and the resulting mixture was stirred for 16 h under a nitrogen atmosphere. A saturated sodium sulfate solution was then added dropwise until the appearance of a white precipitate. The aqueous layer was separated and extracted with ether. The combined ethereal extracts were washed with water, dried, and concentrated in vacuo to give 90.8 mg of 1-phenyl-5-(4′-hydroxybutyl)-6-*exo*-hydroxymethylbicyclo[3.1.0]hexane as a clear, colorless oil. This oil was subjected to preparative TLC on a silica gel (E. Merck, PF_{254}) plate (20 × 20 cm) using anhydrous ether as eluent. Pure 1-phenyl-5-(4′-hydroxybutyl)-6-*exo*-hydroxymethylbicyclo[3.1.0]hexane, 71.4 mg (68.3%), was obtained from a band with an R_f of 0.53. The spectral and physical properties of this compound were identical with those of independently synthesized material.

Synthesis of 1-Phenyl-5-(4′-hydroxybutyl)-6-*endo*- and *exo*-hydroxymethylbicyclo[3.1.0]hexane. 2-(4′-Bromobutyl)-2-carboxycyclopentanone Methyl and Ethyl Esters (14). To a solution of 273.5 g of the potassium salts of 2-carbethoxycyclopentanone methyl and ethyl esters in 1 l. of absolute ethanol, 819.0 g (3.8 mol) of 1,4-dibromobutane was added and the mixture was stirred at reflux for 16 h. The precipitated inorganic salt was removed by filtration. The filtrate was fractionally distilled to give 163.2 g (121.3 g ethyl + 41.9 g methyl esters) of 2-(4′-bromobutyl)-2-carbethoxycyclopentanone methyl and ethyl esters, bp 181–195 °C (12 mm).

Spectral data are as follows: NMR ($CDCl_3$) δ 1.1–3.2 (m, 12–15 H, $-CH_2-$ and $-CH_3$), 3.3–3.6 (t, J = 6.0 Hz, 2 H, $-CH_2Br$), 3.7 (s, 3 H, $-CO_2CH_3$), and 3.9–4.4 (q, J = 7.5 Hz, 2 H, $-CO_2CH_2-$); ir (neat) 3.35, 3.45, 5.70, 5.78, 6.89, 7.10, 7.30, 7.91, 8.12, 8.60, 9.20, 10.38, 11.76, 12.12, 13.60, and 15.50 μm.

Anal of GLC purified ethyl ester. Calcd for $C_{12}H_{19}O_3Br$: C, 49.50; H, 6.58. Found: C, 49.75; H, 6.60.

2-(4′-Bromobutyl)cyclopentanone (15). To 163.2 g (0.4 mol ethyl ester and 0.2 mol methyl ester) of a mixture of 2-(4′-bromobutyl)-2-carbethoxycyclopentanone methyl and ethyl esters, 815 ml of 48% HBr was added and the resulting mixture was stirred vigorously at reflux for 3 h. The dark green organic layer was separated and added to 1 l. of water. After extraction with ether, the combined ethereal extracts were concentrated in vacuo and fractionally distilled, giving 67.8 g (54.5%) of 2-(4′-bromobutyl)cyclopentanone, bp 143–154 °C (15 mm).

Spectral data are as follows: NMR ($CDCl_3$) δ 1.0–2.5 (m, 13 H, $-CH_2-$, CH–) and 3.3–3.6 (t, J = 6.0 Hz, 2 H, $-CH_2Br$); ir (neat) 3.40, 3.49, 5.80, 6.91, 7.12, 7.72, 7.89, 8.01, 8.12, 8.31, 8.70, 9.00, 9.17, 9.39, 9.62, 9.99, 10.32, 10.78, 12.18, 12.50, 13.20, 13.65, and 15.50 μm.

Anal. Calcd. for $C_8H_{13}OBr$: C, 49.33; H, 6.90; Br, 36.47. Found: C, 49.38; H, 6.95; Br, 36.28.

2-(4′-Acetoxybutyl)cyclopentanone (16). To a solution of 76.11 g (0.93 mol) of sodium acetate and 5.15 g (0.31 mol) of sodium iodide in 475 ml of glacial acetic acid, 67.77 g (0.31 mol) of 2-(4′-bromobutyl)cyclopentanone was added and the resulting mixture was stirred for 39 h at reflux. After cooling to room temperature, 1 l. of water was added and the solution was extracted with ether. The combined ethereal extracts were washed with a water–pyridine mixture (5 drops pyridine to 50 ml water), dried, and concentrated in vacuo, yielding a brown oil which was fractionally distilled to give 59.16 g (96.6%) of 2-(4′-acetoxybutyl)cyclopentanone as a yellow oil, bp 151–157 °C (8 mm).

Spectral data are as follows: NMR ($CDCl_3$) δ 1.1–2.5 (m, 13 H, $-CH_2-$, –CH–), 2.1 (s, 3 H, CH_3CO_2-), and 4.0–4.3 (t, J = 7.0 Hz, 2 H, $-CO_2CH_2-$); ir (neat) 3.39, 3.48, 5.79, 6.89, 7.11, 7.21, 7.32, 8.08, 8.68, and 9.64 μm.

Anal. Calcd. for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15. Found: C, 66.42; H, 9.12.

1-Phenyl-2-(4′-hydroxybutyl)cyclopentene (17). To a solution of 49.65 g (0.59 mol) of phenyllithium in 260 ml of 30% ether–benzene, 16.74 g (0.08 mol) of 2-(4′-acetoxybutyl)cyclopentanone in 400 ml of anhydrous ether was added dropwise under a nitrogen atmosphere with good stirring. After this mixture was stirred for 24 h at room temperature and cooled to 0 °C, 552 ml of 15% (by volume) sulfuric acid was added dropwise and the resulting solution was stirred at room temperature for an additional 24 h. The aqueous layer was then separated and extracted with ether. The ethereal extracts were combined with the original ethereal layer, washed with water, dried, and concentrated in vacuo to give a dark brown oil, which was chromatographed on an alumina (MCB, activated, 80–200 mesh) column (740 × 50 mm), eluting with 21.2 l. of 1% ether–hexane and 22.7 l. of 30% ether–hexane and collecting 20-ml fractions while monitoring the eluent by uv at 254 nm. Fractions 594–1583, upon concentration, gave 15.28 g of a brown oil consisting of mainly 1-phenyl-5-(4′-hydroxybutyl)cyclopentene. This material was then equilibrated at 60 °C in 800 ml of benzene saturated with *p*-toluenesulfonic acid for 24 h; the benzene solution was washed with water, dried, and concentrated in vacuo to give 15.28 g (83.5%) of 1-phenyl-2-(4′-hydroxybutyl)cyclopentene as a brown oil. A pure sample was obtained by GLC.

Spectral data are as follows: NMR ($CDCl_3$) δ 0.8–2.9 (m, 12 H, $-CH_2-$), 3.3–3.7 (t, J = 6.5 Hz, 2 H, $-CH_2O-$), and 7.1–7.4 (m, 5 H, aromatic); ir (neat) 2.98, 3.23, 3.26, 3.29, 3.40, 3.49, 5.05, 5.15, 5.36, 5.55, 6.26, 6.70, 6.88, 6.93, 7.28, 8.22, 9.40, 9.72, 10.23, 11.02, 13.21, and 14.37 μm.

Anal. Calcd. for $C_{15}H_{20}O$: C, 83.29; H, 9.32. Found: C, 83.11; H, 9.25.

1-Phenyl-2-(4′-acetoxybutyl)cyclopentene (18). To a solution of 4.71 g (0.02 mol) of 1-phenyl-2(4′-hydroxybutyl)cyclopentene in 71 ml of anhydrous benzene with 0.53 g (0.02 mol) of magnesium powder suspended, 4.6 ml of acetyl chloride was added and the mixture stirred at 60 °C for 3 h under anhydrous conditions. This mixture was then filtered, concentrated in vacuo, and the crude product chromatographed on a silica gel (Davison, grade 923, 100–200 mesh) column (740 × 50 mm). Elution was with 3.9 l. of 40% ether–hexane while monitoring the eluent at 254 nm; 20-ml fractions were collected. Fractions 46–195 gave upon concentration 4.81 g (85.6%) of pure 1-phenyl-2-(4′acetoxybutyl)cyclopentene.

Spectral data are as follows: NMR ($CDCl_3$) δ 0.6–2.9 (m, 12 H, $-CH_2-$), 2.0 (s, 3 H, CH_3CO_2-), 3.9–4.2 (t, J = 6.0 Hz, 2 H, $-CO_2CH_2-$), and 7.1–7.5 (m, 5 H, aromatic); ir (neat) 3.26, 3.30, 3.38, 3.43, 3.48, 3.51, 5.12, 5.32, 5.78, 6.02, 6.26, 6.70, 6.92, 7.23, 7.33, 7.86, 8.10, 8.50, 8.69, 8.95, 9.34, 9.70, 10.32, 10.62, 10.91, 11.00, 11.88, 13.28, and 14.32 μm.

Anal. Calcd. for $C_{17}H_{22}O_2$: C, 79.03; H, 8.58. Found: C, 78.49; H, 8.41.

***endo*- and *exo*-1-Phenyl-5-(4′-hydroxybutyl)bicyclo[3.1.0]hexyl-6-carboxylic Acid (19 and 20).** To 10.29 g (0.04 mol) of 1-phenyl-2-(4′-acetoxybutyl)cyclopentene, 2.60 g (0.04 mol) of zinc powder, and 3.94 g (0.04 mol) of cuprous chloride in 10 ml of *n*-octane at 135 °C under a nitrogen atmosphere with good stirring was added 27.21 g (0.24 mol) of ethyl diazoacetate very slowly. This mixture was then stirred an additional 1 h at 135 °C and cooled to 100 °C. NaOH solution (400 ml, 10% by wt) was added and the resulting dark mixture was stirred under reflux for 13 h. The aqueous mixture was then washed with ether, acidified with hydrochloric acid to pH 1, and extracted with chloroform. The ethereal washings after drying and concentrating in vacuo gave 5.10 g of recovered 1-phenyl-2-(4′-hydroxybutyl)cyclopentene. The chloroform extracts were washed with water, dried, and concentrated in vacuo to give 3.95 g of a crude mixture containing *endo*- and *exo*-1-phenyl-5-(4′-hydroxybutyl)-bicyclo[3.1.0]hexanecarboxylic acids. This mixture was chromatographically separated into the isomeric acids on a silica gel (Davison, grade 923, 100–200 mesh) column (740 × 50 mm). Elution was with 27.9 l. of 35% ether–hexane while monitoring the eluent at 254 nm; 20-ml fractions were collected. Fractions 701–866 gave 0.90 g (8.2%) of *endo*-1-phenyl-5-(4′-hydroxybutyl)bicyclo[3.1.0]hexyl-6-carboxylic acid as an oil, and fractions 963–1394 gave 0.85 g (7.8%) of the exo acid as a light brown solid.

The endo acid for analysis was further purified by TLC on a silica gel (Baker, 7GF) plate (20 × 20 cm), eluting with anhydrous ether. The material collected had an R_f of 0.67. The exo acid was further purified by first chromatographing on a 5% (by volume) activated charcoal (Fischer, Darco G-60) in silica gel (Davison, grade 923, 100–200 mesh) column (24 × 1.2 cm), eluting with 17% ether–hexene, then recrystallizing the obtained solid from hexane–acetone. This procedure gave a white crystalline material, mp 121.5–123 °C.

Spectral data for the endo acid are as follows: NMR ($CDCl_3$) δ 0.4–2.9 (m, 13 H, $-CH_2-$ and cyclopropyl methine), 3.1–3.8 (m, 2 H, $-CH_2OH$), 6.8–7.1 (br s, 2 H, $-OH$ and $-CO_2H$), and 7.1–7.5 (m, 5 H, aromatic); ir (neat) 2.70–4.60, 3.28, 3.30, 3.40, 5.18, 5.25, 5.37, 5.92, 6.28, 6.72, 6.98, 7.88, 8.20, 8.50, 9.58, 10.28, 10.44, 11.02, 11.40, 13.20, and 14.32 μm; high resolution mass spectrum (70eV), calcd for $C_{17}H_{22}O_3$ (*m/e*) 274.1568, found (*m/e*) (rel intensity) 274.1573 (38.4), 256 (13.7), 228 (8.9), 215 (18.8), 214 (61.6), 201 (40.1), 197 (30.2), 196 (28.2), 156 (34.2), 155 (100.0), 143 (34.5), 129 (56.5), 115 (41.8), 79 (12.3), and 55 (29.5).

Spectral data for the exo acid are as follows: NMR ($CDCl_3$) δ 0.9–2.9 (m, 13 H, $-CH_2-$ and cyclopropyl methine), 3.3–3.7 (m, 2 H, $-CH_2OH$), 5.4–6.0 (br s, 2 H, $-OH$ and $-CO_2H$), and 6.9–7.4 (m, 5 H, aromatic); ir (KBr) 3.01, 3.40, 3.48, 3.78 (br), 5.99, 7.15, 7.60, 7.99, 8.43, 8.50, 8.81, 9.40, 9.90, 10.68, 11.32, 13.08, and 14.23 μm; high resolution mass spectrum (70 eV), calcd for $C_{17}H_{22}O_3$ (*m/e*) 274.1568, found (*m/e*) (rel intensity) 274.1573 (60.9), 256 (9.6), 228 (9.9), 215 (29.5), 214 (31.7), 201 (27.9), 197 (79.8), 196 (13.8), 156 (28.2), 155 (100.0), 143 (28.2), 129 (31.7), 115 (42.3), 79 (12.5), and 55 (14.7).

1-Phenyl-5-(4′-hydroxybutyl)-6-*endo*-hydroxymethylbicyclo-[3.1.0]hexane (11). To a solution of 149.9 mg (0.06 mmol) of 1-phenyl-5-(4′-hydroxybutyl)bicyclo[3.1.0]hexane-6-*endo*-carboxylic acid in 15 ml of anhydrous ether, 124.4 mg (3.3 mmol) of lithium aluminum hydride was added and the resulting gray mixture was stirred at room temperature under a nitrogen atmosphere for 24 h. The excess lithium aluminum hydride was destroyed by addition of a saturated sodium potassium tartrate solution. The resulting mixture was extracted with ether. The ethereal extracts were then washed with water, dried, and concentrated in vacuo, giving an oil which was purified by preparative TLC on a silica gel (Merck, PF_{254}) plate (20 × 20 cm) using ether as eluent. The band at R_f 0.31 yielded 18.6 mg (13.1%) of 1-phenyl-5-(4′-hydroxybutyl)-6-*endo*-hydroxymethylbicyclo[3.1.0]hexane.

Spectral data are as follows: NMR ($CDCl_3$) δ 0.4–2.8 (m, 13 H, $-CH_2-$ and cyclopropyl methine), 3.0–3.8 (m, 4 H, $-CH_2OH$), and 6.9–7.6 (m, 5 H, aromatic); ir (neat) 3.00, 3.22, 3.24, 3.28, 2.20, 5.15, 5.40, 5.68, 5.89, 6.28, 6.72, 6.98, 7.39, 8.21, 9.53, 9.78, 11.03, 13.18, and 14.32 μm; high resolution mass spectrum (70eV), calcd for $C_{16}H_{24}O_2$ (*m/e*) 260.1776, found (*m/e*) (rel intensity) 260.1776 (45.6), 242 (14.1), 229 (11.5), 215 (20.0), 213 (1.5), 197 (38.2), 187 (38.2), 183 (23.5), 169 (91.2), 156 (23.5), 155 (69.1), 143 (44.1), 141 (47.1), 129 (50.0), 128 (38.2), 117 (29.4), 115 (41.2), and 91 (100.0).

1-Phenyl-5-(4′-hydroxybutyl)-6-*exo*-hydroxymethylbicyclo-[3.1.0]hexane (12). To a solution of 102.8 mg (0.4 mmol) of 1-phenyl-5-(4′-hydroxybutyl)bicyclo[3.1.0]hexane-6-*exo*-carboxylic acid in 15 ml of anhydrous ether, 85.3 mg (2.2 mmol) of lithium aluminum hydride was destroyed by dropwise addition of a saturated sodium potassium tartrate solution. The resulting mixture was extracted with ether. The ethereal extracts were then washed with water, dried, concentrated in vacuo, and purified by preparative TLC on a silica gel (Merck, PF_{254}) plate (20 × 20 cm) with ether as eluent. The band at R_f 0.18 gave 89.3 mg (25.4%) of 1-phenyl-5-(4′-hydroxybutyl)-6-*exo*-hydroxymethylbicyclo[3.1.0]hexane.

Spectral data are as follows: NMR ($CDCl_3$) δ 0.5–3.2 (m, 13 H, $-CH_2-$ and cyclopropenyl methine), 3.3–4.0 (m, 4 H, $-CH_2OH$), and 6.9–7.6 (m, 5 H, aromatic); ir (neat) 3.00, 3.23, 3.27, 3.31, 3.40, 3.49, 5.15, 5.22, 5.34, 5.50, 6.28, 6.71, 6.89, 6.95, 9.50, 9.78, 11.02, 13.20, and 14.34 μm, high resolution mass spectrum (70 eV), calcd for $C_{17}H_{24}O_2$ (*m/e*) 260.1776, found (*m/e*) (rel intensity) 260.1778 (48.8), 242 (22.6), 229 (48.8), 215 (34.2), 213 (33.3), 197 (61.8), 187 (39.8), 183 (27.5), 169 (73.2), 156 (19.5), 155 (63.4), 143 (43.1), 141 (40.6), 129 (42.3), 128 (26.0), 117 (32.5), 115 (24.4), and 91 (100.0).

Equipment and Procedures for Quantum Yield Determinations. Quantum yields were measured using a "linear optical bench" system equipped with a high-pressure, 500-W mercury vapor lamp (Osram HBO-500-w/2), the output of which was focused and passed through a quartz-faced, water-cooled, three-compartment filter solution cell containing, separately, 2 M $NiSO_4 \cdot 6H_2O$ in 5% H_2SO_4, saturated $CoSO_4 \cdot 7H_2O$ in 5% H_2SO_4, and 2×10^{-4} M $BiCl_3$ in 10% H_2SO_4. This combination of filter solutions gave relative transmission characteristics as follows: 230 nm, 0.11%; 250 nm, 36.1%; 275 nm, 84.4%; 300 nm, 63.1%; and 325 nm, 4.4%. The filtered light then passed through two quartz-faced, water-cooled cells aligned in series. During actinometry runs, both the front and back cells were filled with 0.006 M potassium ferrioxalate.[28] During photolysis runs the front cell contained di-π-methane substrate and the back cell the potassium ferrioxalate solution. Light output was determined before and after each photolysis run and was found to be extremely constant (±1.6%).

The quantum yield for the conversion of **6** to **7** was run on a 2.6×10^{-3} M solution of **6** in purified acetonitrile under nitrogen at 29 °C. Product analysis was accomplished by GLC (5 ft × ⅛ in., 1.5% OV-101, 179 °C, 24 ml/min) using benzophenone as an internal standard added after irradiation. The quantum efficiency was found to be 0.013 ± 0.001 at 8.6% conversion.

The quantum yield for the conversion of **23** to **24** was run on a 2.6×10^{-3} M solution of **23** in purified acetonitrile under nitrogen at 29 °C. Product analysis was accomplished by GLC (10 ft × ⅛ in., 1.5% OV-101, 152 °C, 24 ml/min) using benzoin as an internal standard added after irradiation. The quantum efficiency was found to be 0.029 ± 0.002 at 24.5% conversion.

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(11) Despite indications of homogeneity of this material using GLC, LC, and from its ^{1}H NMR and uv spectra, it appears to contain a trace impurity on the basis of exceptionally small spikes seen in its ^{13}C NMR spectrum. Since microanalysis of this material gave an atomic composition exceptionally close to calculated, we assume that the impurity present is a regioisomer of **6**, perhaps having the spiro-1,8-diene structure. This would derive from conjugate addition of hydride to the aluminum complexed allylic alcohol intermediate in the conversion of dienone to diene. Evidence for this type of reaction is present in the literature.[12]

(12) H. J. Williams, *Tetrahedron Lett.*, 1271 (1975), and references cited therein.

(13) Yield is based upon recovered **6**.

(14) By all estimates based upon energetic considerations of simpler transfused model systems, the tricyclic undecene **8** should be of excessively high energy: (a) K. B. Wiberg and A. de Meijere, *Tetrahedron Lett.*, 519 (1969); (b) J. V. Paukstelis and J. L. Kao, *J. Am. Chem. Soc.*, **94**, 4783 (1972).

(15) Energy transfer from both benzophenone (E_t , 68 kcal/mol) and acetophenone (E_T = 74 kcal/mol) triplet to **6**, having a styryl chromophore (E_T = 64 kcal/mol) is expected to occur with a diffusion-controlled rate.[16]

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(17) G. S. Hammond, R. P. Foss, and W. M. Moore, *J. Am. Chem. Soc.*, **83**, 2789 (1961).

(18) The quantum efficiency for formation of the triplet product, 1-phenyl-5-methyl-6-*endo*-(*trans*-1-propenyl)bicyclo[3.1.0]hexane,[1b] was found to be 0.010 ± 0.001.

(19) In other investigations we have found that di-π-methane conformation is also influential in determining the singlet reaction stereochemistry: P. S. Mariano and D. G. Watson, *Tetrahedron Lett.*, 3439 (1975).

(20) Alternately, the conversion of **6** to **7** could follow a nonconcerted reaction pathway through both cyclopropyldicarbinyl and 2-vinyltrimethylene diradical intermediates. Although possible, this mechanism seems unlikely in view of previous observations,[19] which demonstrate that when concerted rearrangement via anti-disrotatory pathways are blocked, the reaction remains stereospecific. Thus, the concerted syn-disrotatory route appears to be the energetically next best mechanistic route for the singlet di-π-methane rearrangement.

(21) The spirodiene and propenylcyclohexene systems being compared have similar structures. Importantly, the two π moieties in each contain the same substitution patterns; one π moiety in each is of the α-alkylstyryl variety and the other of the *cis*-alkylvinyl variety. Indeed, Zimmerman and coworkers have found from single photon counting studies that substituents at C-1, C-3, and C-5 of the 1,4-diene grouping are very important in determining the singlet lifetime, i.e., rate of singlet decay, of di-π-methane systems. As a result of these considerations, it seems reasonable to expect that the spirodiene and propenylcyclohexene will have nearly the same rates of singlet excited-state decay. In that event, the ratio of the quantum yields for reaction would be equivalent to the ratio of rate constants for singlet reaction. H. E. Zimmerman, K. S. Kamm, and D. P. Werthemann, *J. Am. Chem. Soc.*, **96**, 439 (1974).

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(24) Earlier observations in the literature[24a] had shown that cyclopropyldicarbinyl diradical intermediates generated by photodecarbonylation of bicyclo[3.1.0]-hexanones rearrange to vinylcyclopropanes. More recently, Zimmerman and co-workers[24b] have presented compelling evidence that triplet diradicals of this type, generated by sensitized photodecompositions of parent polycyclic diazenes, rearrange in a similar way as do the triplet states of hydrocarbon analogues having barrelene-like structures; (a) L. D. Hess and J. N. Pitts, *J. Am. Chem. Soc.*, **89**, 1973 (1967); (b) H. E. Zimmerman, R. J. Boettcher, N. E. Buehler, and G. Keck, *ibid.*, **97**, 5635 (1975).

(25) An accumulation of results[19,26] have sharpened the initial postulate to include structural constraints which limit free rotation about only the π moiety of lowest triplet energy.

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(27) Another interesting conclusion derives from the postulate presented. The lack of triplet reactivity of **6** and the stereospecificity of the triplet rearrangement of **23** suggest that the conversions of initially formed triplet cyclopropyldicarbinyl diradicals to their corresponding vinylcyclopropanes do not proceed through intermediate 2-vinyltrimethylene diradicals.

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Cyclohexadienyl Cations. 6. Methyl Group Isotope Effects in the Dienone–Phenol Rearrangement

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Abstract: Rates of rearrangement of 4,4-di(trideuteriomethyl)cyclohexadienone (**1-DD**) and 4-methyl-4-trideuteriomethylcyclohexadienone (**1-HD**) are compared with the unlabeled material (**1-HH**). The observed isotope effects are k_{HH}/k_{DD} = 1.149 ± 0.017 and k_{HH}/k_{HD} = 1.060 ± 0.012. The product isotope effect obtained from **1-HD** by converting the rearrangement product to 3,4-dimethyl-4-dichloromethylcyclohexadienone and NMR integration of the two methyl resonances is 1.36 ± 0.05. Suitable combination of these results give $\kappa_H{}^{\alpha}$ (methyl migrational isotope effect) = 1.25 and $\kappa_H{}^{\beta}$ (remnant methyl group isotope effect) = 0.92. The magnitude and direction of these isotope effects are compared with others in the literature.

Introduction

One of the ultimate goals of physical organic chemistry is to obtain structural information for the transition state similar to that now available for stable molecules. However, the lifetime of the transition state prohibits all attempts at studying these high-energy species directly using presently available spectroscopic techniques and structural information must be obtained indirectly. Unfortunately, ordinary substituent effects which might be used to obtain charge distributions for the transition state are very likely to alter in some degree that property which is being determined. On the other hand, isotopic substitution is known[1] not to affect the potential energy surface of a given molecule or transition state. Thus a comparison of rates of reaction which differ only because of isotopic substitution constitutes very nearly a noninteracting probe.

Secondary deuterium isotope effects have been shown to be a powerful tool in the evaluation of force constant changes attending the formation of the transition state.[2,3] An interesting application of the use of secondary deuterium isotope effects has been achieved recently by Schubert and LeFevre.[4,5] They have shown that the secondary isotope effects in a characteristic 1,2-methyl migration (the pinacol rearrangement of 1,1-diphenyl-2-methyl-1,2-propanediol) are 1.205 for the migrating methyl group and 0.978 for the nonmigrating methyl group (remnant methyl group). In a related paper Schubert and Henson[6] have shown that the absence of an appreciable methyl group kinetic isotope effect in the solvolysis of a neopentyl arenesulfonate required that methyl migration was not coincident with ionization. Winnik, Stoute, and Fitzgerald[7] have determined the migrational ($C_6H_5CH_2$, migrating) and