Photochemistry of Bicyclic Compounds. Di-π-methane Rearrangement of 5-Methylene-2-norbornenes[1]

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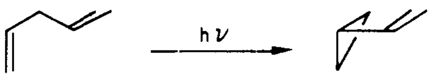
The direct and sensitized photolysis of three substituted methylenenorbornenes, 2–4, has been explored. 5-Benzylidene-2-norbornene (2) undergoes an efficient E–Z photoisomerization from the triplet excited state and a moderate ($\Phi_E = 0.043$, $\Phi_Z = 0.032$) regiospecific di-π-methane rearrangement from the singlet excited state to give 6. Triplet 2 does not rearrange. In contrast, the aliphatic dienes 3 and 4 both give di-π-methane rearrangement products, 8 and 9, respectively, from the triplet [Φ_8(acetone) = 0.32, Φ_9(acetone) = 0.02]. 3 and 4 undergo rearrangement also upon direct irradiation ($\lambda < 254$ nm). The results indicate a distinct substituent effect on the triplet rearrangement efficiency. The role of rotational deactivation processes in governing rearrangement multiplicity and aspects of regiospecificity are discussed.

The di-π-methane (DPM) vinylcyclopropane photorearrangement (eq 1) continues to generate considerable interest as a tool for mechanistic studies of solution photochemistry. The intensive investigations made in the last decade in understanding structure–reactivity relationship in the DPM rearrangement[2] have largely been focused on two subjects: (a) the effect of rotational deactivation processes[3] on the rearrangement efficiency (also called the "free rotor" effect)[4] and (b) the regiospecificity of the rearrangement.



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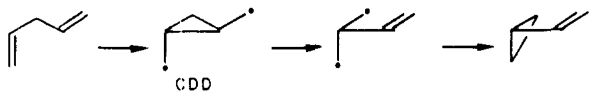
Regarding the former, the ability of 1,4-dienes to undergo DPM rearrangement in competition with rotational deactivation processes has been observed in a wide variety of acyclic,[5–8] monocyclic,[3,9–11] and particularly bicyclic[12–21] systems. This observation led gradually to extension of the "free rotor" rule, first established by Swenton[22] and Zimmerman.[4] Additional rate-governing factors which affect the efficiency of the DPM rearrangement have been introduced including steric effects,[6,23] structural constraint,[19,21,24] energy localization, and radical stabilization substituents.[3,8]



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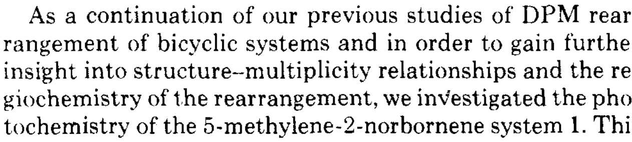
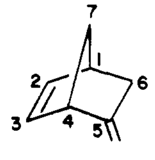
Regiospecificity in DPM rearrangements[2] was first recognized by Zimmerman and Pratt[25] and attributed to the maintenance of maximum delocalization of electrons in the excited state as one proceeds from the transient cyclopropyldicarbinyl diradical (CDD) to product (eq 2). This electronic feature favors the formal 1,2 migration of the less conjugated double bond (eq 3).



3

Several deviations from this rule have been encountered, suggesting alternate factors which might control the direction of rearrangement such as the excited stae multiplicity,[3,20,26] the site of energy localization,[3,27] HOMO–LUMO interaction of the two ethylenic chromophores,[28] and the polarization of the zwitterion excited state.[29]

As a continuation of our previous studies of DPM rearrangement of bicyclic systems and in order to gain further insight into structure–multiplicity relationships and the regiochemistry of the rearrangement, we investigated the photochemistry of the 5-methylene-2-norbornene system 1. This system represents a simple rigid DPM with an exocyclic double bond serving as a built-in potential "free rotor", which can be substituted without major spatial changes of the diene system. However, since the parent compound 1 and its 8-methyl derivative gave only very poor yields of rearrangement products upon direct and sensitized irradiations,[30] we turned our attention to the study of the more promising derivatives 5-benzylidene-2-norbornene (2) and the aliphatic dienes 5-methylene- and 5-ethylidenespiro[bicyclo[2.2.1]hept-2-ene-7,1′-cyclopropane] (3 and 4, respectively).[31,32]



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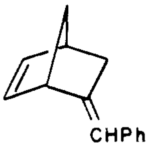

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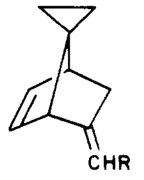

3 R = H

4 R = CH_3

Results

Synthesis and Photochemistry. 5-Benzylidene-2-norbornene (2) (Scheme I). The synthesis of the stereoisomeric mixture of 2 (E and Z) was accomplished by the Wittig reaction of 2-norbornen-5-one (5), prepared according to Freeman,[33] and benzylidenetriphenylphosphorane in THF solution. The mixture consisted of an ca. 2:1 ratio of **2Z**/**2E** by GLC. Alternatively, the reaction of 5 with benzyl diethylphosphonate–NaH in glyme afforded a different mixture consisting of a **2Z**/**2E** ratio of 0.5. The two isomers were separated by GLC and identified by elemental and spectroscopic analyses. The NMR spectra of the isomers resembled each other and that of the parent diene 1. In addition to the aromatic and vinylic protons signals, the spectra consisted of two high-field (δ 1.8–2.7) AB quartets of the two geminal proton pairs at C_6 and C_7, which are further split by the corresponding vicinal protons, and two broad signals at lower field (δ 2.1–3.8) for the two allylic protons, H_1 and H_4. The E–Z configurational assignments were based mainly on the high-field resonance of H_4 in **2Z** (δ 3.24) compared with that of its isomer **2E** (δ 3.72). This upfield shift is due to the phenyl anisotropic effect (see Experimental Section).

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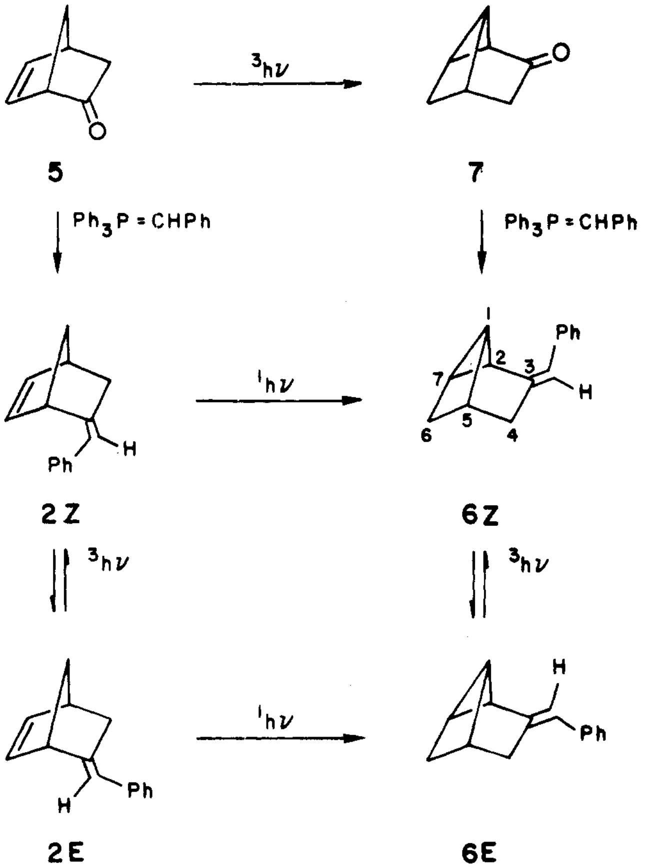
Scheme I. Synthesis and Photochemistry of Benzylidenenorbornene 2



Direct irradiation of either the isomeric mixture or the separate isomers of **2**, at 254 nm (quartz filter), resulted in a fast *E–Z* photoequilibration with the concomitant formation of two isomeric products. These were separated by GLC and identified as **6Z** and **6E** by comparison of their spectral data with those of authentic samples prepared via a Wittig synthesis on ketone **7**, a triplet photo-oxa-DPM product of **5**.[14]

The NMR spectra of the separate isomers show the characteristic features of a tricyclo[3.2.0.0^{2,7}]heptane system,[34,35] particularly as for the high-field H_6 endo proton resonating at $\delta \sim 1.0$ (doublet of doublets, $J = 8.5$ and 2.5 Hz) and H_7 appearing as a multiplet at $\delta \sim 1.7$. The other aliphatic protons form an unresolved complex multiplet at $\delta \sim 2.0$–2.8. Although it was impossible to verify the configuration assignment from these spectra, indirect evidence from irradiation of the separate isomers (vide infra) and the general trend observed in the quantum yield measurements (Table I) support our assignment.

When the separate isomers were directly irradiated to the extent of <5% conversion, a stereospecific rearrangement was observed, indicating the transformations **2Z** → **6Z** and **2E** → **6E**.

The sensitized irradiation of **2** with acetone at 300 nm resulted in isomerization with an *E/Z* photoequilibrium ratio of 1.26 and the formation of only a minute amount of **6** and other unidentified products (<1%).

5-Methylene- and 5-Ethylidenespiro[bicyclo[2.2.1]-hept-2-ene-7,1′-cyclopropane] (3 and 4) (Scheme II). Samples of the aliphatic dienes **3** and **4**, prepared by Ipaktschi,[14,32] were purified by GLC. **4** consisted of a mixture of the two stereoisomers, which could not be separated on a variety of GLC columns. However, it was possible to determine the isomeric ratio by integration of the two different methyl signals (doublets). Upon photoequilibration in acetone, a 1.5 ratio was obtained.

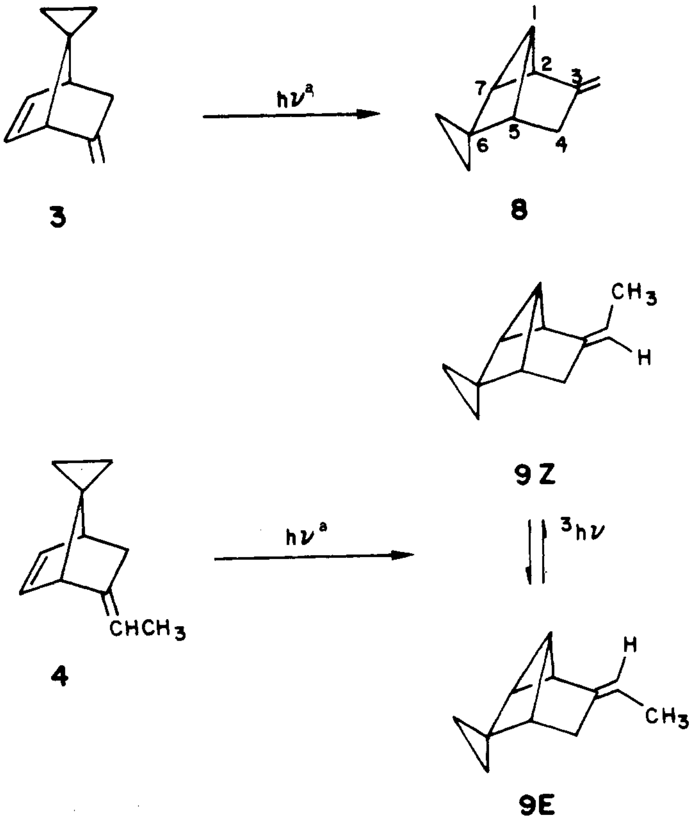
Table I. Quantum Yields of Direct and Sensitzed Irradiations of 5-Methylene-2-norbornenes

	Φ_{DPM}	Φ_E	Φ_Z
	direct[a]		
2E	0.032		0.37
2Z	0.043	0.59	
6E			0.36
6Z		0.54	
	sensitized		
2E[b]	<0.001		0.32
2Z[b]	<0.001	0.62	
6E[b]			0.34
6Z[b]		0.55	
3[b]	0.32		
3[c]	0.44		
4[b,d]	0.02		
4[c,d]	0.08		
9Z[b]		0.42	

[a] Cyclohexane, RPR-2537Å source, quartz filter. [b] Acetone, RPR-3000Å source, chromate filter.[36] [c] Benzene, RPR-2537Å source, quartz filter. [d] *E,Z* mixture.

Direct irradiation (quartz) of **3** in cyclohexane solution using a 450-W medium-pressure mercury lamp afforded a 45% yield of a single isomeric product identified as **8**.[14] Similarly, following Ipaktschi's procedure, acetone-sensitized irradiation of **3** gave a 41% yield of isolated **8**.[14] Photoproduct **8** was also obtained upon benzene-sensitized irradiation of **3** using RPR-2537Å lamps. The NMR spectrum shows, similarly to **6**, characteristics of a tricyclo[3.2.0.0^{2,7}]heptane.[34,35] In addition to the cyclopropane protons multiplet at δ 0.4 and the methylene protons at δ 4.86 and 4.98, the spectrum displayed two multiplets for H_7 and H_5 at δ 1.48 and 2.68, respectively, a triplet at δ 1.98 ($J = 5$ Hz) for H_2, a split AB pattern for the

Scheme II. Photochemistry of Spiromethylenenorbornenes 3 and 4



[a] Direct and sensitized irradiation.

$2H_4$ protons centered at δ 2.18 (J = 14 Hz), and an H_1 multiplet at δ 2.24.

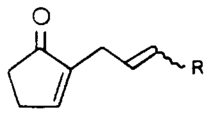
Under similar conditions, irradiation of the isomeric mixture 4, either directly or by sensitization with acetone or benzene, afforded, in addition to a fast isomerization, the two isomers of the DPM rearrangement **9E** and **9Z.** They were separated by GLC and identified by their NMR spectrum, which closely resembled the spectrum of 8 (see Experimental Section). The assignment of configuration was based on the deshielding effect of the C_8 methyl on the H_2 triplet of **9Z** appearing at δ 2.02 as compared to the H_2 signal of **9E** resonating at δ 1.92. Conversely, the upfield part (doublet) of the AB quartet of the H_4 protons moved to a lower field in **9E** as compared to the same signal in **9Z.**

Quantum Yield. Measurements were conducted in deoxygenated cyclohexane solutions for the direct irradiation runs, using RPR-2537Å lamps for the benzylidene compounds (**2,** and **6**). The quantum yields of the sensitized runs were measured using RPR-3000Å lamps for acetone sensitization and the RPR-2537Å lamps for the benzene runs. The cyclopentanone–pentenal actinometer[19,36] was employed. Results are summarized in Table I.

Discussion

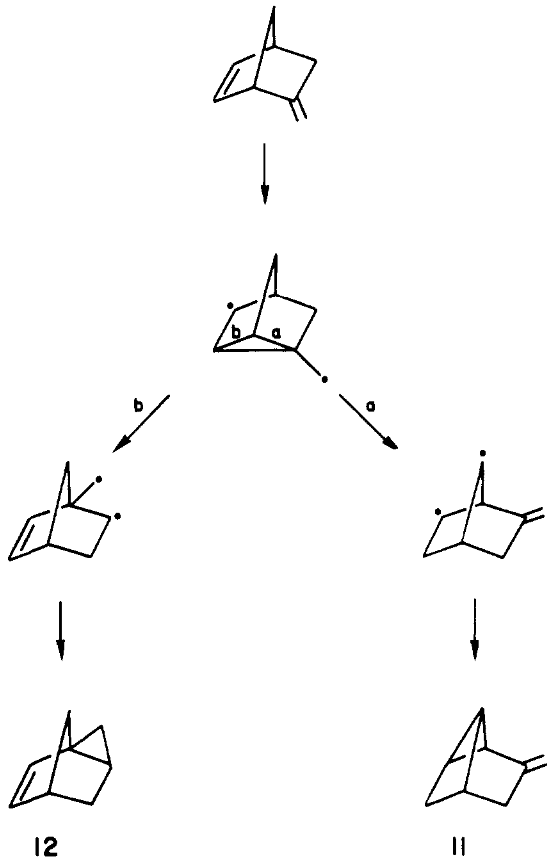
Obviously, the photochemistry of the methylenenorbornene derivatives (**2, 3,** and **4**) involves two competing processes: an *E–Z* isomerization and a regiospecific DPM rearrangement. Both processes have no obvious structural constraints which might prevent their occurrence. The extent of the "free rotor effect" is directly reflected by the *E–Z* isomerizations of **2,** and **4,** while in **3** this rotational deactivation process is a hidden one. The 1,4-diene moeity represents a rigid transoid[37] DPM system in which the two chromophores have a favorable stereochemistry for interaction in the excited state to form the regiochemical guidepost CDD transient en route to vinylcyclopropane (eq 2). Furthermore, it is clear that due to the rigid geometry of the diene system the observed differences in reactivity between the isomers become essentially a function of substituent effects.

Considering first the effect of multiplicity on the mode of reaction, we note that benzylidenenorbornene **2** undergoes a DPM rearrangement only from a singlet excited state, expending the triplet excited state solely for *E—Z* isomerization. In contradistinction, however, aliphatic analogues **3** and **4** undergo a simultaneous isomerization as well as rearrangement from the triplet manifold. Moreover, if we compare the quantum yields of the sensitized reactions (Table I) we note two significant points. Firstly, the quantum yield of DPM rearrangement of **3** [Φ(acetone) = 0.32, Φ(benzene) = 0.44] is of the same magnitude as that of a typical *E–Z* isomerization [e.g., Φ_{9Z}(benzene) = 0.42], indicating that both have practically the same efficiency. Secondly, we observe a substantial decrease in the quantum yield of rearrangement due to methyl substitution in **4** [Φ(acetone) = 0.02, Φ(benzene) = 0.08] as compared to **3** (vide supra). Interestingly, this latter substituent effect has been previously reported by Bullivant and Pattenden[9] in the nonconstrained dienone **10,** where the substitution of methylene (in **10a**) by an ethylidene group (**10b**) completely quenched triplet DPM rearrangement. This rather dramatic substituent effect apparently indicates that the more we stabilize the CDD transient (eq 2) the less efficient will be the triplet DPM rearrangement as compared with rotational deactivation. Assuming other factors to be constant, the efficiency decreases in the order Ph < CH_3 < H for substituents positioned at the end of a free DPM double bond.



10 a. R = H
b. R = CH_3

Scheme III. Mechanism of Di-π-methane Rearrangement of Methylenenorbornene

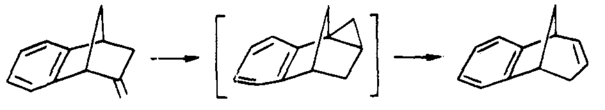


It should be noted at this juncture that the low triplet reactivity of **2E** and **2Z** may be attributed to triplet energy localization in the styryl portion of the molecule (E_T(styrene) = ~62 kcal/mol, E_T(olefin) >75 kcal/mol], which is the site of the competing rotational deactivation process. This argument, presented as a viable rationale for reactivity by Swenton[3] and Hixson,[11] has been recently discussed critically by Zimmerman and Klun.[8]

A further comment is required regarding the effects of substituents at the central carbon of the DMP system in facilitating the rearrangement.[3] Thus, the high reactivity of **3** and **4** as compared with the parent compound **1** (and its 8-methyl derivative) may reflect the cyclopropylcarbinyl stabilization of the diradical transient following the CDD (eq 2).[40]

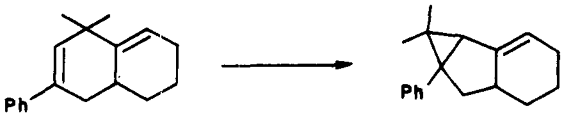
The direct irradiation of **3** and **4** at λ < 254 nm also resulted in DPM rearrangement and isomerization. However, we could not measure the absolute quantum yields nor determine the multiplicity. Nevertheless, since the irradiation in benzene as solvent might to some extent lead to energy transfer from singlet benzene,[38] it is perhaps possible to assess the extent of singlet transfer from the difference between the quantum yields in benzene and in acetone, provided that no solvent effects are involved.

We may now turn to the question of the rearrangement regiochemistry in our system. We note first that the rearrangement is regiospecific, leading to a tricyclic vinylcyclopropane **11** in which the exocyclic double bond is retained regardless of substituents or the excited state multiplicity. This corresponds to route a of the conventional mechanism of DPM rearrangement depicted in Scheme III. For the two aliphatic dienes **3** and **4** this route is expected since maximum odd-electron stabilization during opening of the CDD is maintained.[2,25] However, the same consideration for the phenyl-substituted system **2** would anticipate the preference for route b. We are thus led to the conclusion that route a is exclusively favored in order to avoid the production of the strained vinylcyclopropane **12** obtained via route b. It should be noted that route b is utilized, albeit with low efficiency, in the singlet rearrangement of benzomethylenenorbornene **13**, resulting in the relaxed benzobicyclo[3.2.1]octadiene **14**[39] (eq 4).



13 14 4

A second point of interest is the comparison between the quantum yield efficiencies of the rearrangement of **2** ($\Phi_Z = 0.043$, $\Phi_E = 0.032$) and of the closely related system **15** ($\Phi = 0.097$), recently reported by Zimmerman and Tolbert[37] (eq 5). We clearly observe that although **2** rearranges to **6** via the unexpected route b, it does so with nearly the same efficiency as the anticipated transformation **15** → **16** (via route a), yielding the more stable regioisomeric vinylcyclopropane.



15 16 5

In conclusion, the methylenenorbornene system **1** joins a large group of rigid 1,4-diene systems in which DPM rearrangement from both the singlet and triplet excited states competes with rotational deactivation processes. This work has again demonstrated the importance of substituent effects in determining the efficiency of triplet DPM rearrangements and has confirmed[3] the deactivating effect of a conjugated phenyl group. Finally, it has also been shown that regiospecificty may be controlled by structural constraints of the product vinylcyclopropane.

Experimental Section

General. UV spectra were measured with a Perkin-Elmer Model 402 spectrophotometer. NMR spectra were recorded on a Varian HA-100 spectrometer with Me_4Si as an internal standard. GLC separations were conducted using a Varian Model 90-P chromatograph. GLC analyses were made on a Packard Model 824 chromatograph equipped with a Hewlet-Packard Model 3370B integrator. Analyses were performed at Alfred Bernhard Laboratories, W. Germany.

(*Z*)- and (*E*)-5-Benzylidene-2-norbornene (2). To a THF solution (30 mL) of benzylidenetriphenylphosphorane, prepared from 15.1 g (35 mmol) of benzyltriphenylphosphonium bromide and 14 mL (30 mmol) of 20% BuLi in hexane, was added, under N_2, a solution of 2 g (18.5 mmol) of **5**[14] in 20 mL of dry THF. The mixture was refluxed for 3 h. Acetone (5 mL) was added followed by 20 mL of pentane and anhydrous $MgSO_4$. The mixture was filtered and the solvent removed under vacuum. The residue was distilled (Kugelrohr) at 80 °C/0.15 mm to give 2.9 g (87%) of **2** ($E/Z = 2$). Anal. Calcd for $C_{14}H_{14}$: C, 92.30; H, 7.70. Found: C, 92.02; H, 7.80.

The two isomers were separated on a 2-m 5% Carbowax 20M on Chromosorb W column. Spectral data for **2Z** were as follows: m/e 182; UV (cyclohexane) λ_{max} 253 sh nm (ϵ 22 400), 261 (22 800), 270 (16 100), 285 (1850); NMR (CCl_4) δ 1.52 (2 H, split AB q, J = 8 Hz), 2.24 (2 H, split AB q, J = 14 Hz), 3.04 (1 H, s), 324 (1 H, br s), 6.06 (2 H, br s), 6.36 (1 H, s), 7.15 (5 H, aromatic m). Spectral data for **2E** were as follows: m/e 182; UV (cyclohexane) λ_{max} 255 nm (ϵ 21 500), 296 (590); NMR (CCl_4) δ 1.51 (2 H, split AB q, J = 8 Hz), 2.12 (2 H, split AB q, J = 14 Hz), 2.92 (1 H, br s), 3.72 (1 H, s), 6.12 (3 H, m), 7.15 (5 H, aromatic m).

Alternatively, **2** may be prepared by the following procedure. Sodium hydride (240 mg, 50% in mineral oil) was washed with petroleum ether and covered with dry glyme (20 mL). A solution of benyzyl diethylphosphonate (1.15 g, 5 mmol) and ketone **5** (540 mg, 5 mmol) in 20 mL of dry glyme was added, and the mixture was heated under reflux for 0.5 h. The mixture was decomposed with 100 mL of H_2O and extracted with ether. The ethereal solution was washed with water and dried over $MgSO_4$. Removal of ether and distillation afforded 0.53 g (58%) of **2** (vide supra).

(*Z*)- and (*E*)-3-Benzylidenetricyclo[3.2.0.0^{2,7}]heptane (6). To a THF solution (15 mL) of benzylidenetriphenylphosphorane, prepared from 1.3 g (3 mmol) of benzyltriphenylphosphonium bromide and 1.2 mL (2.5 mmol) of 20% BuLi in hexane, was added 350 mg (1.9 mmol) of ketone **7**[14] in 5 mL of dry THF. The mixture was refluxed for 4 h. Acetone (2 mL) was added followed by 10 mL of pentane and anhydrous $MgSO_4$. The mixture was filtered and concentrated, and the residue distilled at 82 °C/0.1 mm (Kugelrohr) to give 245 mg (70%) of **6** ($Z/E = 1.5$). Anal. Calcd for $C_{14}H_{14}$: C, 92.30; H, 7.70. Found: C, 92.21; H, 7.65.

Spectral data for **6Z** were as follows: m/e 182; UV (cyclohexane) λ_{max} 265 nm (ϵ 19 000), 299 sh (1400); NMR (CCl_4) δ 0.96 (1 H, dd, J = 8.5 and 2.5 Hz), 1.66 (1 H, m), 2.0–2.6 (6 H, m), 6.45 (1 H, br s), 7.15 (5 H, aromatic m). Spectral data for **6E** were as follows: m/e 182; UV (cyclohexane) λ_{max} 263 nm (ϵ 18 000), 299 sh (1150); NMR (CCl_4) δ 1.11 (1 H, dd, J = 8.5 and 2.5 Hz), 1.86 (1 H, m), 2.1–2.8 (6 H, m), 6.4 (1 H, s), 7.2 (5 H, aromatic m).

5-Methylenespiro[bicyclo[2.2.1]hept-2-ene-7,1′-cyclopropane] (3)[14] and the mixture of (*Z*)- and (*E*)-5-ethylidenespiro[bicyclo[2.2.1]hept-2-ene-7,1′-cyclopropane] (4), prepared by Ipaktschi by the Wittig reaction of the corresponding ketone,[32] were purified for preparative photolysis by distillation and further by GLC on a 4-m 15% Carbowax 6000 on Chromosorb W column for quantum yield measurements.

Direct Photolysis of 2. Oxygen-free N_2 was bubbled for 5 min into a solution of 500 mg of **2** in 250 mL of hexane placed in a quartz tube. The solution was irradiated with RPR-2537Å lamps in a Rayonet Model RPR-100 photochemical reactor. Product formation was followed by GLC on a 2-m 8% SE-30 on Chromosorb W column. The irradiation was stopped when there was no further increase in product formation. Removal of solvent and distillation afforded 80 mg of an isomeric mixture of **4E** and **4Z**, identical in all respect with the isomers obtained by direct synthesis (vide supra).

3′-Methylenespiro[cyclopropane-1,6′-tricyclo[3.2.0.0^{2,7}]heptane] (8).[14] Direct Photolysis of 3. A deoxygenated solution of 120 mg of **3** in 50 mL of cyclohexane was irradiated with a 450-W medium-pressure Hg lamp (Hanovia) placed in a water-cooled quartz immersion well. The photolysis was followed by GLC on a 4-m 15% Carbowax 6000 on Chromosorb W column and stopped when there was no increase in product formation. A 54-mg amount of **8** was collected (GLC): NMR (CCl_4) δ 0.40 (4 H, m), 1.48 (1 H, m), 1.98 (1 H, t, J = 5 Hz), 2.18 (2 H, split q, J = 14 Hz), 2.24 (1 H, m), 2.68 (1 H, m), 4.86 (1 H, m), 4.98 (1 H, br s).

Benzene-Sensitized Photolysis of 3. A 103-mg amount of **3** in 20 mL of benzene was irradiated with RPR-2537Å lamps in a quartz tube, affording 42 mg of **8**, identical with that obtained by direct irradiation (vide supra)

(*E*)- and (*Z*)-3′-Ethylidenespiro[cyclopropane-1,6′-tricyclo[3.2.0.0^{2,7}]heptane] (9). Benzene-Sensitized Photolysis of 4. Irradiation of 200 mg of **4** in 100 mL of benzene with RPR-2537Å lamps until no further increase in product formation was observed afforded 64 mg (32%) of a 2:3 isomeric mixture of **9**. Anal. Calcd for $C_{11}H_{14}$: C, 90.41; H, 9.59. Found: C, 90.18; H, 9.47. The isomers were separated on a 4-m 20% Carbowax 6000 on Chromosorb W column. **9E** had the following NMR spectrum: (CCl_4) δ 0.44 (4 H, m), 1.42 (1 H, m), 1.61 (3 H, d, J = 6 Hz), 1.92 (1 H, t, J = 5 Hz), 2.08 (2 H, m), 2.24 (1 H, br s), 2.60 (1 H, m), 5.40 (1 H, split q, J = 6 Hz). **9Z** had the following NMR spectrum: (CCl_4) δ 0.40 (4 H, m), 1.52 (1 H, m), 1.72 (3 H, dd, J = 6 and 2 Hz), 1.91 (1 H, d, J = 14 Hz), 2.02 (1 H, t, J = 5 Hz), 2.18 (1 H, m), 2.30 (1 H, m, J = 14 Hz), 2.60 (1 H, m), 5.32 (1 H, split q, J = 6 Hz).

Quantum yield measurements were performed as previously described,[19] employing the cyclopentanone–pentenal actinometer.[36] Direct irradiations were conducted in cyclohexane solution using NMR quartz tubes placed in a merry-go-round apparatus equipped with an RPR-2537Å lamp. The same conditions were employed in the benzene-sensitized runs. For the acetone-sensitized measurements, RPR-3000Å lamps were employed. The 313-nm region was isolated using the potassium chromate filter solution.[36] Irradiation was conducted in NMR Pyrex tubes. Reactant concentration in the direct runs was high enough to ensure absorption of 99.9% of the light. Low enough concentration was used in the sensitized runs to ensure essentially complete triplet energy transfer. Photolyses were carried out to low conversion (<10%), and the reaction progress was monitored by GLC. Product yields were corrected for variances in detection peak response.

Acknowledgment. We would like to thank Dr. A. Frimer for helpful duscussions. The support of this research by the Bar-Ilan Research Committee under Grant No. 161-84-15-8 is also gratefully acknowledged.

Registry No.—**2E,** 28764-49-0; **2Z,** 28764-48-9; **3,** 37939-96-1; **4E,** 69257-81-4; **4Z,** 69257-82-5; **5,** 694-98-4; **6E,** 69257-78-9; **6Z,** 69257-79-0; **7,** 37939-83-6; **8,** 37939-98-3; **9E,** 69257-83-6; **9Z,** 69257-80-3; benzylidenetriphenylphosphorane, 16721-45-2; benzyltriphenylphosphonium bromide, 1449-46-3; benzyl diethylphosphonate, 1080-32-6.

References and Notes

(1) A preliminary report of these studies has appeared: Z. Goldschmidt and M. Shefi, the 25th IUPAC Congress, Jerusalem, 1975, Abstract No. 19.

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(30) During the preparation of this manuscript a paper appeared by R. G. Weiss and G. S. Hammond, *J. Am. Chem. Soc.*, **100,** 1172 (1978), describing the photochemistry of **1** and some of its derivatives. The low yield of rearrangement, particularly in the sensitized runs, due to side reaction, practically prevented a quantitative study of the DPM rearrangement.

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Photoextrusion of Sulfur Dioxide: General Route to [2.2]Cyclophanes[1]

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The synthesis of cyclophanes **1–5** by the photoextrusion of SO$_2$ from bis sulfones **12–17** is detailed. Yields vary from 32 to 100% and are comparable to the current methods available. The ease of synthesis of the sulfones and the convenience of the cyclophane isolation method suggest that photoextrusion is a useful alternative to other methods. Sensitization with acetophenone is effective for the naphthyl sulfones **15** and **16** while acetone sensitization is ineffective for **12**. Thus, the excited-state precursor is probably a singlet for **1** and a triplet for (±)-**4** and **5**. The reactions occur stepwise going through the monosulfone by loss of the first SO$_2$, followed by photochemical loss of the second molecule of SO$_2$. The intermediate (**24**) can be trapped as a methanol addition product, **23**.

Recent interest in "stacked" π systems[3] and in strained molecules[4] has provided an added stimulus to the search for effective methods for the synthesis of cyclophanes and their analogues[5] and the chemistry of the cyclophanes continues to be a very fruitful area of study.[6] We wish to report the details of our study of the photoextrusion of sulfur dioxide from bis sulfones as a relatively mild, efficient entry into the [2.2]cyclophanes, a subset of this intriguing class of compounds.

Photoextrusion of sulfur dioxide as a route to carbon–carbon single bonds is not a new reaction, having been reported by Cava, Schlessinger, and Van Meter in 1964.[7] However, the method has not found wide application in synthesis[8] and only recently reports by Staab[3c–h] and Boekelheide[4d] have appeared in which substituted cyclophanes have been made by this method.

In conjunction with our studies on the mechanism and scope of the photoextrusion reactions of sulfones,[9a] esters,[9b] and ketones,[9c] the usefulness and application of these reactions to the synthesis of strained molecules was developed. Cyclophanes were chosen as synthetic targets because (1) a wealth of potential applications is available as evidenced by the number of cyclophane analogues known,[3,4,5] (2) the sulfones are readily synthesized, i.e., the sulfide precursors or the sul-