shown in Table II). The mixture was mixed with 2% Na_2CO_3 (200 mL) and was extracted with ether (100 mL × 4). The extract was washed with 1% Na_2CO_3 (100 mL × 2), dried with $MgSO_4$, and concentrated. Kugelrohr distillation of the residual oil gave a mixture of isomers **5** and **6**. Their structures were confirmed by ^1H NMR, GC-MS, and IR spectra. The ratios obtained from peak areas by GLC were corrected according to response factors obtained from mixtures of known concentrations of **5** and **6** (see Table II).

***N*-Methyl-*N*-(2,2-dimethylpropyl)benzylamine (8).** To a mixture of *N*-methylbenzylamine (2.45 g, 20 mmol) and 30% NaOH (7 g) was added pivaloyl chloride (2.60 g, 22 mmol) at 0 °C with vigorous stirring. After the mixture was stirred for 1 h at room temperature, water was added to the mixture. The ethereal extract of the reaction mixture was washed with water, dried, and evaporated to give 3.88 g (94%) of *N*-benzyl-*N*-methylpivalamide: bp 160 °C (12 mmHg, Kugelrohr); ^1H NMR ($CDCl_3$) δ 1.34 (s, 9 H, CH_3), 2.96 (s, 3 H, NCH_3), 4.63 (s, 2 H, NCH_2C), 7.2 (m, 5 H); IR (Nujol) 1635 cm^{-1}; exact mass calcd for $C_{13}H_{19}NO$ 205.1466, obsd 205.1476.

Then a solution of *N*-benzyl-*N*-methylpivalamide (1.527 g, 7.4 mmol) in ether (5 mL) was added slowly to a suspension of $LiAlH_4$ (440 mg, 12 mmol) in ether (5 mL). After the mixture was stirred for 1.5 h at room temperature, the reaction was quenched with a saturated aqueous solution of potassium sodium tartrate, and extracted with ether. The ethereal extract was dried ($MgSO_4$), concentrated, and distilled to give 1.343 g (95%) of **8**: bp 140 °C (120 mmHg, Kugelrohr) [lit. bp 38–41 °C (0.7 mmHg)[7]].

Registry No. **1a**, 51951-99-6; **1b**, 111267-94-8; **1c**, 111267-95-9; **1d**, 111267-96-0; **1e**, 111267-97-1; **2f**, 54600-29-2; **2g**, 17877-17-7; **3a**, 111267-98-2; **3b**, 111267-99-3; **3c**, 111268-00-9; **3d**, 111268-01-0; **3e**, 111268-02-1; **3f**, 111290-73-4; **3g**, 111268-03-2; **5a**, 91338-96-4; **5b**, 70160-72-4; **5c**, 70161-02-3; **5d**, 70160-91-7; **5e**, 6565-69-1; **5f**, 91562-61-7; **5g**, 51180-63-3; **6a**, 73676-26-3; **6b**, 70160-93-9; **6d**, 70160-97-3; **6e**, 5300-21-0; **6f**, 6908-75-4; **6g**, 332-14-9; **7**, 103-83-3; **8**, 68723-29-5; $PhCH_2NHMe$, 103-67-3; $PhCH_2NHPr$-*i*, 102-97-6; *t*-$BuNH_2$, 75-64-9; $PhCH_2NHEt$, 14321-27-8; $ClCH_2TMS$, 2344-80-1; $TMSCH_2NHBu$-*t*, 79250-80-9; $PhCH_2Br$, 100-39-0; $C(Me_3)COCl$, 3282-30-2; $C(Me_3)CON(Me)CH_2Ph$, 73551-24-3; *N*-cyclohexylbenzylamine, 4383-25-9.

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Photosensitized Cope Rearrangement of *syn*-7-(1,2-Butadienyl)bicyclo[2.2.1]hept-2-ene [*syn*-7-(3-Methylallenyl)norbornene]†

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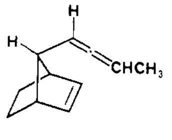

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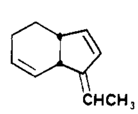

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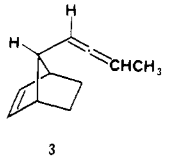

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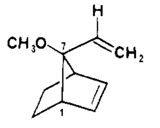

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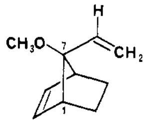

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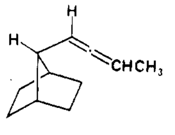

6

Earlier[1] we reported that *syn*-7-(1,2-butadienyl)bicyclo[2.2.1]hept-2-ene (**1**) undergoes a thermal rearrangement above 160 °C to afford racemic trienes **2**, as an approximate 50:50 mixture of *E* and *Z* diastereomers, whereas the anti epimer **3** was found to be thermally stable. Our results were contrasted with those obtained with corresponding vinyl systems.[2] For example,[2b] at 250 °C, *syn*-7-ethenyl-*anti*-7-methoxynorbornene (**4**) and its anti,syn epimer **5** were found to give the same formal Cope product, 1-methoxy-3a,6,7,7a-tetrahydroindene; 2-methoxybicyclo[3.2.2]nona-2,6-diene, a formal [1,3] sigmatropic shift product, was also formed in each case. These results were interpreted in terms of biradical processes initiated by cleavage of the 1,7-bond in **4** or **5**. Furthermore, Berson[3] has found that the parent vinyl hydrocarbon *syn*-7-ethenylnorbornene is stable at 250 °C, and at 320 °C it decomposes without rearrangement. Thus, the allenyl group affords an improved pathway for rearrangement relative to a vinyl group in these systems, and we have interpreted[1b] the **1** → **2** thermal rearrangement in terms of an orbital symmetry allowed[4] $[{}_{\sigma}2_s + {}_{\pi}2_s + ({}_{\pi}2_s + {}_{\pi}2_a)]$ augmented eight-electron pericyclic Cope process.

We now report on a comparative study of the separate triplet-sensitized photochemistry of bicyclic allenes **1** and **3**. In the past[1b] we separated small amounts (<2 mg) of **1** and **3** by reverse-phase HPLC, through a rather tedious procedure and with a low recovery. We have since found that up to 30 μL of a 1/3 mixture can be successfully separated by rotating disk chromatography on a single 1-mm silica gel–silver nitrate rotor by using a hexane–ethyl acetate solvent gradient.

Equal molar amounts of epimers **1** and **3** were separately photolyzed (254 nm) with an equivalent of *p*-xylene in methanol solution. Kropp[5] has reported that irradiation of bicyclo[2.2.1]hept-2-ene (norbornene) in xylene–methanol gave a complex mixture of products including bicyclo[2.2.1]heptane (norbornane), the product of photoreduction. Photolysis of anti allene **3** ($C_{11}H_{14}$) was shown by capillary GC-MS to give a reduced $C_{11}H_{16}$ photoproduct as the only nonpolymeric product. This product was determined to be 7-(1,2-butadienyl)bicyclo[2.2.1]heptane (**6**) by independent synthesis (cf. Experimental Section). As shown in the plot of reaction mixture composition vs irradiation time for **3** → **6** (Figure 1A), the maximum yield of **6** (24%) occurs after about 6 h. Allenylnorbornane (**6**) is remarkably photostable vis a vis **3** (and **1**, see below). When the photolysis was prolonged for a total of 50 h, the yield of **6** only dropped from 24% to 16% in a nearly linear fashion.

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† Taken in part from the 1987 Undergraduate Thesis of K.S.K.

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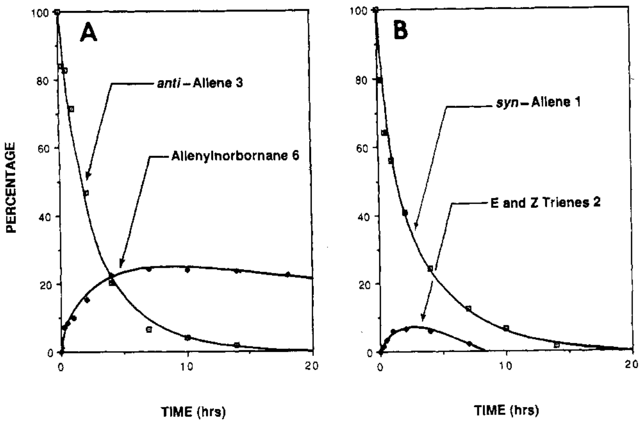
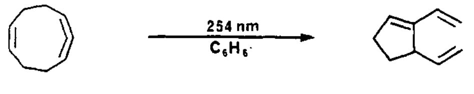


Figure 1. (A) Reaction mixture composition vs irradiation time for the photoreduction of anti allene **3** (7.12 mmol/L initial concentration) to give allenylnorbornane **6**. (B) Reaction mixture composition vs irradiation time for the photoisomerization of syn allene **1** (7.12 mmol/L initial concentration) to *E* and *Z* trienes **2**.

Scheme I

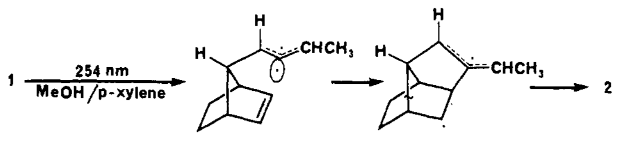


7 **8**

In contrast, the photolysis of syn allene **1** produced no detectable reduced product but rather paralleled the thermal behavior of **1** by affording *E* and *Z* trienes **2** as the only products. Structural identification was made by capillary GC co-injection with authentic material[1b] and by GC-MS. It has not been determined which diastereomer is the major product. Trienes **2** were produced initially (15 min) in a 70:30 ratio of diastereomers, which decreased with time as the trienes polymerized. The photochemistry of cyclic conjugated 1,3-dienes in general appears to be characterized by dimerization and polymerization.[6] A plot of reaction mixture composition vs irradiation time (Figure 1B) depicts a rather low maximum yield for **2** of 8% at about the 2.5-h mark. When a 48:52 diastereomeric mixture of trienes **2** obtained from the thermal rearrangement of **1** in a 1/3 mixture was photolyzed separately, we observed the photoisomerization of one diastereomer to the other as they both polymerized.

The photochemistry of acyclic and monocyclic 1,2,6-trienes has previously been studied by others.[7] To our knowledge, the results reported here are the first involving the photolysis of a 1,2,6-triene which is in part contained in a bicyclic ring system. In the first comprehensive paper on allene photochemistry, Ward and Karafiath[7a] reported that the monocyclic 1,2,6-cyclononatriene (**7**) afforded 2,3-divinylcyclopentene (**8**) upon benzene-sensitized photolysis in the vapor phase (Scheme I). The authors were unable to rule out an indirect mechanism for the **7** → **8** process involving two consecutive [1,3] sigmatropic shifts. This mechanism seems especially implausible in the present case of the **1** → **2** photoisomerization, however, since the first [1,3] sigmatropic shift would not require the double bond of the norbornene ring, and consequently anti allene **3** might be expected to rearrange to **2** as well. Furthermore, under conditions for which **1** and **7** might rearrange by [1,3] sigmatropic shifts, one might expect the remarkably photostable allenylnorbornane **6** to rearrange by a [1,3] sigmatropic shift as well. Similarly, any mechanism involving early cleavage of the 1,7-bond in **1**, such as in the biradical mechanism proposed by Berson[2] for the thermal rearrangement of **4** and **5**, can be discounted.

Scheme II



9 **10**

We currently favor a mechanism for the **1** → **2** process similar to the one envisioned for the **7** → **8** rearrangement by Johnson[8] in a recent review of cumulene photochemistry. The key process is considered to be nonvertical energy transfer to give a bent planar triplet allene. This process is supported by theoretical calculations by Pople and co-workers[9] who have shown that the lowest triplet state of allene is a bent planar species of C_{2v} symmetry found to have an energy of 47.7 kcal/mol above the ground state. It is also found to be 2.4 kcal/mol lower in energy than the lowest energy singlet state and 6.7 kcal/mol lower than the linear D_{2h} planar triplet, as well as to have a CCC angle of 135.4°. Subsequent calculations by Pasto and co-workers[10] are also in general agreement with these results.

The mechanism for the **1** → **2** rearrangement is then expected to involve two intermediate biradicals **9** and **10** in the stepwise Cope rearrangement shown in Scheme II. Ward and Karafiath[7a] originally characterized their observed **7** → **8** photorearrangement as involving a vibrationally excited ground electronic state planar allene, arguing that the **7** → **8** conversion had also been accomplished thermally.[11] This proposal, which would require that the planar ground-state allene be formed (1) by intersystem crossing from the planar triplet, (2) by decay of a planar excited state, or (3) from the decomposition of an allene-photosensitizer adduct, seems unnecessarily complex to us.

An allowed augmented $[{}_\sigma 2_s + {}_\pi 2_s + ({}_\pi 2_s + {}_\pi 2_s)]$ excited-state concerted Cope process, paralleling the allowed $[{}_\sigma 2_s + {}_\pi 2_s + ({}_\pi 2_s + {}_\pi 2_a)]$ pericyclic process we have proposed for the thermal **1** → **2** rearrangement, is unlikely for the triplet-sensitized photorearrangement. Nevertheless, a parallel does appear to exist. The singly occupied hybrid orbital of the conformationally restricted biradical **9**, perpendicular to the allyl radical moiety, is in excellent position for favorable overlap with the π-bond of the norbornene ring in the conformation shown (Scheme II). Thus the **9** → **10** fragment of the overall **1** → **2** photo-Cope process (Scheme II) appears to be augmented by the hybrid orbital perpendicular to the planar allenyl moiety of **9** in much the same way as the antiplanar allenyl component of **1** appears to augment the concerted **1** → **2** thermal process.[1]

As reported by others,[8,12] the field of allene photochemistry has been rather neglected. We hope this study may

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contribute to the rekindling of interest in this general area.

Experimental Section

General. ^{1}H NMR spectra were recorded on a Varian EM-360L (60-MHz) NMR spectrometer with tetramethylsilane as internal standard. IR spectra were recorded on a Beckman IR-8 spectrometer. Mass spectra were obtained at 70 eV on a CEC-21-110B mass spectrometer and GC-MS with a Finnigan Model 4000 mass spectrometer, equipped with an Incos data system. Capillary GC analysis was performed with a Hewlett Packard Model 5790 gas chromatograph equipped with a flame ionization detector and a J&W DB-5 fused silica gel column (30 M × 0.255 mm i.d.; 0.25 μM film thickness). All the analyses were performed with a flow rate of 1 mL/min and with oven, injector, and detector temperatures of 90 °C, 250 °C, and 300 °C, respectively. Integrations and retention times were obtained with a Hewlett Packard Model 3390A integrator. Retention times (min) for compounds **1**, **2**, **3**, **6**, *p*-xylene, and undecane were found to be 11.7, 16.3/16.8, 11.4, 14.0, 3.5, and 9.3, respectively. Preparative GC was performed with a Varian Model 1520 gas chromatograph equipped with a thermal conductivity detector and a 10 ft 3 in. × $^3/_8$ in. column of Carbowax 20M on 80/100-mesh Chromosorb W-NAW. Helium was used as the carrier gas and liquid N_2 was used to condense the samples in collectors protected from moisture with $CaSO_4$. Rotating disk chromatography was performed with a Harrison Research Model 7924T "Chromatotron" using a 1-mm rotor coated with silica gel 60, PF-254 (EM Reagents 7749), and containing 3.85% silver nitrate. The coating of the rotor with silica gel/$AgNO_3$ followed the recipe provided by Harrison Research.

All glassware was cleaned in a KOH/2-propanol bath and then rinsed with dilute acetic acid followed by dilute ammonium hydroxide and finally distilled water before drying in an oven. Methanol (EM Science Omnisolv) was distilled from magnesium methoxide immediately prior to use. Microanalyses were performed by R. Wielesek at the University of Oregon, Eugene, OR.

Preparation of Samples of Syn Allene 1 and Anti Allene 3 for Photolysis. A mixture of **1** and **3** was prepared according to the method previously described.[1] Approximately 30 μL of a 40:60 mixture of **1** and **3** in 300 μL of hexane was applied to a silica gel/$AgNO_3$ rotor of a rotating disk chromatograph and first eluted with 75 mL of hexane. Elution was completed with three 75-mL portions of hexane containing 5%, 10%, and finally 20% by volume of ethyl acetate. In all, 75, 4-mL fractions were collected. Anti allene **3** was found to elute in fractions 31–38 and syn allene **1** in fractions 44–52 by capillary GC analysis. Solutions of **1** and **3** were concentrated below a Vigreux column with gentle heating and then solvent-free samples were obtained from the concentrated solutions by preparative GC (flow rate 40 mL/min, oven temperature 150 °C, injector temperature 150 °C, detector temperature 175 °C, retention time 24 min).

Preparation of a Sample of Trienes 2 for Photolysis. The sample was obtained from the thermal rearrangement of allene **1** on the preparative GC. Three injections of 10 to 15 μL each of a 46:54 mixture of **1** and **3** were made (flow rate 15 mL/min, oven temperature 220 °C, injector temperature 300 °C, detector temperature 230 °C). Approximately 12 mg of a 48:52 mixture of the diastereomers of **2** (retention time 31.5 min) and 20 mg of residual anti allene **3** (retention time 20.3 min) were obtained.

Photolyses of *syn*- and *anti*-7-(1,2-Butadienyl)bicyclo[2.2.1]hept-2-ene (1 and 3) [cf. Figure 1]. A 5.2-mg (35.6 μmol) sample of **1** or **3** was combined with 3.9 mg (36.7 μmol) of *p*-xylene (MCB) and 5.6 mg (35.8 μmol) of undecane (internal standard) in 5 mL of dry methanol in a 13 × 100 mm quartz tube. The tubes were sealed with septa and N_2 was bubbled through the solutions for 15 min immediately prior to irradiation.

The samples were irradiated for up to 50 h at a distance of 6 cm by using a Vicor-filtered Hanovia 450-W medium-pressure mercury arc lamp in a carrousel reaction apparatus. The course of the reactions was followed by monitoring the integrated intensity of the starting materials and products vs undecane on the capillary GC. Allene **1** was found to give *E* and *Z* trienes **2** as the only nonpolymeric product, whereas allene **3** gave only the reduced product **6**. A response ratio of 0.84 was determined for the 1/3 mixture vs undecane and used to correct the integrals for **1**, **3**, and **6**. Similarly, a response ratio of 1.3, determined for the mixture of both diastereomers of **2**, was used to correct the integrals for each separate diastereomer. The results are plotted in Figure 1.

Photolysis of a Mixture of (*E*)- and (*Z*)-1-Ethylidene-3a,4,5,7a-tetrahydroindene (2). This photolysis was carried out in the manner described above on a 20.0-mg (66 μmol) sample of a 48:52 mixture of the two diastereomers of **2**, using an equivalent each of *p*-xylene and undecane. Capillary GC analysis of the reaction mixture monitored over time revealed that one of the trienes first isomerized to the other before both of them completely polymerized over the course of a 28-h period.

Preparation of 7-(1,2-Butadienyl)bicyclo[2.2.1]heptane (6). The general procedure[1] used to prepare a mixture of **1** and **3** was followed with a substitution of 7-bromonorbornane[13] (1.5 g) for the *syn*-7-bromonorbornene: IR (neat) 2960, 2920, 2880, 1980 (C=C=C), 1480, 1460, 1440, 1375, 1350, 1310, 1275, 1255, 1210, 1185, 1135, 1075, 980, 870, 830, 775, 705, 675 cm^{-1}; ^{1}H NMR (60 MHz, $CDCl_3$) δ 0.9–2.1 (m, 11 H), 1.6 (dd, 3 H), 4.8–5.1 (m, 2 H); MS (EI), *m/z* (rel intensity) 148 (M^+, 13), 133 (10), 120 (15), 119 (27), 105 (45), 94 (88), 91 (85), 80 (100), 79 (100), 77 (40), 67 (30); high resolution MS (EI), *m/z* (M^+) calcd 148.125, obsd 148.125. Anal. Calcd for $C_{11}H_{16}$: C, 89.12; H, 10.88. Found: C, 88.83; H, 11.17. The photoreduction product **6** obtained from **3** had the same retention time (14.0 min) on the capillary GC (co-injection) and gave an identical mass spectrum as the product prepared above.

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Addition of *tert*-Butyl Hypoiodite to Selected Olefins

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In a continuation of our investigation of the electrophilic additions of alkyl hypohalites[1,2] to olefins, we report on

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(1) For previous studies on the addition of alkyl hypochlorites to olefins and dienes, see: (a) Heasley, G. E.; McCully, V. M.; Wiegman, R. T.; Heasley, V. L.; Skidgel, R. A. *J. Org. Chem.* **1976**, *41*, 644. (b) Heasley, G. E.; Emery, W. E. III; Hinton, R.; Shellhamer, D. F.; Heasley, V. L.; Rodgers, S. L. *Ibid.* **1978**, *43*, 361. (c) Heasley, V. L.; Shellhamer, D. F.; Gipe, R. K.; Wiese, H. C.; Oakes, M. L.; Heasley, G. E. *Tetrahedron Lett.* **1980**, *21*, 4133. (d) Heasley, V. L.; Gipe, R. K.; Martin, J. L.; Wiese, H. C.; Oakes, M. L.; Shellhamer, D. F.; Heasley, G. E.; Robinson, B. L. *J. Org. Chem.* **1983**, *48*, 3195 and other references included therein.