2h, 100-46-9; **2i**, 110-91-8; **3a**, 1696-17-9; **3b**, 1759-68-8; **3c**, 2782-40-3; **3d**, 10546-70-0; **3e**, 5705-57-7; **3f**, 3278-14-6; **3g**, 18838-10-3; **3h**, 1485-70-7; **3i**, 1468-28-6; **4A**, 868-85-9; **4B**, 762-04-9; **4C**, 1809-20-7; **4D**, 1189-24-8; **4E**, 2283-25-2; **4F**, 1809-15-0; **5A**, 16115-01-8; **5B**, 18104-91-1; **5C**, 74449-29-9; **5D**, 74449-30-2; **5E**, 74449-31-3; **5F**, 74465-43-3; **6**, 16180-99-7; **8**, 33327-40-1; **9**, 33876-85-6; **10**, 3266-66-8; **11f**, 877-95-2; **11h**, 588-46-5; **12**, 20427-93-4; trimethyl phosphite, 121-45-9; triethyl phosphite, 122-52-1; triisopropyl phosphite, 116-17-6; triisobutyl phosphite, 1606-96-8; tri-*sec*-butyl phosphite, 7504-61-2; tris(1-ethylpropyl) phosphite, 19322-55-5; benzoyl chloride, 98-88-4; phosphorus trichloride, 7719-12-2; 3-pentanol, 584-02-1; ethyl diethylphosphinite, 2303-77-7; ethyl dichlorophosphite, 1498-42-6; ethyl bromide, 74-96-4; trimethylsilyl bromide, 2857-97-8; *N*-benzoyl-*N*-cyclohexylbenzamide, 74449-32-4; *N*-benzoyl-*N*-butylbenzamide, 73491-45-9; *N*-benzoyl-*N*-propylbenzamide, 74449-33-5; *N*-benzoyl-*N*-isobutylbenzamide, 73491-46-0; *N*-benzoyl-*N*-phenethylbenzamide, 74449-34-6; *N*-benzoyl-*N*-benzylbenzamide, 19264-38-1.

Thermal Rearrangement of 5,6-Benzotricyclo[3.2.0.0^{2,7}]hept-5-ene into 2-Vinylindene via an Intramolecular Retro-Diels–Alder Reaction

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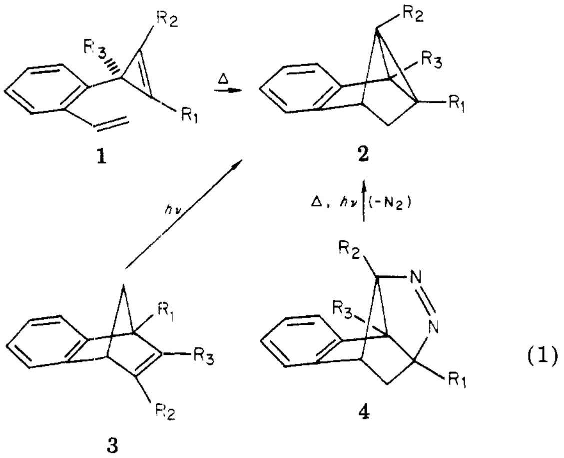
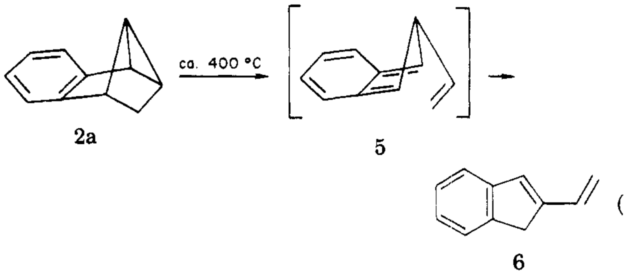
Flash vacuum pyrolysis of the 5,6-benzotricyclo[3.2.0.0^{2,7}]hept-5-ene (**2a**) at ca. 400 °C at 0.7 torr afforded quantitatively 2-vinylindene (**6**). Catalytic hydrogenation of **6** gave 2-ethylindane, thereby unequivocally confirming the proposed 2-vinylindene structure **6**, resulting from intramolecular retrocyclic Diels–Alder reaction of **2a**. Singlet oxygen and PTAD led to the expected cycloadducts, respectively, the endoperoxide **7** and the urazole **8**. It was not possible to trap the postulated isoindene with PTAD.

A recent communication[2] reports the synthetically valuable and mechanistically interesting thermal isomerization of 3-(2-styryl)-substituted cyclopropene **1** into benzotricyclo[3.2.0.0^{2,7}]heptene **2**, the di-π-methane rearrangement product[3] of benzonorbornadienes **3** (eq 1). In connection with our mechanistic work[4] on the thermal and photochemical denitrogenation of azoalkane **4** as an entry into the diradical intermediates that are postulated in the di-π-methane rearrangement **3** → **2**, we examined the thermal stability and behavior of the tricycloalkene **2**. Presently we report our results of this study.



(1)

Preliminary thermolysis attempts on the parent tricycloalkene **2a** in solution at elevated temperatures (>200 °C) led to a complex mixture of products. For this reason we examined the vacuum flash pyrolysis by volatilizing **2** at ca. 60 °C and 0.7 mmHg through a hot Pyrex tube and condensing the effluent in a dry ice cold trap. Exceedingly high temperatures (ca. 400 °C) were necessary under these conditions to effect the thermal decomposition of the tricycloalkene **2**, affording 2-vinylindene (**6**) in quantitative yield (eq 2).



(2)

Confirmation of the indene structure **6** rests on satisfactory elemental composition for $C_{11}H_{10}$ by combustion analysis and ^{1}H NMR, IR, and UV spectral data (cf. Experimental Section). However, since reasonable mechanisms can be envisaged for the production of the isomeric 3-vinylindene, it was essential to conduct chemical transformations for rigorous confirmation of the proposed 2-vinylindene structure **6**. For example, on catalytic hydrogenation (Pd/C) **6** was transformed quantitatively into 2-ethylindane, as confirmed by comparison of the physical constants with the authentic material.[5] Unequivocal assignment of the hydrogenation product as 2-ethyl- rather than 3-ethylindane could be made by ^{13}C NMR. As expected, the more symmetrical 2-ethyl isomer exhibits four

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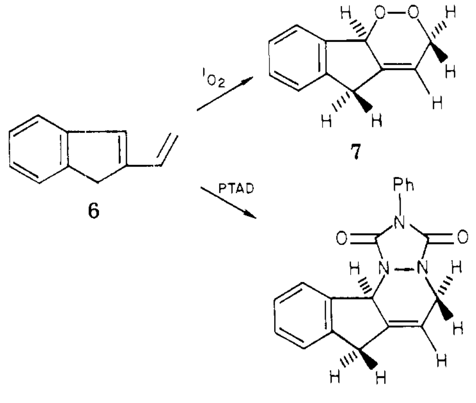
aliphatic carbon resonances, i.e., a quartet and triplet of the ethyl group, a doublet for the methinyl ring carbon, and a triplet for the methylenic ring carbon.

As a chemical structure proof, we examined the cycloaddition of singlet oxygen and *N*-phenyl-1,2,4-triazoline-3,5-dione (PTAD) with indene **6**. For example, singlet oxygenation of **6** in CCl_4 at 0 °C, using tetraphenylporphyrin as sensitizer, gave the expected cycloadduct **7** (eq 3), which exhibited a satisfactory elemental composition for $C_{11}H_{10}O_2$ by combustion analysis. The ^1H NMR spectrum of the singlet oxygen adduct is consistent with the endoperoxide **7** derived from the 2-vinylindene (cf. Experimental Section).[6] Also the (2 + 4) cycloaddition with PTAD again gave the expected urazole **8**. The ^1H NMR spectrum was similar to that of the endoperoxide **7** and consistent with the cycloadduct derived from the 2-vinylindene (cf. Experiment Section). Consequently, the cycloadducts **7** and **8**, respectively, derived from the reaction of $^1O_2$ and PTAD with the thermolysis product of the tricycloalkene **2**, confirm the proposed 2-vinylindene structure **6**.



(3)

A reasonable mechanism for the thermal rearrangement **2a** → **6** is via the intermediary isoindene **5** (eq 2), formed by intramolecular retro-Diels-Alder reaction. Subsequently, a facile hydrogen 1,5 shift in **5** affords the more stable aromatized 2-vinylindene **6**.[7] Indeed, the intermediate temperature (2 + 2) cyclization of *o*-styryl-2-cyclopropenes into tricyclo[3.2.0.0^{2,7}]alkenes (eq 1), followed by high-temperature (2 + 4) retrocyclization into 2-vinylindenes (eq 2), i.e., the overall process **1** → **2** → **6**, should be of synthetic potential, especially in view of its regioselectivity and efficiency.

Experimental Section

Flash Vacuum Pyrolysis of 5,6-Benzotricyclo[3.2.0.0^{2,7}]-hept-5-ene (2a). A 100-mg sample of the tricycloalkene **2a** was placed into a 10-mL, round-bottomed flask and connected to the pyrolysis apparatus, consisting of a heavy-walled Pyrex tube (12-mm o.d.) and heated with Nichrome resistance wire. On heating at ca. 60 °C bath temperature and 0.7 torr, the sample was volatilized through the hot tube kept at ca. 400 °C, condensing the effluent in a dry ice cold trap. A colorless waxy product was obtained quantitatively, which was purified by VPC collection on a 6 ft × 0.25 in. stainless-steel column, packed with 10% SE-30 on Chromosorb W (80–100 mesh), at a column temperature of 100 °C and a carrier gas (He) flow of 25 mL/min. Molecular distillation afforded a colorless wax: mp 42–43 °C; $C_{11}H_{10}$ elemental composition by combustion analysis; ^1H NMR (CCl_4, Me_4Si) δ 3.43 (2 H, br s, H_3), 4.85–5.45 (2 H, AB part of the ABC system, vicinal vinyl H), 6.30–6.70 (1 H, C part of the ABC system), 6.6 (1 H, s, H_1), 6.8–7.35 (4 H, m, C_6H_4); IR (CCl_4) 3080, 3060, 3015, 2990, 2960, 2900, 1623, 1465, 1400, 1360, 1250, 1205, 1135, 985, 900, 870, 715 cm^{-1}.

Hydrogenation of 2-Vinylindene (6). Catalytic hydrogenation of **6** over Pd/C (10%) in ethyl acetate afforded quantitatively 2-ethylindane, which was purified by Kugelrohr distillation: colorless liquid; bp 85 °C (1 torr) [lit.[5] bp 100–105 °C (4 torr)]; n^{26}_D 1.5160; $C_{11}H_{14}$ elemental composition by combustion analysis; ^1H NMR (CCl_4, Me_4Si) δ 0.75–1.10 (3 H, pseudo t, CH_3), 1.20–1.80 (2 H, m, CH_2), 2.10–3.20 (5 H, m, aliphatic ring H), 6.80 (4 H, br s, C_6H_4); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 12.80 (q, CH_3), 28.65 (t, CH_2), 39.19 (t, ring CH_2), 42.11 (d, ring CH), 124.54 and 126.19 (d, aromatic), 143.83 (s, aromatic); IR (CCl_4) 3080, 3050, 3025, 2960, 2940, 2880, 2860, 2840, 1485, 1460, 1380, 1300, 1220, 1085, 1025, 940 cm^{-1}.

Singlet Oxygenation of 2-Vinylindene (6). A 0.1 M solution of **6** in CCl_4, containing ca. 1 mg of tetraphenylporphyrin (TPP), was irradiated with a General Electric 150-W sodium street lamp at 0 °C, while the solution was stirred magnetically and a vivid stream of oxygen was passed through the reaction mixture. The reaction progress was monitored by ^1H NMR. After 2 h the substrate was consumed, the solvent was roto-evaporated [ca. 25 °C (10 torr)], and the residue was Kugelrohr distilled at ca. 100–110 °C (0.7 torr), affording a pale yellow oil in 90% yield: n^{26}_D 1.5790; $C_{11}H_{10}O_2$ elemental composition by combustion analysis; ^1H NMR (CCl_4, Me_4Si) δ 3.53 (2 H, br s), 4.27 and 4.70 (2 H, complex AB pattern, J_{AB} = 16.60 Hz), 5.62 (1 H, narrow m), 5.87 (1 H, narrow m), 7.13 (4 H, br s).

Cycloaddition of PTAD and 2-Vinylindene (6). To a solution of 47 mg (0.33 mmol) of the diene **6** in 5 mL of CH_2Cl_2 was added portionwise 58 mg (0.34 mmol) of freshly sublimed PTAD, while the solution was stirred magnetically at ca. 30 °C. After complete addition of the PTAD, a yellow solution was obtained, the solvent was roto-evaporated [ca. 25 °C at (15 torr)], and the residue was chromatographed on silica gel (ca. 2 g), eluting with CH_2Cl_2. Recrystallization from ethanol afforded colorless plates in 85% yield: mp 168–169 °C; $C_{19}H_{15}N_3O_2$ elemental composition by combustion analysis; ^1H NMR ($CDCl_3$, Me_4Si) δ 3.54 (2 H, br s), 3.5–4.7 (2 H, complex AB pattern, J_{AB} = 18.67 Hz), 5.37 (1 H, br s), 5.65 (1 H, br s), 7.05 and 8.18 (4 H, m, C_6H_4), 7.30 (5 H, m).

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Registry No. 2a, 7213-64-1; **6**, 24459-98-1; **7**, 74420-41-0; **8**, 74420-42-1; 2-ethylindane, 56147-63-8; PTAD, 4233-33-4.

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(7) It is known that isoindenes readily undergo allowed 1,5 sigmatropic shifts, affording indene derivatives.[8] Efforts to trap the isoindene, which was condensed onto a liquid N_2 coldfinger, by reacting the condensate with PTAD at low temperature only afforded adduct **8**.

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