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Kinetic stabilization of the *o*-quinoidal 3,4-benzotropone system

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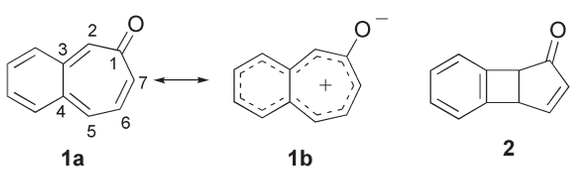
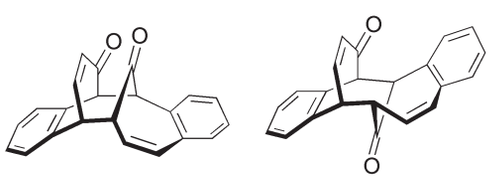
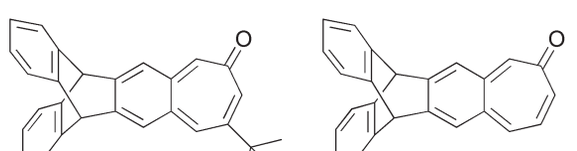
Kinetic stabilization of the *o*-quinoidal 3,4-benzotropone system was investigated. The parent 3,4-benzotropone **1** undergoes rapid [π8 + π10] dimerization in fluid solution even at −78 °C while triptycene-fused derivative **5** having a *tert*-butyl group at the C(6) position of the tropone moiety was found to be stable indefinitely under similar conditions. The relative importance of the triptycene moiety and the *tert*-butyl group in **5** for the kinetic stabilization was evaluated.

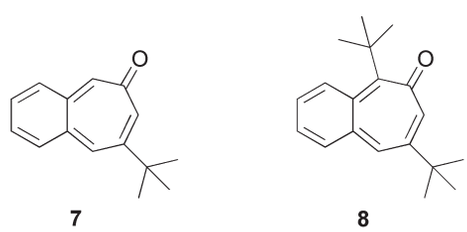
Introduction

3,4-Benzotropones, in which the benzo component is fused to the tropone ring in a manner to form an *o*-quinoidal structure, have long been a subject of theoretical[1] and experimental[2,3] interest. We have previously reported[4] the generation of the parent 3,4-benzotropone **1** using the electrocyclic ring-opening reaction of the corresponding benzocyclobutene isomer **2**. UV-vis and IR spectroscopic studies have revealed that **1** is electronically significantly polarized in the ground state, consistent with a substantial contribution of polarized resonance structure **1b**. Despite the unique electronic structure, however, the thermal instability of **1** has thwarted the exploration of its physical and chemical properties; **1** is persistent only under matrix isolation conditions at low temperature and is rapidly consumed in fluid solution even at −78 °C. We were interested in investigating the kinetic stabilization[5] of **1** to gain a more detailed understanding of this system. The lability of *o*-quinoidal **1** arises from its high propensity to undergo dimerization to form dimers **3** and **4**. This tendency suggests that the system may be kinetically stabilized, to some extent at least, by introducing sterically demanding substituents that specifically shield the reaction sites, and we designed derivatives **5**–**8**. Herein we report the results of synthetic investigation of **5**–**8** aimed at generating the kinetically stabilized derivatives of **1**.









Results and discussion

A major path of the thermal decomposition of **1** is a kinetically controlled [π8 + π10] dimerization at the 2,5- and 2,7-positions to form **3** and **4**.[4] To prevent such dimerization, triptycene-fused derivative **5** having a *tert*-butyl group at the C(6) position was designed as an initial target molecule. Related compounds **6** and **7** were also investigated to evaluate the relative importance of the *tert*-butyl group and the fused triptycene moiety for the kinetic stabilization of this system.

On the basis of our previous successful generation of **1** from the corresponding benzocyclobutene valence isomer **2**, we envisaged **13** as a promising precursor for **5**, and **13** was prepared as outlined in Scheme 1. Thus, addition of benzyne to **9**[6] afforded triptycene derivative **10** in 73% yield. Bromination of **10** followed by dehydrobromination and deprotection afforded enone **12** in 47% yield. 1,2-Addition of *tert*-butyllithium to **12** followed by PCC oxidation produced **13** in 61% yield. On the other hand, 1,2-addition of *tert*-butyllithium to **2**[4] followed by PCC oxidation produced **14** in 58% yield (Scheme 2).

The photochemical generation of **5** from **13** was examined under matrix isolation conditions at low temperature and the reaction was monitored by UV-vis spectroscopy. When a degassed EPA (a 5 : 5 : 2 mixture of ether, isopentane, and ethanol) solution of **13** in a Pyrex tube was frozen at liquid nitrogen temperature (−196 °C) and irradiated with a high-pressure mercury lamp, a new absorption extending to long-wavelength region with λ_{max} around 450 nm was observed (Fig. 1). This newly developed absorption is almost superimposed on that reported[4] for **1** with λ_{max} at 353, 372, 392, 458, 482 (sh), 506 (sh) and 518 (sh) nm. Similarly, irradiation of **12** or **14** in an EPA glass at −196 °C led to the development of a new absorption characteristic of the 3,4-benzotropone system (see experimental section). Thus, we concluded that 3,4-benzotropone derivatives **5**, **6** and **7** were generated photochemically from **13**, **12** and **14**, respectively. The generated orange species **5**–**7** were stable in the frozen EPA glass, but were consumed smoothly in the fluid EPA solution at 0 °C. The decay of the absorption followed second-order kinetics (Fig. 2), so that dimer formation should be still a dominant pathway for their thermal decomposition. The rate constants (Table 1) for the dimerization of **5**, **6** and **7** in EPA at 0 °C were determined to be 30 ± 6 M^{-1} s^{-1}, 166 ± 33 M^{-1} s^{-1} and 60 ± 12 M^{-1} s^{-1}, respectively. These observations demonstrate that

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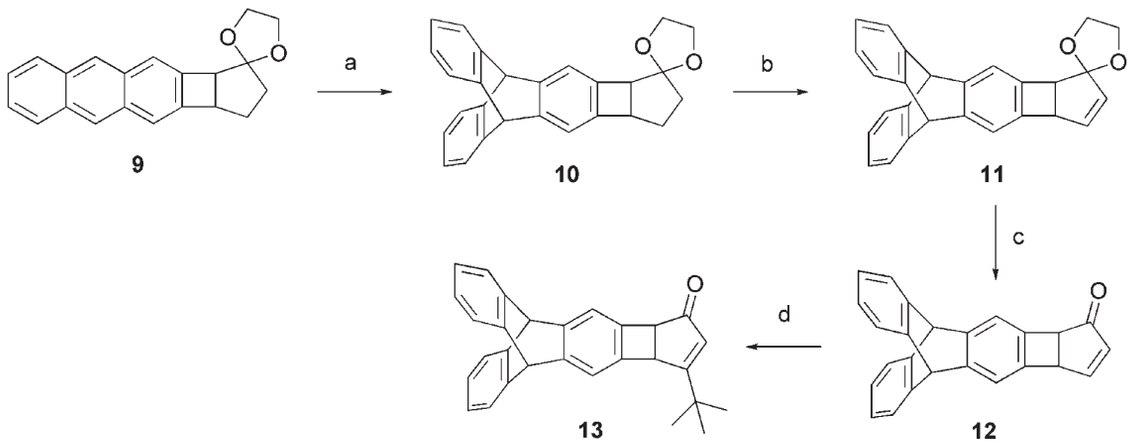
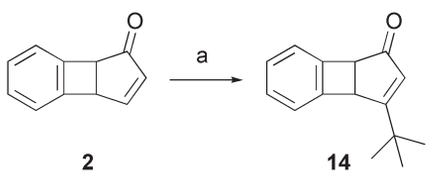


Scheme 1 (a) Anthranilic acid, isopentyl nitrite, refluxing DME, 7 h, 73%; (b) $PyHBr_3$, dichloromethane, room temperature, 5 h, then *t*-BuOK, 18-crown-6, THF, room temperature, 20 h, 52%; (c) aqueous HCl, THF, 50 °C, 3 h, 90%; (d) *t*-BuLi, THF, −78 °C, 1 h, then PCC, dichloromethane, room temperature, 40 h, 61%.



Scheme 2 (a) *t*-BuLi, THF, −78 °C, 1 h, then PCC, dichloromethane, room temperature, 63 h, 58%.

the *tert*-butyl group is more effective than the triptycene moiety for the kinetic stabilization of this system. It is intersting to point out that **5** is stable indefinitely in an EPA solution at −78 °C, whereas parent **1** undergoes dimerization with the rate constant of 12 ± 3 M^{-1} s^{-1} under the same conditions. Unfortunately, however, attempted characterization of **5** by ^1H NMR spectroscopy at low temperature failed, owing to the severe internal filtering of **13** by generating **5** which resulted in limited photochemical conversion of **13**.

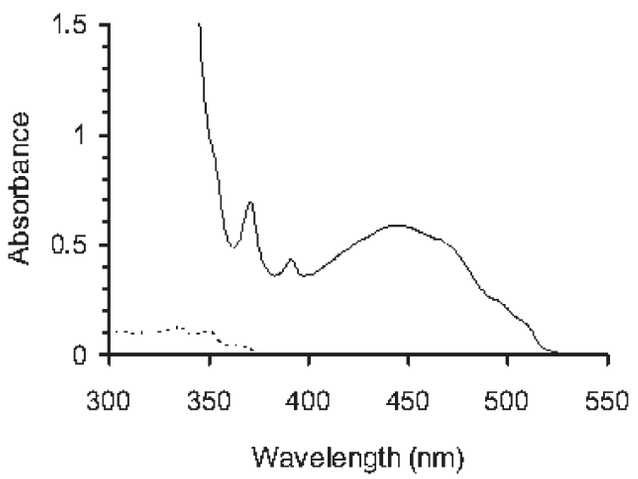


Fig. 1 Absorption spectral changes observed upon irradiation of **13** with a high-pressure mercury lamp through Pyrex in an EPA glass at −196 °C: before irradiation (dashed line) and after irradiation (solid line; λ_{max} 353 (sh), 373, 394, 452, 473 (sh), 498 (sh) and 510 (sh) nm).

We next turned our attention to the generation of **8** having two *tert*-butyl groups at the C(2) and C(6) positions of the tropone moiety in anticipation of generating more stabilized derivative than **5**–**7**. Since the dimerization of **1** proceeds at the 2,5- and 2,7-positions, introduction of the sterically demanding *tert*-butyl group at the C(2) position was expected to be quite effective for the kinetic stabilization. The desired benzocyclobutene precursor **22** was prepared as outlined in Scheme 3. Irradiation of 3-*tert*-butyl-2-cyclopenten-1-one (**15**)[7] with (*E*)-1,4-dichloro-2-butene afforded [π2 + π2] photocycloadduct **16** as a mixture of stereoisomers in 82% yield. Acetalization of **16** followed by two-fold dehydrochlorination produced diene **18** in 86% yield. Diels–Alder reaction

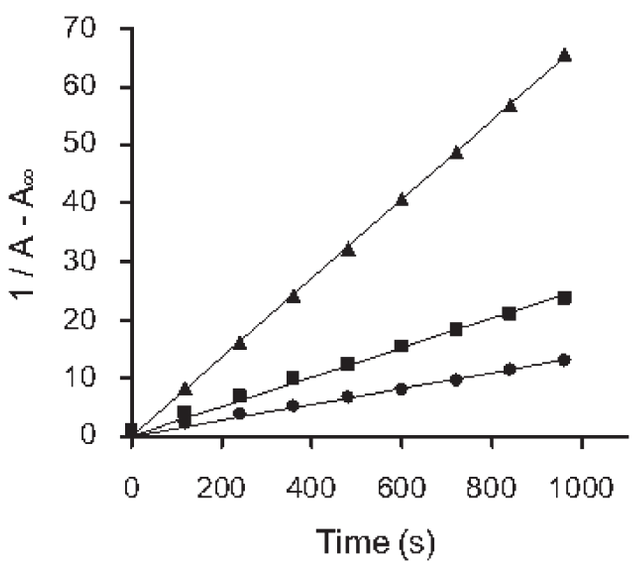


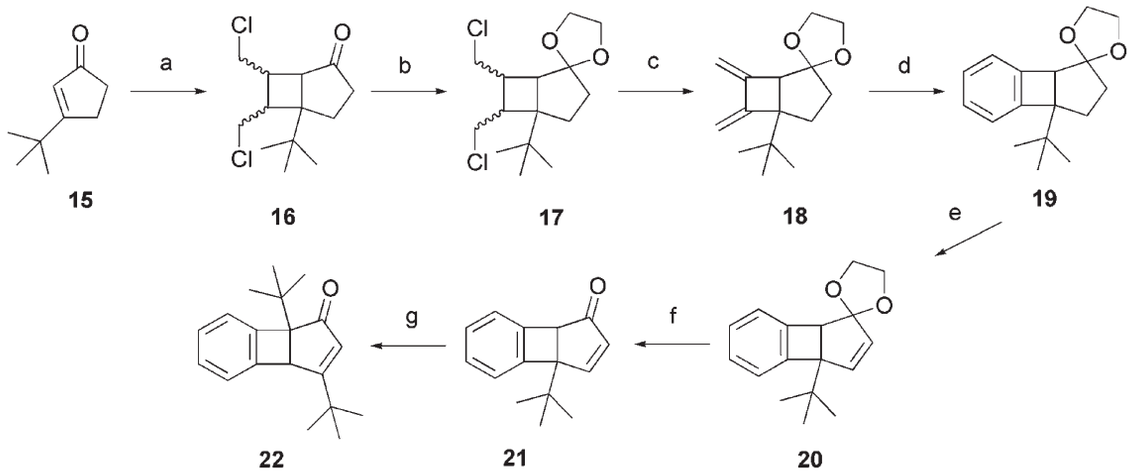
Fig. 2 Plots of the reciprocal of absorbance *vs.* time for the decay of the absorption at 458 nm in EPA at 0 °C: for **5** (●), **6** (▲) and **7** (■).

Table 1 Kinetic stabilities of the 3,4-benzotropones in EPA

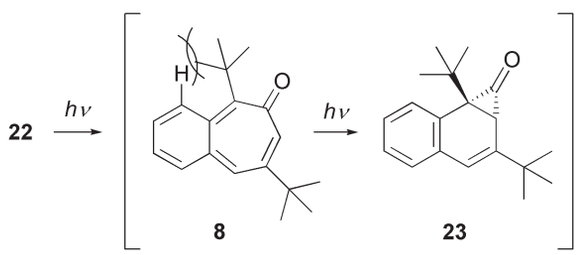
Compound	Temp/°C	k_d/M^{-1} s^{-1}	Reference
1	−78	12 ± 3	reference 4
5	−78	stable	this study
5	0	30 ± 6	this study
6	0	166 ± 33	this study
7	0	60 ± 12	this study

of **18** with 1-(ethynylsulfonyl)-4-methylbenzene[8] followed by dehydrogenation gave **19** in 83% yield. Bromination of **19** followed by dehydrobromination and deprotection afforded **21** in 52% yield. 1,2-Addition of *tert*-butyllithium to **21** followed by PCC oxidation produced **22** in 32% yield.

The photochemical generation of **8** from **22** was examined as described for **5**–**7**. However, unexpectedly, when a degassed EPA solution of **22** in a Pyrex tube was irradiated with a high-pressure mercury lamp at −196 °C, development of no absorption extending to long-wavelength region characteristic of the 3,4-benzotropone system was observed, even after prolonged irradiation. Molecular modeling suggests that **8** would be distorted from its ideal planar structure due to the steric repulsion between the *tert*-butyl group at the C(2) position and the hydrogen atom at the *peri*-position (Scheme 4). To relieve the steric repulsion, **8** may undergo, if it is generated, rapid pericyclic ring-closing photochemical reaction to form norcaradiene derivative **23**. A similar photochemical transformation has been reported for related compounds.[2,6c]



Scheme 3 (a) (*E*)-1,4-dichloro-2-butene, *hν*, 12 °C, 10 h, 82%; (b) ethylene glycol, TsOH, refluxing benzene, 2 h, 91%; (c) *t*-BuOK, 18-crown-6, THF, room temperature, 3 h, 95%; (d) 1-(ethynylsulfonyl)-4-methylbenzene, refluxing benzene, 5 h, 83%; (e) $PyHBr_3$, dichloromethane, room temperature, 40 h, then *t*-BuOK, 18-crown-6, refluxing THF, 5 d, 61%; (f) aqueous HCl, THF, 50 °C, 15 h, 86%; (g) *t*-BuLi, THF, −78 °C, 1 h, then PCC, dichloromethane, room temperature, 46 h, 32%.



Scheme 4 A possible explanation for the non-observation of **8**.

Conclusions

The lability of *o*-quinoidal 3,4-benzotropone **1** arises from its high propensity for undergoing dimerization and this tendency suggests that the system may be kinetically stabilized by introducing sterically demanding substituents that specifically shield the reaction sites. In fact, the skeleton of **1** is kinetically stabilized in derivatives **5**–**7**. The related stabilities of **5**–**7** in EPA at 0 °C indicate that the *tert*-butyl group at the C(6) position is more effective than the fused-triptycene moiety for kinetic stabilization of the 3,4-benzotropone system. Preparation of **8** having two *tert*-butyl groups at the C(2) and C(6) positions of the tropone moiety was also examined using the corresponding benzocyclobutene derivative **22** as a precursor. However, photochemical generation of **8** from **22** could not be confirmed even under matrix isolation conditions at low temperature, possibly because of the photochemical lability of **8** for intramolecular rearrangement.

Experimental

General

^1H and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively, on a JEOL EX-300 spectrometer using tetramethylsilane as an internal reference. IR spectra were taken on a Hitachi 270-30 infrared spectrometer. Electronic absorption spectra were measured on a Hitachi U-3500 spectrophotometer. Mass spectra were recorded on a JEOL JMS-SX102A spectrometer. GLC work was done on Hitachi 163 gas chromatographs. Preparative chromatography was performed on Merck Kieselgel 60 (70–230 mesh). The light source for photochemistry was a Halos (Eiko-sha, Japan) 450 W high-pressure Hg lamp.

6,7-{2′,3′-(9′,10′-Dihydro-9′,10′-benzenoanthro)}bicyclo-[3.2.0]hept-6-en-2-one ethylene acetal (10). To a refluxed solution of **9**[6b] (1.46 g, 4.83 mmol) in DME (70 mL) was added a solution of anthranilic acid (16.5 g, 121 mmol) in DME (70 mL) and isopentyl nitrite (14.1 g, 121 mmol) from respective dropping funnels over 7 h. The mixture was cooled to room temperature, poured into water (500 mL) and extracted with benzene (3 × 500 mL). The extracts were combined, washed successively with water (2 × 500 mL), 5% aqueous HCl (2 × 500 mL), 10% aqueous $NaHCO_3$ (2 × 500 mL) and brine (3 × 500 mL), dried with Na_2SO_4, and concentrated. The residue was chromatographed on silica gel eluted with ethyl acetate/hexane (1 : 9) to give **10** (1.33 g, 73%); mp 241–243 °C (ether); (Found 378.1610, $C_{27}H_{22}O_2$ requires 378.1620); υ_{max} (KBr)/cm^{-1} 1460, 1326 and 1066; δ_H (300 MHz; $CDCl_3$) 1.52–1.88 (m, 4 H), 3.40 (d, J = 3.3 Hz, 1 H), 3.71 (dd, J = 7.1 and 3.3 Hz, 1 H), 3.90–4.02 (m, 4 H), 5.37 (br s, 2 H), 6.90–7.00 (m, 4 H), 7.09 (s, 1 H), 7.18 (s, 1 H) and 7.31–7.36 (m, 4 H); δ_C (75 MHz, $CDCl_3$) 25.61, 31.92, 45.30, 51.64, 54.55, 54.65, 63.97, 65.10, 115.63, 117.97, 119.02, 122.77, 123.33, 123.40, 123.47, 123.83, 124.98, 125.01, 125.03, 140.29, 143.38, 144.79, 145.25, 145.27, 145.32, 145.55 and 145.58; *m*/*z* (FD) 378 (M^+, 100%).

6,7-{2′,3′-(9′,10′-Dihydro-9′,10′-benzenoanthro)}benzobicyclo[3.2.0]hepta-3,6-dien-2-one ethylene acetal (11). To a solution of **10** (1.33 g, 3.51 mmol) in dichloromethane (80 mL) was added pyridinium tribromide (1.13 g, 3.51 mmol) in portions, and the mixture was stirred at room temperature for 5 h and then poured into 10% aqueous $Na_2S_2O_3$ (100 mL). The organic layer was separated, washed with brine (100 mL), dried with Na_2SO_4, and concentrated. The residue was dissolved in 100 mL of dry THF and used for the next reaction without further purification. To the THF solution was added potassium *tert*-butoxide (3.39 g, 30.3 mmol) and the mixture was refluxed for 20 h, cooled to room temperature, and evaporated. Water (80 mL) was added to the residue and the mixture was extracted with ethyl acetate (2 × 100 mL). The extracts were combined, washed with brine (100 mL), dried with Na_2SO_4, and concentrated. The residue was chromatographed on silica gel eluted with ethyl acetate/hexane (1 : 9) to give **11** (0.68 g, 52%); mp 237–239 °C (ether); (Found 376.1469, $C_{27}H_{20}O_2$ requires 376.1463); υ_{max} (KBr)/cm^{-1} 1364, 1142, 990 and 740; δ_H (300 MHz; $CDCl_3$) 3.74 (d, J = 3.8 Hz, 1 H), 3.96–4.15 (m, 4 H), 4.24 (dd, J = 3.8 and 2.5 Hz, 1 H), 5.34 (s, 1 H), 5.37 (s, 1 H), 5.50 (d, J = 5.5 Hz, 1 H), 6.30 (dd, J = 5.5 and 2.5 Hz, 1 H), 6.92–6.97 (m, 4 H), 7.11 (s, 1 H), 7.24 (s, 1 H) and 7.31–7.35 (m, 4 H); δ_C (75 MHz, $CDCl_3$) 51.74, 52.64, 54.89, 54.91, 64.69, 65.79, 115.61, 118.03, 121.47, 123.76, 123.79, 123.82, 124.21, 125.42, 125.43, 125.46, 130.85, 130.87, 139.34, 139.36, 140.51, 145.04, 145.10, 145.42, 145.48, 145.87 and 147.05; *m*/*z* (FD) 376 (M^+, 100%).

6,7-{2′,3′-(9′,10′-Dihydro-9′,10′-benzenoanthro)}bicyclo-[3.2.0]hepta-3,6-dien-2one (12). To a solution of **11** (0.60 g, 1.6 mmol) in THF (50 mL) was added 10% aqueous HCl (5 mL) and the mixture was heated at 50 °C for 3 h. The mixture was cooled to room temperature, diluted with chloroform (100 mL), washed successively with 10% aqueous $NaHCO_3$ (50 mL) and

brine (50 mL), dried with Na_2SO_4, and concentrated. The residue was chromatographed on silica gel eluted with ethyl acetate/hexane (1 : 9) to give **12** (0.50 g, 90%); mp 256–257 °C (ether); (Found 332.1196, $C_{25}H_{16}O$ requires 332.1191); υ_{max} (KBr)/cm^{-1} 1696; δ_H (300 MHz; $CDCl_3$) 3.97 (d, J = 3.0 Hz, 1 H), 4.45 (dd, J = 3.0 and 2.6 Hz, 1 H), 5.38 (s, 1 H), 5.39 (s, 1 H), 5.95 (d, J = 5.5 Hz, 1 H), 6.95–7.00 (m, 4 H), 7.21 (s, 1 H), 7.26 (s, 1 H), 7.32–7.40 (m, 4 H) and 7.70 (dd, J = 5.5 and 2.6 Hz, 1 H); δ_C (75 MHz, $CDCl_3$) 49.87, 51.83, 54.17, 54.25, 118.39, 119.54, 123.22, 123.25, 123.37, 123.41, 124.96, 123.98, 125.02, 125.07, 133.44, 137.95, 137.97, 143.22, 144.65, 144.71, 144.73, 144.79, 145.20, 161.53 and 205.06; *m*/*z* (FD) 332 (M^+, 100%).

4-*tert*-Butyl-6,7-{2′,3′-(9′,10′-dihydro-9′,10′-benzeno-anthro)}bicyclo[3.2.0]hepta-3,6-dien-2-one (13). To a solution of **12** (64 mg, 0.19 mmol) in dry THF (5 mL) was added 1.6 M *tert*-butyllithium in pentane (0.24 mL, 0.38 mmol) over 1 min at −78 °C. The mixture was stirred at the same temperature for 1 h, allowed to warm to room temperature, diluted with ethyl acetate (50 mL), washed with brine (30 mL), dried with Na_2SO_4, and concentrated to give the crude alcohol as a brown oil (58 mg), which was diluted in 5 mL of dry dichloromethane and added to a suspension of PCC (50 mg, 0.23 mmol) and molecular sieves 4A (50 mg) in dichloromethane (2 mL). After 40 h at room temperature, ether (50 mL) was added and the mixture was filtered through a short pad of Florisil. The filtrate was washed with water (30 mL), dried with Na_2SO_4, and concentrated. The residue was subjected to chromatography on silica gel eluted with ethyl acetate/hexane (1 : 9) followed by preparative GPC (chloroform) to give **13** (45 mg, 61%); mp 280–281 °C (ether); (Found 388.1825, $C_{29}H_{24}O$ requires 388.1823); υ_{max} (KBr)/cm^{-1} 1696, 1592 and 1460; δ_H (300 MHz; $CDCl_3$) 1.26 (s, 9 H), 3.99 (d, J = 3.0 Hz, 1 H), 4.44 (d, J = 3.0 Hz, 1 H), 5.37 (s, 1 H), 5.40 (s, 1 H), 5.77 (s, 1 H), 6.96–7.00 (m, 4 H), 7.27 (s, 1 H), 7.26 (s, 1 H) and 7.33–7.39 (m, 4 H); δ_C (75 MHz, $CDCl_3$) 29.08, 35.26, 49.37, 53.89, 54.33, 54.50, 119.31, 119.59, 123.39, 123.52, 123.58, 123.64, 125.17, 125.22, 125.29, 127.15, 138.82, 143.87, 144.90, 144.93, 145.00, 145.05, 145.07, 145.09, 145.32, 187.28 and 204.81; *m*/*z* (FD) 388 (M^+, 100%).

4-*tert*-Butyl-6,7-benzobicyclo[3.2.0]hepta-3,6-dien-2-one (14). To a solution of **2**[4] (50 mg, 0.32 mmol) in dry THF (5 mL) was added 1.6 M *tert*-butyllithium in pentane (1.02 mL, 1.63 mmol) over 1 min at −78 °C. The mixture was stirred at the same temperature for 1 h, allowed to warm to room temperature, diluted with ether (50 mL), washed with brine (30 mL), dried with Na_2SO_4, and concentrated to give the crude alcohol as a brown oil (50 mg), which was diluted in 5 mL of dry dichloromethane and added to a suspension of PCC (100 mg, 0.46 mmol) and molecular sieves 4A (100 mg) in dichloromethane (2 mL). After 63 h at room temperature, ether (50 mL) was added and the mixture was filtered through a short pad of Florisil. The filtrate was washed with water (30 mL), dried with Na_2SO_4, and concentrated. The residue was subjected to chromatography on silica gel eluted with ether/hexane (1 : 4) followed by preparative GPC (chloroform) to give **14** (40 mg, 58%) as a viscous oil; (Found 212.1210, $C_{15}H_{16}O$ requires 212.1201); υ_{max} (neat)/cm^{-1} 1698; δ_H (300 MHz; $CDCl_3$) 1.26 (s, 9 H), 3.99 (d, J = 3.0 Hz, 1 H), 4.44 (d, J = 3.0 Hz, 1 H), 5.38 (s, 1 H) and 7.17–7.25 (m, 4 H); δ_C (75 MHz, $CDCl_3$) 28.93, 35.08, 50.07, 54.63, 123.02, 123.24, 127.06, 127.32, 127.60, 141.92, 146.85, 187.18 and 204.39; *m*/*z* (FD) 212 (M^+, 100%).

5-*tert*-Butyl-6,7-bis(chloromethyl)bicyclo[3.2.0]heptan-2-one (16). A degassed solution of 3-*tert*-butyl-2-cyclopenten-1-one (**15**)[7] (2.78 g, 20 mmol) and (*E*)-1,4-dichloro-2-butene (25.2 g, 200 mmol) in dichloromethane (70 mL) was irradiated with a 450 W high-pressure mercury lamp through Pyrex at 12 °C. The reaction was monitored by GLC (5% Silicon SE30, 0.5 m, 100–270 °C) and the irradiation was terminated after 10 h (90% GLC conversion). After evaporation of the reaction mixture, the residue was subjected to chromatography on silica gel eluted with ether/hexane (1 : 4) to give **16** (4.3 g, 82%) as a mixture of stereoisomers; (Found 262.0886, $C_{13}H_{20}OCl_2$ requires 262.0891); υ_{max} (neat)/cm^{-1} 1730; δ_H (300 MHz; $CDCl_3$) 0.91 (s, 9 H), 2.02–2.09 (m, 2 H), 2.22–2.44 (m, 2 H), 2.53–2.59 (m, 2 H), 2.80–2.86 (m, 1 H) and 3.61–3.78 (m, 4 H); *m*/*z* (FD) 266 (M^+ + 4, 11.2%), 264 (M^+ + 2, 63.8%) and 262 (M^+, 100%).

5-*tert*-Butyl-6,7-bis(chloromethyl)bicyclo[3.2.0]heptan-2-one ethylene acetal (17). A mixture of **16** (0.87 g, 3.3 mmol), ethylene glycol (0.41 g, 6.6 mmol), and *p*-toluenesulfonic acid monohydrate (62 mg, 0.3 mmol) in benzene (90 mL) was heated under reflux for 2 h while water was removed with a Dean–Stark trap. The mixture was cooled, diluted with ether (100 mL), washed successively with aqueous $NaHCO_3$ (80 mL), water (100 mL), and brine (100 mL), dried with Na_2SO_4, and concentrated. The residue was chromatographed on silica gel eluted with ether/hexane (1 : 9) to give **17** (0.93 g, 91%) as a mixture of stereoisomers; (Found 306.1142, $C_{15}H_{24}O_2Cl_2$ requires 306.1153); υ_{max} (neat)/cm^{-1} 1100; δ_H (300 MHz; $CDCl_3$) 0.91 (s, 9 H), 1.49–1.56 (m, 1 H), 1.82–1.93 (m, 2 H), 2.03–2.11 (m, 3 H), 2.46–2.49 (m, 1 H), 3.46–3.72 (m, 4 H) and 3.88–3.95 (m, 4 H); *m*/*z* (FD) 310 (M^+ + 4, 14.4%), 308 (M^+ + 2, 66.2%) and 306 (M^+, 100%).

5-*tert*-Butyl-6,7-bismethylenebicyclo[3.2.0]heptan-2-one ethylene acetal (18). To a solution of **17** (358 mg, 1.17 mmol) in dry THF (50 mL) was added potassium *tert*-butoxide (392 mg, 3.5 mmol) and the mixture was stirred at room temperature under argon for 3 h and then evaporated. Water (100 mL) was added to the residue and the mixture was extracted with ether (3 × 70 mL). The extracts were combined, washed with brine (100 mL), dried with Na_2SO_4, and concentrated. The residue was chromatographed on silica gel eluted with ether/hexane (1 : 9) to give **18** (260 mg, 95%) as a colorless oil; (Found 234.1608, $C_{15}H_{22}O_2$ requires 234.1620); υ_{max} (neat)/cm^{-1} 1098; δ_H (300 MHz; $CDCl_3$) 0.94 (s, 9 H), 1.80–2.20 (m, 4 H), 2.77 (s, 1 H), 3.92–3.96 (m, 4 H), 4.81 (br s, 1 H), 4.84 (br s, 1 H), 5.23 (br s, 1 H) and 5.25 (br s, 1 H); *m*/*z* (FD) 234 (M^+, 100%).

5-*tert*-Butyl-6,7-benzobicyclo[3.2.0]hept-6-en-2-one ethylene acetal (19). A solution of **18** (0.48 g, 2.1 mmol) and 1-(ethynylsulfonyl)-4-methylbenzene[8] (0.37 g, 2.0 mmol) in benzene (5 mL) was refluxed for 5 h. The mixture was cooled to room temperature, diluted with ethyl acetate (50 mL), washed with water (50 mL), dried with Na_2SO_4, and concentrated. To the residue was added DMSO (75 mL), water (75 mL), $Na_2S_2O_4$ (0.95 g, 5.4 mmol) and $NaHCO_3$ (1.0 g, 11.9 mmol) and the mixture was refluxed for 1 h. After cooling, the mixture was diluted with water (100 mL) and extracted with ether (4 × 100 mL). The extracts were combined, washed successively with aqueous water (2 × 100 mL), and brine (100 mL), dried with Na_2SO_4 and concentrated. The residue was chromatographed on silica gel eluted with ether/hexane (1 : 9) to give **19** (0.43 g, 83%); mp 167.5–168 °C (hexane); (Found 258.1612, $C_{17}H_{22}O_2$ requires 258.1620); υ_{max} (KBr)/cm^{-1} 1090; δ_H (300 MHz; $CDCl_3$) 0.91 (s, 9 H), 1.58–1.70 (m, 2 H), 1.94–2.05 (m, 2 H), 3.33 (s, 1 H), 3.90–4.04 (m, 4 H), 7.03–7.06 (m, 1 H), 7.10–7.13 (m, 1 H) and 7.17–7.22 (m, 2 H); *m*/*z* (FD) 258 (M^+, 100%).

5-*tert*-Butyl-6,7-benzobicyclo[3.2.0]hepta-3,6-dien-2-one ethylene acetal (20). To a solution of **19** (400 mg, 1.55 mmol) in dichloromethane (12 mL) was added pyridinium tribromide (545 mg, 1.71 mmol) in one portion, and the mixture was stirred at room temperature for 40 h and then poured into a mixture of benzene (100 mL) and 10% aqueous $Na_2S_2O_3$ (50 mL). The organic layer was separated, washed with brine (50 mL), dried with Na_2SO_4, and concentrated. The residue was dissolved in 50 mL of dry THF and used for the next reaction without further purification. To the THF solution was added 18-crown-6 (787 mg, 3.0 mmol) and potassium *tert*-butoxide (335 mg, 3.0 mmol) and the mixture was refluxed for 5 days, cooled to room temperature, and evaporated. Water (100 mL) was added to the residue and the mixture was extracted with chloroform (3 × 50 mL). The extracts were combined, washed with brine (100 mL), dried with Na_2SO_4, and concentrated.

The residue was subjected to chromatography on silica gel eluted with ether/hexane (1 : 9) followed by preparative GPC (chloroform) to give **20** (236 mg, 61%); mp 162–164 °C (hexane); (Found 256.1474, $C_{17}H_{20}O_2$ requires 256.1463); υ_{max} (KBr)/cm^{-1} 1152, 1072 and 1020; δ_H (300 MHz; $CDCl_3$) 1.03 (s, 9 H), 3.70 (s, 1 H), 3.98–4.12 (m, 4 H), 5.49 (d, J = 4.2 Hz, 1 H), 6.38 (d, J = 4.2 Hz, 1 H) and 7.06–7.19 (m, 4 H); *m*/*z* (FD) 256 (M^+, 100%).

5-*tert*-Butyl-6,7-benzobicyclo[3.2.0]hepta-3,6-dien-2-one (21). To a solution of **20** (200 mg, 0.78 mmol) in THF (30 mL) was added 10% aqueous HCl (3 mL) and the mixture was heated at 50 °C for 15 h. The mixture was cooled to room temperature, diluted with chloroform (50 mL), washed successively with 10% aqueous $NaHCO_3$ (30 mL) and brine (30 mL), dried with Na_2SO_4, and concentrated. The residue was chromatographed on silica gel eluted with ether/hexane (1 : 4) to give **21** (143 mg, 86%); mp 182–183 °C (hexane); (Found 212.1209, $C_{15}H_{16}O$ requires 212.1201); υ_{max} (KBr)/cm^{-1} 1706; δ_H (300 MHz; $CDCl_3$) 1.08 (s, 9 H), 3.97 (s, 1 H), 5.92 (d, J = 5.8 Hz, 1 H), 7.16–7.19 (m, 4 H), 7.83 (d, J = 5.8 Hz, 1 H); *m*/*z* (FD) 212 (M^+, 100%).

1,4-Di-*tert*-butyl-6,7-benzobicyclo[3.2.0]hepta-3,6-dien-2-one (22). To a solution of **21** (100 mg, 0.47 mmol) in dry THF (5 mL) was added 1.6 M *tert*-butyllithium in pentane (1.18 mL, 1.89 mmol) over 1 min at −78 °C. The mixture was stirred at the same temperature for 1 h, allowed to warm to room temperature, diluted with ether (70 mL), washed with brine (30 mL), dried with Na_2SO_4, and concentrated to give the crude alcohol as a brown oil (90 mg), which was diluted in 5 mL of dry dichloromethane and added to a suspension of PCC (100 mg, 0.46 mmol) and molecular sieves 4A (100 mg) in dichloromethane (2 mL). After 46 h at room temperature, ether (40 mL) was added and the mixture was filtered through a short pad of Florisil. The filtrate was washed with water (30 mL), dried with Na_2SO_4, and concentrated. The residue was subjected to chromatography on silica gel eluted with ether/hexane (1 : 4) followed by preparative GPC (chloroform) to give **22** (32 mg, 32%) as a viscous oil; (Found 268.1819, $C_{19}H_{24}O$ requires 268.1827); υ_{max} (neat)/cm^{-1} 1702; δ_H (300 MHz; $CDCl_3$) 1.03 (s, 9 H), 1.30 (s, 9 H), 4.65 (s, 1 H), 5.80 (s, 1 H), 7.16–7.19 (m, 3 H), 7.26–7.30 (m, 1 H); *m*/*z* (FD) 268 (M^+, 100%).

Measurement of the electronic absorption spectra of 5–7. A solution of precursor **12**, **13** or **14** in EPA was placed in a Pyrex tube and degassed by freeze–thaw cycles. The sealed tube was immersed in liquid nitrogen in a Dewar having two parallel windows facing each other and the sample was irradiated through the window with a high pressure Hg lamp. When a solution of the precursor (3.2×10^{-4} M) in EPA was irradiated at −196 °C for 10 min, development of a new absorption assigned to **5–7** was observed. For **5**: λ_{max} 331 (sh), 353 (sh), 373, 394, 452, 473 (sh), 498 (sh) and 510 (sh) nm. For **6**: λ_{max} 331 (sh), 352 (sh), 371, 392, 445, 472 (sh), 496 (sh) and 507 (sh) nm. For **7**: λ_{max} 351, 369, 389, 453, 482 (sh), 503 (sh) and 517 (sh) nm. The absorption assigned to **5** remained unchanged for more than 10 h at −78 °C, but disappeared rapidly at 0 °C. The decay of the absorption followed second-order kinetics and the rate constant determined by monitoring the decay at 458 nm was 30 ± 6 M^{-1} s^{-1} in EPA at 0 °C. The molar absorptivity of **5–7** at 458 nm in EPA was estimated to be 2500 ± 500.[4] Similarly, the rate constants for the dimerization of **6** and **7** in EPA at 0 °C were determined to be 166 ± 33 M^{-1} s^{-1} and 60 ± 12 M^{-1} s^{-1}, respectively.

Attempted photochemical generation of 8 from 22. A degassed EPA solution of **22** (3.0×10^{-4} M) in a Pyrex tube was irradiated with a high pressure Hg lamp at −196 °C and the reaction was monitored by UV-vis spectroscopy. In contrast to the photolysis of **12**–**14** described above, development of no absorption extending to long-wavelength region characteristic of the 3,4-benzotropone system was observed, even after irradiation for 150 min. TLC analysis of the photolysate showed complete consumption of **22** together with the formation of two products. However, preparative scale photolysis of **22** (16 mg, 0.06 mmol) in EPA (50 mL) at 12 °C resulted in the formation of a complex mixture. Similar medium dependent photochemical behavior has been reported[4a] for parent **2**.

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