nucleophile (H_2O). However, we see that k_2 (Scheme I) is actually less than the rate constant for the attack of H_2O on 4 (or 1), perhaps as a consequence of a larger steric encumbrance of the transition state. Hence, the more likely origin of the plateau region of Figure 1 stems from an intramolecular general-base role for the imidazole in Im. Consistent with this is the observed kinetic solvent isotope effect of $k_{H_2O}/k_{D_2O} = 2.8$ in the plateau region. Similar solvent isotope effects are observed in other intramolecular imidazole general-base-assisted hydrolytic processes.[2,3]

The efficacy of the intramolecular imidazole catalyst can be assessed by determining its "effective molarity".[8] This was determined by assessing the intermolecular general-base catalysis effected by 2-methylimidazole buffers on the hydrolysis of 4. As in the imidazole-catalyzed hydrolysis of other acylimidazoles,[1] the buffer acts as both a general-acid and general-base catalyst. The respective values of 5.6×10^{-5} and 1.13×10^{-3} M^{-1} s^{-1} are obtained from the plots of the second-order catalytic constant against percent free base. The pK_a for 2-methylimidazole is 7.59[9a,b] while the Brønsted β value for general-base catalysis of the hydrolysis of acetylimidazole is 0.55.[1c] If that β value also obtains for 4 then an intermolecular general base of pK_a 6.60 (pK_2 in Scheme I) possesses a catalytic constant of $\sim 3.3 \times 10^{-4}$ M^{-1} s^{-1}. Thus, the effective molarity of the intramolecular imidazole in 3 is 1.02×10^{-3} $s^{-1}/3.3 \times 10^{-4}$ M^{-1} s^{-1} = 3.1 M, consistent with the normal range observed in the hydrolysis of esters.[8]

Acknowledgment. We gratefully acknowledge the financial assistance of the U.S. Army Medical Research and Development Command (Contract No. DAMD17-85C-5173), the University of Alberta, and the Natural Sciences and Engineering Research Council of Canada (UV instrumentation grant).

Supplementary Material Available: Tables S1 and S2, giving hydrolytic rate constants for 3 and 4 (3 pages). Ordering information is given on any current masthead page.

(8) (a) Kirby, A. J. *Adv. Phys. Org. Chem.* **1980**, *17*, 183. (b) Kirby, A. J. *Stud. Org. Chem. (Amsterdam)* **1981**, *10*, 219.

(9) (a) The pK_a of 2-methylimidazole at 7.85 at μ = 0.04–0.11 M is reported in: Perrin, D. D. In *Dissociation Constants of Organic Bases in Aqueous Solution*; Butterworths: London, 1965. (b) pK_a = 7.59, μ = 0.3 M: Skorey, K. I. unpublished observation.

Synthesis and Photochemistry of 1-Diazo-2-cyclopentene and 2-Diazobicyclo[3.2.0]hepta-3,6-diene

Orville L. Chapman* and Christopher J. Abelt

Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90024

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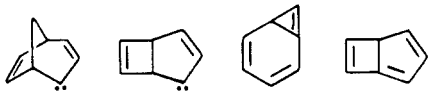
A potentially general route to cyclic α,β-unsaturated diazo compounds via enone tosylhydrazones is described. The unsaturated tosylhydrazone is generated by sulfoxide elimination. Syntheses of 2-diazobicyclo[3.2.0]hepta-3,6-diene and 1-diazo-2-cyclopentene are reported. Photolysis of 2-diazobicyclo[3.2.0]hepta-3,6-diene in an argon matrix at 10 K gives cycloheptatetraene, and similar irradiation of 1-diazo-2-cyclopentene gives cyclopentadiene.

Vinyl carbenes continue to be a rich source of interesting chemistry.[1] Murahashi[2] has found that bicyclo[3.2.1]-octa-2,6-dien-4-ylidene (1) rearranges to styrene. We were intrigued in that styrene is also produced in the pyrolysis of tolyldiazomethanes by way of tolylmethylene–methylcycloheptatetraene interconversions.[3] We sought to investigate the lower homologue, bicyclo[3.2.0]hepta-2,6-dien-4-ylidene (2), to examine its possible role in the phenylmethylene–cycloheptatetraene and related interconversions on the C_7H_6 energy surface.[4] If Murahashi's mechanism operates in this system, then bicyclo[4.1.0]-hepta-2,4,6-triene (3) ought to be produced. 2 also offers a potential route into triene 4 either by a C–H insertion or by a 1,2-shift of the 1,5-bond. Triene 4 is thought to be a critical intermediate in the high-temperature ring contraction of phenylmethylene to fulveneallene and cyclopentadienylacetylene.[5] Finally, 2 has been implicated in the pyrolysis of norbornadienyl acetate.[6]

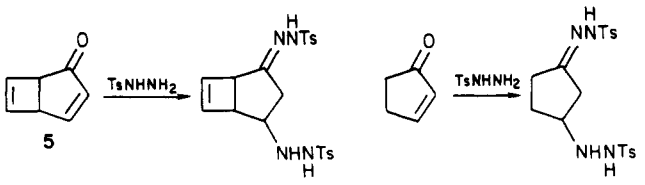


1 2 3 4

The generation of 2 is accomplished by photolysis of the corresponding diazo compound which, in turn, is generated from pyrolysis of the corresponding tosylhydrazone sodium salt. Tosylhydrazones are routinely prepared by reaction of tosylhydrazine with ketones or aldehydes. This simple reaction fails with enone 5 because tosylhydrazine first adds in a Michael fashion. 1,4-Addition has been observed with other reactive enones such as 2-cyclopentenone.[7] This paper describes a convenient preparation for the

(1) Hartzler, H. D. In "Carbenes"; Moss, R. A.; Jones, M., Jr., Eds.; Robert E. Krieger: Malabar, Florida, 1973; Vol. 2, pp 57–73.
(2) Murahashi, S.-I.; Okumura, K.; Naota, T.; Nagase, S. *J. Am. Chem. Soc.* **1982**, *104*, 2466–2475. Freeman, P. K.; Swenson, K. E. *J. Org. Chem.* **1982**, *47*, 2033–2039.
(3) Chapman, O. L.; McMahon, R. J.; West, P. R. *J. Am. Chem. Soc.* **1984**, *106*, 7973–7974. Chapman, O. L.; Tsou, U.-P. E. *J. Am. Chem. Soc.* **1984**, *106*, 7974–7976.
(4) West, P. R.; Chapman, O. L.; LeRoux, J.-P. *J. Am. Chem. Soc.* **1982**, *104*, 1779–1782. McMahon, R. J.; Abelt, C. J.; Chapman, O. L.; Johnson, J. W.; Kreil, C. L.; LeRoux, J.-P.; Mooring, A. M.; West, P. R. *J. Am. Chem. Soc.*, in press.
(5) Wentrup, C. In "Reactive Intermediates"; Abramovitch, R. A., Ed.; Plenum Press: New York, 1980; Vol. 1, pp 263–297.
(6) Hoffman, R. W.; Loof, I. H.; Wentrup, C. *Justus Liebigs Ann. Chem.* **1980**, 1198–1206.
(7) Kirmse, W.; Ruetz, L. *Justus Liebigs Ann. Chem.* **1969**, *726*, 30–35. Royals, E. E. "Advanced Organic Chemistry"; Prentice-Hall: New York, 1954; p 668.

0022-3263/87/1952-1218$01.50/0



tosylhydrazones of such enones.

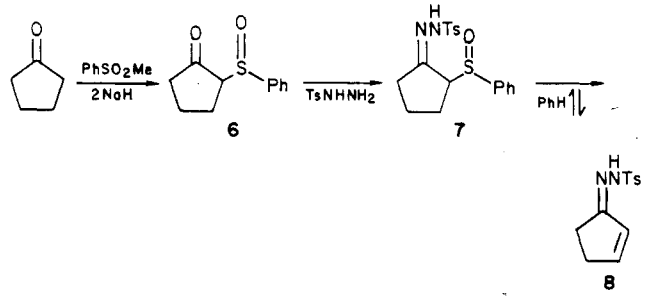
Results and Discussion

Synthesis of Enone Tosylhydrazones. The simplest way to circumvent Michael addition is to generate the C–C double bond after the tosylhydrazone has been formed. There are many ways to generate double bonds next to carbonyl groups, but the presence of the tosylhydrazone renders some of these ineffective. For example, enone **5** can be made by base-catalyzed elimination of acetic acid from the β-acetoxy ketone.[8] Such elimination might also occur with the β-acetoxytosylhydrazone; however, its attempted synthesis is thwarted by the basicity of tosylhydrazine which acts as a base and induces elimination instead of tosylhydrazone formation. Thus, the group responsible for generation of the double bond must be insensitive to base or nucleophilic attack if it is in place before tosylhydrazone formation.

Selenoxide elimination is a more general route for generating double bonds next to ketones.[9] The phenylselenyl moiety is easily introduced adjacent to ketones, and tosylhydrazine reacts smoothly with these ketones giving α-(phenylselenyl)tosylhydrazones. However, oxidation ($NaIO_4$, MCPBA, or *t*-BuOOH) of the compounds is messy, and at best gives clean regeneration of the ketone. That is, the imine of the tosylhydrazone is more susceptible to oxidation than the selenide. Thus, no oxidation can be done once the tosylhydrazone has been formed.

Sulfoxide elimination[10] is the method of choice for generating a double bond next to a tosylhydrazone. Sulfoxides are conveniently introduced adjacent to a ketone by direct sulfinylation with the ester of an aryl sulfinic acid.[11] Tosylhydrazine adds smoothly to these α-arylsulfinyl ketones, and the subsequent elimination proceeds at reflux in benzene or acetonitrile. This methodology was first worked out on the appropriate model system, 2-cyclopentenone tosylhydrazone (**8**).

Sulfinylation of cyclopentanone ($PhSO_2CH_3$, 2 NaH, DME, reflux) affords a poor 23% yield of 2-(phenylsulfinyl)cyclopentanone (**6**). Other methods[12] offer better yields, but this method is quicker and cleaner. Addition of tosylhydrazine provides 2-(phenylsulfinyl)cyclopentanone tosylhydrazone (**7**) in 71% yield. The elimination proceeds in benzene heated at reflux for 24 h, and 2-cyclopentenone tosylhydrazone (**8**) crystallizes out in 67% yield. More product is obtained from the mother liquor and washings boosting the yield to 78%.



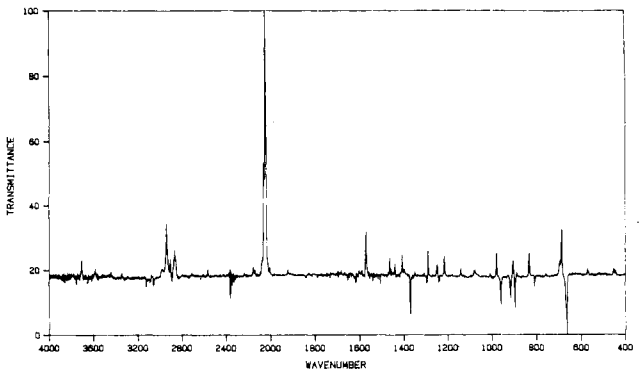
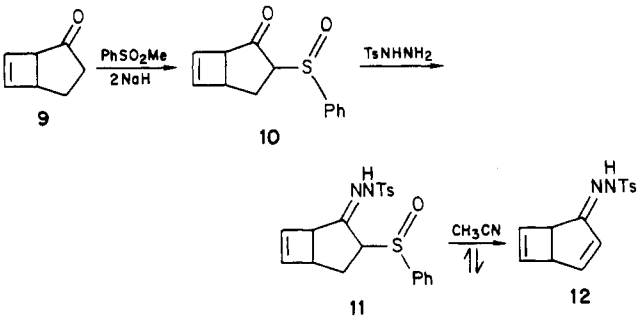
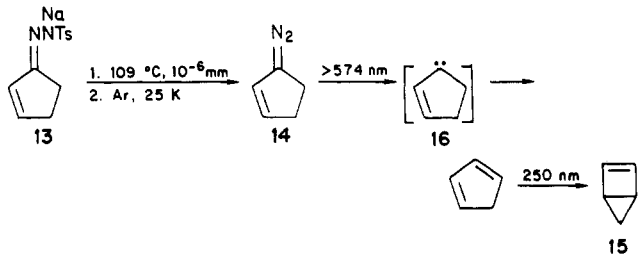


Figure 1. IR difference spectrum showing cyclopentadiene (positive absorbances) being produced upon irradiation (>574 nm) of 1-diazo-2-cyclopentene (negatives absorbances).

In contrast to cyclopentanone, sulfinylation of bicyclo[3.2.0]hepta-6-en-2-one (**9**)[13] affords a reasonable 64% yield of α-phenylsulfinyl ketone **10**. Reaction with tosylhydrazine gives the α-(phenylsulfinyl)tosylhydrazone **11** in 71% yield. The elimination step is more complicated than in the model system. Unlike **7**, **11** does not dissolve in boiling benzene or even boiling CH_3CN. Heating **11** at reflux in CH_3CN until the solution just clears (ca. 90 min) offers the best preparation of bicyclo[3.2.0]hepta-3,6-dien-2-one tosylhydrazone (**12**). Further heating results in side reactions involving the newly generated double bond. In this way, **12** is obtained in 49% yield based on recovered starting material.



Photochemistry of Diazocyclopentenes. The tosylhydrazones provide easy access to the corresponding diazo compounds.[14] Pyrolysis of the tosylhydrazone sodium salt **13** at 109 °C and condensation of the volatile products with Ar onto a CsI window cooled to 25 K affords matrix-isolated 1-diazo-2-cyclopentene (**14**). Evidence for **14** includes the infrared spectrum (Figure 1) which shows



(8) Sugihara, Y.; Morokoshi, N.; Murata, I. *Tetrahedron Lett.* **1977**, 3887–3888.
(9) Reich, H. J.; Renga, J. M.; Reich, I. L. *J. Am. Chem. Soc.* **1975**, *97*, 5434–5447.
(10) Trost, B. M.; Salzman, T. N.; Hiroi, K. *J. Am. Chem. Soc.* **1976**, *98*, 4887–4902.
(11) Montiero, H. J.; DeSouza, J. P. *Tetrahedron Lett.* **1975**, 921–924. Coates, R. M.; Pigott, H. D. *Synthesis* **1975**, 319–320.
(12) Grieco, P. A.; Pogonowski, C. S. *Chem. Commun.* **1975**, 72–73.
(13) Svensson, T. *Chem. Scr.* **1973**, *3*, 171–175. Scouten, C. G.; Barton, F. E., Jr.; Burgess, J. R.; Story, P. R.; Garst, J. F. *Chem. Commun.* **1969**, 78–79.
(14) No attempt was made to characterize these diazo compounds at room temperature.

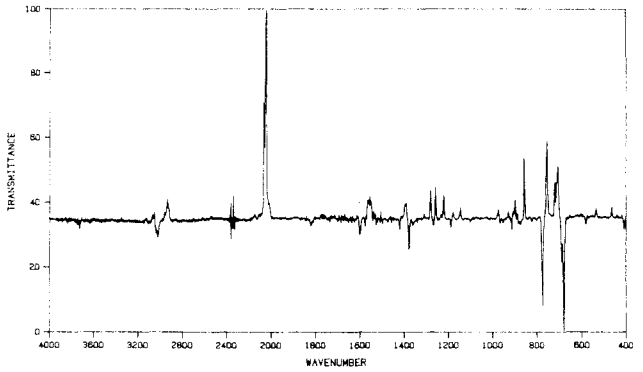
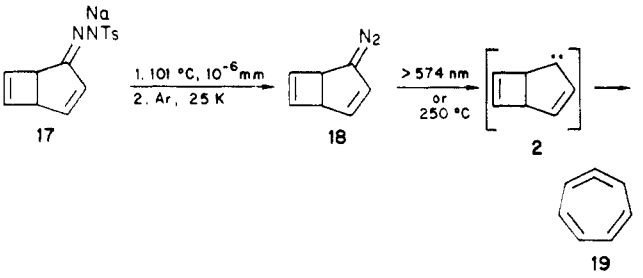


Figure 2. IR difference spectrum showing cycloheptatetraene (positive absorbances) being produced upon irradiation (>574 nm) of 2-diazobicyclo[3.2.0]hepta-3,6-diene (negative peaks).

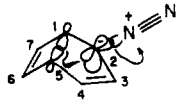
strong absorptions at 2045, 1568, and 685 cm^{-1} as well as the subsequent photochemistry. Irradiation with very long wavelengths (>574 nm) results in destruction of **14** and formation of cyclopentadiene as the sole observable photoproduct (Figure 1). Furthermore, irradiation with shorter wavelengths (250 ± 9 nm) gives only cyclopentadiene and bicyclo[2.1.0]pentene (**15**).[15] No spectroscopic evidence (ESR, IR) was obtained for the intermediacy of cyclopent-1-en-3-ylidene (**16**) or the formation of vinylallene, which could arise by ring opening in analogy with the photochemistry of **18** (vide infra).

Pyrolysis of the tosylhydrazone sodium salt **17** at 101 °C and condensation of the volatile products with Ar onto a CsI window cooled to 25 K provides matrix-isolated 2-diazobicyclo[3.2.0]hepta-3,6-diene (**18**) as evidenced by



17 18 2 19

the infrared spectrum (Figure 2) which shows absorptions at 2045, 854, 752, 718, and 704 cm^{-1}. Again, the subsequent photochemistry corroborates the existence of **18**. Irradiation with long wavelengths (>574 nm) destroys **18** with concomitant formation of cycloheptatetraene (**19**) as the sole observable photoproduct. The identity of **19** was confirmed by comparison with an authentic spectrum produced in the photolysis of phenyldiazomethane.[4] Cycloheptatetraene shows absorptions at 1818, 1810, 1600, 1376, 771, 687(sh), and 667 cm^{-1} (Figure 2). Again, **2** was not observed spectroscopically (ESR, IR). This experiment does not rule out the possibility that the triene **4** is formed initially, but undergoes photolytic ring opening faster than it is formed. This possibility is unlikely, owing to the fact that pyrolysis of **18** at 250 °C prior to condensation with

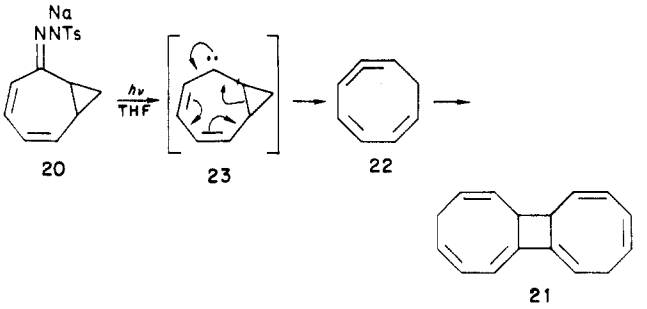


18

Ar also produces cycloheptatetraene. The triene is known to survive at temperatures up to 300 °C.[16]

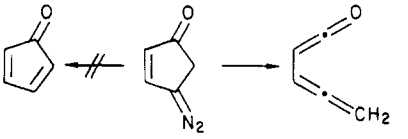
Ring opening dominates the chemistry of **2** as a result of two reinforcing effects. First, C–H insertion or 1,2-bond migration is disfavored because it would produce a strained exocyclic double bond. On the other hand, ring opening is favored because it relieves a minimum of 30 kcal/mol of strain imparted by the cyclobutene moiety. If cycloheptatetraene formation occurs directly with loss of nitrogen, then ring opening happens as a result of the interaction of the $C_{1,5}$-bond with the backside of the C–N σ-bond. Unfortunately, this study cannot answer whether reaction occurs directly from the diazo compound or from the carbene.

This facile ring opening observed with **2** occurs with other carbenes adjacent to small rings. For example, photolysis of **20** gives rise to a 70% yield of allene dimer **21**. The allene **22** is formed through ring opening of the



20 23 22 21

cyclopropane in carbene **23**.[17] We have also found that ring opening occurs when C–H insertion would give an antiaromatic system in the case of 3-diazo-4-cyclopentenone (**24**).[18]



24

Experimental Section

Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. ^{1}HMR spectra were recorded on a Bruker WP-200 spectrometer and reported in ppm relative to Me_4Si. IR spectra were recorded on a Perkin-Elmer Model 580B spectrometer. UV–vis spectra were obtained from a Beckman ACTA-CV spectrometer. Mass spectra were run on an AEI MS-9 or MS-902 spectrometer by the UCLA Chemistry mass spectrometer facility. Microanalytical determinations were performed by Spang Microanalytical Laboratory, Eagle Harbor, Michigan. The matrix isolation technique used in these laboratories is described elsewhere.[19]

2-(Phenylsulfinyl)cyclopentanone (6).[12] A solution of cyclopentanone (2.2 g, 26 mmol) in DME (5 mL, distilled from Na^0) was added dropwise to a slurry of NaH (2.3 g, 60% in oil, 58 mmol) and methyl benzenesulfinate[20] (4.5 g, 29 mmol) in DME (40 mL) heated at reflux under N_2. An exothermic reaction took place after one-third of the cyclopentanone solution had been added. Relux continued overnight. After cooling, excess NaH was quenched with EtOH (5 mL), and the reaction was diluted with H_2O (100 mL), acidified to pH 0, and extracted with Et_2O (2 ×

(15) Braumann, J. I., van Tamelen, E. E.; Ellis, L. E. *J. Am. Chem. Soc.* **1971**, *93*, 6145–6151.

(16) Jones, W. M.; Brown, W. T. *J. Org. Chem.* **1979**, *44*, 3090–3092.

(17) Oda, M.; Ito, Y.; Kitahara, Y. *Tetrahedron Lett.* **1975**, 2587–2590.

(18) Chapman, O. L.; Abelt, C. J. "Abstracts of Papers", 184th National Meeting of the American Chemical Society, Kansas City, Missouri, Sept 1982; American Chemical Society: Washington, D.C., 1982; ORGN 137.

(19) McMahon, R. J.; Chapman, O. L.; Hayes, R. A.; Hess, T. C.; Krimmer, H.-P. *J. Am. Chem. Soc.* **1985**, *107*, 7597–7606.

(20) Field, L.; Locke, J. M. "Organic Syntheses"; Wiley: New York, 1973; Collect. Vol. V, pp 723–726.

100 mL). The organic layers were combined and extracted with 5% aqueous NaOH (2 × 100 mL). The base layers were combined, acidified to pH 0, and extracted with Et_2O (2 × 150 mL). The Et_2O layers were combined, washed with saturated aqueous NaCl (200 mL), dried (Na_2SO_4), and concentrated in vacuo. The residue was chromatographed on silica gel (10% CH_3CN/CH_2Cl_2, R_f 0.25) giving 2-(phenylsulfinyl)cyclopentanone as a mixture of diastereomers (1.26 g, 6.05 mmol, 23%): ^{1}HMR ($CDCl_3$) δ 7.28–7.63 (m, 5 H), 3.78 (dd, 8.6 and 6.0 Hz, 0.21 H), 3.31 (dd, 8.8 and 8.8 Hz, 0.79 H), 1.67–2.62 (m, 6 H); IR ($CDCl_3$) 3063, 2974, 2887, 1737, 1475, 1444, 1403, 1314, 1274, 1263, 1190, 1143, 1084, 1048, 1000, 825 cm^{-1}; UV (EtOH) 252 nm (log ε 3.59); MS (16 eV), *m/e* (% base) 208 (95.9), 126 (100), 125 (44.8), 110 (16.4), 83 (84.0), 82 (48.5), 78 (45.5), 55 (24.4).

2-(Phenylsulfinyl)cyclopentanone Tosylhydrazone (7). $TsNHNH_2$ (1.08 g, 5.80 mmol) was added in one portion to a solution of 2-(phenylsulfinyl)cyclopentanone (1.26 g, 6.05 mmol) in EtOH (2 mL). More EtOH (3 mL) was added, and the solution was warmed until the $TsNHNH_2$ completely dissolved. The mixture was stirred under N_2 overnight. The resulting solid was filtered and washed with cold 95% EtOH. Air-drying gave the crude tosylhydrazone 7 as a white solid (1.56 g, 4.14 mmol, 71%). This product was used without purification. Chromatography on silica gel (gradient elution: 0–9% CH_3CN/CH_2Cl_2, R_f 0.48 in 10% CH_3CN/CH_2Cl_2) gave an analytical sample, mp 142–143 °C: ^{1}HMR ($CDCl_3$) δ 7.98 (d, 8.3 Hz, 2 H), 7.06–7.52 (m, 7 H), 4.60 (dd, 8.9 and 7.4 Hz, 1 H), 2.51 (s, 3 H), 2.14–2.51 (m, 2 H), 1.51–1.72 (m, 1 H), 1.32–1.48 (m, 1 H), 1.09–1.28 (m, 1 H), 0.84–1.01 (m, 1 H); IR ($CDCl_3$) 3064, 2974, 2870, 1596, 1444, 1349, 1168, 1119, 1047, 814, 673, 599 cm^{-1}; UV (EtOH) 232 nm (sh, log ε 4.02), 268 nm (sh, log ε 3.70); MS (16 eV), *m/e* (% base) 250 (4.0), 157 (11.2), 126 (52.9), 125 (33.1), 110 (11.9), 109 (25.1), 95 (58.4), 94 (17.0), 78 (73.1), 77 (10.7), 67 (100), 66 (33.6), 65 (15.2); $m^+ - C_6H_6SO$ calcd 250.0773, obsd 250.0789.

2-Cyclopentenone Tosylhydrazone (8). A solution of crude 2-(phenylsulfinyl)cyclopentanone tosylhydrazone (1.56 g, 4.14 mmol) in benzene (disilled and stored over 4-Å molecule sieves) was heated at reflux for 18 h. After cooling, the precipitate was filtered, washed with cold 95% EtOH, and air-dried giving crude 2-cyclopentenone tosylhydrazone (690 mg, 2.76 mmol, 67%). Recrystallization of the combined washings and mother liquor gave a second crop (253 mg, 1.01 mmol, 78% combined yield): ^{1}HMR ($CDCl_3$) δ 7.87 (d, 8.2 Hz, 2 H), 7.32 (d, 8.2 Hz, 2 H), 6.66 (d of t, 5.7 and 2.7 Hz, 1 H), 6.24 (d of t, 5.7 and 2.1 Hz, 1 H), 2.56–2.64 (m, 2 H), 2.36–2.42 (m, 5 H); IR ($CDCl_3$) 3292, 3214, 3052, 2923, 1624, 1596, 1495, 1444, 1400, 1363, 1333, 1304, 1231, 1166, 1091, 1033, 844, 813, 676, 561 cm^{-1}; UV (95% EtOH) 219 nm (log ε 4.10), 251 nm (log ε 4.09); MS (16 eV), *m/e* (% base) 250 (24.3), 95 (100), 94 (68.9), 66 (29.7); m^+ calcd 250.0773, obsd 250.0774.

Anal. Calcd for $C_{12}H_{14}N_2O_2S$: C, 57.58; H, 5.64; N, 11.19; S, 12.81. Found: C, 57.65; H, 5.52; N, 11.19; S, 12.89.

NaH (103 mg, 60% in oil, 2.57 mmol) was added to a solution of 2-cyclopentenone tosylhydrazone (538 mg, 2.15 mmol) in THF (20 mL, distilled from Na^0–benzophenone), and the reaction was stirred under N_2 for 4 h. The slurry was diluted with petroleum ether (200 mL), and the salt was filtered and washed with petroleum ether (100 mL). Drying in vacuo gave the sodium salt **13** (590 mg, 2.17 mmol, 100%).

3-(Phenylsulfinyl)bicyclo[3.2.0]hept-6-en-2-one (10). A solution of bicyclo[3.2.0]hept-7-en-2-one[13] (1.98 g, 18.3 mmol) in DME (10 mL, distilled from Na^0) was added dropwise over 5 min to a slurry of NaH (1.55 g, 60% in oil, 38.8 mmol), methyl benzenesulfinate[20] (3.15 g, 20.2 mmol), and DME (20 mL) heated at reflux under N_2. An exothermic reaction took place after one-third of the solution had been added, and the reaction mixture turned green. Relux was maintained for 10 min after addition was complete, and the reaction was allowed to cool to room temperature. EtOH (2 mL) was added to quench any residual NaH, and the viscous mixture was dissolved in 5% aqueous NaOH (100 mL). The solution was washed with Et_2O (100 mL) and acidified to pH 0. The aqueous layer was extracted with Et_2O (2 × 100 mL), and the combined organic layers were washed with saturated aqueous $NaHCO_3$ (2 × 100 mL), dried (Na_2SO_4), and concentrated in vacuo giving a diastereomeric mixture of crude 3-(phenylsulfinyl)bicyclo[3.2.0]hept-7-en-2-one (2.72 g, 11.7 mmol, 64%) as a dark viscous liquid. This product was used without further purification. Chromatography on silica gel (gradient elution: 0–12% CH_3CN/CH_2Cl_2, R_f 0.35 in 10% CH_3CN/CH_2Cl_2) gave an analytical sample: ^{1}HMR ($CDCl_3$) δ 7.48–7.61 (m, 5 H), 6.28 (d, 2.5 Hz, 1 H), 6.08 (d, 2.5 Hz, 1 H), 3.97 (dd, 10.6 and 8.8 Hz, 1 H), 3.46–3.50 (m, 2 H), 2.55–2.73 (m, 2 H), 1.54 (dd, 13.9 and 8.8 Hz, 1 H); IR ($CDCl_3$) 3052, 2950, 1733, 1479, 1445, 1325, 1254, 1163, 1086, 1048, 828, 748, 692 cm^{-1}; UV (MeOH) 247 nm (log ε 3.80), 301 nm (sh, log ε 2.76); MS (16 eV), *m/e* (% base) 232 (10.8), 126 (79.1), 110 (39.4), 107 (21.8), 106 (41.0), 79 (23.2), 78 (100); m^+ calcd 232.0555, obsd 232.0499.

3-(Phenylsulfinyl)bicyclo[3.2.0]hept-6-en-2-one Tosylhydrazone (11). A mixture of crude 3-(phenylsulfinyl)bicyclo[3.2.0]hept-7-en-2-one (2.72 g, 11.7 mmol) and $TsNHNH_2$ (2.18 g, 11.7 mmol) in MeOH (8 mL) was stirred for 24 h. The solution was cooled in an ice bath, and the precipitate was filtered, washed with cold 95% EtOH, and air-dried for 1.5 h, giving the tosylhydrazone as a white solid (3.30 g, 8.24 mmol, 70%), mp 160–161 °C: ^{1}HMR (CD_2Cl_2) δ 7.91 (d, 8.4 Hz, 2 H), 7.44 (d, 8.4 Hz, 2 H), 7.07–7.55 (m, 5 H), 6.03 (m, 2 H), 5.12–5.27 (m, 1 H, obscured by CH_2Cl_2), 2.49–2.57 (m, 1 H), 2.52 (s, 3 H), 2.31 (br d, 3.8 Hz, 1 H), 2.10 (ddd, 16.1, 10.0, and 4.2 Hz, 1 H), 1.91 (ddd, 16.1, 9.4, and 3.8 Hz); IR (Nujol) 1443, 1348, 1187, 1167, 1045, 1014, 933, 851, 816, 746, 687, 656 cm^{-1}; UV (95% EtOH) 237 nm (sh, log ε 3.81), 266 nm (sh, log ε 3.51), 273 nm (sh, log ε 3.49); MS (16 eV), *m/e* (% base) 274 (5.2), 126 (100), 125 (28.2), 119 (78.1), 118 (40.2), 110 (29.3), 92 (42.9), 91 (82.7), 90 (67.7), 78 (81.9); $m^+ - C_6H_6SO$ calcd 274.0773, obsd 274.0764.

Bicyclo[3.2.0]hepta-3,6-dien-2-one Tosylhydrazone (12). A slurry of 3-(phenylsulfinyl)bicyclo[3.2.0]hept-6-en-2-one tosylhydrazone (1.03 g, 2.57 mmol) in CH_3CN (50 mL) was heated at reflux under N_2 until the solution cleared (ca. 90 min). Solvent was removed under vacuum (0.01 torr), and the residue was dissolved in a minimum amount of CH_2Cl_2. After a few minutes a solid precipitated, and it was isolated by using a centrifuge. The solid was washed with Et_2O (5 mL) and dried in vacuo giving unreacted starting material (150 mg, 0.39 mmol, 15%). The mother liquor and washing were combined and concentrated in vacuo. Recrystallization (CH_2Cl_2/Et_2O) gave bicyclo[3.2.0]hepta-3,6-dien-2-one tosylhydrazone (292 mg, 1.07 mmol, 49% based on recovered **11**, combination of three crops), mp 155–156 °C: ^{1}HMR ($CDCl_3$) δ 7.85 (d, 8.2 Hz, 2 H), 7.58 (br s, 1 H), 7.31 (d, 8.2 Hz, 2 H), 6.63 (dd, 5.7 and 2.8 Hz, 1 H), 6.33 (d, 2.6 Hz, 1 H), 6.17 (d, 2.6 Hz, 1 H), 6.16 (d, 5.7 Hz, 1 H), 3.95 (dd, 2.8 and 2.5 Hz, 1 H), 3.81 (d, 2.5 Hz, 1 H); IR ($CDCl_3$) 3284, 3210, 3056, 2930, 1620, 1596, 1399, 1359, 1331, 1167, 1088, 1034, 812, 558 cm^{-1}; UV (95% EtOH) 264 nm (sh, log ε 4.05), 312 nm (sh, log ε 3.13); MS (16 eV), *m/e* (% base) 274 (21.5), 167 (17.3), 119 (76.4), 118 (100), 92 (16.9), 91 (24.5), 90 (72.1); m^+ calcd 274.0773, obsd 274.0776.

Anal. Calcd for $C_{14}H_{14}N_2O_2S$: C, 61.29; H, 5.14; N, 10.21; S, 11.69. Found: C, 61.05; H, 5.09; N, 10.07; S, 11.64.

A solution of bicyclo[3.2.0]hepta-3,6-dien-2-one tosylhydrazone (160 mg, 0.58 mmol) in CH_2Cl_2 (5 mL) was added all at once to NaH (28 mg, 60% in oil, 0.70 mmol) which had been washed once with petroleum ether. The mixture was stirred under N_2 for 1.5 h and diluted with petroleum ether (100 mL). The solid was filtered and dried in vacuo at 40 °C giving the sodium salt **17** (110 mg, 0.37 mmol, 64%).

Pyrolysis of Tosylhydrazone Sodium Salts. The finely ground sodium salt was placed into a cylindrical glass bulb that fits directly into a port on our matrix isolation apparatus. Pyrolysis was performed with a Kugelrohr oven, and the effluent was cocondensed with argon onto a CsI window cooled to 25 K.

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Registry No. **6** (isomer 1), 98877-45-3; **6** (isomer 2), 98877-46-4; **7**, 98877-47-5; **8**, 98877-48-6; **9**, 1072-77-1; **10**, 98877-49-7; **11**, 98877-50-0; **12**, 98877-51-1; **13**, 98877-52-2; **14**, 98877-53-3; **15**, 5164-35-2; **17**, 98877-54-4; **18**, 98877-55-5; **19**, 52783-93-4; PhS(O)OMe, 670-98-4; $TsNHNH_2$, 1576-35-8; cyclopentadiene, 542-92-7; cyclopentanone, 120-92-3.