aromatic H); mass spectrum, *m/e* (relative intensity) 222 (M$^+$, 69), 105 (100), 77 (51). Anal. Calcd for $C_{16}H_{14}O$: C, 86.45: H, 6.35. Found: C, 86.44; H, 6.40.

After extraction, the residual solid, insoluble in ether, consisted of aniline hydrochloride, 0.25 g (98%).

Pyrolysis of 5. A solution of **5** (2 mmol) in xylene (10 mL) was refluxed until TLC showed the absence of **5** (~3 h). The solvent was distilled off under reduced pressure, and the residue was recrystallized from benzene-hexane to give **9**. Results are shown in Table II.

Photolysis of 5. A solution of **5** (1 mmol) in benzene (50 mL) was irradiated at room temperature under nitrogen with a high-pressure mercury lamp through a Pyrex filter. After TLC showed the disappearance of **5**, the resulting solution was concentrated, and the residue was chromatographed to give **9** (a satisfactory isolation was not achieved) and a complex mixture of products. Results are shown in Table II.

Registry No. 3a, 4425-82-5; **3a** (polymer), 79918-16-4; **3b**, 1836-87-9; **4a**, 622-37-7; **4b**, 2101-86-2; **4c**, 2101-87-3; **4d**, 3296-05-7; **4e**, 1516-60-5; **5a**, 79918-17-5; **5b**, 79918-18-6; **5c**, 79918-19-7; **5d**, 79918-20-0; **9a**, 3920-79-4; **9b**, 79918-21-1; **9c**, 79918-22-2; **9d**, 79918-23-3; **9e**, 79918-24-4; **10a**, 79918-25-5; **10b**, 79918-26-6; **10c**, 79918-27-7; **10d**, 79918-28-8; **10e**, 79918-29-9; **11c**, 5455-02-7; **18**, 42540-65-8; **20**, 5685-39-2.

Supplementary Material Available: Characterization data of **5b–d**, **9c–e**, and **10b–e** (4 pages). Ordering information is given on any current masthead page.

Pyrolysis of the Tosylhydrazone Sodium Salts of Two Bicyclic Lactones

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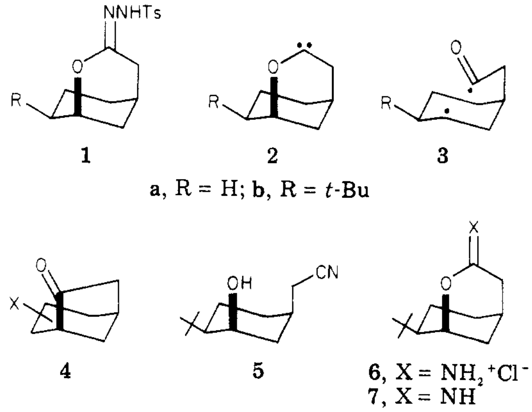
Lactone tosylhydrazone sodium salt **17a** was prepared from lactone **10** by way of thionolactone **14**. The *tert*-butyl homologue **17b** was available by way of hydroxy nitrile **5**. Pyrolysis of these salts led to enol ethers **18a,b** and the ring-contracted ketones **19a,b**. Together with earlier work, our results suggest that biradical **3** is probably an intermediate in conversion of alkoxycarbene **2** to ketone **4** and that the activation energy for this biradical coupling is ~2–3 kcal/mol.

Earlier investigations in our laboratory demonstrated that pyrolysis of lactone tosylhydrazone sodium salts leads to cyclic alkoxycarbenes that generally undergo both a 1,2-shift of hydrogen and also carbon–oxygen bond scission to furnish alkyl acyl biradicals.[1,2] These biradicals collapse to cyclic ketones and, depending on the specific case, may also yield other products. In an investigation related to this earlier work, we have now prepared the bicyclic ketone tosylhydrazones **1a,b**, pyrolyzed the derived salts, and examined the products formed by way of the presumed alkoxycarbenes **2a,b** (Chart I). Our main purpose was to study the behavior of biradicals **3a,b** derived from the carbenes, to compare their behavior with each other, and to compare the behavior of these thermally generated singlet biradicals with that of closely related biradicals reached photochemically on irradiation of a number of substituted bicyclo[3.2.1]octan-6-ones (**4**).[3] Erratic distribution of pyrolytic products interfered with attainment of these goals, but the results do provide useful information on these topics and add to the rather meager information available on thermally generated alkoxycarbenes.[4] Preparative experiments are given first, followed by pyrolytic studies.

Chart I

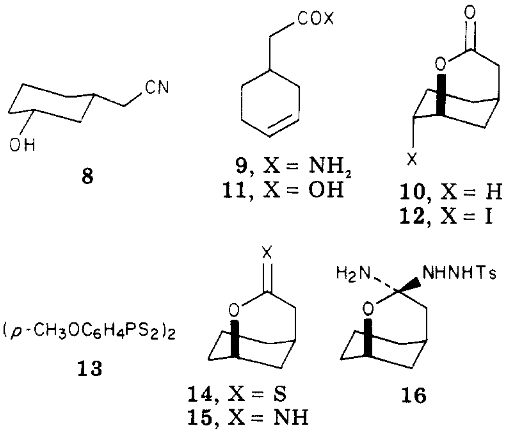


1 2 3

a, R = H; b, R = *t*-Bu

4 5 6, X = NH$_2^+$Cl$^-$
7, X = NH

Chart II



8

9, X = NH$_2$
11, X = OH

10, X = H
12, X = I

13

14, X = S
15, X = NH

16

Preparative Experiments

The starting material for **1b** was the hydroxy nitrile **5** the preparation of which we have described elsewhere.[5] This substance underwent slow cyclization to the imidolactone hydrochloride **6** on exposure to dry hydrogen chloride in benzene.[6] Severe steric congestion about the

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[1] Foster, A. M.; Agosta, W. C. *J. Am. Chem. Soc.* **1972**, *94*, 5777; **1973**, *95*, 608. Smith, A. B., III; Foster, A. M.; Agosta, W. C. *Ibid.* **1972**, *94*, 5100.

[2] Yates, P.; Loutfy, R. O. *Acc. Chem. Res.* **1975**, *8*, 209 and references cited therein.

[3] Agosta, W. C.; Wolff, S. *J. Am. Chem. Soc.* **1976**, *98*, 4182, 4316; **1977**, *99*, 3355.

[4] The statement that "alkoxycarbenes have proven extremely difficult to prepare by conventional synthetic methods" (Lucchese, R. R.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1978**, *100*, 298) is perhaps excessive, but it is certainly true that apart from photochemical work only a few studies of these species are on record.

[5] Ayral-Kaloustian, S.; Agosta, W. C. *J. Org. Chem.* **1981**, *46*, 4880.

0022-3263/82/1947-0284$01.25/0

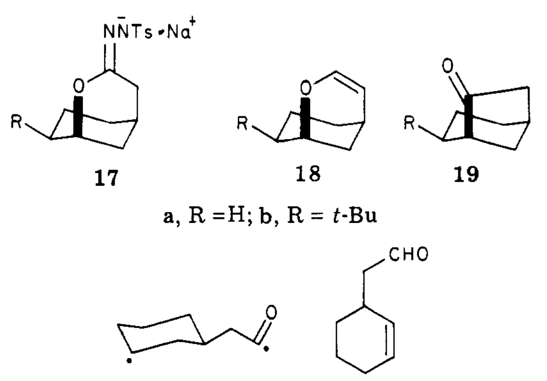
hydroxyl group of **5** and related compounds is manifest in a number of other reactions,[5] and in the present instance the Pinner reaction is slow probably because the cyano group is preferentially turned away from the hydroxyl to minimize the 1,3-diaxial interaction. Treatment of **6** with base furnished the free imidate **7**, which reacted with tosylhydrazine in ethanol, yielding the desired lactone tosyldrazone **1b**. We found it necessary to use the free imidate here, since, contrary to simpler examples,[1,7] the hydrochloride **6** was nearly inert to tosylhydrazine.

Attempts to develop a parallel synthesis of **1a** from the parent *cis*-3-hydroxycyclohexaneacetonitrile (**8**,[5] Chart II) were unsuccessful, as were attempts based on several other 1,3-disubstituted cyclohexanes. We were also disappointed in efforts to adapt to the amide **9**[8] the earlier successful cyclization of an open-chain unsaturated amide in the presence of halogens or mineral acid.[9] It was apparent that the various approaches using **8** and related cyclohexanes failed to overcome the problem presented by their preferred diequatorial conformation.

These observations suggested that the oxabicyclononane skeleton of **1a** be prepared in some convenient form and subsequently manipulated without ring opening to provide the desired hydrazone. We exploited this approach with success starting from the known[10] simple δ-lactone **10**. It was convenient to prepare **10** through iodolactonization[11] of 3-cyclohexene-1-acetic acid (**11**), followed by reductive removal of iodine from the iodolactone **12**[11] with tributylstannane.[12] The obvious limitation to use of **10** as a starting material is that most reagents that attack an ester carbonyl group lead to acyl–oxygen cleavage, the change expressly to be avoided here. A possibly useful reaction, however, was suggested by the fact that both open-chain esters and simple lactones are smoothly transformed into the corresponding thionoesters and thionolactones on reaction with the dimer of "*p*-methoxyphenylthionophosphine sulfide" (**13**).[13,14] This observation implies that thionation of lactone **10** should proceed without ring cleavage. In the event this was correct, treatment of **10** with sulfide **13** in hot toluene furnished the thiolactone thionolactone in 75–80% crude yield.

Previous investigators have found that thionoesters react in a variety of ways with hydrazines[15] but are often converted to imidates on quite mild treatment with primary amines.[16] Our experience with **14** is in agreement with these reports; exposure of **14** to hydrazine or tosylhydrazine led to complex mixtures, but reaction with liquid ammonia proceeded smoothly to furnish the imido lactone **15** in 75–80% yield. This in turn reacted[1,7] with tosylhydrazine to give **1a** as desired. The yield in this last reaction was low, probably as a result of stereoelectronic control.[17] From examination of molecular models it appears that in tetrahedral intermediate **16** (or its epimer) carbon–oxygen cleavage is stereoelectronically favored in all conformations. Loss of ammonia from **16**, on the other hand, requires a sterically hindered conformation in order to benefit from stereoelectronic factors. In the *tert*-butyl-substituted series, conversion of **7** to **1b** was more successful. Presumably competitive carbon–oxygen cleavage here could be reversible, since the relevant groups are locked in a cis diaxial conformation. This would then afford greater opportunity for irreversible expulsion of ammonia.

Chart III



17 **18** **19**

a, R = H; b, R = *t*-Bu

20 **21**

Results and Discussion

The lactone tosylhydrazones **1a,b** were converted to their sodium salts **17a,b**, respectively (Chart III), by treatment with methanolic sodium methoxide and then decomposed by rapid heating to 190 or 310 °C at 0.2–0.4 torr in a closed system without solvent. Decomposition was slower at the lower temperature, but experiments with salt **17b** yielded similar results at the two temperatures. The pyrolytic products were purified by vapor-phase chromatography (VPC) and identified through their spectroscopic properties which are given in detail in the Experimental Section. From **17a** the major products, formed in 65–70% yield, were enol ether **18a** and ketone **19a**, and from **17b** (70–80%) they were the corresponding *tert*-butyl-substituted products **18b** and **19b**. The two enol ethers and ketone **19b** gave spectra quite similar to those of previously described and closely related compounds on hand from other work,[3] and **19a** was identical with an authentic sample of this ketone.[3,18] The yields in these thermolyses were reproducible, but the product distributions were not. While **19a** was occasionally 30–55% of the product from decomposition of **17a**, this reaction usually gave largely **18a**. In four sequential runs from the same batch of tosylhydrazone salt **17b**, ketone **19b** constituted from 9% to 83% of the total volatile products, with an average of 45%. The reasons for this erratic behavior were not identified, despite considerable effort. Our results indicate, however, that the preferred pathway generally followed by the alkoxycarbenes **2a,b** is a 1,2-shift of hydrogen, rather than ring contraction to ketone.

Earlier investigations have shown that an important reaction of **3a** generated on photochemical α cleavage of

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(6) Neilson, D. G. In "The Chemistry of Amidines and Imidates"; Patai, S., Ed., Wiley: New York, 1975; pp 389–394 and references cited therein.

(7) Crawford, R. J.; Raap, R. *Can. J. Chem.* **1965**, *43*, 126.

(8) Boehme, W. R. *J. Org. Chem.* **1961**, *26*, 2107. Kugatova-Shemyakina, G. P.; Poskiene, R. A. *Zh. Org. Khim.* **1966**, *2*, 844.

(9) Craig, P. N. *J. Am. Chem. Soc.* **1952**, *74*, 129. See also: Goodman, L.; Winstein, S. *Ibid.* **1957**, *79*, 4788. Peter, H.; Brugger, M.; Schreiber, J.; Eschenmoser, A. *Helv. Chim. Acta* **1963**, *46*, 577. Stirling, C. J. M. *J. Chem. Soc.* **1960**, 255.

(10) Mori, K.; Matsui, M.; Sumiki, Y. *Agric. Biol. Chem.* **1961**, *25*, 205.

(11) Klein, J. *Isr. J. Chem.* **1963**, *1*, 385.

(12) Cf.: Lythgoe, B.; Manwaring, R.; Milner, J. R.; Moran, T. A.; Nambudiry, M. E. N.; Tideswell, J. *J. Chem. Soc., Perkin Trans. 1* **1978**, 387. Kuivila, H. G. *Acc. Chem. Res.* **1968**, *1*, 299.

(13) Pedersen, B. S.; Scheibye, S.; Clausen, K.; Lawesson, S.-O. *Bull. Soc. Chim. Belg.* **1978**, *87*, 293. Scheibye, S.; Kristensen, J.; Lawesson, S.-O. *Tetrahedron* **1979**, *35*, 1339.

(14) This compound is the crystalline product formed from reaction of anisole with phosphorus pentasulfide: Lecher, H. Z.; Greenwood, R. A.; Whitehouse, K. C.; Chao, T. H. *J. Am. Chem. Soc.* **1956**, *78*, 5018.

(15) Walter, W.; Weiss, H.; Reubke, K.-J. *Justus Liebigs Ann. Chem.* **1970**, *736*, 166.

(16) Barnikow, G.; Strickmann, G. *Chem. Ber.* **1966**, *100*, 1661. Raap, R. *Can. J. Chem.* **1968**, *46*, 2255.

(17) Deslongchamps, P. *Tetrahedron* **1975**, *31*, 2463.

(18) Wiberg, K. B.; Hess, B. A., Jr. *J. Org. Chem.* **1966**, *31*, 2250.

19a is conformational inversion to **20** followed by disproportionation to 2-cyclohexene-1-acetaldehyde (**21**).[3] In photolysis of ketones yielding biradicals in which conformational inversion is disfavored, on the other hand, the corresponding aldehyde is less important or absent as a product.[3] These photochemical reactions then show a product distribution that is dependent on the conformational properties of the intermediate biradicals. The present study, in contrast, reveals that **2a** and **2b** behave about the same, despite the differences in conformational preference expected for **3a** and **3b**. With these facts in mind, we were particularly interested in determining whether **21** was among the products from **17a**. Control experiments indicated as little as a 2% yield of **21** would have been recovered and readily detected, but none was found.

These results suggest that if biradical **3a** is indeed an intermediate in the thermal reaction, collapse of **3a** to **19a** competes successfully with inversion to **20**. Since the barrier to inversion of **3a** is ∼5 kcal/mol,[3] this requirement would be met if the activation energy for collapse of **3a** is no more than 2–3 kcal/mol. Activation energies for coupling of such singlet biradicals are not yet well established; a barrier of 2–3 kcal/mol here seems low but credible.[19] We note also that for the reverse photochemical isomerization of certain ketones to alkoxycarbenes[2] both concerted[20] and biradical[21] paths have been proposed. Our present finding that aldehyde **21** is not among the products from **17a** is, in itself, consistent with concerted isomerization of **2a** to **19a**. A concerted rearrangement seems less likely, however, in view of earlier results implicating a biradical mechanism for the thermal process.[1]

Experimental Section

General Methods. All VPC was carried out on a Varian Aerograph Model 920 gas chromatograph using a column prepared from aluminum tubing (0.25 in. × 8 ft) packed with 25% QF-1 on 40/60 Chromosorb W and operating at a helium flow rate of 95–120 mL/min. Unless otherwise specified, IR and NMR spectra were obtained for CCl_4 solutions, the former on a Perkin-Elmer Model 237 B spectrophotometer and the latter on a Varian T-60A (60 MHz) spectrometer. All NMR signals are reported relative to tetramethylsilane (∼1% internal reference; 0 ppm). Melting points were obtained on a Thomas-Hoover apparatus in sealed capillaries and are corrected. Unless otherwise noted, solutions were dried over $MgSO_4$, K_2CO_3, or Na_2SO_4, and solvents were removed in vacuo with a rotary evaporator. High-resolution mass spectra were determined at the Mass Spectrometry Center of the University of Pennsylvania.

***endo*-8-*tert*-Butyl-3-imino-2-oxabicyclo[3.3.1]nonane Hydrochloride (6).** A solution of *cis*-4-*tert*-butyl-*cis*-3-hydroxycyclohexaneacetonitrile (**5**; 125 mg, 0.64 mmol)[5] in benzene (1.25 mL) was saturated with anhydrous HCl (bubbled through the solution for 15 min at 0–5 °C), sealed in a container, and stored for 3 days at room teperature. Removal of solvent gave a yellowish solid, 145 mg (98%). A sample purified by recrystallization from CH_2Cl_2/ether was characterized as **6**: mp 145.5–146.5 °C; IR ($CHCl_3$) 3640 (w), 3500–2375 (s), 1647 (s), 1539 (w), 1464 (s), 1394 (m), 1364 (w), 1347 (w), 1325 (w), 1303 (vw), 1289 (vw), 1278 (vw), 1119 (s), 1083 (m), 1039 (w), 1006 (w), 972 (vw), 955 (w), 937 (w), 889 (w), 872 (w) cm^{-1}; NMR ($CDCl_3$) δ 11.30 (br d, $J \approx 32$ Hz, 2 H), 5.23 (br s, 1 H), 3.13 (br, 2 H), 2.80–1.15 (m, 8 H), 1.00 (br s, 9 H).

Anal. Calcd for $C_{12}H_{22}ClNO$: C, 62.18; H, 9.57; N, 6.04. Found: C, 61.98; H, 9.58; N, 5.94.

***endo*-8-*tert*-Butyl-2-oxabicyclo[3.3.1]nonan-3-one Tosylhydrazone (1b).** Hydrochloride **6** was dissolved in cold water and the solution washed with one portion of cold ether. The yellowish ether layer was discarded, and the aqueous phase was neutralized with saturated aqueous $NaHCO_3$ and extracted with several poritons of ether. The combined ether solution was dried and the solvent removed to yield a viscous oil (87%), identified as **7** from the following spectral properties: IR ($CHCl_3$) 3450–3050 (w), 2945 (s), 2855 (w), 1646 (s), 1479 (w), 1450 (w), 1397 (m), 1388 (m), 1363 (w), 1344 (w), 1316 (w, split), 1294 (m), 1274 (w), 1084 (s), 1008 (m), 957 (w), 944 (w), 908 (vw), 895 (vw), 875 (w) cm^{-1}; NMR ($CDCl_3$) δ 6.20 (br s, 1 H, variable), 4.63 (m, 1 H), 3.00–2.20 (m, $J \approx 16.5$, 5.5, 2.0 Hz, 2 H), 2.30–1.10 (m, 8 H), 0.96 (s, 9 H).

A solution of **7** (164 mg, 0.84 mmol) and tosylhydrazine (156 mg, 0.84 mmol) in EtOH (2.4 mL) was sealed under argon and stored for 6 days at room temperature. Most of the solvent was removed, and the crude mixture was diluted with CH_2Cl_2 and purified by thick-layer chromatography (two 20 × 20 cm Analtech "Uniplates", 2000-μm-thick silica gel with UV-254 zinc silicate phosphor indicator; eluted with ether). The major band (R_f 0.67–0.79) was extracted with CH_2Cl_2 and EtOAc. Removal of the solvent gave a crude solid (∼45%) consisting of the desired product (∼75%) and a carbonyl compound (10–30%). Recrystallization from CCl_4/pentane gave a white solid (102 mg, 33%) identified as **1b**: mp 107.0–109.0 °C; IR ($CHCl_3$) 3275 (w, br), 3000 (w), 2940 (s), 2850 (m), 1638 (s), 1596 (w), 1455 (w, split), 1421 (w), 1387 (m), 1372 (m), 1324 (w, split), 1288 (w), 1250 (m), 1155 (vs), 1084 (m), 1012 (m, with sh), 986 (w), 963 (w), 926 (vw), 800 (w) cm^{-1}; NMR ($CDCl_3$) δ 7.76 (d, $J \approx 8$ Hz, 2 H), 7.57 (br s, 1 H), 7.24 (d, $J \approx 8$ Hz, 2 H), 4.73 (s, 1 H), 2.90–2.30 (m, 2 H, with s at 2.42, 3 H), 2.30–1.00 (m, 8 H), 0.87 (s, 9 H).

Anal. Calcd for $C_{19}H_{28}N_2O_3S$: C, 62.62; H, 7.74; N, 7.69. Found: C, 62.38; H, 7.60; N, 7.74.

Preparation and Pyrolysis of Sodium Salt 17b. A solution of **1b** (19.8 mg, 0.054 mmol) in anhydrous MeOH (200 μL) was treated with a freshly prepared solution of $NaOCH_3$ in MeOH (50 μL, containing 0.058 mmol of $NaOCH_3$). After 30 min, removal of the solvent on a rotary evaporator gave the salt **17b** (22 mg) as a thin-film coating the bottom of the flask (5 mL, roundbottom). This was used without further handling for the pyrolysis described below. A similarly prepared sample of **17b** was recrystallized from ether as a white powder: mp 119.5–121.5 °C; IR ($CHCl_3$) 2940 (s), 2927 (w), 1628 (m), 1597 (w), 1385 (w), 1362 (w), 1318 (w), 1288 (w), 1212 (s, br), 1154 (w), 1115 (s), 1075 (s, with sh), 1030 (s, split), 970 (w), 947 (w), 926 (w, with sh), 888 (w, with sh), 800 (w) cm^{-1}; NMR (CD_3OD) δ 7.70 (d, $J \approx 8.5$ Hz, 2 H), 7.13 (d, $J \approx 8.5$ Hz, 2 H), 4.75 (br s, 1 H), 3.00–2.20 (m, 2 H, with s, 2.33, 3 H), 2.20–1.10 (m, 8 H), 0.93 (s, 9 H).

The flask containing the film of salt was connected to a bent bulb-to-bulb distillation apparatus, evacuated (initial pressure of 0.08 torr), and immersed in a 190 °C oil bath with the receiving end simultaneously immersed in a −78 °C bath. The solid appeared to melt and decompose slowly, forming a condensate above the heated flask. The stopcock leading to the pump was opened two or three times (pressure 0.2–0.4 torr), and the condensates were gently warmed with a heat gun to induce distillation. After 1 h the apparatus was removed from the bath, the flask containing the solid residue was disconnected, and the remaining parts were rinsed with pentane. Aliquots of the resulting pentane solution were analyzed by VPC (135 °C) to determine the yields by comparison with standards. The two major products (5.5- and 18.0-min retention times, 40% and 36% yields, respectively) were collected and identified as *endo*-8-*tert*-butyl-2-oxabicyclo[3.3.1]non-3-ene (**18b**) and *endo*-4-*tert*-butylbicyclo[3.2.1]octan-6-one (**19b**). (Two or more products more volatile than **18b**, amounting to ≤4% were observed. Another 2–4% yield of the volatile products appeared to be absorbed on the solid residue.) For **18b**: colorless oil; IR 3050 (w), 2950 (s), 1638 (m, split), 1476 (w), 1442 (w), 1387 (w), 1365 (w), 1227 (s), 1204 (w), 1083 (w), 1054 (m), 960 (w), 938 (w) cm^{-1}; NMR (Varian HR-220) δ 6.39 (d, $J = 6.0$ Hz, 1 H), 4.56 (ddd, $J \approx 6.0$, 6.2, 1.6 Hz, 1 H), 4.45 (m, 1 H), 2.40–1.00 (m, 8 H), 0.95 (s, 9 H); mass spectrum, m/z 180.1518

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[19] Wagner, P. J. "Rearrangements in Ground and Excited States"; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol 3, Chapter 20, p 414 and references cited therein.

[20] Stohrer, W.-D.; Jacobs, P.; Kaiser, K. H.; Wiech. G.; Quinkert, G. *Fortschr. Chem. Forsch.* **1974**, *46*, 181. Quinkert, G.; Jacobs, P.; Stohrer, W.-D. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 197. Quinkert, G.; Jacobs, P. *Chem. Ber.* **1974**, *107*, 2473.

[21] Turro, N. J.; McDaniel, D. M. *J. Am. Chem. Soc.* **1970**, *92*, 5727. Turro, N. J.; Morten, D. R. *Ibid.* **1971**, *93*, 2569. Morton, D. R.; Turro, N. J. *ibid.* **1973**, *95*, 3947.

(M$^+$; calcd for $C_{12}H_{20}O$, 180.1515). For **19b**: white solid; mp 36.0–37.5 °C; IR 2937 (s), 2860 (m), 1738 (s), 1475 (w), 1455 (w), 1389 (w), 1363 (m), 1230 (w), 1158 (w), 1142 (m), 1132 (w), 1108 (w), 1054 (w), 855 (w) cm^{-1}; NMR δ 2.65–2.28 (br d, $J \approx 6$ Hz, 2 H), 2.23–1.15 (m, 9 H), 0.90 (s, 9 H); mass spectrum, m/z 180.1514 (M$^+$; calcd for $C_{12}H_{20}O$, 180.1515). Various pyrolyses at 190 and 310 °C (Wood's metal bath; complete pyrolysis in ca. 15 min.) gave a 70–80% yield of the two major products. **19b** was usually 35–50% of the mixture, with a range of 9–83% under nominally identical conditions.

2-Oxabicyclo[3.3.1]nonane-3-thione (14). Jones oxidation of 3-cyclohexene-1-ethanol (Aldrich) gave the carboxylic acid **11**, which was iodolactonized according to Klein.[11] The product (**12**) was converted to lactone **10**[10] with tributylstannane and azobis(isobutyronitrile) catalyst.[12]

A solution of **10** (795 mg, 5.68 mmol) and reagent **13** (1.44 g, 3.58 mol)[13,14] in toluene (8.5 mL) was heated for 3 h at reflux and stirred overnight at room temperature. The white precipitate was filtered, washed with warm CH_2Cl_2, and discarded. The solution and washings were concentrated, and the mixture was purified by column chromatography (16 × 2.2 cm Woelm active silica gel; 70–150 mesh) with benzene/ether as the eluant [300 (benzene), 40 (3:1), 20 (1:1), 20 (1:3), and 100 mL (ether)]. Fractions containing the desired product (followed by TLC) were combined, and the solvent was removed to yield a solid (75–80% pure). Sublimation [40–65 °C (0.1 torr)] gave a pale yellow solid identified as **14**: mp 68.5–70.0 °C; IR 2950 (s), 2875 (w), 1449 (w), 1380 (m), 1361 (w), 1350 (w), 1328 (w), 1297 (m), 1233 (s), 1214 (s), 1169 (w), 1150 (s), 1097 (s), 1069 (m), 1031 (w), 1014 (w), 950 (m), 905 (w) cm^{-1}; NMR δ 4.93 (br s, 1 H), 3.15 (d, fine structure, $J \approx$ Hz, 2 H), 2.40–1.35 (m, 9 H).

Anal. Calcd for $C_8H_{12}OS$: C, 61.52; H, 7.75. Found: C, 61.50; H, 7.65.

2-Oxabicyclo[3.3.1]nonan-3-one Tosylhydrazone (1a). Thiolactone **14** (203 mg, 1.30 mmol) was placed in a 25-mL two-necked flask fitted with a dry ice condenser and a septum. The system was flushed with argon and cooled (−70 °C) while anhydrous ammonia was introduced through the septum with constant magnetic stirring. After 12–13 mL of ammonia had condensed in the flask (ca. 45 min), the gas inlet was removed and the cold bath warmed to −20 °C (15 min) and maintained at that temperature for 3.5 h. Finally the dry ice condenser and cold bath were removed to allow the ammonia to evaporate under a gentle stream of argon. When most of the solvent was gone, CH_2Cl_2 (3–4 mL) was added through the septum and all the remaining solvent removed at room temperature (45 min to 1 h). This gave a viscous oil containing **15** as the major product: 78–80% (by NMR); IR ($CDCl_3$) 3700–3100 (w), 2950 (s), 2890 (w), 2870 (w), 1638 (s), 1450 (w), 1388 (m), 1337 (m), 1313 (w), 1275 (w), 1245 (w), 1235 (m), 1210 (m), 1114 (w), 1100 (m), 1068 (m), 1039 (w) cm^{-1}; NMR ($CDCl_3$) δ 7.30 (br s, ~1 H, variable), 4.47 (br s, 1 H), 3.03–2.23 (m, 2 H), 2.30–0.90 (m, 9 H plus excess due to minor product). The minor product appeared (TLC, NMR) to be the hydroxy thio amide from ring opening of **14**. The mixture was used without further handling.

A solution of the crude oil (~1.01 mmol of **15**) from above and $TsNHNH_2$ (210 mg, 1.13 mmol) in anhydrous EtOH (2 mL) was sealed under argon and stored for 6 days at room temperature (see preparation of **1b**). Chromatography as before (two plates, eluted with 1:1 ether/toluene; R_f 0.47–0.58) followed by recrystallization (benzene/pentane) gave a white solid (31 mg, 10%) identified as **1a**: mp 137.5–139.5 °C; IR ($CHCl_3$) 3300 (br, m), 3030 (w), 2955 (s), 2890 (w), 2875 (w), 1639 (s), 1598 (w), 1488 (w), 1450 (w), 1377 (s), 1330 (s), 1312 (w), 1301 (w), 1287 (w), 1247 (s), 1160 (vs), 1100 (m), 1087 (m), 1072 (w), 1012 (s, br), 960 (m), 897 (w), 862 (w), 803 (w) cm^{-1}; NMR ($CDCl_3$) δ 7.79 and 7.28 (2 d, $J \approx 8$ Hz, overlapping with one variable proton, 5 H), 4.53 (br s, 1 H), 3.00–2.20 (m, with s at 2.42, 5 H), 2.30–0.90 (m, ~9 H).

Anal. Calcd for $C_{15}H_{20}N_2O_3S$: C, 58.43; H, 6.54; N, 9.09. Found: C, 58.56; H, 6.52; N, 9.06.

Preparation and Pyrolysis of Lactone Tosylhydrazone Sodium Salt 17a. A solution of **1a** (18.5 mg, 0.060 mmol) was treated with $NaOCH_3$ (0.065 mmol) to give **17a** (see **1b** → **17b**) which was used directly for pyrolysis. Spectra were obtained on a separate sample: IR ($CDCl_3$) 2950 (s), 1637 (m), 1488 (w), 1420 (w), 1385 (w), 1345 (w), 1285 (w), 1211 (w), 1162 (s), 1120 (m), 1082 (s, with sh), 1026 (m), 1005 (m), 803 (w) cm^{-1}; NMR ($CDCl_3$) δ 7.67 (d, $J \approx 8$ Hz, 2 H), 7.10 (d, $J \approx 8$ Hz, 2 H), 4.40 (br s, 1 H), 3.00–2.10 (m, 5 H), 2.10–0.90 (m, ~9 H).

Pyrolysis at 190 °C (as for **17b**) gave an ~70% total yield of 2-oxabicyclo[3.3.1]non-3-ene (**18a**) and bicyclo[3.2.1]octan-6-one (**19a**) (ratio of ~14:1). Ether **18a** was collected by VPC (110 °C, $t_R = 3.5$ min) as a waxy white solid and characterized from the following data: IR 3085 (w), 2960 (s), 2872 (w), 1633 (s), 1439 (w), 1250 (w), 1225 (s), 1207 (w), 1100 (w), 1044 (m), 1012 (w), 880 (w) cm^{-1}; NMR (Varian HR-220) δ 6.44 (d, $J = 6.0$ Hz, 1 H), 4.57 (ddd, $J \approx 6, 6, 1.5$ Hz, 1 H), 4.25 (s, 1 H), 2.29 (br s, 1 H), 2.00–0.70 (m, ~8 H); mass spectrum, m/z 124.0883 (M$^+$; calcd for $C_8H_{12}O$, 128.0888).

Ketone **19a** was the minor product (6–7%) in several runs of the pyrolysis. However, it was ≥30% of the mixture in two runs (310 and 190 °C) and ≥50% in another (190 °C). This product was also collected (110 °C, $t_R = 15$ min) and identified by its spectral properties (IR, NMR) that were identical with those of an authentic sample.[3,18]

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On the Thermal Isomerization of *trans*-Cyclooctene to *cis*-Cyclooctene

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The thermal isomerization of *trans*-1,2-dideuteriocyclooctene in adequately conditioned Pyrex ampules gives *cis*-1,2-dideuteriocyclooctene, a result which excludes radical chain, [1,3] hydrogen shift, and [1,2] hydrogen shift mechanisms. When inadequately conditioned ampules are employed, deuterium scrambling is evident in the *cis*-cyclooctene formed but not in the *trans*-cyclooctene recovered.

The ground-state properties of *trans*-cyclooctene[1] have been well-defined. The lowest energy conformation of this dissymmetric strained olefin is the "twist" or "crown" form **1**, with a C(8)–C(1)–C(2)–C(3) dihedral angle of 136°.[2-5]