0.10 g of off-white crystalline powder: mp 137–139 °C; IR (KBr) 3380 (m), 3170 (m), 1650 (s), 1590 (m-s), 1560 (s), 1468 (m), 1440 (m), 1390 (s) cm^{-1}.

Anal. Calcd for $C_9H_{12}N_2O_3$: C, 55.09; H, 6.17; N, 14.28. Found: C, 53.73; H, 6.64; N, 12.92. Material obtained from other runs of this reaction likewise failed to give good C, H, and N analyses; attempts at further purification of the salt resulted in decomposition.

Reaction of 4-Methylphthalimide with Ammonium Hydroxide. When 4-methylphthalimide was treated with NH_4OH as described above, an off-white powder was obtained. Recrystallization of the powder from water–ethanol afforded white crystals: mp 172–173 °C (melting point was not consistent from batch to batch); IR (KBr) 3420 (m-s), 3180 (m-s), 1710 (w), 1670 (m), 1620 (m-s), 1578 (m), 1538 (m-s), 1410 (m-s), 1390 (m-s) cm^{-1}.

Anal. Calcd for $C_9H_{12}N_2O_3$: C, 55.09; H, 6.17; N, 14.28. Found: C, 54.84; H, 6.15; N, 14.29.

A sample of the salt was treated with 10% hydrochloric acid. After the solvent had evaporated the residue was extracted with ethyl acetate. Addition of heptane to the extract induced crystallization of 4-methylphthalic acid: mp 156–157 °C (lit.[7] 152 °C); IR (KBr) ν_{CO} 1690 (s, br) cm^{-1}.

To a slurry of the salt (1.0 g) in 12 mL of DMF which was cooled to ca. −10 °C was added dropwise 1.7 mL of thionyl chloride. After the addition was complete, the temperature was allowed to rise to 24 °C and stirring was continued for 16 h. The reaction mixture was poured over 50 mL of ice and then filtered to collect 0.82 g (90%) of a white powder, spectroscopically identical with an authentic sample of 4-methylphthalimide.

A 50-mg sample of the salt was heated in an evacuated glass vessel for 15 min at 196 °C. Recrystallization of the cool melt from benzene–heptane afforded 33 mg (79%) of white powder: mp 194–195.5 °C (lit.[6] 196 °C), spectroscopically identical with 4-methylphthamide.

3-Methylphthalamide. A 3-oz glass pressure vessel was charged with 4.01 g (24.9 mmol) of 3-methylphthalimide and 4 mL of dry DMF. The suspension was cooled to 0 °C and the ammonia gas was bubbled in for 30 min. The vessel was pressurized to 50 psi and then heated for 8 h at 45 °C. After cooling to room temperature the pressure was carefully released. Acetonitrile (20 mL) was added with stirring and the mixture was suction filtered. After vacuum drying (70 °C) 3.38 g of 3-methylphthalamide (76% yield) was obtained as a white powder: mp 225 °C; IR (KBr) 3420 (m-s), 3330 (m), 3200 (m), 1680 (m), 1655 (s), 1610 (m-s), 1582 (w-m) cm^{-1}.

Anal. Calcd for $C_9H_{10}N_2O_2$: C, 60.66; H, 5.66; N, 15.72. Found: C, 60.34; H, 5.72; N, 15.75.

3-Methylphthalimide (1.07 g) was recovered from the filtrate and could be recycled.

4-Methylphthalamide. A 3-oz glass pressure vessel was charged with 4.01 g of 4-methylphthalimide and 40 mL of absolute ethanol. After the mixture was cooled to 0 °C, ammonia was bubbled into the suspension for 30 min. The reaction mixture was pressurized with ammonia until a pressure of 50 psi was maintained, and the mixture was then heated for 18 h at 50 °C. After cooling to room temperature, the pressure was carefully released and the mixture was filtered. Pure 4-methylphthalamide, 3.56 g (80% yield), was obtained: mp 188 °C (lit.[7] 188 °C); IR (KBr) 3435 (m-s), 3235 (m), 3200 (m), 1690 (m), 1655 (s), 1630 (sh), 1605 (m-s), 1582 (w-m) cm^{-1}.

3-Methylphthalonitrile. Method A. A flask was charged with 1.00 g of 3-methylphthalamide, 15 mL of dry DMF, and a magnetic stir bar, and was capped with a rubber septum and cooled to 0 °C (ice bath). Thionyl chloride (1.49 g) was added with stirring over a 30-min period (via syringe). The reaction mixture was allowed to slowly warm to room temperature and was then poured over 80 g of ice. The water-insoluble product was collected by filtration, washed with water, and dried. The yield of 3-methylphthalonitrile was 0.638 g (80%): mp 143 °C (lit.[8] 143 °C); IR (KBr) ν_{CN} 2230 cm^{-1}.

Method B. A suspension of 3.77 g (21.2 mmol) of 3-methylphthalamide in 20 mL of dry DMF was added to a solution of 3.9 mL (53 mmol) of thionyl chloride in 9 mL of DMF which had been cooled to 0 °C. The addition was made over a 30-min period; after an additional 30 min, the reaction mixture was poured over ice (150 g). The product was collected by filtration and dried to afford 1.18 g (39%) of the dinitrile.

4-Methylphthalonitrile. Method A. A flask was similarly charged with 1.00 g of 4-methylphthalamide, 15 mL of dry DMF, and a magnetic stir bar, and was capped with a rubber septum and cooled to −12 °C (NaCl–ice bath). Thionyl chloride (1.48 g) was added (via syringe) with stirring over a 30-min period. The reaction mixture was allowed to warm to room temperature and stirring was continued for ca. 16 h. The reaction mixture was poured over 83 g of ice and the insoluble product was collected by filtration, washed with water, and dried. The yield of 4-methylphthalonitrile was 0.39 g (48%): mp 120 °C (lit.[6] 120 °C); IR (KBr) ν_{CN} 2255 cm^{-1}.

Method B. A suspension of 3.90 g (21.9 mmol) of 4-methylphthalamide in 20 mL of dry DMF was added to a solution of 4.0 mL (55 mmol) of thionyl chloride in 20 mL of DMF which had been cooled to 0 °C. The addition was carried out over a 20-min period, after which the mixture was allowed to warm to room temperature. The reaction mixture was poured over ice and the product collected by filtration. A white powder (mp 122 °C) was obtained in 84% yield (2.62 g).

Registry No.—3-methyl-**2**, 7251-82-3; 4-methyl-**2**, 40314-06-5; 3-methyl-**3**, 63089-46-3; 4-methyl-**3**, 63089-47-4; 3-methyl-**4**, 63089-48-5; 4-methyl-**4**, 63089-49-6; 4-methyl-**5**, 4316-23-8; 3-methyl-**6**, 36715-97-6; 4-methyl-**6**, 63089-50-9.

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The Bimolecular Elimination of *trans*-2-Methylcycloocytl Tosylate. A Reinvestigation

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Our continuing interest in the synthetically useful reactions of eight-membered rings[1a–c] has recently led us to reinvestigate the elimination reaction of *trans*-2-methylcycloocytl tosylate. In 1966, Brown and Klimisch published preliminary results[2] on that reaction as part of a study of E2 eliminations in a series of *trans*-2-methylcycloalkyl tosylates, using potassium *tert*-butoxide in *tert*-butyl alcohol. For the five-, six-, and seven-membered rings, they obtained a 99:1 ratio of 3-methylcycloalkene to the 1-methyl isomer. However, this expected selectivity (based on the well-documented stereoelectronic requirement for an anti-periplanar transition state

Table I

Conditions[a]	cis-1-Methylcyclooctene	*cis*-3-Methylcyclooctene
Literature[2]	1	1
50 °C, 3 h, KO-*t*-Bu, *t*-BuOH	2	1
50 °C, 3 h, Na_2CO_3, *t*-BuOh	2.5	1
25 °C, 30 min, KO-*t*-Bu, Me_2SO	1	23

[a] Both alkenes are stable to these reaction conditions.

in such reactions) was not followed by the eight-membered tosylate, which afforded a 1:1 ratio of olefins.

We were intrigued by this anomolous behavior of the cyclooctane ring, and especially by the possibility that the 1-methyl iosmer could have resulted from a trans elimination toward the methyl group, giving *trans*-1-methylcyclooctene,[3] which the reported acidic workup might well have isomerized to the observed *cis*-1-methylcyclooctene. However, repetition of the experiment followed by a careful, nonacidic workup yielded no such trans olefin.

It has long been known that the introduction of sp^2 centers into a saturated eight-membered ring significantly relieves nonbonded interaction (I-strain) in the ring;[4] it seemed possible that such an effect could so favor an E1 process[5] as to render it competitive with the E2 reaction. Accordingly, a series of experiments was run (summarized in Table I) including a solvolysis where *trans*-1-methylcyclooctyl tosylate was treated in *tert*-butyl alcohol with heterogeneous carbonate as the only base.[6] Under conditions identical with the butoxide experiments (50 °C, 3 h), a product ratio of 2.5:1 (1-methylcyclooctene to 3-methylcyclooctene, respectively) was obtained in high yield. In one repetition of the original experiment, we observed a rate qualitatively equal to that reported,[2] but a product ratio favoring the 1-methyl isomer. Given these results, it appears likely that the observed 1-methycyclooctene actually results from a solvolytic, E1 reaction with a rate comparable to that of the bimolecular elimination being studied. To test this hypothesis, a reaction was run with potassium *tert*-butoxide in dimethyl sulfoxide at room temperature, since these conditions should favor the E2 mechanism at the expense of E1; indeed, after 30 min a nearly quantitative yield of alkenes was obtained with 3-methylcyclooctene highly favored (>20:1).

In conclusion, we feel that cyclooctyl sulfonates do not provide an exception to the anti-periplanar rule; thus, for synthetic purposes, the direction of bimolecular eliminations in these systems can be predicted with the same confidence as for other alkyl tosylates.

Experimental Section

Elimination Reaction Using Carbonate and *tert*-Butyl Alcohol. To a 0.32 M solution of *trans*-2-methylcyclooctyl tosylate[2] in dry *tert*-butyl alcohol was added 1 equiv of solid sodium carbonate (to bind any tosyl acid formed). This heterogeneous solution was stirred under nitrogen at 50 °C for 3 h. The resulting mixture was diluted with water and extracted three times with pentane. The combined pentane extracts were dried with 4-Å molecular sieves and concentrated (by distilling the pentane at 760 mm) to give the crude product, analyzed by gas chromatography (Carbowax 20 M). The gas chromatogram showed two peaks, in the ratio of 2.5:1, whose retention times were identical with those for authentic samples of *cis*-1-methylcyclooctene and *cis*-3-methylcyclooctene, respectively. The combined yield was >95% (GC).

Elimination Reaction Using Potassium *tert*-Butoxide in Me_2SO. *trans*-2-Methylcyclooctyl tosylate was dissolved in dry dimethyl sulfoxide and 2.5 equiv of solid potassium *tert*-butoxide was added under nitrogen (the resulting solution was 0.5 M in base). The reaction mixture immediately became dark green and slightly warm. After 30 min, isolation was effected as above. The yield of *cis*-3-methylcyclooctene, identified by NMR (^1H and ^{13}C), was determined to be 93%, while *cis*-1-methylcyclooctene was produced in 4% yield.

Elimination Reaction Using Potassium *tert*-Butoxide in *tert*-Butyl Alcohol. A solution of *trans*-2-methylcyclooctyl tosylate and 2.5 equiv of potassium *tert*-butoxide in dry *tert*-butyl alcohol (0.26 M in tosylate, 0.65 M in base) was stirred under nitrogen at 50 °C for 3 h. Isolation as before provided a 2:1 ratio of the 1-methyl- to 3-methylcyclooctene in a combined yield of 65%.

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Registry No.—*trans*-2-Methylcyclooctyl tosylate, 6597-13-3; *cis*-3-methylcyclooctene, 15840-65-0; *cis*-1-methylcyclooctene, 15840-64-9.

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A Novel Intramolecular C Alkylation Involving a 1,4-Benzoquinone Derivative

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Part of our investigations, related to the synthesis of substituted 1,4-benzoquinones,[1] dealt with the oxidation of 2-[3-(2,5-dihydroxyphenyl)-1-oxopropyl]cyclopentanone (1)[2] with 1 equiv of silver(I) oxide (Ag_2O). In this reaction two products, a quinone (A), mp 86–87 °C, and a white crystalline compound (B), mp 230–232 °C, were obtained in 26 and 35% yield, respectively. When 2 equiv of silver oxide was used, only A was obtained in 60% yield. The formation of the expected 1,4-benzoquinone, **2**, was ruled out by the fact that reduction of compound A with sodium dithionite did not produce the starting hydroquinone **1**, but gave a hydroquinone identical to compound B. Elemental analysis and the mass spectrum (*m/e* 244) of A indicated the molecular formula to be $C_{14}H_{12}O_4$. The ^1H NMR spectrum exhibited a sharp singlet at δ 6.70 which integrated to two benzoquinone protons.

The analytical data indicate intramolecular O or C alkylation of the 1,4-benzoquinone by the 1,3-diketone side chain. In order to differentiate between the C-alkylation product **3** and the O-alkylation product **4**, the catalytic hydrogenation of A was attempted. In this reaction only B was obtained, indicating an absence of a double bond in A. Further evidence was provided by ^{13}C NMR spectroscopy. The ^{13}C NMR spectrum of A exhibited two different carbonyl carbon signals at 212.44 and 204.59 ppm, which were assigned to a cyclopentanone (213.9 ppm) and a cyclohexanone (208.8 ppm)