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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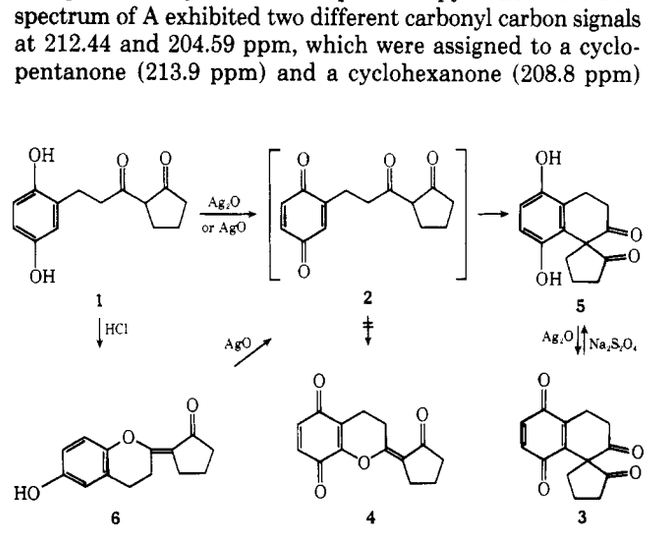
Part of our investigations, related to the synthesis of substituted 1,4-benzoquinones,[1] dealt with the oxidation of 2-[3-(2,5-dihydroxyphenyl)-1-oxopropyl]cyclopentanone (1)[2] with 1 equiv of silver(I) oxide (Ag_2O). In this reaction two products, a quinone (A), mp 86–87 °C, and a white crystalline 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.

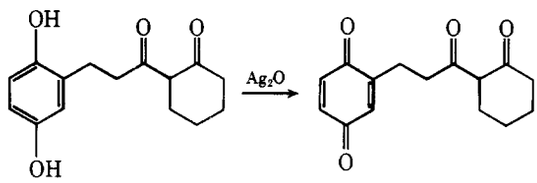
The analytical data indicate intramolecular O or C alkylation of the 1,4-benzoquinone by the 1,3-diketone side chain. In order to differentiate between the C-alkylation product **3** and the O-alkylation product **4**, the catalytic hydrogenation of A was attempted. In this reaction only B was obtained, 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)



moiety, respectively.[3] All evidence indicates that the sole oxidation product A of 1 is the intramolecular C-alkylation product **3**, and compound B is its reduction product **5**.

The mechanism of this reaction involves the intermediate formation of **2**, followed by cyclization to give the hydroquinone **5**, which is further oxidized to the final oxidation product **3**. The hydroquinone derivative **1** undergoes cyclodehydration at room temperature in the presence of strong mineral acids, such as hydrochloric acid, to give 6-hydroxy-2-(2′-oxocyclopentylidene)benzopyran (**6**) in virtually quantitative yield. The formation of **3** from **6** involves initial oxidative dealkylation to give **2**, which undergoes cyclization and further oxidation. This mechanism is supported by the fact that hydroquinone dimethyl ethers undergo oxidative demethylation with silver(II) oxide to give the corresponding 1,4-benzoquinones.[4] Furthermore, oxidation of **1** with silver(II) oxide also produced **3** in approximately 40% yield. No other quinones could be isolated.

The C alkylation of 1,4-benzoquinones is a well-known reaction; however, more drastic conditions and a Lewis acid catalyst are always required.[5] The observed facile C alkylation is surprising and prompted us to test the generality of this reaction. The cyclohexanone analogue of **1**, compound **7**, was synthesized by the procedure used in the preparation of **1**.[6] Oxidation of **7** with both silver(I) oxide and silver(II) oxide



7 **8**

produced solely the 1,4-benzoquinone derivative **8** in quantitative yield. No cyclization of **7** was observed even with anhydrous zinc chloride both at room temperature and at 90 °C. The difference in the stability of the 1,4-benzoquinone derivatives **8** and **2** can only be explained by the acidity differences between the two diketones. The ionization constants of 2-acetylcyclopentanone and 2-acetylcyclohexanone are reported to be 1.5×10^{-8} and 8.1×10^{-11}, respectively.[7] Thus, 2-acetylcyclopentanone is a stronger acid by about 2 pK_a units, which may be sufficient to explain the difference in reactivity of **2** and **8**.

Experimental Section

Infrared spectra were recorded on a Beckman AccuLab 5. ^1H NMR spectra were obtained on a Varian T-60 spectrometer and ^{13}C NMR were obtained on a Varian CFT-20 spectrometer. Mass spectra were obtained on a Varian CH-5 mass spectrometer. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. The melting points are uncorrected.

Oxidation of 2-[3-(2,5-dihydroxyphenyl)-1-oxopropyl]-cyclopentanone (2). Silver(I) Oxide (Ag_2O). A solution of **1** (5.0 g, 20 mmol) in 150 mL of ethyl acetate was suspended with Ag_2O (5.0 g, 21 mmol) and anhydrous sodium sulfate (5.6 g, 39 mmol) and stirred. After 18 h, the insolubles were filtered and TLC (6:4 chloroform–ether, silica gel plates) examination showed that it contained one *p*-benzoquinone component. The unconverted starting **2** was removed as a copper complex by stirring with a hot solution of cupric acetate, which amounted to 2.7 g. From the organic layer, after washing with 1 N H_2SO_4, followed by water, and drying (anhydrous $MgSO_4$), 2.2 g of brown viscous liquid was isolated. TLC (6:4 chloroform–ether, silica gel plate) examination revealed that it contained two components. This liquid was chromatographed over 75 g of silica gel (Biosil A, 100–200 mesh). With chloroform was isolated 0.6 g (26%) of **3** as a yellow solid, mp 84–86 °C. After recrystallization from methanol it melted at 86–87 °C: ^1H NMR ($CDCl_3$) δ 2.0–3.2 (m, 10, aliphatic protons of two fused rings), 6.70 (s, 2, *p*-benzoquinone); IR ($CHCl_3$) 1655 cm^{-1} (C=O, benzoquinone), 1700 cm^{-1} (C=O cyclohexanone), 1735 cm^{-1} (C=O cyclopentanone); mass spectrum *m/e* 244 (M^+).

Anal. Calcd for $C_{14}H_{12}O_4$: C, 68.85; H, 4.95. Found: C, 68.91; H, 5.06.

Further elution with chloroform–ether (6:4) gave a brown liquid which when triturated with ether gave 0.8 g (35%) of **5**, mp 230–232 °C. It was once recrystallized from *n*-hexane–ethyl acetate: mp 234–236 °C; ^1H NMR (acetone-d_6) δ 1.90–3.20 (m, 10), 6.56 (s, 2, aromatic), 7.40 (br s, 2, phenolic OH); IR (KBr) 1698 cm^{-1} (C=O cyclohexanone), 1725 cm^{-1} (C=O cyclopentanone); mass spectrum *m/e* 246 (M^+).

Anal. Calcd for $C_{14}H_{14}O_4$: C, 68.28; H, 5.73. Found: C, 68.37; H, 5.68.

When the oxidation was carried out with 2 equiv of Ag_2O (10.0 g, 42 mmol) for 5 days, 3.0 g (60%) of **3** was isolated by similar workup.

Oxidation of 1 with Silver(II) Oxide (AgO). To a suspension of AgO (1.7 g, 13.7 mmol) in 40 mL of THF (freshly distilled over CaH_2) containing **1** (1.0 g, 4 mmol) was added 4 mL of 6 N HNO_3 under stirring and after 5 min diluted with 160 mL of chloroform and 40 mL of water. Evaporation of the organic layer gave a liquid which partly solidified. Chromatography over 45 g of silica gel using benzene as solvent yielded 0.4 g (40%) of **3**, mp 84–86 °C (mixture melting point and IR spectral comparison with that of **3** from Ag_2O oxidation of **1**).

Reduction of (6-Oxo-5,6,7,8-tetrahydro-1,4-naphthoquinone)-5,1′-(2′-oxocyclopentane) (3) with Sodium Dithionite. A solution of **3** (0.5 g) in 100 mL of ethyl acetate was shaken with an aqueous solution of a sodium dithionite (5%) and instantly the quinone was reduced as evidenced by a change in color from light orange to colorless. The organic layer was separated, washed with water, dried (anhydrous $MgSO_4$), and evaporated to give 0.5 g of **5** (100% yield), mp 230–232 °C.

Preparation of 6-Hydroxy-2-(2′-oxocyclopentylidene)benzopyran (6). To **1** (5.0 g, 20 mmol) was added 25 mL of concentrated HCl. The solution turned yellow and solidified. After 5 min, it was diluted with ice-cold water and the resulting white solid was filtered, washed with excess water, and dried to give 4.5 g (97%) of **6**, mp 204–206 °C. It melted at 207–209 °C after one recrystallization from ethyl acetate.

Anal. Calcd for $C_{14}H_{14}O_3$: C, 73.02; H, 6.13. Found: C, 73.58; H, 6.40.

Oxidation of 6 with Silver(II) Oxide (AgO). The oxidation of **6** (0.9 g, 3.9 mmol) was conducted similarly to the AgO oxidation of **1**, to give 0.4 g (41%) of **3**, identical with the quinone isolated in the oxidation of **1** (mixture melting point and IR spectral comparison).

Oxidation of 2-[3-(2,5-Dihydroxyphenyl)-1-oxopropyl]cyclohexanone (7)[6] with Silver(I) Oxide (Ag_2O). The diketone **7** (2.0 g, 7.6 mmol) in 100 mL of ethyl acetate was stirred with Ag_2O (5.1 g, 21 mmol) and anhydrous sodium sulfate (5.6 g, 20 mmol) for 18 h. The reaction mixture was filtered and TLC (6:4 chloroform–ether, silica gel) showed that it contained one component. Evaporation of the solvent gave 2.0 g (100%) of orange-brown solid, mp 85–87 °C. It was recrystallized from 2-propanol to give orange needles of **8**: mp 87–88 °C; ^1H NMR ($CDCl_3$), δ 6.50–6.65 (m, 1, benzoquinone H adjacent to side chain), 6.70 (s, 2, benzoquinone).

Anal. Calcd for $C_{15}H_{16}O_4$: C, 69.21; H, 6.20. Found: C, 69.50; H, 6.58.

Reduction of **8** with sodium dithionite gave the starting material **7**.

Oxidation of 7 with Silver(II) Oxide. The oxidation of **7** (1.0 g, 3.8 mmol) was carried out in a manner similar to that of **1** with AgO. The resulting quinone (100% yield) was identical with **8** obtained by Ag_2O oxidation.

Registry No.—**1**, 50714-97-1; **2**, 63216-56-8; **3**, 63250-61-3; **5**, 63216-57-9; **6**, 63216-58-0; **7**, 63216-59-1; **8**, 63216-60-4.

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