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Synthesis and Chemistry of Sesquibicyclo[2.2.2]octene and a Tetradecacyclic-Caged Sesquibicyclo[2.2.2]octene

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Abstract. Cationic rearrangements of functionalized spiro(norbornane-7,3'-bicyclo[2.2.2]octan-2'-ols) provide synthetic access to two novel polycarbocyclic alkenes, i.e., **5** and **10** ("sesquibicyclo[2.2.2]octene"). X-ray crystallographic analysis of **5** and **10** reveals that each alkene C=C double bond is planar in the crystalline solid. MCPBA promoted epoxidation of **5** produced the corresponding oxirane, **11**. Ring opening of the highly labile oxirane moiety in **11** occurred in the presence of mild Lewis acids (e.g., silica gel) or bases (e.g., $NaHCO_3$), thereby affording the corresponding *cis*-diol, **12**. MCPBA promoted epoxidation of **7** afforded the corresponding oxirane, **13**. Oxirane **13** proved to be considerably less labile than **11** toward acidic and/or basic media.

Introduction. Recently, we reported the syntheses of a variety of cage-functionalized pinacols and their respective acid-promoted rearrangements to cage-functionalized pinacolones.[1-5] In some cases, pinacol rearrangements of this type occur with remarkable regioselectivity.[3] We now report the synthesis of a novel pinacol, **2**, derived from heptacyclo[$6.6.0.0^{2,6}.0^{3,13}.0^{4,11}.0^{5,9}.0^{10,14}$]tetradecan-7-one (**1**)[6] and its acid-promoted rearrangement[7] to the corresponding pinacolone, 8-(heptacyclo[$6.6.0.0^{2,6}.0^{3,13}.0^{4,11}.0^{5,9}.0^{10,14}$]tetradecan-7-yl)heptacyclo[$7.6.0.0^{2,6}.0^{3,14}.0^{4,12}.0^{5,10}.0^{11,15}$]pentadecan-7-one (**3**). Subsequent conversion of **3** into a novel, cage functionalized alkene, i.e., **5**, also has been performed.[8] In addition, a "bisnorbornyl analog" of pinacol **2**, i.e., **7**, has been converted into tetracyclo[$6.2.2.2^{3,6}.0^{2,7}$]tetradec-2-ene (i.e., "sesquibicyclo[2.2.2]octene", **10**), a close structural analog of **5**. Finally, some interesting aspects of the structure and chemistry of **5** and **10** are presented.

Syntheses of Polycarbocyclic Alkenes 5 and 10. The procedure that was used to prepare **2** and to perform its subsequent acid promoted rearrangement to **3** is shown in Scheme 1. Polycarbocyclic cage ketone **3** was converted subsequently into a rearranged polycyclic alkene, **5**, via a straightforward two-step procedure (Scheme 1). A key feature of this synthesis involves acid promoted dehydration of cage alcohol **4**, a process that most likely proceeds via an intermediate carbocation that undergoes concomitant skeletal rearrangement, ultimately affording the target alkene, **5**. The structure of **5** was established unequivocally via application of X-ray crystallographic methods (see X-ray structure drawing, Figure 1).

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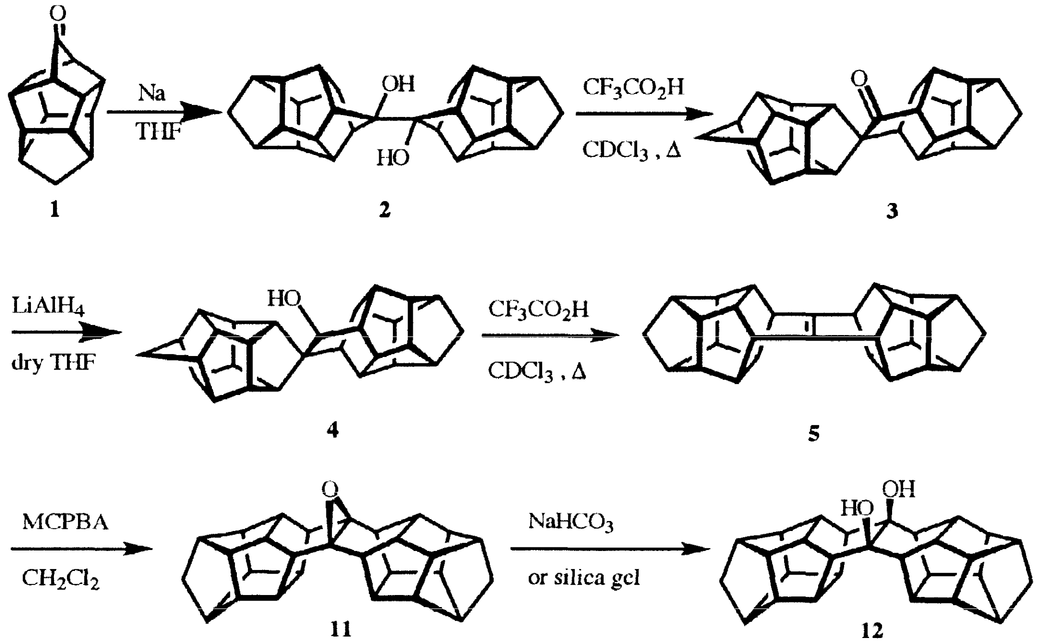
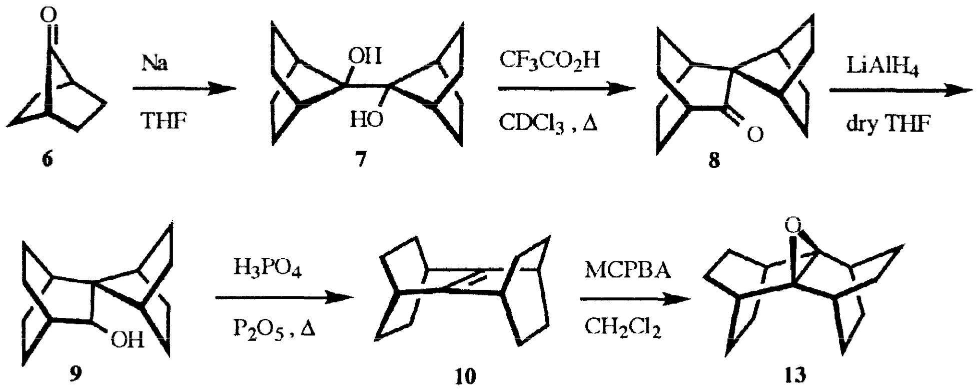
Scheme 1



A closely analogous sequence of reactions, shown in Scheme 2, was employed to synthesize **10** (i.e., "sesquibicyclo[2.2.2]octene",[9] a tetracyclic analog of **5**) from norbornan-7-one[10,11] (i.e., **6**). An X-ray structure drawing of **10** is shown in Figure 1.

Scheme 2



Some Features of the Structures of 5 and 10. The molecular symmetry associated with the C=C double bonds in **5** and **10** suggest that each of these bonds should be planar in the isolated molecule. X-ray structure data obtained for each compound indicates that this expectation is also realized in the solid state (see Figures 1 and 2).

Relevant bond length and bond angle data in the vicinity of the C=C double bond in **5** and **10** also appear in Figure 1. Here, it will be noted that <C-C=C bond angles generally lie in the range 113°-116° and thus vary significantly from the ideal C(sp^2) bond angle (i.e., 120°). Since the C=C bonds in **5** and in **10** remain planar, the cumulative angle strain imposed on the double bonds in these novel alkenes by their respective rigid polycarbocyclic frameworks expresses itself through shortening of those C=C bonds; the observed C=C bond lengths in **5** and **10** are 1.334 (7) Å (T = 208 K) and 1.327 (4) Å (T = 295 K), respectively. Interestingly, the C=C double

bond stretching vibrations as determined via Raman spectroscopic examination of solid **5** and **10** appear to be essentially "normal". Thus, for **5**, we find $\nu_{C=C}$ = 1662 cm^{-1} (w) and for **10**, $\nu_{C=C}$ = 1649 cm^{-1} (w).

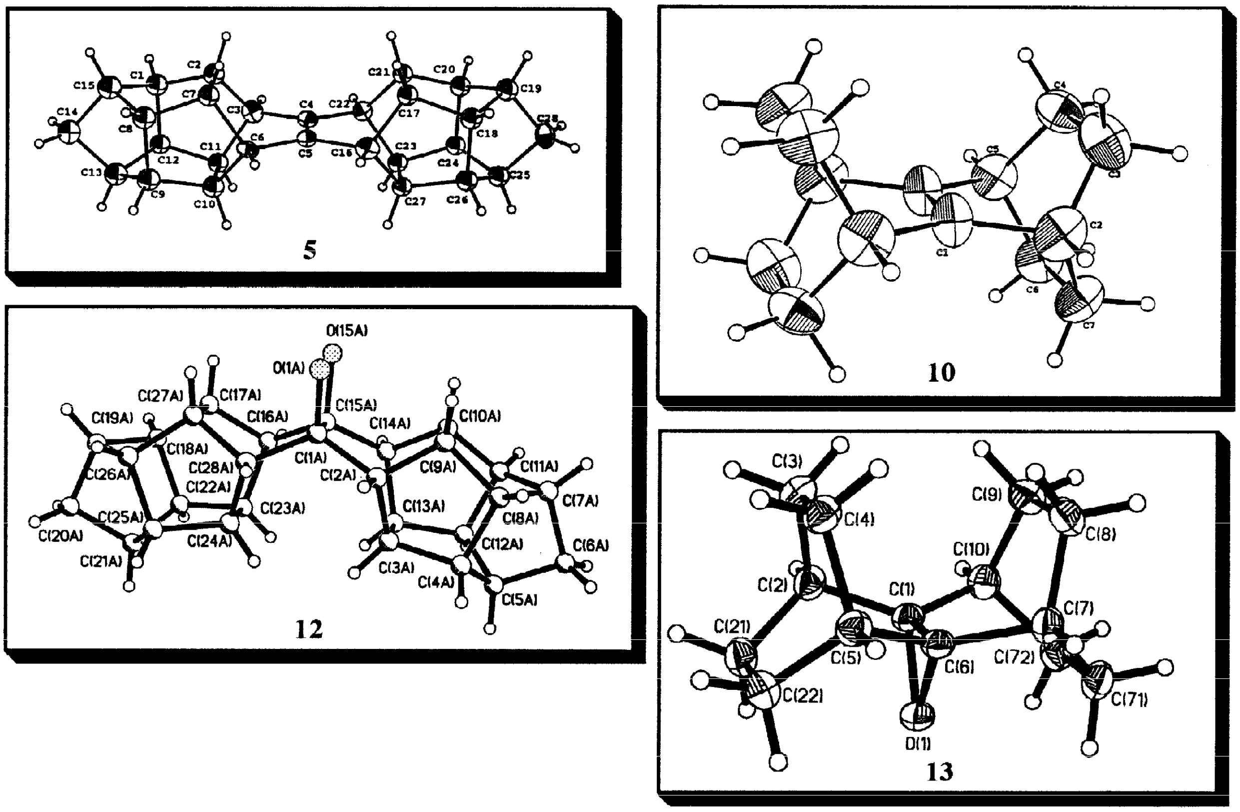
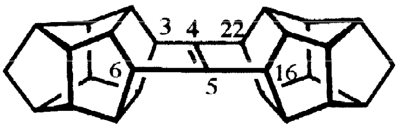


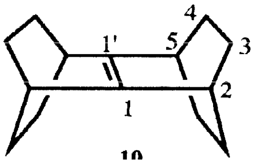
Figure 1. X-ray structure drawings of **5**, **10**, **12**, and **13**.



5

Bond length: C(4)=C(5) = 1.334 (7) Å

Bond angles: C(3)-C(4)=C(5) = 113.7 (4) °
C(4)=C(5)-C(6) = 115.1 (4) °
C(4)=C(5)-C(16) = 113.4 (4) °
C(5)=C(4)-C(22) = 115.7 (4) °



10

Bond length: C(1)=C(1') = 1.327 (4) Å

Bond angles: C(2)-C(1)=C(1') = 114.8 (3) °
C(5)-C(1')=C(1) = 113.8 (3) °

Figure 2. Selected bond lengths and bond angles in **5** and **10**.

MCPBA Promoted Epoxidation of the C=C Double Bonds in 5 and 10. As part of this study, we investigated MCPBA promoted oxirane formation in systems **5** and **10**. The results thereby obtained are summarized in Schemes 1 and 2, respectively. Interestingly, we find that oxirane **11** is highly labile; it readily undergoes hydration upon treatment with aqueous NaHCO$_3$ or during attempted purification via column chromatography on silica gel, thereby affording the corresponding ring-opened *cis*-diol, **12**. By way of contrast, oxirane

13 appears to be quite stable under comparable conditions and is not as readily hydrated. X-ray structure drawings of **12** and **13** are shown in Figure 1.

Particularly noteworthy is our observation that both nucleophilic and electrophilic hydration of the oxirane ring in **11** proceed stereoselectively *cis*, i.e., contrary to the normal mode of oxirane hydration which leads to the formation of the corresponding *trans*-diol.[12] In both cases, it seems likely that ring opening proceeds via an intermediate carbocation that suffers nucleophilic attack by either H_2O or $HO:^-$ to afford the corresponding (thermodynamically favored) *cis*-diol.[13]

At present, work in our laboratory is directed toward further exploration of reactions of various electrophilic agents with the highly sterically shielded, planar C=C double bonds in **5** and **10**. We plan to report details of the results of these studies shortly.

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