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Ring Enlargement of Geminal Dibromocyclopropanes with Silver Tosylate. An Approach to Medium Sized Rings

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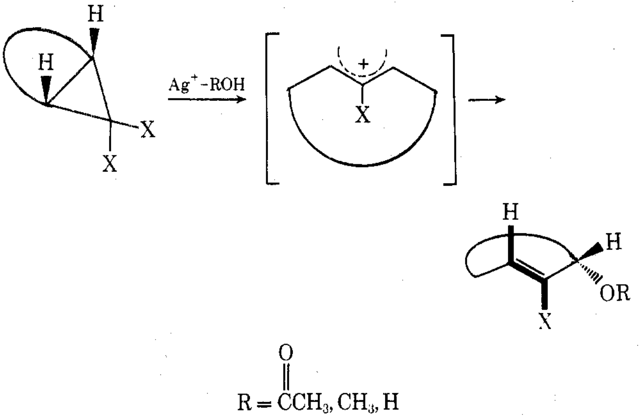
Received May 19, 1975

The reaction of geminal dihalocyclopropanes with silver perchlorate under solvolytic conditions has recently attracted attention as a synthetically useful approach for ring enlargement.[1-4] These reactions obey the Woodward–Hoffmann rules of conservation of orbital symmetry and proceed in a disrotatory manner.[5,6] The allylic system formed has been postulated to have the trans conformation, obtained by release of the exo halogen atom.



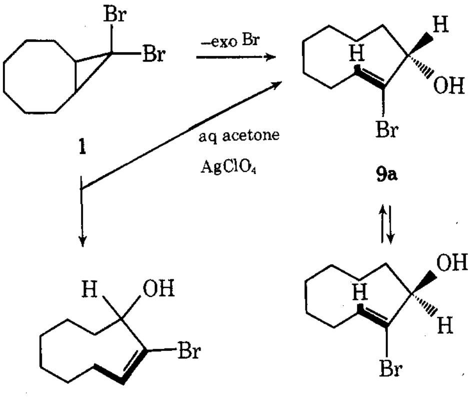
$R = \overset{O}{\overset{\|}{C}}CH_3, CH_3, H$

The nucleophile attacks at the same site of the incipient allylic system where the halogen atom is departing and thus leads to the formation of one single diastereoisomer in most cases.

In the absence of silver salts severing of the exo halogen atom is preferred on steric considerations, unless the expanded ring would become too small to accommodate a trans double bond. In the latter case the endo halogen is lost, leading to a cis allylic system.[7a,b]

We now wish to present a highly stereospecific method to generate tosylated medium sized rings by ring opening of dibromocyclopropanes in one step and with excellent yields. Reaction of the bicyclic systems **1–4** for 2 hr with a slight excess of silver tosylate in refluxing acetonitrile led in a smooth reaction to the tosylates **5–8** (Table I). Examination of the reaction products (TLC, ^1H NMR) revealed that in all four cases one single diastereoisomer had been formed. The ring opening of **3** and **4** proceeds mechanistically in a similar fashion as the above-mentioned reactions. This could easily be demonstrated by synthesizing compounds **7** and **8** by tosylation of the corresponding alcohols with known stereochemistry.[1] Therefore, the tosylates **7** and **8** have the configuration as assigned in Table I.

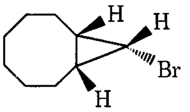
The formation of tosylates **5** and **6** deserves some comment. Earlier literature concerning the silver perchlorate catalyzed solvolysis of **1** showed that two diastereoisomeric trans alcohols were formed, which were rapidly equilibrating at room temperature.[2] However, in our hands, besides the trans alcohols **9a,b**, also considerable and reproducible amounts of the cis alcohol **10** could be isolated (ca. 30%).[8]



1 **9a** **9b** **10**

Tosylation of the cis alcohol **10** gave the tosylate **4**, whereas the product obtained by reaction of the mixture of diastereoisomers **9a** and **9b** with tosyl chloride proved to be quite different (NMR spectrum displayed multiplet structures at δ 4.87 and 6.05 for the allylic part of the spectrum). A possibility of initial formation of a trans tosylate followed by an Ag$^+$-assisted isomerization to the cis conformer could be ruled out easily by refluxing the trans tosylate of **9a,b** with excess silver tosylate in acetonitrile; no traces of **5** could be detected.

Disrotatory ring opening of **1** with release of the sterically less accessible endo bromine atom leading to a cis-allylic system seems very improbable. Upon treating *endo*-9-bromobicyclo[6.1.0]nonane (**11**) with silver tosylate in refluxing acetonitrile no noticeable reaction was observed. A similar observation was made in the expansion of the nine-membered compound **2**.



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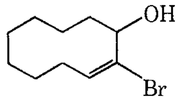
In this case we found that besides the expected 2-bromo-3-hydroxy-*trans*-cyclodec-1-ene (**12**)[11] also the 2-bromo-3-hydroxy-*cis*-cyclodec-1-ene (**13**) could be isolated in 30% yield by ring expansion with silver perchlorate in 5% aqueous acetone.

The tosylate derived from **13** proved to be identical with **6**, whereas the trans alcohol **12** gave a tosylate displaying



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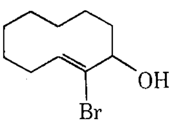

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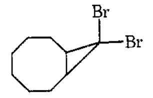
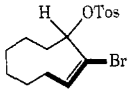
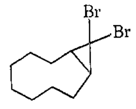
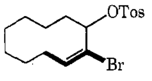
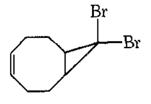
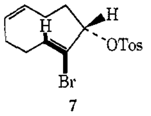
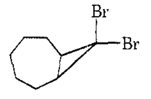
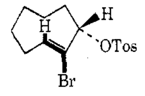
Table I

Starting compd	Product[a]	Mp, °C	Yield, %[b]	NMR data ($CDCl_3$), δ
 1	 5	91–93	93	6.04 (t, 1, olefin H, J = 8 Hz), 5.52 (dd, 1, methine H, J = 10 and 5 Hz), 2.40 (s, 3, CH_3)
 2	 6	108–111	81	5.75 (m, 2, olefin H and methine H), 2.41 (s, 3, CH_3)
 3	 7	89–91	89	5.85 (t, 1, olefin H, J = 8 Hz), 5.27 (m, 2, H cis double bond), 4.85 (dd, 1, methine H, J = 10 and 6 Hz), 2.39 (s, 3, CH_3)
 4	 8	80–82	85	6.10 (dd, 1, olefin H, J = 11 and 5 Hz), 4.92 (t, 1, methine H, J = 8 Hz), 2.42 (s, 3, CH_3)

[a] Satisfactory analytical data were obtained (±0.3% for C and H). [b] Yields are based upon isolated crude material (purity >95%).

triplets at δ 4.95 (J = 7 Hz) and 6.18 (J = 8.5 Hz). From these observations we must conclude that silver ion assisted ring opening of 1 and of 2 is leading initially to the free trans allylic cation which rapidly isomerizes to the cis allylic cation before reacting with the weakly nucleophilic tosylate anion.

The ring opening of 3 and of 4 leads exclusively to the trans allylic tosylates, because a free trans cation would require a sterically very unfavorable geometry, and therefore, these reactions must proceed completely concertedly leading to 7 and 8.

Experimental Section

General. Starting materials 1–4 were prepared by the reaction of dibromocarbene with the appropriate olefins according to known procedures.[9] *endo*-9-Bromobicyclo[6.1.0]nonane (11) was obtained from reduction of 1 with tri-*n*-butyltin hydride.[8] Silver tosylate was prepared from silver oxide and *p*-toluenesulfonic acid, according to the procedure of Kornblum et al.[10] NMR spectra were obtained on a Varian T-60 spectrometer using Me_4Si as an internal standard. The ring expansion reaction with silver tosylate is exemplified with the preparation of 7.

2-Bromo-3-tosyloxycyclonona-*trans,cis*-1,5-diene (7). To a solution of 2.80 g (0.01 mol) of 3 in 10 ml of acetonitrile was added a solution of 3.10 g (0.011 mol) of silver tosylate in 15 ml of acetonitrile. The mixture was stirred with gentle reflux for 2 hr. After cooling and addition of an equal volume of ether the precipitate was filtered and the filtrate evaporated to dryness. The resulting gummy product was chromatographed through a short silica gel column and afforded 3.3 g (89%) of white, crystalline tosylate 7. Recrystallization from diisopropyl ether gave analytical material, mp 89–91°. Anal. Calcd for $C_{16}H_{19}BrO_3S$: C, 51.75; H, 5.12. Found: C, 51.64; H, 5.12.

2-Bromo-3-hydroxycyclonon-1-ene (9, 10). To a solution of 5.64 g (0.02 mol) of 1 in 50 ml of 5% aqueous acetone was added a solution of 5.36 g (0.026 mol) of silver perchlorate in 25 ml of 5% aqueous acetone. The mixture was stirred at ambient temperature for 2 hr. After addition of 50 ml of saturated sodium chloride solution stirring was prolonged for an additional 5 min. The precipitate was filtered; the filtrate was diluted with 200 ml of water and extracted with ether. Upon washing, drying, and evaporation of the organic phase 3.19 g (73%) of the product was left as a colorless oil. The product consisted of two components. Chromatography (silica gel, chloroform–2% methanol as eluent) afforded 0.89 g of the cis alcohol 10 (R_f 0.29) and 2.29 g of the diastereomeric mixture of trans alcohols **9a,b**[2a] (R_f 0.22). The cis alcohol was recrystallized from petroleum ether: mp 72–74°; NMR ($CDCl_3$) δ 4.75 (m, 1, methine H), 6.18 (t, 1, olefin H, J = 11 Hz). Anal. Calcd for $C_9H_{15}BrO$: C, 49.31; H, 6.84. Found: C, 49.29; H, 6.80.

2-Bromo-3-hydroxycyclodec-1-ene (12, 13). A solution of 5.92 g (0.02 mol) of 2 and 5.36 g (0.026 mol) of silver perchlorate in 75 ml of 5% aqueous acetone was stirred for 3 hr at room temperature. Work-up in a similar manner as described for 9 and 10 afforded 3.21 g (71%) of product. Chromatography over silica gel (chloroform–2% methanol as eluent) afforded 2.55 g of trans alcohol 12 (R_f 0.38) as a colorless oil: NMR ($CDCl_3$) δ 4.18 (dd, 1, methine H, J = 9 and 5 Hz), 6.24 (t, 1, olefin H, J = 9 Hz). The other component (0.75 g, R_f 0.44) was the cis alcohol 13: mp 48–50° (petroleum ether); NMR ($CDCl_3$) δ 4.82 (t, 1, methine H, J = 8 Hz), 5.98 (dd, 1, olefin H, J = 12 and 6 Hz). Anal. Calcd for $C_{10}H_{17}BrO$: C, 51.50; H, 7.29. Found: C, 51.62; H, 7.31.

Registry No.—**1**, 32644-18-1; **2**, 57129-79-0; **3**, 54809-08-4; **4**, 52750-35-3; **5**, 57090-95-6; **6**, 57090-96-7; **7**, 57344-75-9; **8**, 57344-76-0; **10**, 32726-58-2; **12**, 57090-97-8; **13**, 57090-98-9; silver tosylate, 16836-95-6.

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(11) The two diastereoisomers of trans alcohol 12 equilibrate at room temperature at such a rate that only one NMR signal is observed.[2b]

Ring Opening of 5,7-Dimethyl-*v*-triazolo[1,5-*a*]pyrimidine by Halogenating Agents

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Received June 13, 1975

In earlier publications, we demonstrated that electrophilic attack by halogens took place in the five-membered ring