Silver ion assisted ring expansions of some geminal dibromobicyclo[n.1.0]alkanes. Evidence for free cationic intermediates

Silver Ion Assisted Ring Expansions of Some Geminal Dibromobicyclo[*n*.1.0]alkanes. Evidence for Free Cationic Intermediates

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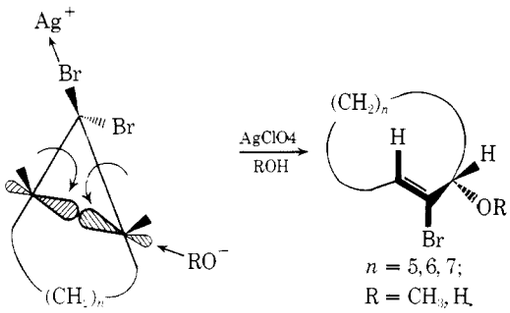
Geminal dibromocyclopropanes, annelated to seven-, eight-, and nine-membered rings, represent well-adapted precursors for the construction of medium-sized rings via ring expansion. Though the exo bromine atom is lost, the products do not always possess the expected trans allylic configuration. Reaction of **1** and **2** with silver nitrate in acetonitrile gives the trans nitrate esters **6** and **7**. However, **3** gives exclusively the cis product **8**, and the nine-membered precursor **4** affords a mixture of trans and cis nitrate **9** and **10**. In connection with the results obtained from reaction of **1**–**4** with silver tosylate, it became apparent that, though the exo halogen atom was lost, both ring size and nucleophilicity of the counterion might be the final configuration determining parameters. In order to demonstrate this, compound **3** was solvolyzed with silver perchlorate in a number of alcohols with different nucleophilicity. The percentage of cis product proved to increase in the order $CH_3OH < C_2H_5OH < i\text{-}C_3H_7OH < t\text{-}C_4H_9OH$. A free trans cation which can isomerize to a cis cation is assumed to be the intermediate.

Silver ion promoted ring expansions of geminal dibromobicyclo[*n*.1.0]alkanes represent a useful approach for the construction of medium sized rings.[1a-h] The ring opening, when performed in the presence of strong nucleophiles (H_2O or CH_3OH), generally leads to cyclic structures with a trans geometry. The mechanism of formation, which has been discussed recently by Reese et al., is visualized in Scheme I.

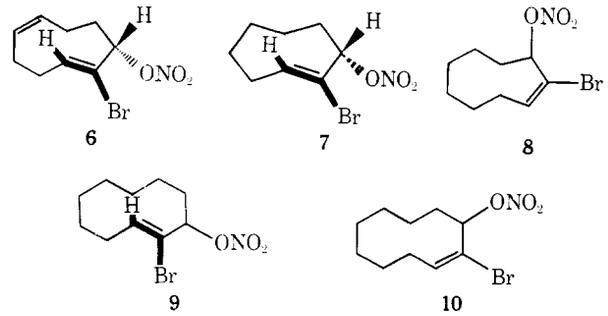
Scheme I

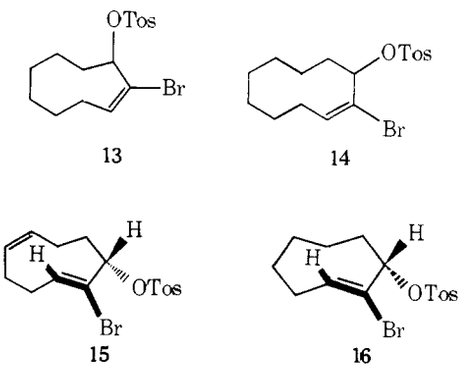


Essential features of this mechanism consist in a disrotatory ring opening, according to the rules of conservation of orbital symmetry, with departure of the exo bromine atom.[2-4]

In most cases only one diastereoisomer was formed. This could be explained by assuming that attack of the nucleophile should be concerted with the ring opening. From these observations the intermediacy of a free trans cation was made questionable.

Recently we presented a method which permits the stereospecific synthesis of medium-sized rings by the reaction of geminal dibromobicyclo[*n*.1.0]alkanes with silver tosylate in acetonitrile.[5] We observed that on reacting 9,9-dibromobicyclo[6.1.0]nonane (**3**) and 10,10-dibromobicyclo[7.1.0]decane (**4**) with silver tosylate only cis products were formed though the exo bromine atom was released; viz., *cis*-2-bromo-3-tosyloxycyclonon-1-ene (**13**) and *cis*-2-bromo-3-tosyloxycyclodec-1-ene (**14**), respectively. The formation of such cis products was rationalized by assuming the intermediacy of a free trans cation in both cases, which isomerizes rapidly to the cis cation before reacting with the weakly nucleophilic tosylate anion.





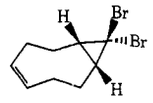
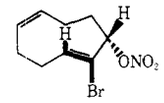
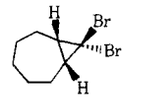
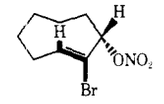
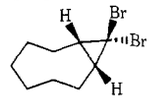
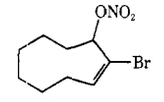
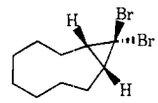
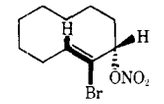
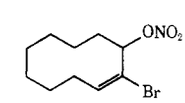
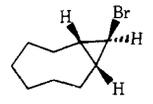
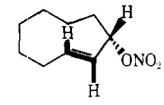
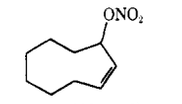
Ring expansion of 9,9-dibromobicyclo[6.1.0]non-4-ene (**1**) and of 8,8-dibromobicyclo[5.1.0]octane (**2**) with silver tosylate led to *trans,cis*-2-bromo-3-tosyloxycyclonona-1,6-diene (**15**) and *trans*-2-bromo-3-tosyloxycyclooct-1-ene (**16**), respectively. This result is not surprising since the full development of a trans cation in these latter systems would represent an energetically unfavorable situation and consequently the tosylate anion enters simultaneously with the ring opening.

A series of ring expansions we performed with silver nitrate, in order to investigate the scope and limitations of this reaction, corroborated the assumed tendency (vide supra). Reaction of the dibromides **1** and **2** led, as expected, to *trans,cis*-2-bromocyclonona-1,6-dien-3-yl nitrate (**6**) and *trans*-2-bromocyclooct-1-en-3-yl nitrate (**7**), respectively, whereas **3** gave the *cis*-2-bromocyclonon-1-en-3-yl nitrate (**8**).

In contrast to the silver tosylate promoted ring opening the reaction of **4** with silver nitrate afforded a 1:1 mixture of *trans*- and *cis*-2-bromocyclodec-1-en-3-yl nitrate (**9** and **10**), respectively. However, this could be reconciled easily with the proposed mechanism. The nitrate anion, which is a slightly better nucleophile than the tosylate anion, reacts more rapidly with the transient cation and thus suppresses partially the isomerization in the less strained ten-membered system (see Table I). The conformations of the newly formed double bonds were established in a chemical way, on synthesizing **6**–**10** by nitration of their corresponding alcohols with acetyl nitrate.[6a,b]

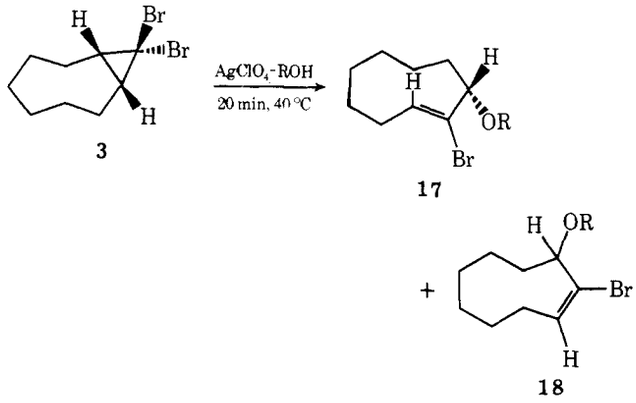
From all these observations it became apparent to us that both the nature of the initial bicyclic system and the nucleo-

Table I. Nitrate Esters

Substrates	Products (ratio)	NMR data ($CDCl_3$), δ	Yield, %[a]	Reaction time, h
 1 (54809-08-4)[b]	 6 (60996-34-1)	6 08 (dd, 1, olefin H, J = 8 and 6 Hz), 5.35 (m, 2, cis double bond), 5.14 (m, 1, methine H)	62	3
 2 (52750-35-3)	 7 (60996-35-2)	6.37 (t, 1, olefin H, J = 8 Hz), 5.76 (t, 1, methine H, J = 8 Hz)	71	4
 3 (32644-18-1)	 8 (60996-36-3)	6.33 (t, 1, olefin H, J = 9 Hz), 5.86 (m, 1, methine H)	78	4
 4 (51129-79-0)	 9 (1) (60996-37-4)  10 (1) (60996-38-5)	trans: 6.37 (t, 1, olefin H, J = 8 Hz), 5.21 (t, 1, methine H, J = 7 Hz) cis: 5.82–6.32 (m, 2, olefin H and methine H)	83	3
 5 (1551-94-6)	 11 (2) (60996-39-6)  12 (60996-40-9)	trans: 4.72–5.28 (m, 1, methine H), 5.36–6.03 (m, 2, olefin H), 0.70–2.60 (aliphatic H) cis: 5.20–6.08 (m, 3, methine H + olefin H), 1.05–2.20 (aliphatic H) [^{13}C (ppm downfield from external Me_4Si), 86.8 (methine C, trans), 82.9 (methine C, cis)]	72	0.5

[a] Yields were based on pure isolated products after chromatography. [b] Registry no.

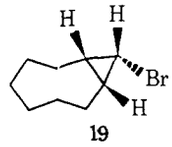
Table II



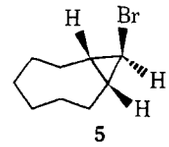
	R	17a–d (trans, %)	18a–d (cis, %)	Total yield, %
a	CH_3	90	10	81
b	C_2H_5	61	39	86
c	i-C_3H_7	47	53	85
d	t-C_4H_9	36	64	82

philicity of the attacking anion might be the main parameters in determining the percentage of cis and trans products in the silver ion assisted ring expansion reactions. In order to demonstrate this we performed a series of silver ion assisted alcoholysis reactions which unambiguously support this theorem.

Relying on the previously presented data it is clear that 9,9-dibromobicyclo[6.1.0]nonane (**3**) is the most interesting substrate to submit to the silver ion assisted ring opening, because it is the smallest ring in this series which obviously possesses the property of undergoing ring opening in a "semiconcerted" manner leading to a strained transient trans cation. Its lower homologue **2** has been shown to react always completely concerted, apparently without intermediate cations, leading to trans eight-membered systems. A number of ring expansions were performed by reacting **3** in a 1 M solution of silver perchlorate in a series of alcohols with varying nucleophilicity, viz., methanol, ethanol, 2-propanol, and *tert*-butyl alcohol. All these reactions were carried out at 40 °C with a twofold molar excess of silver perchlorate. After 20 min of reaction the starting material had disappeared (the reactions were monitored by TLC, using benzene as eluent). The results from the alcoholysis reaction of **3** have been presented in Table II. From these results it is readily recognized that decreasing nucleophilicity ($CH_3OH > C_2H_5OH > i\text{-}C_3H_7OH > t\text{-}C_4H_9OH$) leads to an increase of cis isomer in the final product. On performing the alcoholysis in *tert*-butyl alcohol the cis product even predominates. It should be mentioned that under the conditions applied for the ring opening of **3** the 9-*endo*-bromobicyclo[6.1.0]nonane (**19**) proved to be nearly



19



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unreactive.[8] The results achieved with this number of alcohols undoubtedly give ample proof for our original idea of a free trans cation[5] (see Chart I).

Chart I

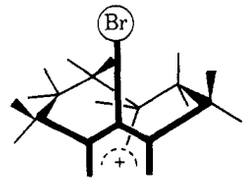
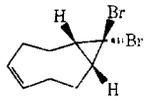
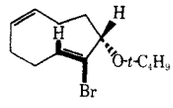
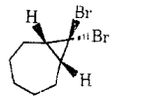
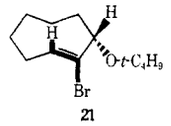
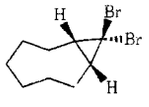
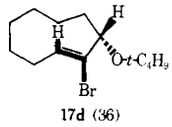
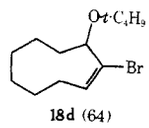
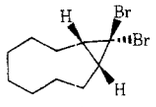
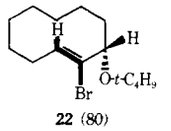
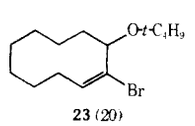
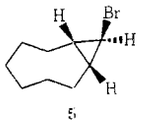
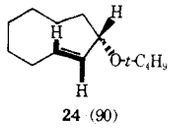
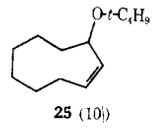


Table III. Solvolysis Reactions in 1 M $AgClO_4$ Solution in *tert*-Butyl Alcohol (40 °C)

Substrate	Products (ratio)	Yield, %	Reaction time, min
 1	 20	79	15
 2	 21	83	20
 3	 17d (36)  18d (64)	82	20
 4	 22 (80)  23 (20)	90	10
 5	 24 (90)  25 (10)	81	10

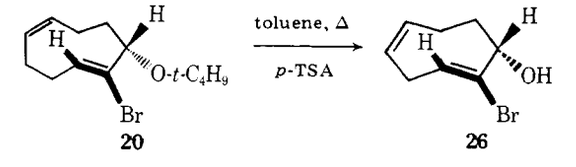
When 9-*exo*-bromobicyclo[6.1.0]nonane (**5**) was treated with silver perchlorate in *tert*-butyl alcohol at 40 °C a very rapid reaction took place, which led to the formation of nearly pure *trans*-3-*tert*-butoxycyclonon-1-ene (**24**); see Table III. Only a minor amount of the corresponding cis isomer was formed. This result is not surprising since the absence of the bulky bromine atom decreases the severe steric strain in the transient cation and thus diminishes the propensity for isomerization to the cis cation. It is interesting to note that a similar tendency is also observed in the ring expansion of **5** with silver nitrate. In this case predominantly *trans*-cyclonon-1-en-3-yl nitrate (**11**) is formed. A significant release of strain can also be effected by extension of the carbon chain by one carbon atom. So, on treatment of the next higher homologue **4** with silver perchlorate in *tert*-butyl alcohol mainly *trans*-2-bromo-3-*tert*-butoxycyclodec-1-ene (**22**) was formed. The corresponding cis isomer (**23**) represented only 20% of the product.

Finally, we wish to note that 8,8-dibromobicyclo[5.1.0]-octane (**2**) and 9,9-dibromobicyclo[6.1.0]non-4-ene (**1**) afforded only trans products on reaction with silver perchlorate in *tert*-butyl alcohol, viz., *trans*-2-bromo-3-*tert*-butoxycyclooct-1-ene (**21**) and *trans,cis*-2-bromo-3-*tert*-butoxycyclonona-1,6-diene (**20**), respectively. It was nearly self-evident that these reactions would proceed in a completely concerted manner.

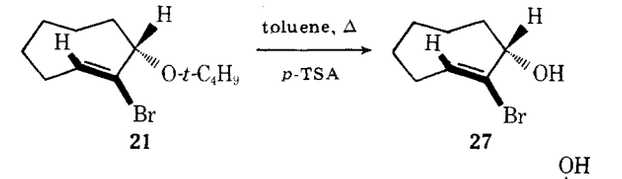
Structure Assignments. The configurations of products **17a–d** and **18a–d** arising from the ring expansion of **3** were determined with the aid of their ^1H and ^{13}C NMR spectra (see Table IV). In the proton spectrum the trans products **17a–d** exist as two rapidly equilibrating diastereoisomers (rotation of the trans double bond through the loop of the ring).[6b] Their spectra display typical double doublets for the olefinic region. The methine part of the spectrum shows a characteristic double doublet and a lower field multiplet. The corresponding cis structures **18a–d** can be detected readily by their typical olefinic triplet and by the signal of the methine proton: a multiplet which resonates always at lower field than the methine protons of the trans diastereoisomers. These observations are in good agreement with recently reported data for similar compounds.[1h] An additional and valuable method of determining the structures of the products consisted in comparison of the ^{13}C spectra. Of importance is the resonance of the allylic carbons. One of these, to which the alkoxy substituent is attached, may readily be found.

For the cis isomers this latter allylic carbon resonates generally at 5–10 ppm upfield relative to the allylic signal of the corresponding trans diastereoisomers.[9] In this way the mixtures **22, 23** and **24, 25** were analyzed unambiguously, as well as the mixture of *cis*- and *trans*-cyclonon-1-en-3-yl nitrate (**11** and **12**).

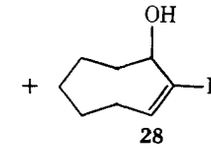
The structural assignments of the two trans compounds **20** and **21** were made in accordance with their ^1H NMR spectra. The coupling constants were in good agreement with the values measured in analogous compounds. Chemical evidence was obtained in the following way: on refluxing a solution of **20** in toluene containing a catalytic amount of *p*-toluenesulfonic acid for 10 min the parent alcohol **26** was obtained. In



20 **26**



21 **27**



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a similar way the *tert*-butoxy group was removed from **21**. This afforded a 3:2 mixture of *trans*- and *cis*-2-bromocyclooct-1-en-3-ol (**27** and **28**, respectively).[10]

Experimental Section

General. The dibromides **1–4** were prepared by reaction of the appropriate olefins with dibromocarbene, generated from bromoform

and potassium *tert*-butoxide in pentane.[11] Cyclononene, required for the preparation of **4**, was obtained from 9,9-dibromobicyclo[6.1.0]nonane (**3**) by conversion to cyclonona-1,2-diene and subsequent reduction.[12] 9-*exo*-Bromobicyclo[6.1.0]nonane (**5**) was obtained from the dibromide **3** by reduction with dimsyl anion in Me_2SO.[13] The corresponding 9-*endo*-bromobicyclo[6.1.0]nonane (**19**) was obtained via tri-*n*-butyltin hydride reduction of **3**.[14] ^1H NMR spectra were obtained on a Varian T-60 spectrometer and ^{13}C NMR spectra were measured on a Varian HA-100 apparatus at 25.12 MHz.

A typical experimental procedure for the preparation of the nitrate esters is exemplified with the preparation of **8**. The alcoholysis reactions were performed at 40 °C, starting with an initial 1 M concentration of silver perchlorate; a typical experiment is illustrated by the preparation of **21**.

***cis*-2-Bromocyclonon-1-en-3-yl Nitrate (8).** A solution of 2.82 g (0.01 mol) of 9,9-dibromobicyclo[6.1.0]nonane (**3**) and 3.38 g (0.02 mol) of silver nitrate in 20 ml of acetonitrile was refluxed with stirring for 4 h (progress of the reaction was monitored by TLC). After cooling the reaction mixture was poured onto 100 ml of saturated sodium chloride solution and 75 ml of ether. Stirring was continued for 10 min and the mixture was filtered through Celite. The organic layer was separated and washed twice with water. The product which remained after drying and concentrating was separated from some TLC immobile material by chromatography through a short silica gel column, using pentane as eluent. Upon bulb to bulb distillation 1.86 g (78%) of **8** was obtained as a colorless oil. NMR data are presented in the table; IR (neat) 2930, 2860, 1630, 1460, 1440, 1360, ,1320, 1290, 1270, 1160, 1020, 1005, 970, 962, 946, 920, 890, 845, 750 cm^{-1}.

Anal. Calcd for $C_9H_{14}NO_3Br$: C, 40.91; H, 5.30; N, 5.30. Found: C, 40.99; H, 5.36; N, 5.19.

Product **8** was obtained also by nitration of *cis*-2-bromocyclonon-1-en-3-ol. To 3 ml of acetic anhydride was added 265 mg (1.1 mmol) of $Cu(NO_3)_2 \cdot 3H_2O$. After the appearance of the typical precipitate of cupric acetate the mixture was stirred for an additional 15 min and then cooled to 0 °C. A solution of 210 mg (1 mmol) of *cis*-2-bromocyclonon-1-en-3-ol[5] in 2 ml of methylene chloride was added in 1 min. The mixture was stirred for an additional 5 min and then poured onto 20 ml of water. After neutralization with solid sodium bicarbonate the product was extracted with ether. The oil which remained after evaporation of the organic phase was chromatographed over a short silica gel column (pentane as eluent) and afforded 240 mg (91%) of **8**.

***trans,cis*-2-Bromocyclonona-1,6-dien-3-yl Nitrate (6).** This compound was prepared in 62% yield by refluxing a solution of 2.80 g (0.01 mol) of **1** and 3.38 g (0.02 mol) of silver nitrate in 20 ml of acetonitrile for 3 h. Some TLC immobile material was separated by chromatography through silica gel using pentane as eluent. Analytical material was obtained by microscale distillation. NMR data are presented in the table; IR (neat) 3000, 2925, 2860, 1625, 1540, 1530, 1440, 1360, 1295, 1270, 1260, 1215, 1192, 1170, 1078, 972, 955, 924, 900, 845, 787, 750, 748 cm^{-1}. Anal. Calcd for $C_9H_{12}BrNO_3$: C, 41.22; H, 4.58; N, 5.34. Found: C, 41.16; H, 4.69; N, 5.27.

***trans*-2-Bromocyclooct-1-en-3-yl Nitrate (7).** The nitrate was obtained in 71% yield as an oil from reaction of 2.68 g (0.01 mol) of **2** and 3.38 g (0.02 mol) of silver nitrate on refluxing 4 h in 20 ml of acetonitrile. The crude product was chromatographed through a short column of silica gel, using pentane as eluent, to remove some traces of TLC immobile material. NMR data are presented in the table; IR (neat) 2925, 2850, 1630, 1450, 1360, 1315, 1277, 1248, 1217, 1119, 1035, 1009, 990, 959, 892, 848, 750 cm^{-1}. Anal. Calcd for $C_8H_{12}BrNO_3$: C, 38.40; H, 4.81; N, 5.61. Found: C, 38.12; H, 4.59; N, 5.30.

2-Bromocyclodec-1-en-3-yl Nitrate (9 and 10). A mixture of 2.96 g (0.01 mol) of dibromide **4** and 3.38 g (0.02 mol) of silver nitrate in 25 ml of acetonitrile was refluxed for 3 h and worked up in the usual manner. After chromatography through a short column of silica gel (pentane) 2.72 g (83%) of a colorless oil was obtained which according to the NMR spectrum consisted of a 1:1 mixture of **9** and **10**. An analytical sample was obtained by evaporative bulb to bulb distillation. Anal. Calcd for $C_{10}H_{16}BrNO_3$: C, 43.17; H, 5.76; N, 5.04. Found: C, 43.01; H, 5.77; N, 5.12. The individual isomers were synthesized from the corresponding alcohols[5] as described for **8**. The NMR data of the individual isomers are presented in the table. IR (neat) for **10:** 2930, 2850, 1730, 1470, 1445, 1355, 1320, 1270, 1200, 945, 930, 845 cm^{-1}. IR (neat) for **9:** 2930, 2860, 1730, 1465, 1440, 1360, 1305, 1270, 955, 845 cm^{-1}.

Cyclonon-1-en-3-yl Nitrate (11 and 12). A solution of 2.03 g (0.01 mol) of **5** and 3.38 g (0.02 mol) of silver nitrate in 25 ml of acetonitrile was refluxed for 0.5 h. After workup in the usual manner, the resulting product was chromatographed over silica gel (hexane) and afforded 440 mg of *cis*-cyclonon-1-en-3-yl nitrate (**12**) (R_f 0.25) and 890 mg of *trans*-cyclonon-1-en-3-yl nitrate (**11**) (R_f 0.21). The total yield amounted to 72%. Analytical material was obtained by microdistillation. Anal. Calcd for $C_9H_{15}NO_3$: C, 58.38; H, 8.11; N, 7.57. Found: 58.60; H, 8.29; N, 7,31. The NMR data for the individual isomers are presented in Table I. IR (neat) for **11:** 2930, 2860, 1620, 1450, 1305, 1290, 1275, 1265, 975, 937, 855 cm^{-1}. ^{13}C spectrum ($CDCl_3$) 21.2, 23.6, 27.5, 31.7, 31.9, 33.4, 86.8, 128.0, 133.7 ppm. IR (neat) for **12:** 3020, 2930, 2860, 1620, 1450, 1300, 1270, 970, 945, 925, 855, 775, 740 cm^{-1}. ^{13}C spectrum ($CDCl_3$) 24.2, 26.6, 27.4, 28.9, 31.5, 82.9, 128.0, 134.7 ppm.

Table IV. NMR Data[a]

Compd[b]	^1H NMR, δ (CCl_4 solutions)	^{13}C NMR, ppm downfield from external Me_4Si in $C_2Br_2F_4$
17a, 18a	3.91 and 3.47 (m and dd, methine H-3, trans, J = 5 and 10 Hz), 4.20 (m, methine H-3, cis)	56.9 (CH_3O), 79.2 (C-3, cis), 85.9 and 87.2 (C-3, trans)
17b, 18b	3.62 and 4.02 (m and dd, methine H-3, trans, J = 5.5 and 10 Hz), 4.35 (m, methine H-3, cis)	64.7 (CH_3C_2O), 77.4 (C-3, cis), 84.1 and 85.4 (C-3, trans)
17c, 18c	4.11 (m, methine H-3, trans), 4.40 (m, methine H-3, cis), 6.20 (t, J = 0 Hz, olefin H-1, cis)	69.2 [$(CH_3)_2C$], 74.2 (C-3, cis), 81.3 and 82.7 (C-3, trans)
17d, 18d	3.72 and 4.07 (m and dd, trans, methine H-3, J = 5 and 10 Hz), 4.41 (m, cis, methine H), 6.02 (t, olefin H-1, J = 9 Hz, cis)	70.4 (C-3, cis), 74.7 [$(CH_3)_3C$], 78.1 and 79.3 (C-3, trans)
20	5.78 (t, 1, H-1, J = 8 Hz), 5.19 (m, 2, H-5 and H-6), 3.84 (m, 1, methine H-3)	
21	5.99 (dd, 1, H-1, J = 11 and 4.5 Hz), 3.96 (t, 1, H-3, J = 8 Hz)	75.1 [$C(CH_3)_3$], 78.7 (C-3, trans)
22, 23	6.24 (t, J = 8 Hz, trans, H-1), 5.82 (dd, H-1, cis, J = 12 and 6 Hz), 4.49 (m, H-3, cis), 3.99 (m, H-3, trans)	69.2 (C-3, cis), 75.0 [$C(CH_3)_3$], 77.6 (C-3, trans)
24, 25	3.59 (m, methine H, trans), 4.06 (m, methine H, cis), 5.21 (m, olefinic H)	68.9 (C-3, cis), 73.9 [$C(CH_3)_3$], 75.9 (C-3, trans)

[a] Only the most significant signals were tabulated, because in the methine region the signals are often overlapped by alkoxy protons, whereas in the olefinic region the protons of cis and trans structures coincide. [b] Registry no. are, respectively, 26994-06-9, 61045-43-0, 61045-44-1, 61045-45-2, 60996-41-0, 60996-42-1, 60996-43-2, 60996-44-3 60996-45-4, 60996-46-5, 60996-47-6, 60996-48-7, 60996-49-8, 60996-50-1.

***trans*-2-Bromo-3-*tert*-butoxycyclooct-1-ene (21).** To a solution of 4.14 g (0.02 mol) of silver perchlorate in 20 ml of *tert*-butyl alcohol (~15 g) was added to 40 °C with vigorous stirring 2.68 g (0.01 mol) of **2**. Precipitation of silver bromide began immediately. After 20 min the starting bromide had disappeared (as evidenced by the thin layer chromatogram, Merck silica gel plates, benzene as eluent). Then 20 ml of saturated sodium chloride solution was added. The mixture was stirred for about 5 min and filtered through Celite. After dilution with 100 ml of water the product was extracted twice with ether. Upon washing, drying, and evaporation of the solvent 2.16 g (83%) of pure **21** remained as a colorless oil.[10] The NMR data are presented in Table IV.

A solution of 1,3 g (0.005 mol) of **21** in 10 ml of toluene, containing about 100 mg of *p*-toluenesulfonic acid, was refluxed for 10 min. The mixture was washed twice with 10% Na_2CO_3 solution and once with

water. After drying and evaporation of organic phase 0.75 g (74%) of a 3:2 mixture of trans and cis alcohol **27** and **28**, respectively, was obtained. These two alcohols were separated by column chromatography (silica gel, chloroform–2% methanol as eluent): R_f (cis, **28**) 0.35; R_f (trans, **27**) 0.29. NMR ($CDCl_3$) for **27**: δ 4.18 (dd, 1, methine H-3, J = 10 and 5 Hz), 6.11 (dd, 1, olefin H-1, J = 10.5 and 4.5 Hz). NMR ($CDCl_3$) for **28**: δ 4.71 (dd, 1, methine H-3, J = 10 and 5 Hz), 6.21 (t, 1, olefin H-1, J = 8.5 Hz).

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Registry No.—**27**, 61045-46-3; **28**, 60996-51-2; silver nitrate; 7761-88-8; *cis*-2-bromocyclonon-1-en-3-ol, 32726-58-2; *cis*-bromocyclodec-1-en-3-ol, 57090-98-9; *trans*-2-bromocyclodec-1-en-3-ol, 57090-97-8; *tert*-butyl alcohol, 75-65-0.

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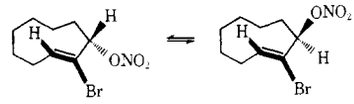
(6) (a) T. Sato, T. Akima and K. Uno, *J. Chem. Soc. C*, 891 (1973). (b) The *trans*-cyclononene derivatives generally do exist as two rapidly equilibrating diastereoisomers which are readily recognized from their ^1H NMR spectra. This phenomenon has been discussed exhaustively in the literature; see



(a) A. C. Cope, K. Banholzer, H. Keller, B. A. Pawson, J. J. Whang, and H. J. S. Winkler, *J. Am. Chem. Soc.*, **87**, 3644 (1965); (b) G. Binsch and J. D. Roberts, *ibid.*, **87**, 5157 (1965). *trans*-Cyclonon-1-en-3-yl nitrate, which was prepared from the corresponding trans alcohol, could be characterized in this way.
The NMR spectrum (CCl_4) displayed an olefinic multiplet at δ 6.23, whereas the methine part was splitted in two signals, viz., a triplet at δ 5.33 (J = 5 Hz) and a double doublet at δ 5.02 (J = 10 and 4 Hz).
(7) Excess of silver perchlorate is necessary to obtain a high reaction rate and a quantitative conversion.
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Specific Ortho Bromination.[1] 2. Aluminum Trichloride Catalyzed Transalkylation

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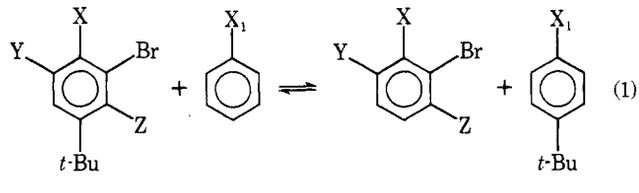
Transalkylation between 2-bromo-4-*tert*-butyl derivatives of substituted benzenes (donors) and various aromatics (acceptors) was found (under the conditions of this study) to be catalyzed by solid $AlCl_3$. The equilibrium constant of the reversible process was determined at different temperatures. The enthalpy of the reaction was calculated and discussed.

Direct bromination of monosubstituted aromatic compounds yields a mixture of the three possible monobrominated isomers. The separation of the isomers in most cases is difficult owing to their similarity in physical properties. In order to overcome this difficulty methods for an indirect bromination specifically at the ortho position have been developed.[1]

Tertiary butyl and other bulky hydrocarbons were used as blocking groups in the synthesis of ortho-disubstituted benzene derivatives. Various catalysts, temperatures, substrates, and solvents were used for the removal of the blocking groups.[2–8]

It has been reported[9–15] that bromine attached to benzene or substituted benzene shifts along the aromatic nuclei or even cleaves under alkylation reaction conditions.

We have recently reported that catalytic amounts of $AlCl_3$ promote the transfer of *tert*-butyl group from the donor to the acceptor, in a reversible process according to eq 1.[1]



(1)

Results and Discussion

At least 5 mol % of $AlCl_3$ is needed to disproportionate bromobenzene to benzene and dibromobenzene.[13] Our results show that transfer of *tert*-butyl group from the donor to the acceptor is accomplished with 1–2 mol % of $AlCl_3$ without concurrent bromine transfer.

Crump,[16] who investigated the $AlCl_3$-catalyzed isomerization of bromotoluenes, suggested that the $AlCl_3$ catalysis is heterogeneous in nature.