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Bromination of benzobicyclic system with 1,2-dibromotetracholoroethane: unusual radical rearrangement

Arif Dastan*

Department of Chemistry, Atatürk University, 25240 Erzurum, Turkey

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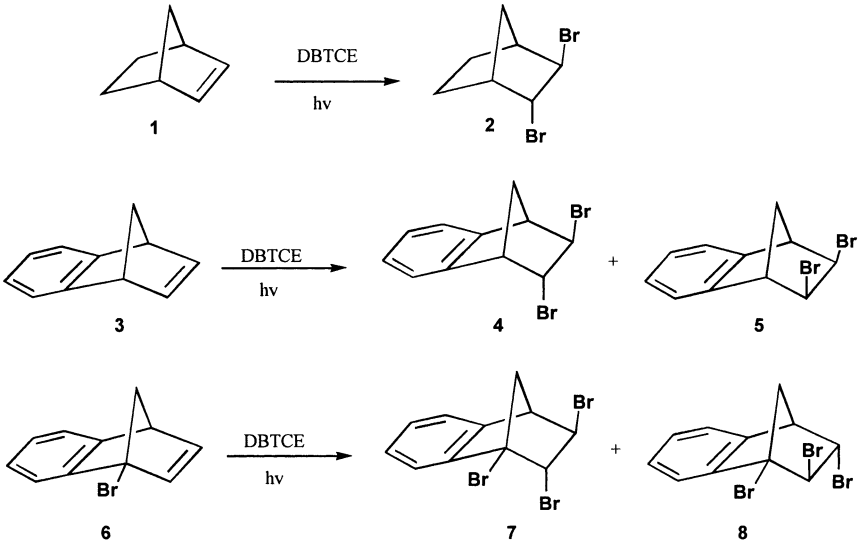
Abstract—The bromination reaction of a benzobicyclic system with 1,2-dibromotetracholoroethane (DBTCE) was studied. For tricyclo-[6.2.2.0^{2,7}]dodeca-2,4,6,9,11-pentaene, rearranged and non-rearranged products were obtained. Bromination of 11-oxatricyclo[6.2.1.0^{2,7}]-undeca-2,4,6,9-tetraene with DBTCE gave non-rearranged products whereas brominations of (1*R*(*S*),8*R*(*S*))-9-bromotricyclo[6.2.2.0^{2,7}]-dodeca-2,4,6,9,11-pentaene and (1*S*(*R*),8*S*(*R*))-9,10,11-tribromotricyclo[6.2.2.0^{2,7}]dodeca-2,4,6,9,11-pentaene with DBTCE gave only rearranged products. In addition, the reaction of (1*S*(*R*),8*S*(*R*))tricyclo[6.3.1.0^{2,7}]dodeca-2,4,6,9-tetraene with the same reagent resulted in the formation of allylic bromination products. The radicalic reaction mechanism is discussed. All compounds are characterized properly, in particular by NMR spectra and by chemical transformation.

1. Introduction

In addition to numerous industrial applications as pesticides, plastics, fire retardants and pharmaceutical chemicals, the halogen derivatives of a compound are valuable as a model for synthesizing other derivatives. Therefore, the halogenation of organic compounds is an important process. The addition of bromine to the carbon–carbon double bond with molecular bromine is formally one of the simplest reactions typical of unsaturated compounds.[1] The nature of the intermediates of the addition depends on temperature, steric factors, torsional effects, π- and σ-participation in the transition state and the formation of non-classical ions or a fast equilibrium of classical ions.[2] The bromination of unsaturated bicyclic systems with molecular bromine leads to rearrangements of the molecular skeleton.[2,3]



Scheme 1.

Keywords: bromination; polybromides; 1,2-dibromotetracholoroethane.
* Tel.: +90-442-2311758; fax: +90-442-2331062; e-mail: adastan@atauni.edu.tr
Abbreviations: DBTCE, 1,2-dibromotetracholoroethane; AIBN, azoisobutyronitrile.

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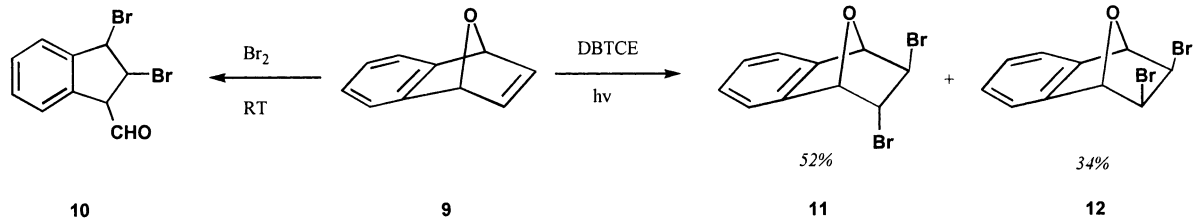


Scheme 2.

Furthermore, we have shown previously that high temperature bromination of a bicylic system gives mainly non-rearrangement products.[3]

1,2-Dibromotetracholoroethane (DBTCE) is a mild bromination reagent first used by Huyser and DeMott[4] to brominate allylic positions. Later, Fry and co-workers[5] studied norbornene (**1**), and Wilt and Cheiner[6] studied benzonorbornadiene (**3**), showing that the bromination of these systems with DBTCE gives only non-rearranged products rather than allylic brominated products. Paquette and Burke[7] obtained non-rearranged products from the bromination of 1-bromobenzonorbornadiene (**6**) with DBTCE (Scheme 1). Similarly, the bromination of different benzonorbornadiene analogues with DBTCE gives non-rearranged products.[8]

In this paper, several new bromination reactions using DBTCE have been investigated.

2. Results and discussion

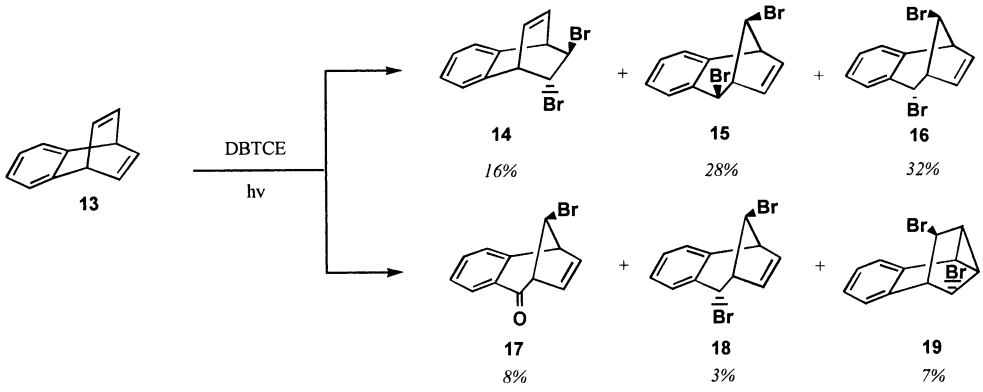
The starting materials (**9**[9], **13**[10], **20**[11], **29**[12] and **37**[10]) were prepared by published methods. Firstly, the bromination of 7-oxabenzonorbornadiene (**9**) with DBTCE was investigated. The solution of **9**, DBTCE and AIBN in carbon tetrachloride was irradiated with a 150 W sun lamp at 77°C. ^{1}H NMR spectroscopic studies revealed that the reaction mixture consisted of two products. This mixture was submitted to silica gel column chromatography, and two non-rearranged products (**11**–**12**) were isolated in nearly quantitative yield as expected (Scheme 2). In contrast, the bromination of **9** with molecular bromine at rt gives dibromoaldehyde **10** as described in the literature.[3f]

While bromination of benzobarrelene (**13**) with molecular bromine was accompanied by only rearrangement of skeletal,[3a] the bromination of **13** with DBTCE gave predominantly rearranged products (**15**–**19**) in 78% yield and non-rearranged product **14** in only 16% yield (Scheme 3). Cationic and radical system often behave similarly and radicalic rearrangements are also possible. But, these results at first glance unexpected, since the previous results obtained bromination of norbornene and benzonorbornadiene systems with DBTCE mentioned only conservation of skeletal.[5–8]

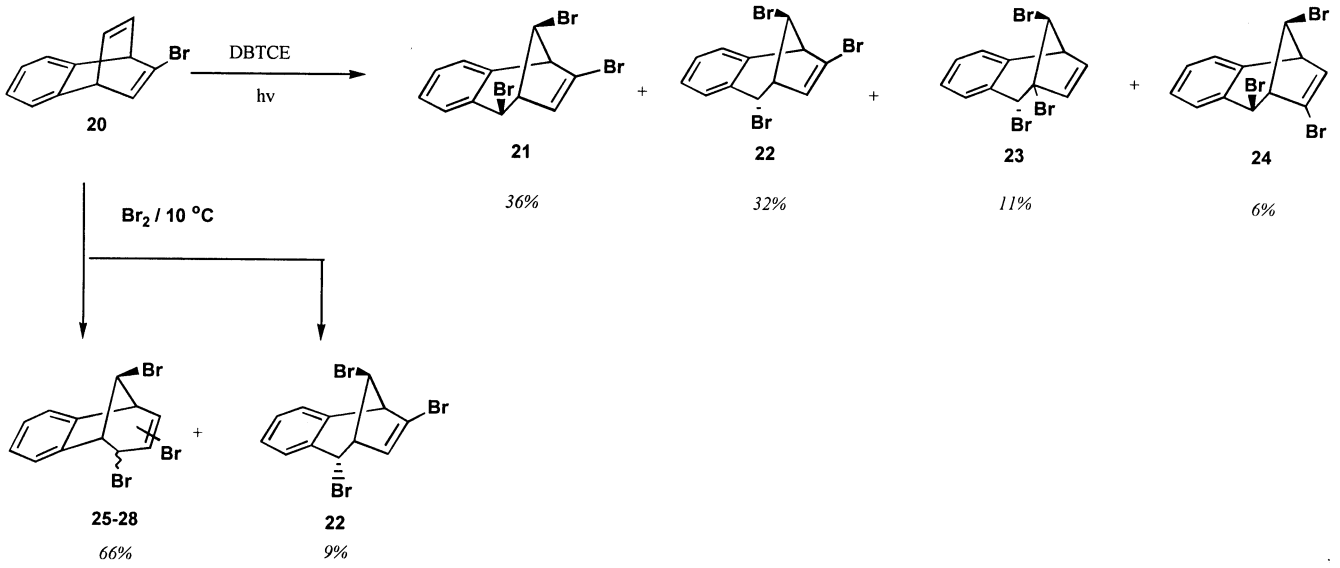
In order to test the behavior of bromine-substituted benzobarrelene, the bromination of mono-, and tribromobenzobarrelene with DBTCE was studied. The bromination of 2-bromobenzobarrelene (**20**) with DBTCE gave only rearranged products via alkyl migration, while bromination of **20** at 10°C with bromine gave[2b] predominantly aryl migration products (**25**–**28**). Furthermore, non-rearranged products were not observed in this reaction (Scheme 4).

Although the reaction of 2,3,5-tribromobenzobarrelene (**29**) with molecular bromine at 10°C gave only non-rearranged products[12] (**35**,**36**), surprisingly, it was observed that bromination of **29** with DBTCE gave only rearranged products (**30**–**33**) via alkyl migration (Scheme 5). From this reaction was also obtained HBr addition product **34**, the formation mechanism of which is discussed in Section 2.1.

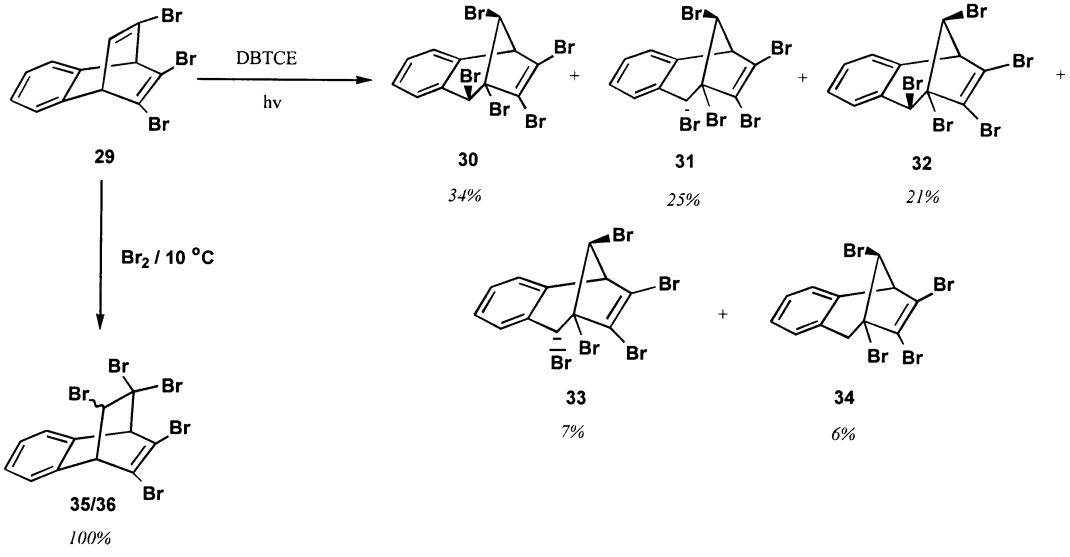
Lastly, bromination of homobenzonorbornadiene (**37**), which has both active allylic protons and a strained double bond, was studied. Bromination of **37** with DBTCE gave only alyllic-brominated products **38** rather than rearranged and non-rearranged addition products. The further bromination of products **38** gave dibromide **39** in high yield (Scheme 6). This observation shows that allylic bromination occurs more readily than addition to a double bond with DBTCE,



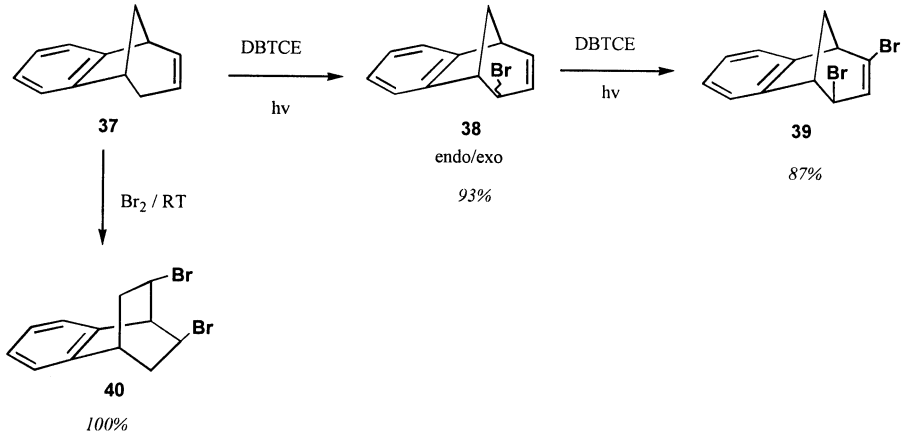
Scheme 3.



Scheme 4.

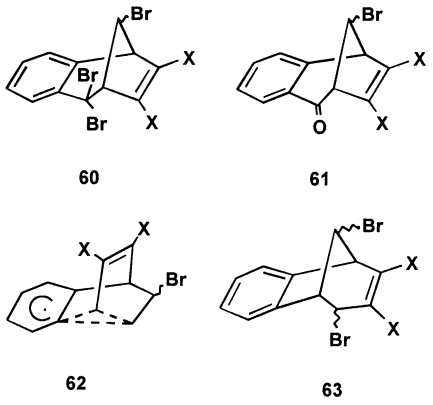


Scheme 5.



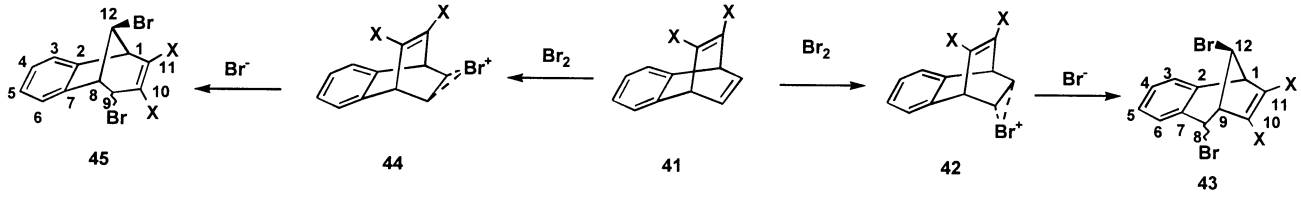
Scheme 6.

even a molecule with a strained double bond. However, the bromination of **37** with molecular bromine gives only addition product **40** rather than allylic bromination.[10]



2.1. Mechanism for bromination with DBTCE

It is clear that bromination of a bicylic system with molecular bromine at low temperature gives rearranged products by way of aryl and alkyl migration. In these reactions, the addition of bromine to the double bond takes place stereoselectively.[3] For the products obtained by aryl migration, the bromine atom at C_{12} carbon is absolutely *syn*, while for the products obtained by alkyl migration bromine atom at C_{12} carbon is absolutely *anti* according to the benzene ring (Scheme 7).



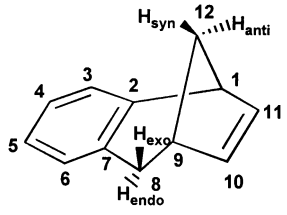
Scheme 7.

However, there is no stereoselectivity in the radical mechanism. It was observed that bromination of these compounds with DBTCE gave both *anti* and *syn* bromine atoms at C_{12} carbon. The *anti*-configuration of the bromine in molecules (**15**, **17**, **18**, **21**, **24**, **32**, **33**) cannot be explained by an ionic mechanism. It can be explained only by a radical mechanism in which stereochemical control of configuration cannot be achieved in most cases. Therefore, for the formation of the rearranged products, the following general reaction mechanism is proposed (Scheme 8). The initially formed radicals **46** and **47** may either form non-rearranged products **48**–**50** or change radical-vinyl bridged intermediates **51/53** to form **52/54**. Radical-vinyl bridged intermediates **51/53** also open to the benzylic radicals **55/58**, which are then captured either by the bromine radical to form **43/57** or by the hydrogen radical to form **56/59** by means of HBr obtained during the allylic bromination.

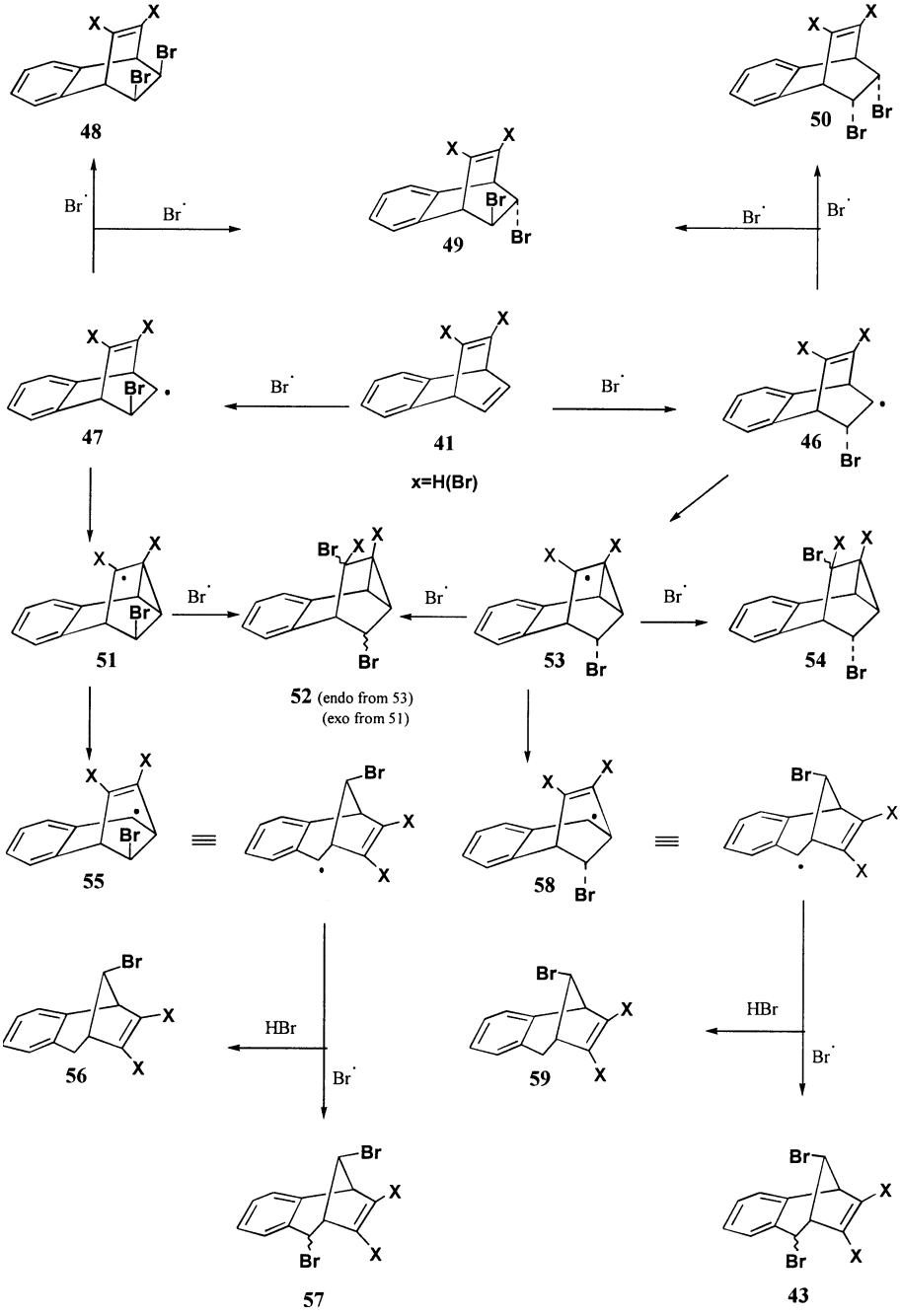
For the bromination of the benzobarrelene derivatives, the last fractions of the column show that there were ketones, like **61**, derived from allylic brominated compounds like **60**, but only **17** was isolated. Therefore it was obvious that the source of HBr was revealed from allylic bromination of dibromides. It was also assumed that during the reaction the radicals **46/47** were not able to turn into aryl-radical bridged intermediate **62**. If they had, it would have been necessary to obtained rearranged products like **63**. This also shows that benzo-vinyl bridging is not favorable. So, bromination of norbornene and benzonorbornadiene derivatives with DBTCE gives only non-rearranged products because they cannot form benzo-vinyl bridging radicals like **62**. Contrary to norbornene and benzonorbornadiene derivatives, benzobarrelene derivatives, which is also eligible to vinyl–vinyl bridging (Scheme 8), gives rearranged products via radical intermediates.

2.2. NMR spectral studies and configurational assignments

The structures of these compounds have been elucidated on the basis of ^{1}H and ^{13}C NMR spectral data and extensive double resonance experiments and by comparison of some spectral data of known compounds and related systems reported in the literature.[3,13] For the new compounds, which completely follow skeletal systems, the structural analysis was achieved according to coupling constant and chemical shifts. A synopsis of the proton coupling constants exhibited by these closely related [3.2.1]octadienes is given in Section 4.



The coupling patterns that are important for stereochemical characterization of this dual are $J_{9,12syn}$, $J_{9,12anti}$, $J_{9,8exo}$ and $J_{9,8endo}$. As a consequence of the rigid geometry and reliability of the Karplus rule[14] in [3.2.1]octane systems[3,13], the dihedral relationship of the H_9 proton to H_{12anti} (~40°), and to H_{12syn} (~80°) is sufficiently distinctive to be revealed by the magnitude of the spin–spin interaction. Thus, the high value of $J_{H12anti}$ (J=4.0–5.0 Hz) is uniquely accommodated by the *syn*-orientation of the bromine atom bonded to the bridge atom. H_{12syn} gives a singlet with line broadening ($J \leq 1$ Hz). The configuration of bromine at the C_8 atom was determined from the coupling constants ($J_{8,9}$). Inspection of Dreiding models indicates that the dihedral angle between

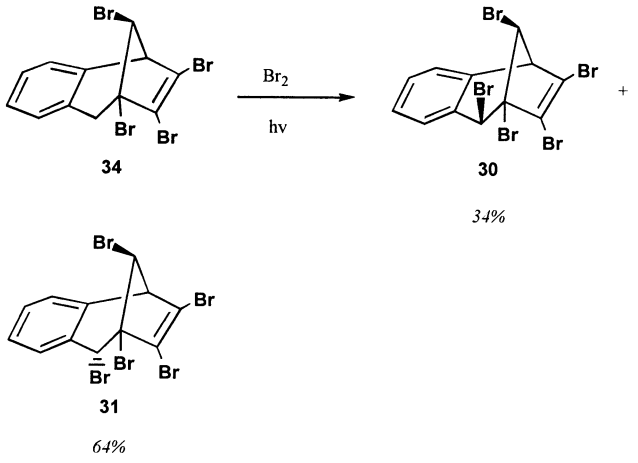


Scheme 8.

protons H_9 and H_{8exo} is approximately 40° whereas the dihedral angle between H_9 and H_{8endo} is 60°. Large coupling constants of J=4.0–5.0 Hz are observed in the case of *endo*-orientation of bromine (*exo*-proton) and J=0.0–2.0 Hz in the case of *exo*-orientation of bromine (*endo*-proton). Aryl shift products can also be easily distinguished in the typical pattern of aromatic resonance.[3a]

For the compounds (**23**, **30**–**34**) that have no hydrogen at C_9 carbon, the configuration of bromine at C_8 carbon was easily determined by chemical shifts. Data published in the literature[13] and described in our study[3a] show that the chemical shift of H_{endo} at C_8 carbon resonates at a weak field in comparison to H_{exo} at C_8 carbon ($\Delta\delta$=0.25–0.60 ppm). These observations confirm the proposed structures. Furthermore, H_{12syn} protons at the C_{12} carbon atom are affected by the *exo*-bromine atom at C_8 carbons and resonate down field. This (γ-*gauche effect*) supports the proposed structures.

The structure of HBr addition product **34** was also supported by chemical transformation. When pure HBr addition product **34** was subjected to radicalic bromination by photobromination with molecular bromine, penta bromides **30** and **31** were obtained in high yield. This observation also supports the proposed structure.



3. Conclusions

The results of the present work demonstrate that bromination with DBTCE is a useful synthetic method for generating non-rearranged bromine addition products in norbornene, benzonorbornadiene and oxa-benzonorbornadiene, which have a great tendency to undergo Wagner–Meerwein rearrangement. In this study, this behaviour of DBTCE was shown to be limited to a few molecules. The bromination of the benzobarrelene system with DBTCE gives predominantly rearranged products. Furthermore, 2,3,5-tribromobenzobarrelene (**29**), which does not have a tendency toward rearrangements with molecular bromine, gives only rearranged products by DBTCE. These results show that rearrangements occur via vinyl–vinyl bridging intermediates at radicalic conditions and benzo-vinyl bridging is not favourable. So, bromination of norbornene and benzonorbornadiene derivatives with DBTCE result in conservation of skeletal while bromination of benzobarrelene systems with the same reagent gives mainly rearranged products via vinyl–vinyl bridging intermediates. It was also observed that a molecule comprising both strained double bonded and active allylic protons regio selectively gives only allylic brominated products such as **38/39**.

4. Experimental

4.1. General

Melting points are uncorrected. Infrared spectra were obtained from solution in 0.1 mm cells or KBr pellets on a regular instrument. The ^{1}H and ^{13}C NMR spectra were recorded on 200 (50)-MHz spectrometers. Apparent splittings are given in all cases. Column chromatography was performed on silica gel (60-mesh, Merck). TLC was carried out on Merck 0.2 mm silica gel 60 F_{254} analytical aluminum plates. All substances reported in this paper are in their racemic form.

4.2. Caution

It has been reported[15] that of three laboratory workers who have used dibromides and a bromohydrin derived from norbornadiene, two later developed similar pulmonary disorders, which contributed to their subsequent deaths. The third exhibited minor skin sensitivity reactions. In the case of the dibromide derived from benzonorbornadiene there is no report in the literature about the toxicological effect. However, I recommend that the compounds must be handled only with extreme caution.

4.3. General procedure for bromination with DBTCE

A solution of alkenes, DBTCE (1.0–1.5 equiv.), AIBN (catalytic) in CCl_4 was irradiated with a 150 W sun lamp at reflux temperature in 50 mL flask equipped with condenser. The progress of reaction was monitored by ^{1}H NMR spectra. After completion of reaction, the solvent and tetracholoroethylene formed during bromination were removed under reduced pressure. The residue was purified by column chromatography.

4.4. Bromination of 11-oxatricyclo[6.2.1.0^{2,7}]undeca-2,4,6,9-tetraene (9)[9] with DBTCE

The reaction was carried out according to the above procedure by using 0.5 g (3.47 mmol) of 7-oxabenzonorbornadiene **9** and DBTCE (1.14 g, 3.50 mmol) in 25 mL of carbon tetrachloride. After 14 h, the residue was chromatographed on silica gel (30 g) eluting with hexane/ethyl acetate in ratio 10:1. The first fraction was identified as *(1R(S),8S(R),9S(R),10S(R))-9,10-dibromo-11-oxatricyclo-[6.2.1.0^{2,7}]undeca-2,4,6-triene* (**11**)[3f] (549 mg, 52% yield).

The seconds fractions was identified as *(1R(S),8S(R),9S(R),10R(S))-9,10-dibromo-11-oxatricyclo[6.2.1.0^{2,7}]-undeca-2,4,6-triene* (**12**)[3f] (359 mg, 34% yield).

4.5. Bromination of tricyclo[6.2.2.0^{2,7}]dodeca-2,4,6,9,11-pentaene (13) with DBTCE

The reaction was carried out according to the above procedure by using 110 mg (0.71 mmol) of **13** and DBTCE (255 mg, 0.79 mmol) in 15 mL of carbon tetrachloride After 24 h, the residue was chromatographed on silica gel (80 g) eluting with hexane. The first fraction was identified as unreacted benzobarrelene (6 mg). The second fraction consisted of a mixture of dibromides **14**[3a] (16%), **15**[3a] (28%), **16**[3a] (32%), and **18**[3a] (3%). The third fractions are identified as **19**[3f] (7%). Then the column was eluted with hexane/ethyl acetate (8:2). The last fraction was identified as **17**.

4.5.1. (1*S*(*R*),9*R*(*S*),12*S*(*R*))-12-Bromotricyclo[7.2.1.0^{2,7}]-dodeca-2,4,6,10-tetraen-8-one (17). (14 mg, 8%) mp: 93–94°C colourless crystals from chloroform/hexane (1:5). [Found: C, 59.09; H, 3.58 $C_{12}H_9BrO$ requires C, 57.86; H, 3.64%]; ^{1}H NMR (200 MHz, $CDCl_3$): 7.93–7.17 (m, 4H, aromatic), 6.73 (dd, $J_{10,11}$=5.4, $J_{1,11}$=2.9 Hz, H_{11}, 1H), 6.11 (dd, $J_{10,11}$=5.4, $J_{9,10}$=2.7 Hz, H_{10}, 1H), 4.94 (s, H_{12},1H) 4.04 (d, $J_{9,10}$=2.7 Hz, H_9, 1H), 3.83 (d, $J_{1,11}$=2.9 Hz, H_1, 1H). ^{13}C NMR (50 MHz, $CDCl_3$): 193.60, 146.63, 144.98, 135.48, 130.84, 130.58, 130.34(2C), 127.39, 67.62, 63.65, 59.03. IR (KBr, cm^{-1}): 3063, 2994, 2980, 1670, 1584, 1466, 1320, 1290, 1230, 1112, 1090, 1010, 900, 820.

4.6. Bromination of (1*R*(*S*),8*R*(*S*))-9-bromotricyclo-[6.2.2.0^{2,7}]dodeca-2,4,6,9,11-pentaene (20) with DBTCE

The reaction was carried out according to the above procedure by using 690 mg (2.96 mmol) of **20** and DBTCE (1.16 g, 3.55 mmol) in 20 mL of carbon tetrachloride. After 36 h, the residue was chromatographed on silica gel (100 g) eluting with hexane. Four compounds were isolated: **24** (70 mg, 6%), **22** (372 mg, 32%), **21** (419 mg, 36%), **23** (128 mg, 11%) in that order.

4.6.1. (1*S*(*R*),8*R*(*S*),9*S*(*R*),12*S*(*R*))-8,10,12-Tribromotricyclo[7.2.1.0^{2,7}]dodeca-2,4,6,10-tetraene (24). Colourless crystals, mp 99–100°C from methylene chloride/*n*-hexane 1:3. [Found: C, 36.88; H, 2.28, $C_{12}H_9Br_3$ requires C, 36.68; H, 2.31%]; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.41–6.94 (m, aromatic, 4H), 6.59 (dd, $J_{1,11}$=3.1, $J_{11,12}$=1.2 Hz, H_{11}, 1H), 5.39 (d, $J_{8,9}$=2.0 Hz, H_8, 1H), 5.11 (m, H_{12}, 1H), 3.68 (bd, $J_{1,11}$=3.1 Hz, H_1, 1H), 3.58 (dd, $J_{8,9}$=2.0, $J_{1,9}$=1.1 Hz, H_9, 1H), ^{13}C NMR (50 MHz, $CDCl_3$) δ 142.08, 139.83, 134.06, 133.78, 129.12, 128.79, 126.54, 120.28, 65.55, 57.16, 55.79, 46.84. IR (KBr, cm^{-1}) 3081, 3055, 3020, 2985, 1590, 1490, 1294, 1260, 1230, 1217, 1165, 1140, 834, 808, 757.

4.6.2. (1*S*(*R*),8*S*(*R*),9*S*(*R*),12*S*(*R*))-8,11,12-Tribromotricyclo[7.2.1.0^{2,7}]dodeca-2,4,6,10-tetraene (22). Colourless crystals, mp 111–112°C from methylene chloride/*n*-hexane 1:3. [Found: C, 36.80; H, 2.33 $C_{12}H_9Br_3$ requires C, 36.68; H, 2.31%]; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.35–6.78 (m, aromatic, 4H), 5.91 (d, $J_{9,10}$=3.3 Hz, H_{10}, 1H), 5.38 (d, $J_{8,9}$=4.8 Hz, H_8, 1H), 4.60 (t, $J_{1,12}$=$J_{9,12}$=4.6 Hz H_{12}, 1H), 3.18 (bd, $J_{1,12}$=4.6 Hz, H_1, 1H), 3.13 (ddd, $J_{8,9}$=4.8, $J_{9,10}$=3.3, $J_{1,9}$=1.0 Hz, H_9, 1H), ^{13}C NMR (50 MHz, $CDCl_3$) δ 138.09, 135.56, 134.41, 132.79, 132.37, 130.84, 130.21, 129.32, 58.85, 54.55, 53.81, 49.08. IR (KBr, cm^{-1}) 3055, 3020, 2970, 2953, 1595, 1480, 1450, 1260, 1230, 1145, 1000, 910, 757.

4.6.3. (1*S*(*R*),8*R*(*S*),9*S*(*R*),12*R*(*S*))-8,11,12-Tribromotricyclo[7.2.1.0^{2,7}]dodeca-2,4,6,10-tetraene (21). Colourless crystals, mp 89–90°C from methylene chloride/*n*-hexane 1:3. [Found: C, 36.84; H, 2.32 $C_{12}H_9Br_3$ requires C, 36.68; H, 2.31%]; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.39–7.03 (m, aromatic, 4H), 5.88 (dd, $J_{9,10}$=2.1, $J_{10,12}$=1.0 Hz, H_{10}, 1H), 5.24 (d, $J_{8,9}$=1.9 Hz, H_8, 1H), 5.09 (d, $J_{10,12}$=1.0 Hz, H_{12}, 1H), 3.58 (m, H_1, 1H), 3.55 (m, H_9, 1H), ^{13}C NMR (50 MHz, $CDCl_3$) δ 140.99, 138.23, 135.39, 135.21, 130.86, 130.07, 128.58, 127.46, 63.42, 61.17, 58.05, 49.17. IR (KBr, cm^{-1}) 3081, 3055, 3030, 3004, 2978, 2953, 1472, 1447, 1294, 1268, 1217, 1165, 1140, 834, 808, 757.

4.6.4. (1*S*(*R*),8*R*(*S*),9*R*(*S*),12*R*(*S*))-8,9,12-Tribromotricyclo[7.2.1.0^{2,7}]dodeca-2,4,6,10-tetraene (23). Colourless crystals, mp 91–92°C from methylene chloride/*n*-hexane 1:3. [Found: C, 35.59; H, 2.41 $C_{12}H_9Br_3$ requires C, 36.68; H, 2.31%]; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.56–6.95 (m, aromatic, 4H), 6.45(dd, A part of AB system, $J_{10,11}$=6.1, $J_{1,11}$=3.5 Hz, H_{11}, 1H), 6.17 (d, B part of AB system, $J_{10,11}$=6.1 Hz, H_{10}, 1H) 5.65 (s, H_8, 1H), 4.97 (d, $J_{1,12}$=4.6 Hz, H_{12}, 1H), 3.55 (dd, $J_{1,12}$=4.6, $J_{1,11}$=3.5 Hz, H_1, 1H), ^{13}C NMR (APT, 50 MHz, $CDCl_3$) δ 141.14(−), 138.30(−), 138.25, 136.54, 134.24(−), 130.28(−), 130.15(−), 128.56(−), 70.41, 64.63(−), 58.65(−), 53.52(−). IR (KBr, cm^{-1}) 3081, 3055, 3030, 2978, 2953, 1472, 1446, 1319, 1243, 1191, 1166, 1114, 961, 911.

4.7. Bromination of (1*S*(*R*),8*S*(*R*))-9,10,11-tribromotricyclo[6.2.2.0^{2,7}]dodeca-2,4,6,9,11-pentaene (29) with DBTCE

The reaction was carried out according to the above procedure by using 1.70 g (4.34 mmol) of **29** and DBTCE (2.12 g, 6.52 mmol) in 30 mL of carbon tetrachloride. After 5 days, the residue was chromatographed on silica gel (100 g) eluting with hexane. The first fraction identified as starting material **29** (10 mg). Later, five compounds were isolated: **34** (144 mg, 6%), **32** (503 mg, 21%), **31** (600 mg, 25%), **30** (815 mg, 34%), **33** (168 mg, 7%) in that order.

4.7.1. (1*S*(*R*),9*S*(*R*),12*R*(*S*))-9,10,11,12-Tetrabromotricyclo[7.2.1.0^{2,7}]dodeca-2,4,6,10-tetraene (34). Colourless crystals, mp 173–174°C from methylene chloride/*n*-hexane 1:1. [Found: C, 30.43; H, 1.66 $C_{12}H_8Br_4$ requires C, 30.55; H, 1.71%]; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.35–7.08 (m, aromatic, 4H), 5.03 (d, $J_{1,12}$=4.7 Hz, H_{12}, 1H), 3.70 (d, $J_{1,12}$=4.7 Hz, H_1, 1H), 3.40 (d, A part of AB system, $J_{8en,8ex}$=17.4 Hz, H_{8ex}, 1H), 3.31 (d, B part of AB system, $J_{8en,8ex}$=17.4 Hz, H_{8en} 1H), ^{13}C NMR (50 MHz, $CDCl_3$) δ 135.30, 134.54, 132.13, 131.26, 130.40, 129.93, 128.68, 127.08, 70.32, 60.11, 59.56, 39.96. IR (KBr, cm^{-1}) 3081, 3055, 3004, 2979, 2953, 1574, 1447, 1425, 1243, 1089, 961, 936.

4.7.2. (1*S*(*R*),8*S*(*R*),9*R*(*S*),12*S*(*R*))-8,9,10,11,12-Pentabromotricyclo[7.2.1.0^{2,7}]dodeca-2,4,6,10-tetraene (32). Colourless crystals, mp 181°C from methylene chloride/*n*-hexane 1:1. [Found: C, 25.98; H, 1.33 $C_{12}H_7Br_5$ requires C, 26.17; H, 1.28%]; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.43–7.05 (m, aromatic, 4H), 5.64 (s, H_8, 1H), 5.45 (s, H_{12}, 1H), 3.94 (s, H_1, 1H), ^{13}C NMR (50 MHz, $CDCl_3$) δ 138.80, 137.85, 136.30, 135.11, 131.09, 130.46, 128.57, 123.98, 80.15, 64.58, 62.11, 56.81. IR (KBr, cm^{-1}) 3030, 3004, 2979, 2953, 1600, 1574, 1472, 1191, 1115, 962, 757.

4.7.3. (1*S*(*R*),8*R*(*S*),9*R*(*S*),12*R*(*S*))-8,9,10,11,12-Pentabromotricyclo[7.2.1.0^{2,7}]dodeca-2,4,6,10-tetraene (31). Colourless crystals, mp 182–183°C from methylene chloride/*n*-hexane 1:1. [Found: C, 26.03; H, 1.31 $C_{12}H_7Br_5$ requires C, 26.17; H, 1.28%]; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.69–7.05 (m, aromatic, 4H), 5.75 (s, H_8, 1H), 5.13 (d, $J_{1,12}$=4.7 Hz, H_{12}, 1H), 3.70 (d, $J_{1,12}$=4.7 Hz, H_1, 1H) ^{13}C NMR (50 MHz, $CDCl_3$) δ 135.92, 134.50, 134.19, 133.06, 130.92, 130.68, 129.04, 127.11, 73.12, 61.93, 59.80, 56.56. IR (KBr, cm^{-1}) 3055, 3030, 3004, 2979, 2953, 1600, 1574, 1472, 1447, 1243, 1166, 1114, 961.

4.7.4. (1*S*(*R*),8*S*(*R*),9*R*(*S*),12*R*(*S*))-8,9,10,11,12-Pentabromotricyclo[7.2.1.0^{2,7}]dodeca-2,4,6,10-tetraene (30). Colourless crystals, mp 208°C from methylene chloride/*n*-hexane 1:1. [Found: C, 26.24; H, 1.26 $C_{12}H_7Br_5$ requires C, 26.17; H, 1.28%]; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.69–7.07 (m, aromatic, 4H), 5.48 (s, H_8, 1H), 5.17 (d, $J_{1,12}$=4.5 Hz, H_{12}, 1H), 3.76 (d, $J_{1,12}$=4.5 Hz, H_1, 1H) ^{13}C NMR (50 MHz, $CDCl_3$) δ 137.28, 136.12, 135.71, 135.23, 131.01, 130.40, 128.58, 127.11, 72.32, 61.08, 56.47, 51.69. IR (KBr, cm^{-1})

3055, 3030, 3004, 2953, 1600, 1574, 1472, 1447, 1243, 1191, 1089, 1064, 987.

4.7.5. (1*S*(*R*),8*R*(*S*),9*R*(*S*),12*S*(*R*))-8,9,10,11,12-Pentabromotricyclo[7.2.1.0^{2,7}]dodeca-2,4,6,10-tetraene (33). Colourless crystals, mp 154°C from methylene chloride/*n*-hexane 1:1. [Found: C, 25.53; H, 1.24 $C_{12}H_7Br_5$ requires C, 26.17; H, 1.28%]; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.66–7.05 (m, aromatic, 4H), 5.78 (s, H_8, 1H), 4.80 (s, H_{12}, 1H), 3.91 (s, H_1, 1H) ^{13}C NMR (50 MHz, $CDCl_3$) δ 136.51, 135.68, 134.58, 132.30, 131.08, 130.93, 127.99, 126.23, 77.71, 65.12, 63.57, 57.26. IR (KBr, cm^{-1}) 3055, 3029, 2979, 2928, 1574, 1472, 1243, 1089, 1063, 987, 936.

4.8. Bromination of (1*S*(*R*),8*S*(*R*))tricyclo[6.3.1.0^{2,7}]-dodeca-2,4,6,9-tetraene (37) with DBTCE

The reaction was carried out according to the above procedure by using 100 mg (0.64 mmol) of **37** and DBTCE (208 mg, 0.64 mmol) in 15 mL of carbon tetrachloride After 4 h, the residue was filtered through a silica gel column. The solvent was removed and the mixture was analysed according to spectral data published in our previously report.[3c] The NMR analyses of mixture indicated the formation of a mixture consisting of *endo* and *exo* (**38**) in ratio 78:22 (total 140 mg, 93%).

4.9. Bromination of monobromides 38 with DBTCE

The reaction was carried out according to the above procedure by using 140 mg (0.60 mmol) of **38** and DBTCE (194 mg, 0.60 mmol) in 15 mL of carbon tetrachloride. After 18 h, the residue was filtered through a silica gel column. The solvent was removed and the mixture was analysed according to spectral data published in our previously report.[3c] The NMR analyses of mixture indicated the formation of **39** in 87% yield (163 mg) as oily residue.

4.10. Photobromination of 34

A solution of **34** (50 mg, 0.11 mmol) and bromine (17 mg, 0.11 mmol) in 5 mL of CCl_4 was subjected to direct irradiation with a sun lamp (150 W) at room temperature for 10 min. After the solvent was removed, the residue was filtered on a short silica gel column (5 g) eluted with CCl_4 to give 57 mg (98%) of pure crude products. The ^{1}H NMR analysis of the crude product indicated the formation of a mixture consisting of **30** and **31** in a ratio of 35:65.

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