Imidyl Radicals, 4[+]

Radical Addition of *N*-Bromophthalimide to Linear and Cyclic Alkynes

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Dedicated to Prof. Dr. Werner Tochtermann on the occasion of his 65th birthday

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Addition of *N*-bromophthalimide (**1**) to alkynes **3** via phthalimidyl radicals **2** introduces a bromine atom and an imidyl moiety to vicinal C atoms, and highly functionalized alkenes **5** are generated. The regioselectivity of the radical attack is controlled by steric and electronic effects, whereas the stereochemistry at the newly formed C=C double bond can be explained by the Curtin–Hammett principle. When this free-radical addition is applied to the medium-sized cycloalkyne **8**, the regular addition product **9** is obtained in addition to products resulting from a transannular cyclization. Furthermore, a parallel bromine radical chain is initiated to yield the highly brominated products **11** and **12**.

Introduction

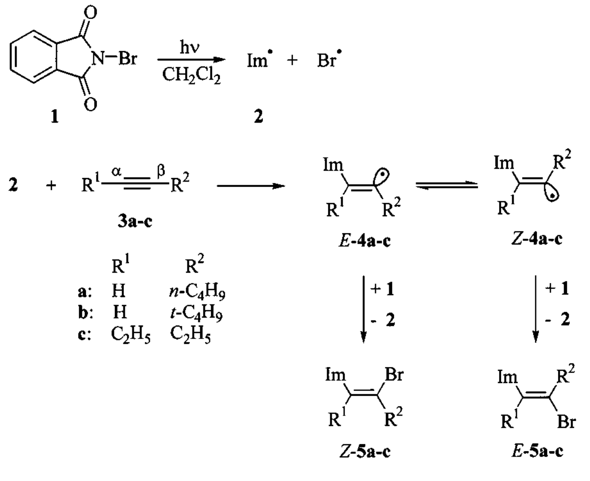
N-Bromosuccinimide has been widely used in synthetic chemistry for benzylic and allylic brominations since the discovery of this reaction by Ziegler et al. in 1942.[1] The reaction involves bromine radicals as hydrogen-abstracting species and not imidyl radical intermediates.[2] On the other hand, imidyl radicals can be generated by photolysis of *N*-bromo- or *N*-chloroimides in dichloromethane, and radical chain reactions with imidyl radicals as chain carriers have been established. Because the addition of *N*-centered radicals to π-systems is a versatile tool for the generation of C−N bonds, some synthetic applications of imidyl radicals have been reported, i.e. aromatic substitution reactions[3] and addition of *N*-bromoimides to alkenes, which introduces a halogen atom and an imidyl moiety to vicinal C atoms of a carbon chain.[4]

Intermolecular radical additions to alkynes have not been carried out very often,[5a] in contrast to cyclizations. The addition of most electrophilic radicals to multiple bonds is not a very useful reaction because two alternative processes compete: fragmentation (for instance of electrophilic alkoxy radicals) and hydrogen atom abstraction in allylic positions.[6a] We were interested in investigating whether *N*-bromophthalimide (**1**) could be added to alkynes by an intermolecular radical addition. Such an addition would be a quick entry to highly functionalized C=C double bonds bearing a bromine substituent and a protected amino group.

Results and Discussion

The addition of **1** to C≡C triple bonds was studied with linear terminal and dialkylated alkynes **3a−c** and with the medium-sized cycloalkyne **8**. The imidyl radical chain reaction was initiated by UV irradiation of a solution of the alkyne and **1** with an [alkyne]/[**1**] ratio of 5−10:1 in dichloromethane (see Experimental Section).

In the case of the linear alkynes **3a−c**, addition of **1** to the C≡C triple bond was observed, resulting in formation of the *Z*- and *E*-substituted alkenes *Z*-**5a−c** and *E*-**5a−c** (Scheme 1 and Table 1). The stereochemistry was assigned by measuring the NOE effects of the allylic methylene groups in both, the *Z* and the *E* stereoisomers.



Scheme 1. Radical addition of *N*-bromophthalimide (**1**) to linear alkynes **3**

The radical addition of *N*-bromophthalimide (**1**) to a multiple bond occurs in two steps: (i) addition of the imidyl radical **2** to the π-system, and (ii) abstraction of a bromine atom from the *N*-bromoimide **1** by the adduct radical **4**. In the case of alkynes **3**, this adduct radical **4** is a vinyl radical.

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Table 1. Yields of the addition products *E*-**5a−c** and *Z*-**5a−c** obtained from the radical chain addition of *N*-bromophthalimide (**1**) to alkynes **3a−c**

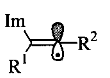
Alkyne	R^1	R^2	Yield (%)[a]	*Z*-**5**/*E*-**5**
3a	H	n-C_4H_9	68	39:61
3b	H	t-C_4H_9	13	5:95[b]
3c	C_2H_5	C_2H_5	74[c]	44:56

[a] Isolated yields unless otherwise stated. − [b] Unseparated mixture. − [c] Yield determined by GC.

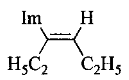
The bromine atoms generated by the photolysis reaction also initiate a radical chain addition, and a dibromide is formed in the first cycle, but only as a by-product. After bromine transfer from **1** to generate the dibromide, phthalimidyl radicals (**2**) are the chain carriers.

If an *N*-bromoimide **1** is added to a nonsymmetrical alkyne such as the terminal alkynes **3a** and **3b**, the formation of regioisomers is possible. But it was observed that the addition of the imidyl moiety occurred exclusively at the less hindered terminal carbon atom (α-position) of the C≡C triple bond. Products resulting from an attack at the β-carbon atom could not be detected. This finding is in agreement with the general behavior of intermolecular radical additions to π-systems. The regiochemistry of the initial radical attack is mainly determined by steric and electronic factors and an α-attack is usually favored.[5b] Thus, in the addition reactions of imidyl radicals to alkenes the α-attack was also strongly preferred.[4b,4c]

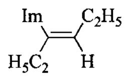
The products of the addition of *N*-bromophthalimide (**1**) to an alkyne **3** are imidyl- and bromo-substituted alkenes **5a−c** which were found as *E*/*Z* mixtures. From the *E*/*Z* ratio of the olefins *E*-**5a−c** and *Z*-**5a−c**, respectively, no information concerning the electronic structure of the intermediate vinylic radical can be deduced. In a vinyl radical, the unpaired electron can either be located in an sp^2 orbital resulting in the σ-vinylic radicals *Z*-**4a−c** and *E*-**4a−c**, respectively.[7] On the other hand, the single electron can be localized in a π-orbital, leading to a linear structure, as shown for the π-vinylic radicals **6a−c**. Generally, the latter structure would only be of importance if steric or conjugation effects were significant.[6b] Unconjugated vinyl radicals are known to be of the σ-type which invert with a low activation barrier.[6b] Therefore, in general, there may be two factors determining the selectivity: (i) the *Z*/*E* equilibrium, and (ii) the rate of bromine atom transfer. The bromine transfer from an *N*-haloimide to a carbon-centered radical is a diffusion-controlled reaction[8] while the *Z*/*E* isomerization of a vinyl radical possesses an activation energy of ca. 8 kJ/mol.[6b]



6a-c



E-**7**



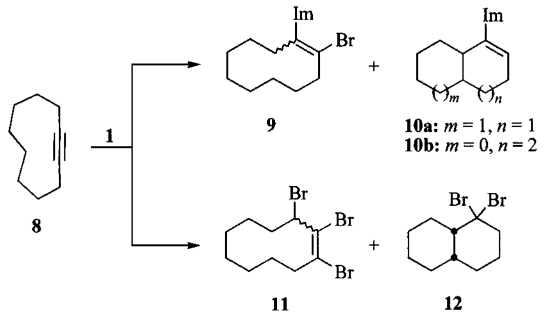
Z-**7**

But with the concentrations chosen ([**1**] < 0.1 M), the equilibration reaction of the intermediate vinylic radicals *E*-**4a** and *E*-**4c**, to yield the respective isomers *Z*-**4a** and *Z*-**4c**, in which the unpaired electron and the imidyl moiety are localized opposite to each other, is at least 100 times faster than the *inter*molecular bromine atom abstraction. Therefore, the preferred formation of the *E*-configured alkenes *E*-**5a** and *E*-**5c** can be rationalized by the Curtin−Hammett principle.[9] In the reaction of **3b** with **1**, a 95:5 mixture of two isomers was obtained which was not separated. From the ^{1}H NMR spectrum of this mixture, and by comparison of the spectroscopical data with the data obtained for *E*-**5a** and *Z*-**5a**, the configuration of the excess alkene **5b** was tentatively also assigned to be *E*.

In the case of the dialkylated alkyne **3c**, additional products (the reduction products *E*-**7** and *Z*-**7**), could be observed by GC/MS, in low yield. These products were obviously formed by hydrogen atom abstraction by the intermediate vinylic radicals *E*-**4c** and *Z*-**4c**, respectively. The excess alkyne or the solvent can act as hydrogen atom donors.

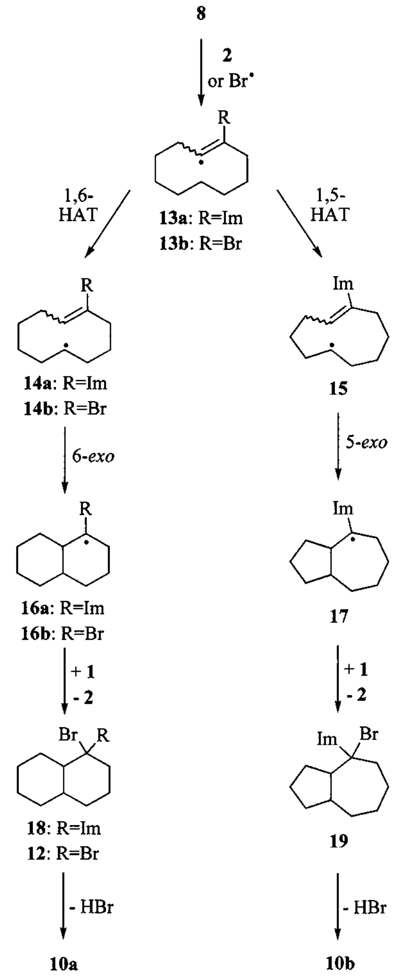
The radical addition of **1** was also applied to a medium-sized cycloalkyne **8**. Radical additions to C≡C triple bonds, which are part of a medium-sized cycloalkyne have not been well investigated yet.[10] Recently, we reported that addition of the electrophilic NO_3 radical to medium-sized cycloalkynes leads to the formation of bicyclic ketones resulting from a transannular radical atom abstraction/cyclization cascade.[11]

In the reaction of **1** with the ten-membered cycloalkyne **8**, numerous reaction products have been detected by GC, and the major products could be isolated and were identified. Besides the cycloalkene **9** resulting from the radical addition of **1** to the alkyne **8** two inseparable isomers, presumably **10a** and **10b**, were also formed. In addition, two more products, **11** and **12**, were obtained, which did not contain an imidyl moiety, but had more than one bromine atom (Scheme 2).



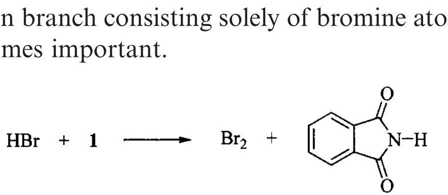
Scheme 2. Radical addition of *N*-bromophthalimide (**1**) to cyclodecyne **8**

The configuration at the C=C double bond in **9** could not be determined from the ^{1}H NMR data, because the relevant proton signals were broadened. In Scheme 3, a reaction scheme leading to the observed and isolated products is shown. Formation of the unsaturated bicyclic compounds **10a** and **10b** may occur by a transannular 1,6- and 1,5-hydrogen atom transfer (HAT) in the intermediate vinylic radical **13a**. The resulting secondary alkyl radicals **14a** and **15** may then cyclize in a 6-*exo*/6-*endo*- and 5-*exo*/7-*endo* fashion[12] to the double bond. Abstraction of a bromine atom from **1** by the resulting radicals **16a** and **17**, and subsequent loss of HBr gives the unsaturated compounds **10a** and **10b**. Considerable steric (i.e. 1,3-steric) interactions at the tetrasubstituted carbon atoms in **18** and **19** may be the reason for the HBr elimination to give the less crowded final products **10a** and **10b**, respectively. At present, the stereochemistry of the ring connection cannot be assigned. It cannot be excluded that **10a** and **10b** are *cis*/*trans* isomers of bicyclic compounds with the same ring size.



Scheme 3. Transannular HAT and subsequent cyclization may explain the formation of the bicyclic reaction products **10a–b** and **12**

The elimination of HBr from **18** and **19** is crucial for the broad product distribution of this reaction, because a parallel reaction branch consisting solely of bromine atom chemistry becomes important.



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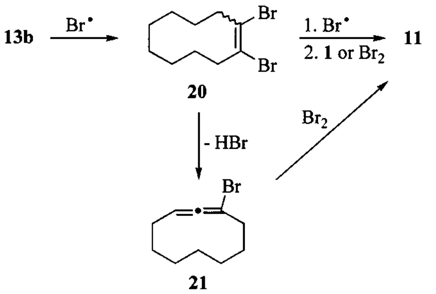
With bromine present, the intermediate vinyl radicals can abstract a bromine atom from **1** or from bromine. In the latter case, a new bromine atom is formed which will add to the alkyne and yield more dibromide than expected from the photolytic initiation alone.

Thus, the formation of the bicyclic dibromo compound **12** can be explained by a transannular reaction sequence in analogy to the formation of **18** as shown in Scheme 3. The ring sizes in **12** were unambiguously determined by NMR using the INADEQUATE technique.[13] The *cis* fusion of both rings was deduced from NOE data. A formation of a [5.3.0]bicyclic compound with geminal dibromo substitution resulting from a 1,5-HAT in **13b** cannot be excluded, but it may be a minor by-product.

The monocyclic tribromo compound **11** may be derived from a dibromo-substituted alkene **20** which may then either undergo an allylic bromination to yield **11** or an elimination of HBr to yield an allenic compound **21**. Ionic addition of molecular bromine would also give the tribromide **11** (Scheme 4).



Scheme 4. Possible pathways to form the tribromocyclodecene **11**

The radical nature of the reaction pathway leading to the bromine-containing products **11** and **12** was independently verified by treating the cycloalkyne **8** with **1**, under radical conditions according to the Ziegler mechanism (NBS).

Conclusion

Alkynes can be good substrates for an intermolecular addition of electrophilic imidyl radicals to form vicinal functionalized alkenes. For mono- and disubstituted alkynes, yields of ca. 70% can be observed. However, steric hindrance as in **3b** or transannular reactions as in **8** limit the synthetic application to less crowded terminal and disubstituted acyclic alkynes. But, in contrast to the intermolecular reaction of most electrophilic radicals with multiple bonds,[6a] [where hydrogen atom abstraction at C–H groups next to the triple bond ("allylic" substitution) is a major side reaction], even in **3c** with four "allylic" hydrogen atoms, the product **5c** was formed in 74% yield.

Experimental Section

General Remarks: See ref.[14], and: – IR: Paragon 1000, Perkin–Elmer. – ^{1}H NMR: Bruker AM 300, Bruker DRX 500. – ^{13}C NMR: Same instruments, frequency 75.5 and 125.8 MHz, respectively. – Melting points: Büchi 510, not corrected. – Elemental analysis: Mikroanalytisches Laboratorium Ilse Beetz, Kronach, Germany. – UV lamp: TQ, Original Hanau 400 W, Heraeus; Philips mercury lamp (12 W). – Dichloromethane used as solvent for the photolysis experiments was dried and filtered through alumina to remove traces of acid, then degassed in an ultrasonic bath for

30 min and saturated with nitrogen prior to use. − For further information see ref.[4b−4d]

General Procedure: To a solution of the alkyne (**3c**, **8**: 5 equiv.; **3a**, **3b**: 10 equiv.) in anhydrous oxygen-free dichloromethane (17 mL/mmol) was added **1**. The reaction mixture was irradiated in a Pyrex flask by means of a UV lamp (distance: 1 cm, room temperature). The end of the reaction was determined by a potassium iodide/starch test. Workup: **3a** and **3c**: The solvent and the excess alkyne were distilled off, the residue was dried in vacuo and purified by column chromatography (SiO_2). **3b**: The crude reaction product was dissolved in ether and washed with aqueous sodium hydrogen carbonate. After drying, the residue was recrystallized from ethanol/water (1:1). **8**: The solvent was evaporated in vacuo and the excess cycloalkyne and the products were isolated by column chromatography (SiO_2).

Addition of 1 to 1-Hexyne (3a)

***E*-5a:** R_f (CH_2Cl_2) = 0.50. − M.p. 83−84°C, colorless solid. − IR (KBr): $\tilde{\nu}$ = 2960 cm^{-1}, 2930, 1770, 1710, 1390, 1110, 895, 725. − ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 7.91 (2 H, m), 7.77 (2 H, m), 6.50 (1 H, s), 2.42 (2 H, t, J = 7.0 Hz), 1.70−1.50 (2 H, m), 1.32 (2 H, m), 0.90 (3 H, t, J = 7.0 Hz). − ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 166.2 (2 s), 134.6 (2 d), 132.8 (s), 131.9 (2 s), 123.9 (2 d), 117.7 (d), 35.7 (t), 29.8 (t), 22.0 (t), 13.8 (q). − MS (CI); *m/z* (%): 310 (96) [M^+ + H, ^{81}Br], 308 (100) [M^+ + H, ^{79}Br], 230 (32), 228 (52). − $C_{14}H_{14}BrNO_2$ (308.18): calcd. C 54.56, H 4.58, N 4.54; found C 54.67; H 4.53, N 4.55.

***Z*-5a:** R_f (CH_2Cl_2) = 0.49, yellow oil. − ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 7.91 (2 H, m), 7.77 (2 H, m), 6.48 (1 H, s), 2.65 (2 H, t, J = 7.0 Hz), 1.67 (2 H, m), 1.43 (2 H, m), 0.98 (3 H, t, J = 7.0 Hz). − ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ = 166.0 (2 s), 134.8 (s), 134.3 (2 d), 132.0 (2 s), 123.7 (2 d), 116.8 (s), 38.8 (t), 30.1 (t), 21.5 (t), 13.8 (q).

Addition of 1 to 3,3-Dimethylbut-1-yne (3b)

***E*/*Z*-5b:** M.p. 87°C, colorless solid. − IR (KBr): $\tilde{\nu}$ = 2970 cm^{-1}, 2930, 1785, 1770, 1720, 1470, 1390, 1365, 1300, 1110, 890, 710. − ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 7.90 (2 H, m), 7.78 (2 H, m), 6.50 (0.95 H, s), 6.40 (0.05 H, s), 1.36 (8.55 H, s), 1.28 (0.45 H, s). − MS (70 eV); *m/z* (%): 309 (< 3) [M^+, ^{81}Br], 307 (< 3) [M^+, ^{79}Br], 294 (6), 292 (6), 228 (100), 210 (33), 160 (53), 148 (13), 104 (32). − $C_{14}H_{14}BrNO_2$ (308.18): calcd. C 54.56, H 4.58, N 4.55; found C 54.61; H 4.42, N 4.46.

Addition of 1 to 3-Hexyne

***E*-5c:** R_f (CH_2Cl_2) = 0.52. − M.p. 82−83°C, colorless solid. − IR (KBr): $\tilde{\nu}$ = 2975 cm^{-1}, 2936, 1719, 1370, 883, 721, 530. − ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.91 (2 H, m), 7.78 (2 H, m), 2.64 (2 H, q, J = 7.4 Hz), 2.32 (2 H, q, J = 7.4 Hz), 1.10 (3 H, t, J = 7.4 Hz), 0.98 (3 H, t, J = 7.4 Hz). − ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 166.9 (2 s), 134.4 (2 d), 132.0 (2 s), 131.7 (s), 129.0 (s), 123.8 (2 d), 30.4 (t), 27.9 (t), 13.0 (q), 10.6 (q). − MS (CI); *m/z* (%): 310 (17) [M^+, ^{81}Br], 308 (19) [M^+, ^{79}Br], 230 (4), 228 (100). − $C_{14}H_{14}BrNO_2$ (308.18): calcd. C 54.56, H 4.58; found C 54.51, H 4.51.

***Z*-5c:** R_f (CH_2Cl_2) = 0.56, colorless oil. − IR (KBr): $\tilde{\nu}$ = 2978 cm^{-1}, 2934, 1718, 1374, 881, 726, 531. − ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.90 (2 H, m), 7.76 (2 H, m), 2.70 (2 H, q, J = 7.5 Hz), 2.49 (2 H, q, J = 7.5 Hz), 1.25 (3 H, t, J = 7.5 Hz), 1.04 (3 H, t, J = 7.5 Hz). − ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 166.6 (2 s), 134.3 (2 d), 131.9 (2 s), 131.5 (s), 130.6 (s), 123.7 (2 d), 30.4 (t), 25.3 (t), 13.5 (t), 11.8 (q). − MS (CI); *m/z* (%): 310 (63) [M^+, ^{81}Br], 308 (69) [M^+, ^{79}Br], 230 (22), 228 (100). − $C_{14}H_{14}BrNO_2$ (308.18): calcd. C 54.56, H 4.58, N 4.55; found C 54.49, H 4.49, N 4.44.

Addition of 1 to Cyclodecyne (8)

***N*-(2-Bromocyclodec-1-enyl)phthalimide (9):** R_f (CH_2Cl_2) = 0.63, yellow oil. − IR (film): $\tilde{\nu}$ = 2924 cm^{-1}, 2865, 1782, 1726, 1473, 1377, 882, 720, 530. − ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.89 (2 H, m), 7.76 (2 H, m), 2.89 (2 H, t, J = 6.4 Hz), 2.68 (2 H, t, J = 6.4 Hz), 1.85−1.45 (12 H, m). − ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = 166.4 (2 s), 134.2 (2 d), 131.9 (2 s), 130.6 (s), 130.5 (s), 123.6 (2 d), 35.5 (t), 29.2 (t), 27.7 (t), 26.7 (t), 24.7 (t), 24.5 (t), 20.9 (t), 19.8 (t). − MS (CI); *m/z* (%): 364 (95) [M^+ + H, ^{81}Br], 362 (100) [M^+ + H, ^{79}Br], 282 (90), 148 (11), 135 (25).

Isomeric Mixture of 10a and 10b: R_f (CH_2Cl_2) = 0.49. − M.p. 141−142°C, colorless solid. − IR (KBr): $\tilde{\nu}$ = 2918 cm^{-1}, 1712, 1467, 1380, 1118, 1078, 722. − ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.86 (4 H, m), 7.73 (4 H, m), 5.74 (2 H, m), 2.25 (7 H, m), 1.90−1.20 (19 H, m). − ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 168.1 (2 s), 167.9 (2 s), 134.0 (4 d), 132.0 (2 s), 131.9 (2 s), 131.9 (2 d), 128.7 (2 d), 123.4 (4 d), 46.5 (d), 40.0 (d), 38.0 (d), 34.4 (t), 33.6 (d), 31.1 (t), 30.5 (t), 29.6 (t), 27.4 (t), 26.3 (t), 25.2 (t), 24.8 (t), 24.5 (t), 23.2 (2 t), 22.1 (t). − MS (CI); *m/z* (%): 282 (68) [M^+ +H], 235 (70), 221 (72), 147 (4), 135 (10), 111 (54), 85 (30), 69 (100). − $C_{18}H_{19}NO_2$: calcd. 281.14157; found 281.14140 (MS).

1,2,3-Tribromocyclodecene (11): R_f (*n*-pentane) = 0.25, colorless oil. − IR (film): $\tilde{\nu}$ = 2934 cm^{-1}, 2855, 1593, 1466, 1444, 1129, 701, 650. − ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 5.51 (1 H, dd, J = 5.2, 11.8 Hz, 3-H), 3.16 (1 H, dd, J = 4.6, 10.3 Hz), 2.45 (2 H, m), 1.95 (2 H, m), 1.46 (7 H, m), 1.17 (2 H, m). − ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 131.6 (s, C-1 or C-2), 129.5 (s, C-1 or C-2), 50.9 (d, C-3), 40.4 (t), 35.2 (t), 27.7 (t), 25.7 (t), 24.3 (t), 22.0 (t), 19.5 (t). − MS (CI); *m/z* (%): 378 (1) [M^+, 3 ^{81}Br], 376 (2) [M^+, ^{79}Br, 2 ^{81}Br], 374 (2) [M^+, 2 ^{79}Br, ^{81}Br], 372 (1) [M^+, 3 ^{79}Br], 297 (2), 295 (4), 292 (2), 215 (31), 213 (32), 133 (100). − $C_{10}H_{15}Br_3$ (374.83): calcd. C 32.02, H 4.03; found C 32.13, H 4.09.

***cis*-2,2-Dibromobicyclo[4.4.0]decane (12):** R_f (*n*-pentane) = 0.56, pale yellow oil. − IR (film): $\tilde{\nu}$ = 2926 cm^{-1}, 2862, 1448, 1130, 871, 710, 628. − ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.58 (1 H, m, 6-H), 2.47 (1 H, m, 3-H_A), 2.37 (1 H, ddd, J = 4.2, 12.6, 14.5 Hz, 3-H_B), 2.31 (1 H, ddt, J = 1.9, 3.7, 12.7 Hz, 1-H), 2.18 (1 H, dddd, J = 1.2, 3.6, 3.6, 13.0 Hz, 10-H_A), 1.89 (1 H, dddd, J = 4.0, 12.5, 13.4, 13.4 Hz, 4-H_A), 1.82 (1 H, ddddd, J = 2.2, 3.5, 3.5, 6.8, 13.0 Hz, 9-H_A), 1.67 (1 H, dddd, J = 4.4, 13.3, 13.3, 13.3 Hz, 5-H_A), 1.60 (1 H, m, 4-H_B), 1.59 (1 H, m, 7-H_A), 1.48 (1 H, ddd, J = 4.7, 12.9, 12.9 Hz, 7-H_B), 1.42 (1 H, dddd, J = 3.6, 12.9, 12.9, 12.9 Hz, 10-H_B), 1.39 (1 H, m, 8-H_A), 1.35 (1 H, m, 8-H_B), 1.30 (1 H, m, 5-H_B), 1.23 (1 H, dddd, J = 3.7, 13.1, 13.1, 14.8 Hz, 9-H_B). − ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ = 81.8 (s, C-2), 54.7 (d), 43.9 (t, C-3), 33.9 (d, C-6), 31.9 (t, C-7), 26.4 (t, C-9), 25.7 (t, C-10), 25.2 (t, C-4), 23.1 (t, C-5), 20.2 (t, C-8). − MS (CI); *m/z* (%): 217 (10) [M^+(^{81}Br) − ^{79}Br], 215 (12) [M^+(^{79}Br) − ^{79}Br], 135 (100).

Acknowledgments

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