Pergamon

Tetrahedron 58 (2002) 8979–8984

TETRAHEDRON

Bromination of an *N*-carbethoxy-7-aza-2,3-benzonorbornadiene and synthesis of *N*-carbethoxy-7-aza-2,3-dibromo-5,6-benzonorbornadiene: high temperature bromination. Part 14

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Dedicated to Professor Waldemar Adam on the occasion of his 65th birthday

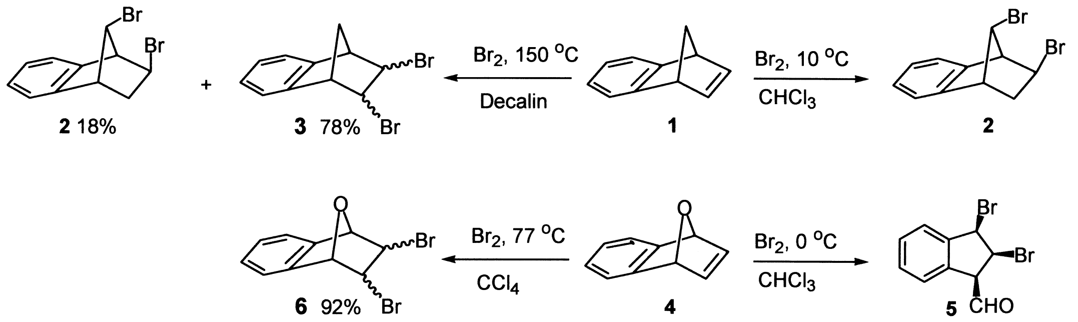
Received 5 July 2002; revised 23 August 2002; accepted 12 September 2002

Abstract—The electrophilic addition of bromine to an *N*-carbethoxy-7-aza-2,3-benzonorbornadiene at 0°C led in high yield to the formation of rearranged dibromides. However, high-temperature bromination of *N*-carbethoxy-7-aza-2,3-benzonorbornadiene in carbon tetrachloride at 77°C while irradiating, gave exclusively non-rearranged products. From the elimination of these non-rearranged products, *N*-carbethoxy-4-bromo-7-aza-2,3-benzonorbornadiene was obtained as the sole product. Similarly, bromination of monobromide *N*-carbethoxy-4-bromo-7-aza-2,3-benzonorbornadiene at 77°C yielded non-rearranged tribromides. The dehydrobromination of these tribromides provided the *N*-carbethoxy-5,6-dibromo-7-aza-2,3-benzonorbornadiene in high yield, which is a synthon for trimerization reaction. © 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction

The mechanism of the electrophilic addition of bromine to alkenes has been widely investigated both from a kinetic and stereochemical point of view.[1] The nature of the intermediates of the addition depends on the structure of the substrate and on the reaction medium, ranging from a strongly bridged bromonium ion to a weakly bridged species or open ions. While bromonium ion intermediates are involved in the bromination of non-conjugated olefins, which give only *anti* adducts irrespective of the reaction medium, non-classical carbocations are involved in the case of unsaturated bicyclic systems to rationalize the rearranged products via Wagner–Meerwein rearrangement.

For example, the electrophilic addition of bromine to benzonorbornadiene (**1**) gives a rearranged dibromide **2** in quantitative yield (Scheme 1),[2] whereas high temperature bromination[3] of **1** at 150°C resulted in the formation of non-rearranged products **3** and rearranged product **2** in a ratio of 4:1.[4] In order to test the behavior of an oxygen bridge in the bicyclic system on the product distribution, we recently investigated the bromination of 7-oxabenzonorbornadiene **4** at 0°C and higher temperatures.[5] We found that the electrophilic addition of bromine to **4** at 0°C led to the formation of **5** in high yield. However, high-temperature bromination of **4** in carbon tetrachloride at 77°C gave an isomeric mixture of non-rearranged products **6**. In this paper, we report the low and high temperature bromination



Scheme 1.

Keywords: bicyclic heterocyclic compounds; aza compounds; rearrangements.
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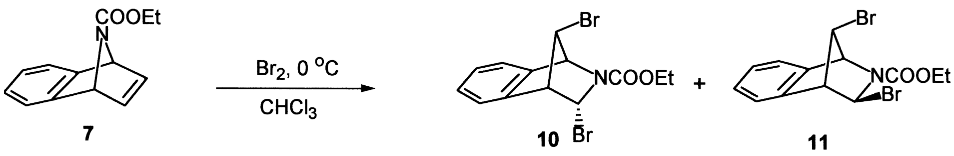
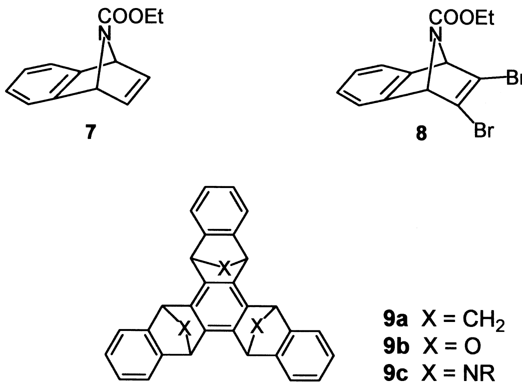
PII: S0040-4020(02)01150-X



Scheme 2.

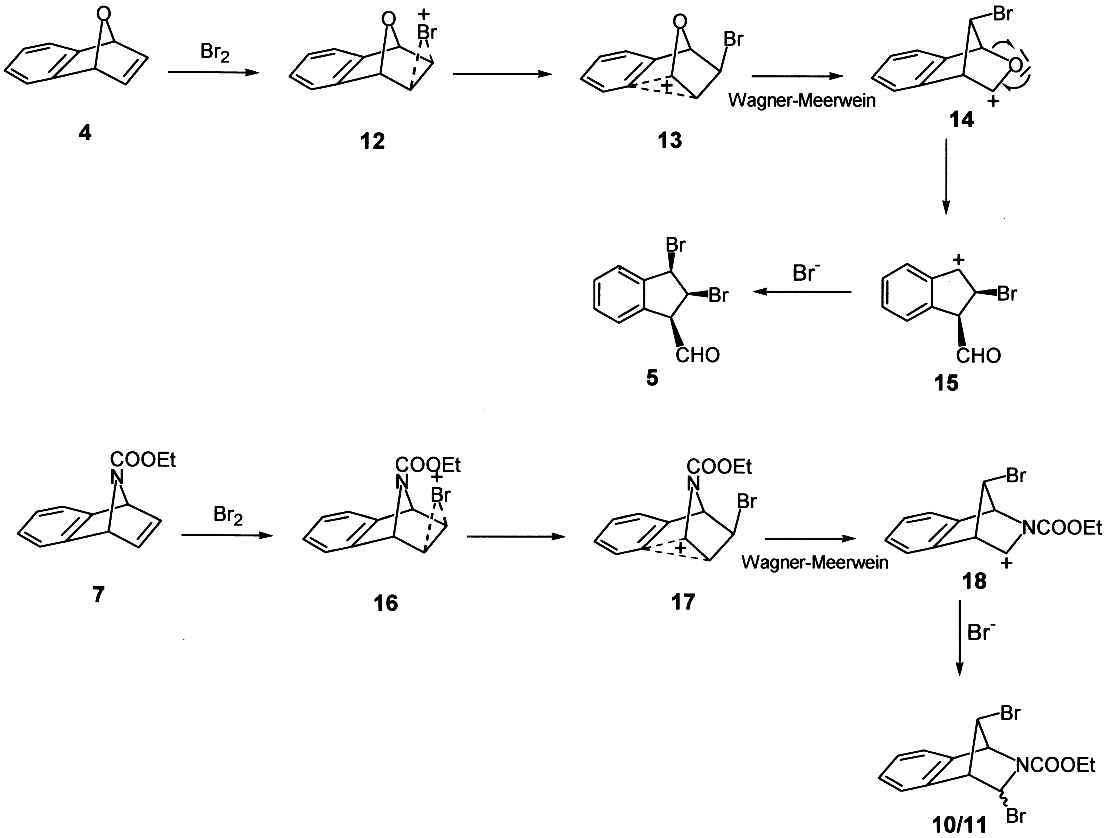
reactions of a substituted 7-aza-benzonorbornadiene **7** to see the effect of a nitrogen atom on the course of the reaction. Furthermore, we were interested in the synthesis of the dibromo-aza-benzonorbornadiene **8** in connection with its use in trimerization reactions. Recently, we succeeded in the synthesis of **9a** which is a basket shaped molecule that displays unusual geometric and electronic features including bond length fixation of the central benzene ring.[6] The dibromo compound **8** is a key compound for the synthesis of **9c**.



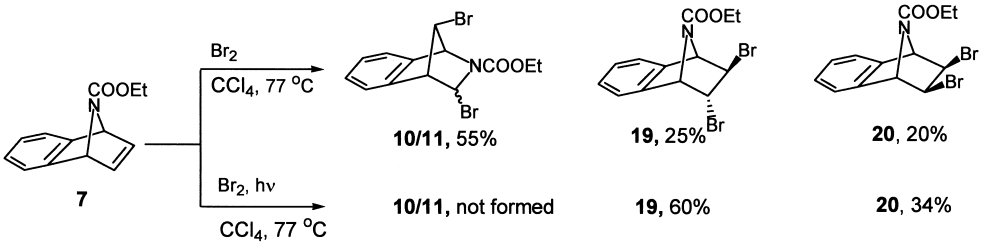
2. Results and discussions

The aza-benzonorbornadiene derivative **7**[7] was synthesized by the addition of benzyne to *N*-carbethoxypyrrole[8] as described in the literature. First, aza-benzonorbornadiene **7** was treated with bromine in chloroform at 0°C. An isomeric mixture consisting of the rearranged dibromides **10** and **11** (in a ratio of 45:55) were formed which were not stable at room temperature (Scheme 2). An attempted low-temperature chromatography to separate the isomers failed. However, the structural assignments to isomers **10/11** was made easily by analysis of the NMR spectra.

In the case of bromination of 7-oxa-benzonorbornadiene **4**, we suggested the following mechanism (Scheme 3). Bromine attacks the double bond from the *exo*-face to generate an *exo*-bromonium cation **12**. The formed intermediate can undergo Wagner–Meerwein rearrangement to form the cation **14**, which can easily rearrange into aldehyde **5**. The driving force for this rearrangement is the formation of a stable carbonyl group. In the case of azacompound **7**, the rearranged intermediate **18** is captured by the bromide anion to form the isomeric mixture **10** and **11**.



Scheme 3.



Scheme 4.

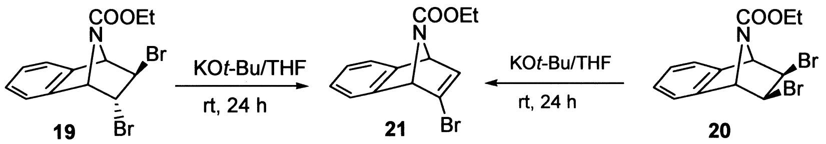
In addition, we studied the high temperature bromination of *N*-carbethoxy-7-aza-2,3-benzonorbornadiene (**7**) at the reflux temperature of CCl_4. For this purpose, a hot bromine solution in CCl_4 was added directly to a refluxing solution of **7** in CCl_4. NMR analysis of the crude product indicated that the reaction mixture consisted of isomeric rearranged products **10/11** and non-rearranged isomers **19** and **20** (Scheme 4).

The reaction mixture was submitted to silica gel column chromatography. Two separable products **19** and **20** were isolated whereas the rearranged products **10** and **11** decomposed on the column. Furthermore, we conducted the bromination reaction of **7** in CCl_4 with bromine while internal irradiating (150 W projector lamp) in refluxing temperature of CCl_4. To our surprise, no trace of the rearranged products **10** and **11** was formed. The exact configuration of these isomeric dibromides **19** and **20** were elucidated on the basis of ^{1}H and ^{13}C NMR data (COSY, DEPT, HMQC and HMBC). Compound **20** exhibits an AA′BB′ system arising from the aromatic protons which indicates the symmetrical structure and the *syn* addition[9] of bromine. Furthermore, an eight-line ^{13}C NMR spectrum is also in agreement with the proposed structure. The *trans* configuration of the bromine atoms in **19** is reflected in the unsymmetrical ^{1}H and ^{13}C NMR spectra.

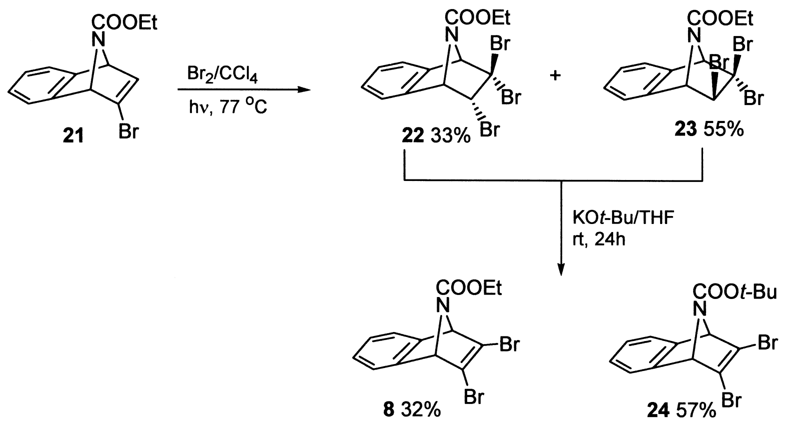
In the case of the high temperature addition of bromine, we assume that bromination is occurring mainly by a free radical mechanism. Radical intermediates are much less likely to rearrange. The formation of rearranged **10/11** and non-rearranged products **19/20** indicates that there is a competition between radical and ionic reactions. However, conducting the bromination reaction at high-temperature, with internal irradiation, completely suppressed the formation of rearranged products. This outcome supports the radical addition mechanism of bromine to the double bond in **7**.

After successful synthesis and characterization of these non-rearranged products **19** and **20** which have the functionality to permit the easy introduction of a double bond, we submitted either pure isomers or an isomeric mixture consisting of **19** and **20** to a dehydrobromination reaction with potassium *tert*-butoxide and isolated **21** in 90% yield (Scheme 5). Structural assignment to **21** was achieved by means of ^{1}H and ^{13}C NMR spectra.

For the synthesis of the target compound **8**, the mono-bromide **21** was further brominated in refluxing CCl_4 with internal irradiation. The ^{1}H and ^{13}C NMR studies of the reaction mixture revealed that two isomers **22** and **23** were formed (Scheme 6). Column chromatography allowed us to isolate the formed isomers in a purity of 90%. The structures of these compounds **22** and **23** were elucidated on the basis of their NMR spectra. Correspondingly, treatment of a



Scheme 5.



Scheme 6.

mixture consisting of **22** and **23** with potassium *tert*-butoxide in THF at ambient temperature for 24 h gave a mixture of the dibromide **8** (32%) and transesterification product **24** (57%). The ^{1}H NMR spectra of **8** and **24** showed an AA′BB′ system for the aromatic protons and a singlet for the bridgehead protons.

From these results, it can be concluded that high temperature bromination is a useful synthetic method to generate non-rearranged bromine addition products in unsaturated bicyclic systems that have a tendency to undergo Wagner–Meerwein rearrangement. With this methodology, we have shown that the application of high temperature bromination to the aza-benzonorbornadiene **7** provides an important synthetic tool for entry into the substituted aza-benzonorbornadiene system. Furthermore, the synthesis of the dibromide **8** and **24** will serve as key compounds for trimerization reactions.

3. Experimental

3.1. General

Melting points are uncorrected. Infrared spectra were obtained from KBr pellets on a regular instrument. The ^{1}H and ^{13}C NMR spectra were recorded on 400 (100) 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.

3.1.1. Bromination of ethyl 11-azatricyclo[6.2.1.0^{2,7}]-undeca-2,4,6,9-tetraene-11-carboxylate (7) with 1 equiv. bromine at 0°C. A solution of **7** (108 mg, 0.50 mmol) in 0.5 mL of $CDCl_3$ was placed into NMR tube and cooled to 0°C. Bromine (80 mg, 0.50 mmol) was added to the solution. The ^{1}H NMR and ^{13}C NMR spectra were recorded immediately. Spectral data indicated the formation of an isomeric mixture of *N*-carbetoxy-2-*exo*-7-*anti*-dibromo-3-aza-benzonorborn-5-ene and *N*-carbetoxy-2-*endo*-7-*anti*-dibromo-3-aza-benzonorborn-5-ene **10** and **11** in a ratio of 45:55 (from ^{1}H NMR spectrum integration). *Isomer* **10** (interchangeable with the isomer **11**). ^{1}H NMR (400 MHz, $CDCl_3$) 7.3–7.5 (m, 4H, aryl), 6.5 (d, J=3.2 Hz, 1H, H_2), 5.38 (br s, 1H, H_7), 4.1 (m, 4H, $-OCH_2-$, H_1 and H_4), 1.3 (t, J=6.9 Hz, 3H, $-CH_3$). *Isomer* **11** (interchangeable with the isomer **10**). ^{1}H NMR (400 MHz, $CDCl_3$) 7.3–7.5 (m, 4H, aryl), 6.43 (d, J=3.1 Hz, 1H, H_2), 5.26 (br s, 1H, H_7), 3.9–4.0 (m, 4H, $-OCH_2-$, H_1 and H_4), 1.28 (t, J=7.0 Hz, 3H, $-CH_3$); ^{13}C NMR spectrum of the mixture (**10** and **11**) (100 MHz, $CDCl_3$) 154.9, 154.4, 142.0, 141.8, 140.0, 139.5, 129.0, 128.9, 128.8, 125.2, 125.1, 124.5, 124.4, 122.1, 67.9, 67.4, 64.4, 64.1, 63.0, 62.7, 59.3, 58.5, 57.0, 56.6, 15.0, 14.7.

3.1.2. Bromination of ethyl 11-azatricyclo[6.2.1.0^{2,7}]-undeca-2,4,6,9-tetraene-11-carboxylate (7) with 1 equiv. bromine at 77°C. A hot solution of bromine (0.60 g, 3.75 mmol) in carbon tetrachloride (20 mL) was added to a refluxing solution of 7-aza-benzonorbornadiene **7** (0.73 g, 3.4 mmol) in CCl_4 (20 mL) in 50 mL flask during 15 min while stirring magnetically. After being cooled to room temperature, the ^{1}H NMR spectrum of reaction solution was recorded immediately. ^{1}H NMR integration indicated the formation of Wagner–Meerwein rearrangement products (**10/11**) and non-rearranged isomers **19** and **20** in a ratio of 55:45.

3.2. Photobromination of ethyl 11-azatricyclo-[6.2.1.0^{2,7}]undeca-2,4,6,9-tetraene-11-carboxylate (7) with 1 equiv. bromine at 77°C

Aza-benzonorbornadiene **7** (0.73 g, 3.4 mmol) was dissolved in CCl_4 (20 mL) in a photochemical reaction apparatus (60 mL) which was equipped with reflux condenser. The solution was heated until carbon tetrachloride started to reflux while stirring magnetically. To the refluxing solution was added dropwise a hot solution of bromine (0.61 g, 3.8 mmol) in carbon tetrachloride (20 mL) over 35 min while irradiating by 150 W projector lamp. After being cooled to room temperature, the solvent was evaporated. The residue was chromatographed on neutral alumina (1:9 ethyl acetate–hexane eluent). The first fraction gave the *trans* dibromide **19**.

3.2.1. Ethyl (1*R*(*S*),8*S*(*R*),9*S*(*R*),10*S*(*R*))-9,10-dibromo-11-azatricyclo[6.2.1.0^{2,7}]undeca-2,4,6-triene-11-carboxylate (19). 0.76 g (60%), colorless crystals from methylene chloride–hexane (1:3), mp 103–104°C. [Found: C, 41.73; H, 3.61; N, 3.81. $C_{13}H_{13}Br_2NO_2$ requires C, 41.63; H, 3.49; N, 3.73%]; ^{1}H NMR (400 MHz, $CDCl_3$) 7.5–7.3 (m, 4H, aryl), 5.32 (br s, H_8, 1H), 5.27 (d, J=4.1 Hz, H_1, 1H), 4.6 (dd, J=4.1, 2.8 Hz, H_{10}, 1H) 4.1 (q, J=7.1 Hz, methylenic, 2H), 3.73 (d, 1H, J=2.8 Hz, H_9, 1H), 1.3 (t, J=7.1 Hz, methyl, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 155.2, 141.8, 141.2, 128.6, 128.0, 124.5, 121.0, 69.8, 66.2, 62.5, 54.4, 52.2, 14.8. IR (KBr, cm^{-1}) 2983, 1707, 1460, 1383, 1271, 1103, 904, 766, 542.

The second fraction consisted of the *exo-cis* dibromide **20**.

3.2.2. Ethyl(1*R*(*S*),8*S*(*R*),9*S*(*R*),10*R*(*S*))-9,10-dibromo-11-azatricyclo[6.2.1.0^{2,7}]undeca-2,4,6-triene-11-carboxylate (20). 0.43 g (34%), colorless crystals from methylene chloride–hexane (1:3), mp 132–133°C. [Found: C, 41.41; H, 3.66; N, 3.80. $C_{13}H_{13}Br_2NO_2$ requires C, 41.63; H, 3.49; N, 3.73%]; ^{1}H NMR (400 MHz, $CDCl_3$) 7.4–7.2 (AA′BB′ system, 4H, aryl), 5.3 (s, H_1 and H_8, 2H), 4.2 (s, H_9 and H_{10}, 2H), 4.1 (q, J=7.1 Hz, methylenic, 2H), 1.2 (t, J=7.1 Hz, methyl, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 156.0, 142.9, 128.8, 121.7, 70.4, 62.4, 52.1, 14.8. IR (KBr, cm^{-1}) 2995, 1699, 1458, 1383, 1267, 1103, 908, 754, 604, 511.

3.3. Elimination of dibromides 19 and 20

To a stirred solution of a mixture of dibromides **19** and **20** (2.93 g, 7.8 mmol) in dry and freshly distilled THF (30 mL) was added (1.3 g, 11.6 mmol) potassium *tert*-butoxide solution in THF (20 mL). The resulting reaction mixture was stirred 24 h at room temperature. The mixture was diluted with water (100 mL) and the aqueous solution was extracted with ether (4×50 mL), washed with water, and dried over $MgSO_4$. After removal of the solvent, the residue was filtered on a short neutral alumina column (20 g) eluted with hexane–ethyl acetate (9:1) to give 2.07 g (90%) of monobromide **21** as the sole product. From the elimination of **19** under the same reaction conditions, monobromide **21** was obtained as the sole product in 90% yield.

3.3.1. Ethyl (1*R*(*S*),8*S*(*R*))-9-bromo-11-azatricyclo-[6.2.1.0^{2,7}]undeca-2,4,6,9-tetraene-11-carboxylate (21). Colorless crystals from ether–hexane (1:3), mp 83–84°C. [Found: C, 53.27; H, 4.24; N, 4.86. $C_{13}H_{12}BrNO_2$ requires C, 53.08; H, 4.11; N, 4.76%]; ^{1}H NMR (400 MHz, $CDCl_3$) 7.33 (m, aromatic, 1H), 7.20 (m, aromatic, 1H), 6.96 (m, aromatic) 2H), 6.84 (br s, olefinic, 1H), 5.51 (br s, bridgehead, 1H), 5.30 (br s, bridgehead, 1H), 4.07 (q, *J*=7.1 Hz, diastereotop methylenic protons, 2H), 1.2 (t, *J*=7.1 Hz, methyl, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) 155.7, 147.1, 146.6, 143.4, 141.0, 126.4, 125.8, 121.9, 121.2, 72.4, 68.6, 62.4, 14.9. IR (KBr, cm^{-1}) 3124, 3080, 2979, 1709, 1477, 1376, 1330, 1253, 1093, 1018, 906, 831, 788, 756, 737, 667, 638, 496.

3.4. Photobromination of ethyl (1*R*(*S*),8*S*(*R*))-9-bromo-11-azatricyclo[6.2.1.0^{2,7}] un-deca-2,4,6,9-tetraene-11-carboxylate (21)

Monobromide **21** (0.80 g, 2.7 mmol) was dissolved in CCl_4 (20 mL) in a photochemical reaction apparatus (60 mL) which was equipped with reflux condenser. The solution was heated until carbon tetrachloride started to reflux while stirring magnetically. To the refluxing solution was added dropwise a hot solution of bromine (0.50 g, 3.1 mmol) in carbon tetrachloride (20 mL) over 30 min while irradiating by a 150 W projector lamp. After being cooled to room temperature, the solvent was evaporated. The residue was submitted to repeated column chromatography on neutral alumina (1:9 ethyl acetate–hexane eluent). The first fraction consisted of the tribromide **22**.

3.4.1. Ethyl (1*S*(*R*),8*R*(*S*),10*R*(*S*)-9,9,10-tribromo-11-azatricyclo[6.2.1.0^{2,7}]undeca-2,4,6-triene-11-carboxylate (22). Purity: 90% determined by NMR. Colorless oily liquid. 0.40 g (33%). ^{1}H NMR (400 MHz, $CDCl_3$) 7.4–6.8 (m, aromatic, 4H), 5.6 (s, bridgehead H8), 5.3 (br s, H_{10}), 5.1 (d, *J*=3.8 Hz, H_1), 4.1 (m, diastereotop methylene, 2H), 1.2 (t, *J*=7.1 Hz, methyl); ^{13}C NMR (100 MHz, $CDCl_3$) 153.8, 141.5, 139.9, 129.2, 128.2, 127.9, 124.3, 76.2, 66.3, 62.5, 62.3, 60.1, 14.9. IR (KBr, cm^{-1}) 2979, 1718, 1250, 1101, 1014, 896, 788, 758, 617. The second fraction consisted of *exo*-tribromide **23**.

3.4.2. Ethyl (1*S*(*R*),8*R*(*S*),10*S*(*R*)-9,9,10-tribromo-11-azatricyclo[6.2.1.0^{2,7}]undeca-2,4,6-triene-11-carboxylate (23). Purity: 90% determined by NMR. Colorless oily liquid. 0.68 g (55%). ^{1}H NMR (400 MHz, $CDCl_3$) 7.4–7.1 (m, 4H, aryl protons), 5.6 (br s, bridgehead, H_1 or H_8), 5.2 (br s, bridgehead H_1 or H_8), 4.22 (s, H_{10}), 4.1 (m, diastereotop methylene, 2H), 1.2 (t, *J*=7.0 Hz, methyl); ^{13}C NMR (100 MHz, $CDCl_3$) 154.4, 142.6, 129.2, 128.3, 127.3, 125.1, 120.9, 71.11, 65.3, 62.5, 61.9, 29.4, 14.9. IR (KBr, cm^{-1}) 2979, 1716, 1464, 1377, 1268, 1099, 1010, 896, 800, 755, 620, 542.

3.5. Elimination of dibromides 22 and 23

To a stirred solution of a mixture of tribromides **22** and **23** (3.06 g, 6.7 mmol) in dry and freshly distilled THF (30 mL) was added (1.12 g, 10 mmol) potassium *tert*-butoxide solution in THF (20 mL). The resulting reaction mixture was stirred 24 h at room temperature. The mixture was diluted with water (100 mL) and the aqueous solution was extracted with ether (4×50 mL), washed with water, and dried over $MgSO_4$. After removal of the solvent, the residue was chromatographed on neutral alumina with hexane–ethyl acetate (9:1). The first fraction consisted of the transesterification product **24**.

3.5.1. *t*-Butyl 9,10-dibromo-11-azatricyclo[6.2.1.0^{2,7}]-undeca-2,4,6,9-tetraene-11-carboxylate (24). 1.6 g (57%). Colorless crystals from ether–hexane (1:2). Mp 100–101°C. [Found: C, 45.16; H, 3.85; N, 3.62. $C_{15}H_{15}Br_2NO_2$ requires C, 44.92; H, 3.77; N, 3.49%]; ^{1}H NMR (400 MHz, $CDCl_3$) 7.27 (AA′ part of AA′BB′ system, aromatic, 2H), 6.98 (BB′ part of AA′BB′ system, aromatic, 2H), 5.28 (br s, bridgehead, 2H), 1.3 (s, methyl, 9H,); ^{13}C NMR (100 MHz, $CDCl_3$) 154.7, 145.5, 134.8, 126.5, 121.7, 81.9, 74.0, 73.8, 28.5. IR (KBr, cm^{-1}) 2978, 1704, 1579, 1475, 1448, 1394, 1338, 1255, 1153, 1079, 1049, 918, 843, 802, 754, 675, 625, 496.

The second fraction consisted of the carbethoxy-dibromide **8**.

3.5.2. Ethyl 9,10-dibromo-11-azatricyclo[6.2.1.0^{2,7}]-undeca-2,4,6,9-tetraene-11-carboxylate (8). 0.84 g (32%). Colorless crystals from ether–hexane (1:2). Mp 110–111°C. [Found: C, 42.07; H, 3.08; N, 3.82%]; $C_{13}H_{11}Br_2NO_2$ requires C, 41.86; H, 2.97; N, 3.75; ^{1}H NMR (400 MHz, $CDCl_3$) 7.34 (AA′ part of AA′BB′ system, aromatic, 2H), 6.99 (BB′ part of AA′BB′ system, aromatic, 2H), 5.37 (br s, bridgehead, 2H), 4.06 (q, *J*=7.1 Hz, methylene, 2H), 1.16 (t, *J*=7.1 Hz, methyl, 3H,); ^{13}C NMR (100 MHz, $CDCl_3$) 155.1, 145.3, 134.6, 126.6, 121.6, 73.4, 62.5, 14.9. IR (KBr, cm^{-1}) 2978, 1704, 1579, 1475, 1448, 1394, 1338, 1255, 1153, 1079, 1049, 918, 843, 802, 754, 675, 625, 496.

Acknowledgements

The authors are indebted to the Department of Chemistry (Middle East Technical University and Gaziosmanpasa University; Grant 2001/31) for financial support. A. T. thanks TUBITAK-BAYG for a postdoctoral fellowship (1999/2000) at METU and Kiymet Berkil for technical assistance.

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