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Highly Functionalized Benzobarrelene Derivatives. Bromination of 2-Bromo-5,6-benzobicyclo[2.2.2]octa-2,6-diene: High Temperature Bromination. 3.[1]

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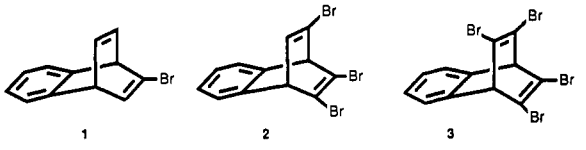
Introduction

In a continuation of our investigation of high-temperature bromination[3] of bicyclic systems we report on the addition of bromine to 2-bromobenzobarrelene (1). Recent work has revealed that bromination of 1 gives five rearranged products via Wagner–Meerwein rearrangement with accompanying aryl and alkyl migration. However, the bromination of 1 at 78 °C resulted in the formation of nonrearranged products with the bicyclo[2.2.2]skeleton. In this paper, we describe the high-temperature reaction of 1 with 2 equiv of Br_2 and the synthesis of tri- and tetrasubstituted benzobarrelene derivatives 2 and 3. These have potential importance for exploring the effect of different substituents in the same molecule on the course of the di-π-methane rearrangement.[4]



1 2 3

Results and Discussion

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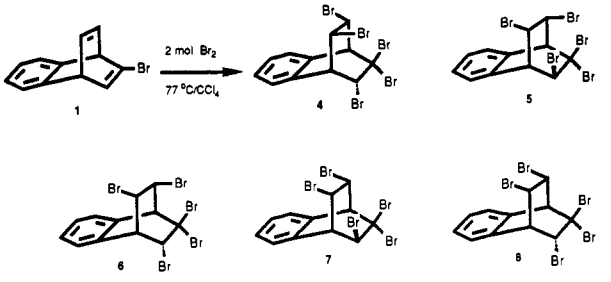
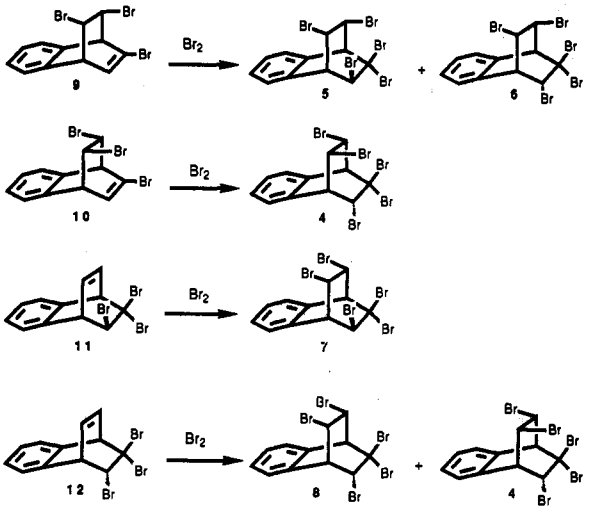
The starting material 1 was prepared by our published method[5] starting from benzonorbornadiene and was subjected to bromination[6] in refluxing carbon tetrachloride. The reaction mixture was kept for 15 min at reflux temperature and led to a considerably complex mixture consisting of five products. The resulting mixture was crystallized from methylene chloride/carbon tetrachloride, and we isolated 4 as the major product in a yield of 36%. The rest of the mixture was subjected to repeated column chromatography, and we isolated four additional products 5–8 in yields of 9, 18, 5, and 7%, respectively (Scheme I). The structure of these compounds has been elucidated on the basis of the spectral data obtained by ^1H NMR and ^{13}C NMR experiments (Table I) and chemical transformations. The ^1H and ^{13}C NMR spectra indicated that only nonrearranged products were formed during this reaction. Because of the very close structural similarity we were not able to make a clear-cut differentiation between the stereochemistry in any of these materials containing five bromine atoms. Therefore, we carried out an X-ray

Scheme I



Scheme II



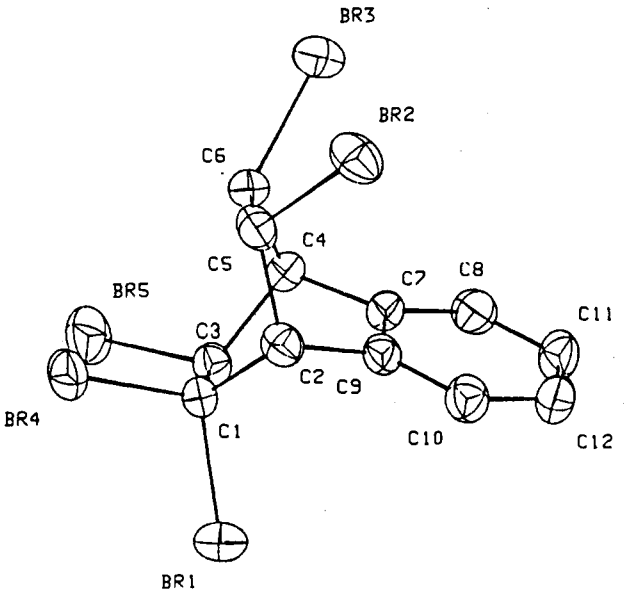


Figure 1. X-ray crystal structure of 7.

(1) For part 2 see: Balci, M.; Çakmak, O.; Hökelek, T. *Tetrahedron*, in press.

(2) Author to whom inquiries regarding the X-ray crystallographic analysis should be addressed.

(3) (a) Çakmak, O.; Balci, M. *Tetrahedron Lett.* **1989**, *31*, 2349. (b) Çakmak, O.; Hökelek, T.; Büyükgüngör, O.; Balci, M. *Tetrahedron Lett.* **1990**, *31*, 2345.

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(6) For bromination of similar systems see: (a) Lobanova, T. P.; Benus, E. I.; Barkash, V. A. *Zh. Obsch. Khim.* **1960**, *39*, 2332. (b) Lobanova, T. P.; Slyko, N. M.; Derendyaev, B. G.; Barkash, V. A. *Zh. Org. Khim.* **1970**, *6*, 2473. (c) Lobanova, T. P.; Derendyaev, B. G.; Kollegova, M. I.; Barkash, V. A. *Zh. Org. Khim.* **1973**, *9*, 1883. (d) Smith, W. B. *J. Org. Chem.* **1985**, *50*, 5731.

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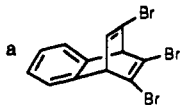
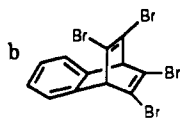
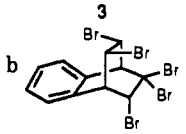
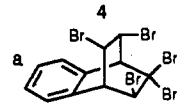
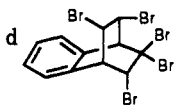
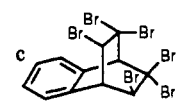
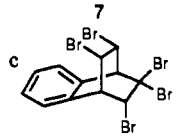
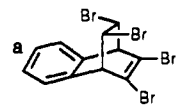
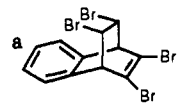
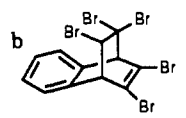
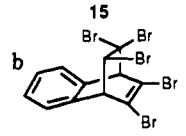
Table I. ^1H and ^{13}C NMR Spectral Data of the Compounds 2–8 and 13–16 (All Values are in ppm, TMS, in $CDCl_3$ Solutions)

compd	H 1	2	3	4	5	6	aromatic-H	^{13}C values	coupling constants in Hz
a  2	4.79 s			4.78 d			7.23–6.81 (5 H)	143.2, 140.13, 136.19, 130.93, 129.95, 128.33, 125.49, 125.0, 123.15, 122.75, 66.92, 59.67	
b  3	5.0 s			5.0 s			7.35–7.1	141.85, 128.40, 125.68, 122.98, 67.30	
b  4	4.11 d		5.53 d	3.37 dd	5.16 dd	4.05 dd	7.25–7.47	134.18, 132.2, 129.22, 128.84, 128.84, 126.43, 67.06, 62.76, 57.55, 55.49, 54.19, 49.71	J_{34} = 1.6, J_{56} = 4.4, J_{15} = 2.0, J_{46} = 2.4
a  5	4.09 d		4.92	3.5 dd	4.07 dd	4.73 dd	7.22–7.39	138.63, 133.38, 129.25, 128.58, 126.66, 125.64, 64.16, 64.1, 60.45, 55.13, 53.98, 46.87	J_{34} = 2.4, J_{56} = 6.4, J_{15} = 1.6, J_{46} = 1.6
d  6	4.22 d		5.03 d	3.54 d	4.21 dd	4.59 dd	7.44–7.0	138.33, 129.56, 129.07, 129.00, 129.00, 125.82, 62.03, 61.93, 60.06, 54.42, 52.38, 51.33	J_{34} = 2.1, J_{56} = 6.6, J_{15} = 2.1, J_{46} = 1.7
c  7	4.5 d		4.77 d	3.5 t	5.05 dd	5.37 dd	7.34–7.2	134.65, 134.10, 129.05, 128.92, 128.62, 126.31, 64.79, 63.07, 62.36, 54.36, 49.78, 44.40	J_{34} = 2.4, J_{56} = 8.0, J_{15} = 2.6, J_{46} = 1.6
c  8	4.24 d		5.05 d	3.57 t	5.38 dd	4.82 dd	7.6–7.20	134.10, 130.45, 129.79, 128.72, 128.59, 128.49, 66.55, 62.52, 60.67, 54.13, 48.63, 47.79	J_{34} = 1.8, J_{56} = 8.4, J_{15} = 2.4, J_{46} = 2.2
a  13	4.36 t			4.43 t	4.57 t	4.63 t	7.3–7.2	138.39, 135.79, 127.87, 127.24, 126.23, 125.14, 124.08, 123.53, 59.60, 59.39, 49.66, 48.49	J_{15} = 1.27, $J_{4,6}$ = 1.27
a  14	4.41			4.41	4.61 AA'BB' system	4.61	7.31	135.85, 127.29, 126.29, 125.20, 50.46, 48.53	
b  15	4.99 s		5.18 d	4.35 d			7.40–7.30	136.98, 133.68, 127.88, 127.64, 126.56, 126.31, 125.60, 124.73, 68.79, 62.83, 60.36, 59.82	J_{34} = 2.4
b  16	4.58 s		4.75 d	4.45 d			7.46–7.27		J_{34} = 2.0

[a] 250-MHz ^1H NMR, 63-MHz ^{13}C NMR. [b] 300-MHz ^1H NMR, 75-MHz ^{13}C NMR. [c] 60-MHz ^1H NMR, 75-MHz ^{13}C NMR. [d] 200-MHz ^1H NMR, 50-MHz ^{13}C NMR. AA'BB' system

analysis of the isomer 7[7] which revealed that Br_2 addition has occurred in a syn fashion contrary to our expectation. Studies concerning the mechanism of syn addition show that the syn adduct can arise either from direct syn collapse of the ion pair or from rotation followed by anti collapse.[8] Because of the rigid skeleton in 1 a bond rotation is out of the question. In this case, we assume that the high-temperature bromination is occurring by a free-

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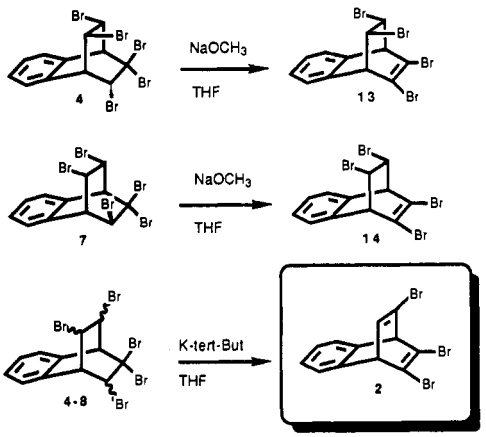
(8) Heasley, G. E.; Bower, T. R.; Dougharty, K. W.; Easdon, J. C.; Heasley, V. L.; Arnold, S.; Carter, T. L.; Yaeger, D. B.; Gipe, B. T.; Shellhamer, D. F. *J. Org. Chem.* **1980**, *45*, 5150.

Scheme III



radical mechanism.[9] Radical intermediates are much less likely to rearrange. This could explain also our stereochemical results, like the formation of cis addition products.

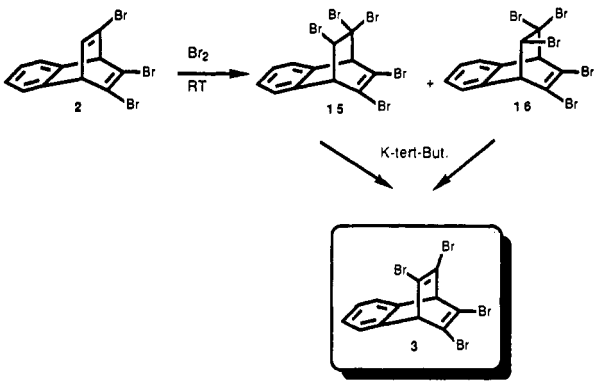
In order to establish the exact stereochemistry of the other isomers, we have synthesized these compounds in an independent way starting from the tribromo species **9–12**, the configurations of which have been determined exactly.[1,3b] The three trans bromides **4–6** have been synthesized by bromination of the trans tribromides **9** and **10** (Scheme II). Careful examination of the reaction mixture resulting from bromination of **9** has revealed the formation of only two isomers in a ratio of 2:1. On the other hand, the reaction of **10** with bromine provided only a single isomer which was identical with **4** obtained as the major product from reaction of **1** with 2 equiv of Br_2. Steric hindrance prevents here the formation of the other possible isomer.

The syn addition products **7** and **8** have also been synthesized by addition of bromine to **11** and **12**.

After successful synthesis of these desired isomers **4–8** which have the requisite skeletal arrangement and the functionality to permit the easy introduction of two double bonds, we submitted the pure isomers **4–7** to dehydrobromination reaction with 1 mol of sodium methoxide and isolated **13** and **14** (Scheme III). In both cases we noticed that the tribromo-substituted linkage was preferentially attacked by base. We used these tribromo-elimination reactions for further confirmation of the proposed structures. In the case of compounds containing a trans bromine configuration (as in cases of **4–6**), we isolated an unsymmetrical compound **13**. On the other hand, both syn addition products **7** and **8** provided the symmetrical compound **14** which has been characterized on the basis of spectral data. The ^{13}C-NMR spectrum of **14** (Scheme I) has six carbon signals, consisting of four sp^2-carbons and two sp^3-carbons in accordance with the proposed structure. The ^1H-NMR spectrum shows a distinct AA′BB′-system as expected from the symmetrical structure. On the other hand, the 12-line ^{13}C-NMR spectrum of **13** supports strongly the unsymmetrical structure. On the basis of these monodehydrobromination reactions the proposed structures **4–8** have been established exactly.

Treatment of a mixture consisting of **4–8** with potassium *tert*-butoxide in THF at reflux temperature proceeded by abstraction of the cis proton and cis elimination (in the cases of **7** and **8**) to give **2** as the single product in a yield of 70% (Scheme III). The structure of **2** was evident from the method of synthesis and from its spectral properties (Table I). In particular, the ^1H NMR spectrum shows a singlet and a doublet for the bridgehead protons (4.79, 4.77 ppm) and a doublet (6.97) for the olefinic proton. The aromatic protons give a multiplet (ABCD-system). With the completion of the synthesis of our target molecule **2** we opened up an entry to the tetrasubstituted benzobarrelene **3**.

Scheme IV



The tribromo compound **2** was subjected to bromination at room temperature. Careful examination of the reaction mixture has indicated clearly the formation of two isomeric pentabromides **15** and **16** which have been separated by fractional crystallization. The NMR and mass spectra and elemental analysis of these isolated products supported the proposed structures (Scheme IV).

Correspondingly, treatment of a mixture consisting of **15** and **16** with potassium *tert*-butoxide in THF at ambient temperature gave the tetrabromobenzobarrelene **3** in 90% yield as a crystalline solid, mp 208–210 °C (Scheme IV). The ^1H NMR spectrum showed a singlet for bridgehead protons (5.0 ppm) and an AA′BB′-system for the aromatic protons, and ^{13}C NMR spectrum is highly symmetrical according to the symmetry in the molecule. The mass spectrum indicates clearly the presence of four bromine atoms.

With the completion of the synthesis of our target molecules **2** and **3** we opened up an entry to the other benzobarrelene derivatives substituted at different positions and showed the application of the *high-temperature bromination* to the benzobarrelene system.

Experimental Section

General. Melting points were determined on a Thomas-Hoover capillary melting point apparatus. Solvents were concentrated at reduced pressure. Infrared spectra were obtained from films on NaCl plates for liquids or from solution in 0.1-mm cells or KBr pellets for solids on a Perkin-Elmer 337 infrared recording spectrophotometer. The ^1H-NMR spectra were recorded on an EM 360 Varian or Brucker WM 200-, 250-, and 300-MHz spectrometers and are reported in δ units with $(CH_3)_4Si$ as internal standard. Apparent splittings are given in all cases. Mass spectra were recorded on a Finnigan-MAT MS Model 4000 mass spectrometer at an ionizing voltage 70 eV. All column chromatography was performed on silica gel (60-mesh, Merck). TLC was carried out on Merck 0.2-mm silica gel 60 F254 analytical alumina plates.

Bromination of 2-Bromo-5,6-benzobicyclo[2.2.0]octa-2,5,7-triene (1) at 77 °C. 2-Bromobenzobarrelene **1** (1165 mg, 5 mmol) was dissolved in 40 mL of CCl_4 in a 100-mL flask which was equipped with reflux condenser. The solution was heated while being stirred magnetically until carbon tetrachloride started to reflux. To the refluxing solution was added a hot solution (65–70 °C) of bromine (1650 mg, 10.3 mmol) in 10 mL of car-

(9) High-temperature bromination of benzonorbornadiene gives nonrearranged products. Conducting of the same reaction in the presence of free-radical inhibitors like 2,4,6-tri-*tert*-butylphenol suppressed the formation of the nonrearranged products. This supports very strongly that there is a competition between radical and ionic mechanism. Daştan, A.; Balci, M. To be published.

bontetrachloride in one portion. The resulting mixture was heated for 15 min at reflux temperature. After being cooled to room temperature the solvent was evaporated. The oily residue was crystallized from 15 mL of CH_2Cl_2/CCl_4 (1:4) to give the pentabromide 4 (600 mg). The residue was left 1 day at room temperature, and 7 was crystallized (170 mg). The solvent was removed under reduced pressure, and the oily residue (1900 mg) was chromatographed on silica gel (140 g) eluting with *n*-hexane. After collection of 2.8 L of eluate, the solvent was changed to $CHCl_3$/*n*-hexane (1:5) and elution was continued (4 L of eluate was collected). 4, 6, and 8 were obtained as pure compounds. 7 was obtained as a mixture with 5. This mixture was separated by fractional crystallization from chloroform/*n*-hexane. In the following elution order we obtained 4, 5, 7, 6, and 8.

For 4: 684 mg, 36%; mp 175–176 °C (from chloroform/*n*-hexane); IR (KBr, cm^{-1}) 3000, 2990, 1480, 1460, 1280, 1190, 1110, 935, 850; MS *m/e* 549/551/553/555/557/559 (M^+), 469/471/473/475/477 (M – Br), 389/391/393/395 (M – 2Br). Anal. Calcd for $C_{12}H_9Br_5$: C, 26.08; H, 1.64. Found: C, 26.02; H, 1.59.

For 5: 170 mg, 9%; IR (KBr, cm^{-1}) 2920, 1480, 1460, 1240, 1210, 1200, 935, 650. Anal. Calcd for $C_{12}H_9Br_5$: C, 26.08; H, 1.64. Found: C, 26.42; H, 1.55.

For 7: 342 mg, 18%; mp 180 °C (from chloroform/*n*-hexane); IR (KBr, cm^{-1}) 2980, 1480, 1460, 1260, 1210, 1100, 935, 885; MS *m/e* 549/551/553/555/557/559 (M^+), 469/471/473/475/477 (M – Br). Anal. Calcd for $C_{12}H_9Br_5$: C, 26.08; H, 1.64; Br, 72.28. Found: C, 25.97; H, 1.51.

For 6: 95 mg, 5%; IR (KBr, cm^{-1}) 3040, 2970, 1460, 1260, 1190, 1100, 975, 935, 860. Anal. Calcd for $C_{12}H_9Br_5$: C, 26.08; H, 1.64; Br, 72.28. Found: C, 26.35; H, 1.53.

For 8: 133 mg, 7%; mp 171 °C (from chloroform/*n*-hexane); IR (KBr, cm^{-1}) 2960, 1480, 1460, 1330, 1290, 1240, 1200, 1190, 1110, 930; MS *m/e* 549/551/553/555/557/559 (M^+), 469/471/473/475/477 (M – Br) 389/391/393/395 (M – 2Br). Anal. Calcd for $C_{12}H_9Br_5$: C, 26.08; H, 1.64; Found: C, 25.92; H, 1.54.

General Procedure for Bromination of 9–12. To a solution of 40 mg (0.1 mmol) of tribromide in 1 mL of chloroform was added a solution of 20 mg (0.1 mmol) of bromine in 1 mL of chloroform at room temperature, and the resulting mixture was stirred. Bromination of 9 and 10 was completed in 1.5 h and bromination of 11 and 12 in 0.5 h. 4 and 7 were formed nearly in quantitative yield. Reaction of 9 and 12 with bromine resulted in the formation 5 and 6 in a ratio of 2:1 and 4 and 8 in a ratio of 53:47, respectively.

General Procedure for Dehydrobromination of 4 and 7. To a solution of 56 mg (0.1 mmol) sodium methoxide in 15 mL of dry and freshly distilled THF was added 553 mg (0.1 mmol) of pentabromide 4 or 7. The resulting reaction mixture was refluxed for 3 h. After being cooled to room temperature the solution was poured into a mixture of hexane (40 mL) and water (40 mL). The layers were separated, and the aqueous phase was extracted with hexane. The combined organic layers were washed with water (2 × 40 mL), dried, and evaporated. The residue was purified by filtration through a short silica gel (5 g) column. Elution with hexane and crystallization from chloroform/hexane gave tetrabromides 13 and 14.

For 13: 425 mg, 90%. Anal. Calcd for $C_{12}H_8Br_4$: C, 30.55; H, 1.71. Found: C, 30.22; H, 1.59.

For 14: 448 mg, 95%; mp 210–212 °C (from chloroform/*n*-hexane); IR (KBr, cm^{-1}) 3000, 1605, 1460, 1455, 1235, 1220. Anal. Calcd for $C_{12}H_8Br_4$: C, 30.55; H, 1.71. Found: C, 30.29; H, 1.61.

2,3,5-Tribromobenzobarrelene (15). To a magnetically stirred solution of 1106 mg (2 mmol) of a mixture consisting of 4–8 (obtained by bromination of 1 at high temperature) in 30 mL of dry and freshly distilled THF was added a solution 450 mg (4 mmol) of potasium *tert*-butoxide in 15 mL of THF. The resulting reaction mixture was refluxed for 3 h. After being cooled to room temperature, the solution was poured into a mixture of hexane (50 mL) and water (50 mL). The organic phase was washed with water, dried, and rotoevaporated. The residue was chromatographed on silica gel (25 g). Elution with petroleum ether and crystallization from methylene chloride/pentane gave tribromide 2.

For 2: 545 mg, 70%; mp 178–179 °C; IR (KBr, cm^{-1}) 3020, 1610, 1455. Anal. Calcd for $C_{12}H_7Br_3$: C, 36.87; H, 1.86; Br, 61.32. Found: C, 36.39; H, 1.81.

Bromination of 2. To a magnetically stirred solution of 1564 mg (4 mmol) of 2,3,5-tribromobenzobarrelene 2 in 25 mL of carbon tetrachloride was added a solution of 440 mg (4.1 mmol) of bromine in 10 mL of carbon tetrachloride at room temperature. The resulting solution was stirred for 45 min. NMR studies indicated the formation of the isomers 15 and 16 in a ratio of 48:52 in quantitative yield. The solvent was evaporated, and products were separated by fractional crystallization from chloroform/*n*-hexane.

For 15: mp 183–184 °C (from chloroform/*n*-hexane); IR (KBr, cm^{-1}) 2990, 2980, 1600, 1475, 1460, 1150, 1100, 1090, 1030, 990, 960.

For 16: mp 153–154 °C (from chloroform/*n*-hexane); IR (KBr, cm^{-1}) 1615, 1600, 1475, 1315, 1250, 1195, 1080, 1025, 970; MS *m/e* 547/549/551/553 (M^+), 469/471/473 (M – Br), 388/390/392/394 (M – 2Br), 284)286/288 (M – 3Br, –2C).

Synthesis of 3. To a magnetically stirred solution of 1102 mg (2 mmol) of a mixture consisting of 15 and 16 (obtained by bromination of 2) in 30 mL of dry and freshly distilled THF was added a solution of 235 mg (2.1 mmol) of potasium *tert*-butoxide in 10 mL of THF. The resulting reaction mixture was refluxed for 3 h. After being cooled to room temperature, the solution was poured into a mixture of hexane (50 mL) and water (50 mL). The organic phase was washed with water, dried, and rotoevaporated. The residue was chromatographed on silica gel (10 g). Elution with carbontetrachloride and crystallization from chloroform/carbontetrachloride gave the tetrabromide 3.

For 3: 844 mg, 90%; mp 208–210 °C; IR (KBr, cm^{-1}) 3080, 3020, 1590, 1460, 1450, 1190, 1140, 1060, 980, 850; MS *m/e* 466/468/470/472/474 (M^+), 387/389/391/393 (M – Br), 308/310/312 (M – 2Br). Anal. Calcd for $C_{12}H_6Br_4$: C, 30.71; H, 1.29; Br, 68.11. Found: C, 30.49; H, 1.34.

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Addition of Fluorinated Olefins to Ester Enolates. Synthesis of Fluorinated Carboxylic Esters and Tetrafluorocyclobutanes

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Introduction

Use of polyhalogenated olefins for the incorporation of fluorine into organic molecules and numerous reactions involving their use as either nucleophilic and electrophilic synthons have been described. In particular, nucleophilic additions to fluorinated olefins by aryl,[1] alkyl,[2] and allyl[3] anions, as well as sulfur and other nucleophiles,[4] have been reported. In addition, lithiotrifluoroethylene,[5] 1-lithio-2,2-difluoroethylene,[6] and 1-lithio-1-chloro-2,2-difluoro-

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