Generation and Trapping of a Highly Strained Bicyclic Alkyne: Tricyclo[6.3.1.0^{2,7}]dodeca-2,4,6-trien-9-yne

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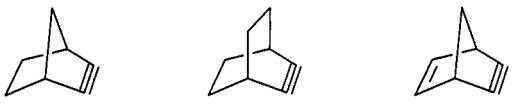
High-temperature bromination of 10-bromotricyclo[6.3.1.0^{2,7}]dodeca-2,4,6,9-tetraene (**8**) resulted mainly in the formation of two isomeric tribromides (**16** and **17**) whose dehydrobromination with DBU afforded the corresponding 9,10-dibromotricyclo [6.3.1.0^{2,7}] dodeca-2,4,6,9-tetraene (**14**). Treatment of **14** with *tert*-butyllithium in THF at −78 °C produces the strained bicyclic alkyne (**10**) which is trapped by 1,3-diphenylisobenzofuran to give two isomeric cycloadducts **12a** and **12b**. The adducts **12a** and **12b** were found to readily rearrange to the isomeric ketones **19a** and **19b** upon chromatography. Upon treatment with potassium *tert*-butoxide, the adducts **12a** and **12b** undergo base-catalyzed double bond isomerization to give four products **20**−**23**. Furthermore, reaction of **14** with one and two mole of potassium *tert*-butoxide has been studied and the mechanism of the product formation is discussed with regard to either an allene or alkyne as a possible intermediate.

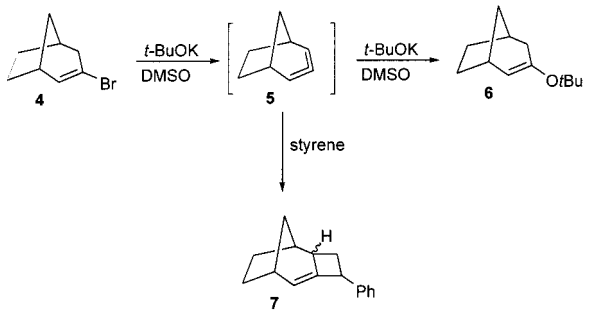
Introduction

An intriguing part of cyclic hydrocarbon chemistry is the synthesis and study of highly strained ring systems. Small-ring cyclic alkynes are of considerable interest in chemistry because of their high strain and reactivity.[1] While cyclononyne and its larger ring homologues are stable and isolable compounds, cycloheptyne, cyclohexyne, and cyclopentyne are unstable and exist only as short-lived intermediates. Intermediacy of these strained ring systems is based exclusively on the observation of trapping products. However, strained bicyclic alkynes have also been reported. Bicyclo[2.2.1]hept-2-yne (**1**)[2] and bicyclo[2.2.2]oct-2-yne (**2**)[3] were generated from the corresponding 2,3-dibromo compounds as reactive intermediates and trapped with appropriate dienes. Quite recently, a highly strained bicyclic alkyne, bicyclo[2.2.1]-hept-2-en-5-yne (**3**), was generated by reaction of a new hypervalent iodine precursor and trapped with 1,3-diphenylisobenzofuran (DPIBF).[4]



1 **2** **3**

Scheme 1



Some years ago, Mohanakrishnan et al.[5] reported that the base-induced (potassium *tert*-butoxide in DMSO) dehydrobromination of **4**[6] gives the highly strained bicyclic allene **5**, which was trapped as either enol ether **6** or as its [2 + 2] cycloaddition product **7** (Scheme 1). An alternate mechanism for the formation of these products was not discussed.

In a previous paper,[7] we initially also proposed the highly strained bicyclic allene **9** as an intermediate in the base-induced elimination of HBr from **8**, which gives allene-like cycloadducts **11** in the presence of 1,3-diphenylisobenzofuran (DPIBF) as a trapping agent. However, as noticed in the same paper, these results also were in agreement with an alternative mechanism for the formation of cycloadducts **11**. According to this mechanism, the

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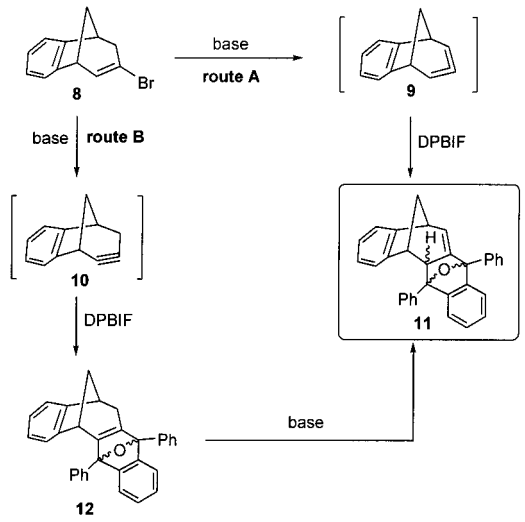
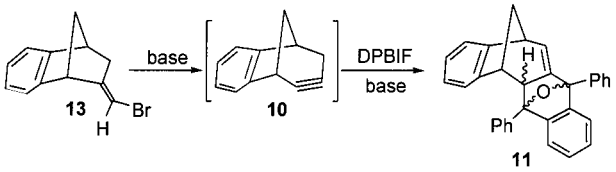
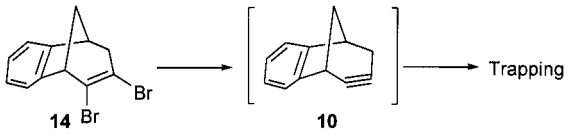
Scheme 2



Scheme 3



Scheme 4



dehydrobromination of **8** yields the bicyclic alkyne **10**, which undergoes cycloaddition with DPIBF to give **12**. The base-promoted isomerization of the double bond in **12** would give the observed products **11** (Scheme 2).

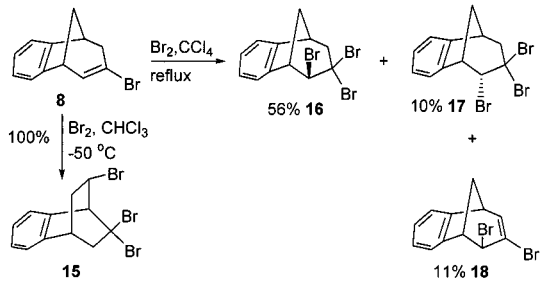
To distinguish between these two possible mechanisms, we recently investigated the generation and trapping of the alkyne **10** by alternative procedures.[8] The alkyne **10** was generated by the base-induced rearrangement of the bromomethylidene compound **13** and trapped with DPBIF to give the alkyne-like cycloadducts **12**, which then isomerize completely to the allene-like products **11** in the presence of excess base (Scheme 3).

Even with these results, allene formation cannot be excluded in the base-promoted reaction of **8**. At this stage, the question "What is the real intermediate in the base-promoted reaction of **8**?" still remained open. To reveal the nature of the intermediate we have undertaken another independent generation of alkyne **10** where the formation of allene **9** was excluded. We now report on the synthesis of 9,10-dibromotricyclo[6.3.1.0^{2,7}]dodeca-2,4,6,9-tetraene (**14**) including its conversion to **10** and the subsequent trapping with DPIBF (Scheme 4).

Results and Discussion

Our synthesis plan toward the dibromide **14** has engaged the techniques of high-temperature bromination, which prevents skeletal rearrangement during the bromination reaction. In a previous work, we have examined the addition of bromine to **8** in $CHCl_3$ at −50 and 0 °C and obtained completely different product distribution.[9] From the reaction at −50 °C we have obtained only the Wagner−Meerwein rearranged product **15** in quantitative yield, which presumably forms via migration of the aryl group in long-lived *exo*-bromonium ion intermediate. In contrast, bromination at 0 °C resulted partly in the formation of rearranged and nonrearranged tribromides (Scheme 5). We noticed that the reaction temperature has a dramatic influence on product distribution. Bromination at room and lower temperatures gives rearranged products via Wagner−Meerwein rearrangement with accompanying alkyl and aryl migration. However, the bromination of these hydrocarbons at higher temperatures (80−150 °C) resulted partly or completely in the formation of nonrearranged products.[10] High-temperature bromination prevents skeletal rearrangement.

Scheme 5



Vinyl bromide **8**, the starting material for the synthesis of **14**, was prepared by a published method[11] and subjected to bromination in CCl_4 at reflux temperature. Three products (**16**−**18**) were isolated after repeated column chromatography in yields of 56%, 10%, and 11%, respectively (Scheme 5). The rearranged tribromide **15** was not detected among the products. The structures of **16**, **17**, and **18** were determined principally by ^{1}H and ^{13}C NMR spectral comparison with literature data.[9]

Our initial attempt to obtain dibromide **14** from the dehydrobromination of *exo*-tribromide **16** using potassium *tert*-butoxide in THF failed probably due to base-catalyzed isomerization of the initially formed product **14** (see also below). The *exo*-dibromide **18** was obtained as the sole product[9] (Scheme 6). In contrast, treatment of *exo*-tribromide **16** with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in refluxing benzene afforded the desired dibromide **14** (65% isolated yield) together with a small amount of the parent bromide **8** in a ratio of 78:22. The latter compound arises from the debromination of **16** under the reaction conditions. Reaction of endo isomer **17** with DBU gave also the dibromide **14** as the only product in high yield (77%) (Scheme 6).

When **14** was treated with *tert*-butyllithium in THF at −78 °C in the presence of DPIBF, two isomeric ketones (**19a** and **19b**) were obtained after chromatographic separation (Scheme 7). The same products (**19a**, **19b**)

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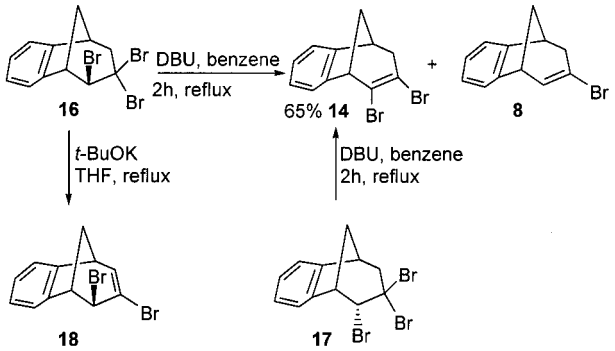
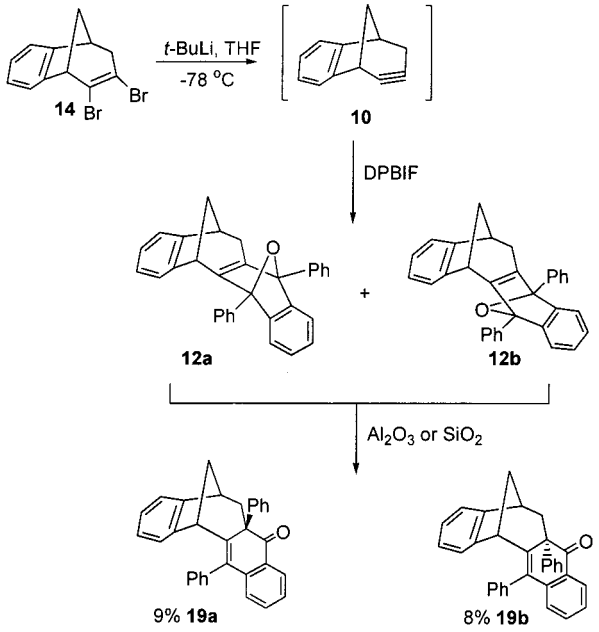
Scheme 6



Scheme 7

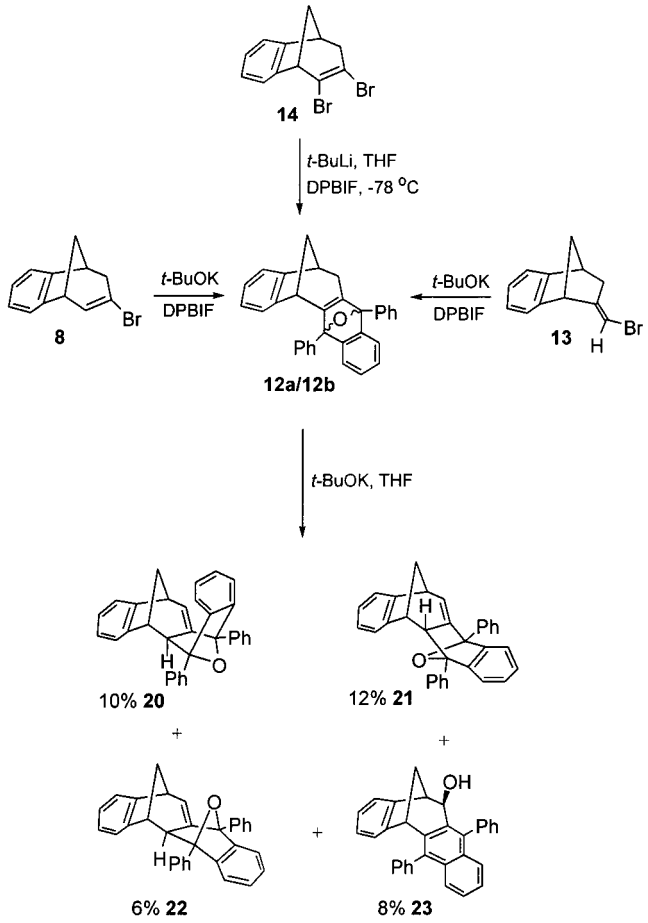


were obtained previously[8] when **13** was reacted with 1 mol of potassium *tert*-butoxide in the presence of DPIBF. We suggest that the isolation of **19a** and **19b** from the debromination of **14** provides strong evidence for the intermediacy of the highly strained bicyclic alkyne **10**. This reactive intermediate initially reacts with DPIBF to give the diastereomeric adducts **12a** and **12b**. These trapping products have been observed by ^{1}H NMR spectroscopy. Attempted isolation of these products **12a** and **12b** failed. This mixture isomerized on the chromatographic column (Al_2O_3 or SiO_2) to give the corresponding ketones **19a** and **19b**.

Reaction of dibromide **14** with *tert*-butyllithium in the presence of DPIBF was repeated under identical conditions, and after workup, the crude product was heated for 6 h with potassium *tert*-butoxide in THF at reflux temperature. Four products (**20**−**23**) were isolated after repeated column chromatography in yields of 10%, 12%, 6%, and 8% (isolated yields), respectively (Scheme 8). This experiment indicates clearly that DPIBF trapping products (**12**) undergo base-promoted double-bond isomerization when treated with base. These products (**20**−**23**) were also obtained by the reaction of **13**[8] and **8**[7a] with excess potassium *tert*-butoxide.

The identical product distribution from the three different reactions, (i) base-promoted reaction of **8** in the presence of DPBIF, (ii) base-promoted reaction of **13** in

Scheme 8



the presence of DPBIF, and (iii) BuLi reaction of **14** in the presence of DPBIF followed by potassium *tert*-butoxide isomerization, strongly suggests that the intermediates have the same structure. Since the allene intermediate cannot be generated from the BuLi reaction of **14**, we conclude once again that the intermediate is the alkyne **10**.

Last, we examined the reaction of **14** with potassium *tert*-butoxide to force the system to generate an allene, since the olefinic proton in **8** is substituted by a bromine. When **14** was treated with 1 mol of potassium *tert*-butoxide in refluxing THF, the ether **25** was obtained as the exclusive product (Scheme 9). No allene dimerization products were detected. This shows that the bromo allene **24** is not formed in this reaction as the intermediate.

Independently, we have shown that the ether **25** is also formed by reaction of the *exo*-dibromide **18** with 1 mol of potassium *tert*-butoxide, which indicates that the dibromide **14** initially undergoes base-promoted double bond isomerization to give *exo*-dibromide **18**. To support the formation of **18** as the intermediate, we have interrupted the reaction of **14** with potassium *tert*-butoxide after 30 min and analyzed the reaction mixture. It has been shown that **18** was formed as the sole product. Nucleophilic displacement of the bromine in **18** (S_N2'-type[12]) by *tert*-butoxide ion yields the ether **25** (Scheme 9). The exo configuration of the *t*-BuO group was determined by measuring the vicinal bridgehead-oxymethine coupling

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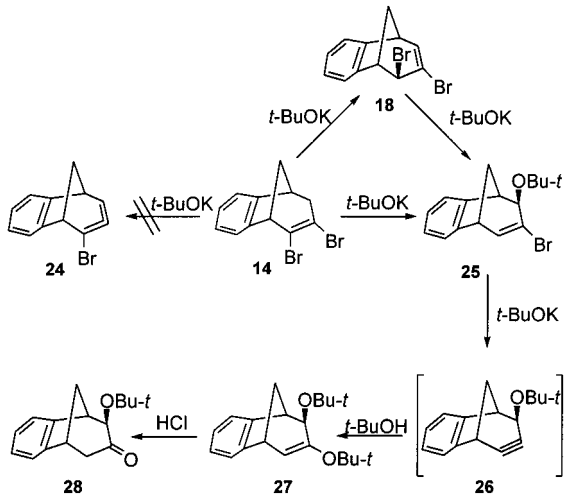
Scheme 9



constant (J = 2.0 Hz), which indicates clearly the exo configuration of the *tert*-butoxide group.[13,14]

On the other hand, treatment of **14** with 2 mol of potassium *tert*-butoxide afforded the enol ether **27**, which was also formed upon reaction of **25** with 1 mol of potassium *tert*-butoxide (Scheme 9). On standing at room temperature or hydrolysis with dilute HCl, **27** converts to the corresponding *exo*-ketone **28**. The structures of **27** and **28** have been elucidated on the basis of spectral data. The exo configuration of the *t*-BuO group in **27** again was determined by measuring the vicinal bridgehead-oxymethine coupling constant (J = 2.3 Hz) as in **25**.

We assume that the alkyne **26** is the reactive intermediate in the dehydrobromination of **25,** which then adds *t*-BuOH to give the enol ether **27**. Because of the unsymmetrical structure of the intermediate alkyne **26**, the formation of two isomeric enol ethers was expected; however, theoretical calculations[15] on analogue alkyne **10** indicated that the unsymmetric triple bond is polarized and the positive end is the site of *tert*-butoxide attack, which explains the formation of only one isomer **27** in the dehydrobromination of **25**.

Experimental Section

General Methods. Melting points were determined on a Büchi model 530 apparatus and are uncorrected. Infrared spectra were recorded on a Mattson model 1000 FT-IR spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on 200 (50)-MHz spectrometers. Mass spectra (electron impact) were recorded at 70 eV. Column chromatography was performed on silica gel (60−200 mesh) and activated alumina (70−230 mesh) from Merck Co. TLC was carried out on Merck 0.2 mm silica gel 60 F_{254} analytical aluminum plates.

Bromination of 10-Bromotricyclo[6.3.1.0^{2,7}]dodeca-2,4,6,9-tetraene 8 at 77 °C. Vinyl bromide **8**[11] (0.5 g**,** 2.13 mmol) was dissolved in 5 mL of CCl_4 in a 25 mL flask that was equipped with a reflux condenser. The solution was heated until carbon tetrachloride started to reflux with magnetic stirring. To the refluxing solution was added dropwise a hot solution of bromine (0.36 g, 2.25 mmol) in 0.5 mL of CCl_4 during 30 s. The color of bromine disappeared immediately. The reaction flask was removed from the oil bath and cooled to room temperature in an ice bath. Evaporation of the solvent gave an oil whose ^{1}H NMR spectrum indicated a mixture of **16**, **17**, and **18** in a ratio of 72:14:14, respectively. The crude product (0.95 g) was purified as described in the literature[9b] to give 470 mg (56%) of *exo*-tribromide **16**, 75 mg (11%) of *exo*-dibromide **18**, and 82 mg (10%) of *endo*-tribromide **17**. Comparison of the spectral data of these compounds (**16**, **17**, and **18**) with those reported in the literature[9b] were in full agreement.

Reaction of *exo*-Tribromide 16 with DBU: 9,10-Dibromotricyclo[6.3.1.0^{2,7}] dodeca-2,4,6,9-tetraene (14). To a stirred solution of *exo*-tribromide **16** (1.25 g, 3.98 mmol) in 40 mL of absolute benzene was added 0.96 g (6.31 mmol) of DBU. The resulting reaction mixture was heated at reflux temperature for 2 h. After the reaction mixture was cooled to room temperature, the insoluble materials were separated by filtration. The filtrate was evaporated, and the residue was treated with water and extracted with ether. The organic phase was washed with saturated $NaHCO_3$ and water and dried over $MgSO_4$. Evaporation of the solvent gave a viscous oil (0.77 g) whose ^{1}H NMR spectrum indicated the presence of a mixture of **14** and **8** in a ratio of 78:22. The oily viscous residue was crystallized from ethanol to give **14** (0.65 g, 65%): colorless crystals; mp 68−69 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.34−7.12 (m, 4H), 3.77 (d, J = 4.0 Hz, 1H), 3.39 (t, J = 4.4 Hz, 1H), 3.06 (dd, A part of AB system, J = 17.2, 4.9 Hz, 1H), 2.48 (bd, B part of AB system, J = 17.2 Hz, 1H), 2.32 (dt, A part of AB system, J = 10.7, 4.4 Hz, 1H), 2.24 (d, B part of AB system, J = 10.7 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 148.4, 145.4, 127.8, 127.2 (2x), 123.9, 121.6, 119.4, 52.8, 44.2, 42.6, 41.8; MS (70 eV) m/z 312/314/316 (M^+, 32), 233/235 (M^+ − Br, 30), 154 (M^+-2Br, 100), 76 (51); IR (NaCl, film, cm^{-1}) 3085−2817, 1617, 1410, 1338, 1162, 1086, 960, 852, 744. Anal. Calcd for $C_{12}H_{10}Br_2$: C, 45.90; H, 3.20. Found: C, 46.29; H, 3.17.

Reaction of *endo*-9,10,10-Tribromotricyclo[6.3.1.0^{2,7}]-dodeca-2,4,6-triene 17 with DBU. The reaction was carried out as described above by using 180 mg (0.45 mmol) of *endo*-tribromide **17** and 130 mg (0.85 mmol) of DBU. Dibromide **14** (110 mg, 77%) was obtained as sole product.

Reaction 14 with *t*-BuLi in the Presence of DPIBF. A solution of 1.7 M *t*-BuLi in pentane (2.1 mL, 3.57 mmol) was added dropwise to a stirred solution of **14** (1.0 g, 3.2 mmol) and diphenylisobenzofuran (0.86 g, 3.2 mmol) in dry THF (20 mL) over 5 min at −78 °C under nitrogen. The reaction mixture was allowed to warm to room temperature and then quenched with wet THF (3 mL). Stirring was continued at room temperature for 2 h. After a major part of the THF was removed, the mixture was treated with water (30 mL). The aqueous layer was extracted with ether (4 × 30 mL) and CH_2Cl_2 (2 × 25 mL). The combined organic layers were washed with water, dried over $MgSO_4$, and filtered. The filtrate was treated with maleic anhydride until the yellow color disappeared to remove the excess DPBIF. After removal of the solvent, the oily residue was chromatographed over alumina (150 g, grade IV, neutral). Elution with petroleum ether−toluene (8:2) gave 117 mg (9%) of *exo*-ketone **19a** and 104 mg (8%) of endo isomer **19b**. The ^{1}H NMR, ^{13}C NMR, and IR spectral data for **19a** and **19b** are identical with those reported in the literature.[8]

Reaction of 14 with *t*-BuLi in the Presence of DPIBF and Followed by Potassium *tert*-Butoxide. The first step of the reaction was carried out as described above by using 2.0 g (6.37 mmol) of dibromide **14**, 1.72 g (6.37 mmol) of diphenylisobenzofuran, and 4.12 mL of *t*-BuLi in pentane (1.7 M, 7.0 mmol). After the usual workup, the residue (3.5 g) was dissolved in 20 mL of dry and freshly distilled THF and potassium *tert*-butoxide (0.71 g, 6.34 mmol) added. The resulting solution was heated at reflux temperature for 6 h under nitrogen with magnetic stirring and worked up in the same way as described above. The crude product was chromatographed over alumina (300 g, grade IV, neutral). As the first fraction we isolated the reduction product **8** (28.5 mg, 22%). The trapping products (**20**−**23**)[8] were isolated after repeated column chromatography with petroleum ether−toluene (8:2, 7:3) in yields of 10%, 12%, 6%, and 8% (isolated yields), respectively. Total yield of the trapping products, determined

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(14) Wege, D. *J. Org. Chem.* **1990**, *55*, 1667−1670.
(15) Balci, M.; Krawiec, M.; Taskesenligil, Y.; Watson, W. H. *J. Chem. Crystallogr.* **1996**, *26*, 413−418.

by ^{1}H NMR integration, was aprroximately 62%. The spectral data of these compounds (**20**−**23**) with those reported in the literature[8] were in full agreement.

Reaction of 14 with Potassium *tert*-Butoxide (1 Equiv). To a stirred solution of dibromide **14** (300 mg, 0.95 mmol) in 20 mL of dry THF was added potassium *tert*-butoxide (120 mg, 1.07 mmol, 10% excess). The reaction mixture was refluxed for 6 h and then cooled to room temperature. The mixture was diluted with water, and the aqueous solution was extracted with ether, washed with water, and dried over $MgSO_4$. After removal of the solvent, the residue was chromatographed on silica gel with hexane−chloroform (9:1) yielding 130 mg (43%) of ether **25** as a colorless liquid: ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.35 (m, 1H), 7.13 (m, 3H), 6.70 (d, J = 7.3 Hz, 1H), 3.95 (d, J = 2.0 Hz, 1H), 3.40 (m, 2H), 2.36 (d, A part of AB system, J = 10.6 Hz, 1H), 2.19 (dt, B part of AB system, J = 10.6, 4.4 Hz, 1H), 1.39 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 154.1, 145.0, 142.2, 128.5, 128.3, 126.7, 124.0, 123.6, 77.2, 76.4, 51.4, 45.4, 39.9, 30.9 (3x); IR (NaCl, film, cm^{-1}) 2978, 2876, 1625, 1479, 1421, 1395, 1344, 1242, 1217, 1038.

Reaction of 14 with Potassium *tert*-Butoxide (2 Equiv): Formation of *exo*-10,11-Di(*tert*-butoxy)tricyclo-[6.3.1.0^{2,7}]dodeca-2,4,6,9-tetraene (27). To a stirred solution of dibromide **14** (500 mg, 1.95 mmol) in 20 mL of dry THF was added potassium *tert*-butoxide (400 mg, 3.57 mmol). The reaction mixture was refluxed for 10 h, cooled to room temperature, and worked up in the same way as described above. The crude product was purified on silica gel with hexane-chloroform (9:1) to yield 270 mg (56%) of the butoxy enol ether **27** as a colorless liquid: ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.29 (m, 1H), 7.06 (m, 3H), 5.65 (d, J = 7.1 Hz, 1H), 3.62 (d, J = 2.3 Hz, 1H), 3.33 (dd, J = 7.1, 4.3 Hz, 1H), 3.25 (m, 1H), 2.28 (d, A part of AB system, J = 9.9 Hz, 1H), 2.07 (dt, B part of AB system, J = 9.9, 4.4 Hz, 1H), 1.31 (s, 9H), 1.15 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 156.4, 150.0, 145.5, 128.1, 127.4, 126.3, 122.7, 119.2, 79.7, 76.2, 74.4, 51.0, 41.9, 40.5, 30.9 (3x), 30.8 (3x); IR (NaCl, film, cm^{-1}) 3080−2876, 1651, 1472, 1395, 1242, 1217, 1191, 757.

***exo*-9-(*tert*-Butoxy)tricyclo[6.3.1.0^{2,7}]dodeca-2,4,6-trien-10-one (28).** To a solution of **27** (160 mg, 0.53 mmol) in 5 mL of CH_2Cl_2 was added dropwise a solution of 10% HCl (0.5 mL). The reaction mixture was stirred at room temperature for 30 min and then quenched with NH_3 solution. The aqueous solution was extracted with CH_2Cl_2, washed with water, and dried over $MgSO_4$. After removal of the solvent, the residue was chromatographed on silica gel with petroleum ether−ether (49:1) to give 75 mg (57%) of ketone **28** as a colorless liquid: ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.24−7.12 (m, 4H), 3.79 (d, J = 3.9, 1H), 3.38−3.28 (m, 2H), 2.94 (dd, A part of AB system, J = 15.1, 3.3 Hz, 1H), 2.64 (d, A part of AB system, J = 11.3 Hz, 1H), 2.36 (bd, B part of AB system, J = 15.1 Hz, 1H), 2.18 (m, B part of AB system, 1H), 1.23 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 211.1, 149.5, 143.4, 129.8, 129.3, 126.4, 125.5, 79.3, 77.7, 50.3, 49.2, 42.5, 38.8, 30.4 (3×); IR (NaCl, film, cm^{-1}) 3055−2902, 1727, 1497, 1370, 1217, 1038, 782.

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