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Bicyclo[3.2.1]octane Synthons from Cyclopropenes: Functionalization of Cycloadducts by Nucleophilic Additions

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It has been known for several decades that a highly functionalized family of tetrahalobicyclo[3.2.1]-octadienes are readily available through the cycloaddition of furan or cyclopentadiene with either tetrachloro- or tetrabromocyclopropene. However, the application of these highly functionalized building blocks in synthesis has remained relatively unexplored in relation to their better-known counterparts derived through oxyallyl cation additions. As a first step toward utilizing these highly versatile intermediates in synthesis, a study of the addition of various nucleophiles to the halogenated nucleus has been conducted. It has been found that these halogenated systems are amenable to a wide range of functionalizations in high yields and with good selectivities.

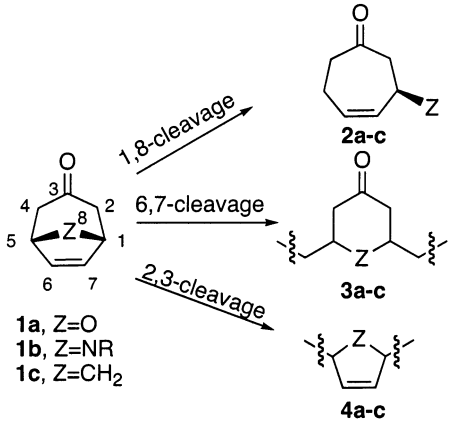
Introduction

The bicyclo[3.2.1]octene systems **1a**−**c** have found widespread use as key intermediates in the synthesis of natural products and other compounds.[1] Embedded within these building blocks are various ring systems (**2a**−**c**, **3a**−**c**, and **4a**−**c**), which are common to a wide array of natural products. Each of these ring systems can be unveiled by the cleavage of one of the three unique bridges in the bicyclic molecules (Scheme 1).

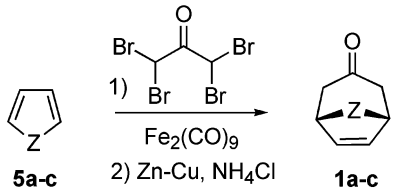
The parent derivatives are typically prepared via the cycloaddition of an oxyallyl cation equivalent to cyclic dienes **5a**−**c**, a reaction popularized by Hoffmann[2] and Noyori[3] (Scheme 2). The oxyallyl cations are typically generated from the haloacetone derivatives, although other methods have been reported.[4] These halogens are subsequently removed to produce the bicyclo[3.2.1]oct-6-en-3-ones, meso compounds that have found wide use in organic syntheses.[5]

Although the oxyallyl cation addition is the method of choice for gaining entry into this family of bridged compounds, there were in fact earlier reports of these types of derivatives accessed through alternative cycloaddition reactions. In 1968, Tobey and Law[6] reported the reaction of furan, substituted furans, and cyclopentadiene with tetrachloro- and tetrabromocyclopropene (Scheme 3).

SCHEME 1. Bridged Bicyclic Synthons



SCHEME 2



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(1) (a) Filippini, M.; Rodriguez, J. *Chem. Rev.* **1999**, *99*, 27. (b) Patil, G. S.; Nagendrappa, G. *J. Indian Chem. Soc.* **2002**, *41*, 1019. (c) Langer, P.; Holtz, E.; Saleh, N. N. R. *Chem.−Eur. J.* **2002**, *8*, 917. (d) Barluenga, J.; Ballesteros, A.; Santamaria, J.; de la Rua, R. B.; Rubio, E.; Tomas, M. *J. Am. Chem. Soc.* **2000**, *122*, 12874.

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(6) (a) Law, D. C. F.; Tobey, S. W. *J. Am. Chem. Soc.* **1968**, *90*, 2376. (b) Tobey, S. W.; Law, D. C. F. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 649. (c) Tobey, S. W.; Law, D. C. F. U.S. Patent 3,538,117, Nov 3, 1970.

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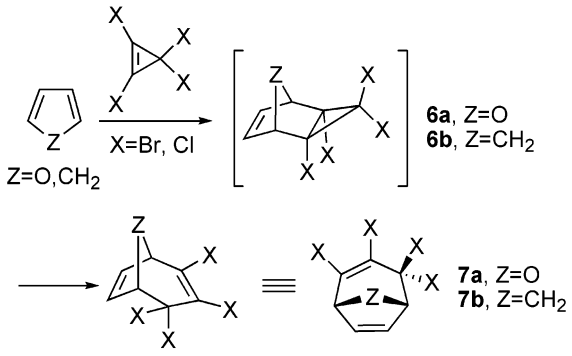
SCHEME 3



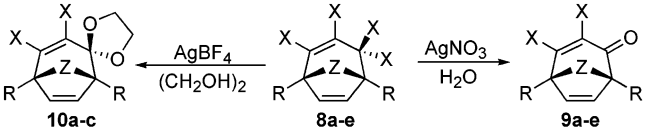
They proposed that the tetrahalocyclopropenes underwent an initial Diels−Alder cycloaddition to produce the cyclopropyl norbornene derivatives **6a** and **6b**, which spontaneously rearrange by way of a halogen atom migration to yield the bicyclo[3.2.1]octadiene nucleus. Although this unusual rearrangement has generated a variety of elegant mechanistic studies,[7] there has been little interest in these compounds from a synthetic perspective.

We have been interested in the use of oxabicyclo[3.2.1]-octane for the syntheses of heterocycles[8] and carbocycles.[9] It is noteworthy that the resulting adducts **7a**,**b**, in addition to having a rigid framework, contain three contiguous functionalized carbons that constitute a perhalogenated allylic system. This substitution pattern suggested that it would be possible to further functionalize this system via a cationic, anionic, or free-radical process. Thus, these molecules are attractive intermediates for the synthesis of natural products and are complementary to those synthons prepared through the oxyallyl-cation route. Initial studies have focused on the functionalization of the halogenated bridge and, in particular, the replacement of the halide groups with oxygen- and carbon-based nucleophiles. Herein, we report our studies on the addition of the nucleophiles to the halogenated positions of the bicyclic system.

Results and Discussion

We initially examined the formation and trapping of the carbocation intermediates by use of a Lewis acid in the presence of latent nucleophiles. It was envisioned that strong Lewis acids could promote the formation of a symmetrical allylic cation and that it should be possible to intercept this cation with a variety of nucleophiles. Useful reactions could only be realized with the use of silver salts.[10] Other Lewis acids such as copper(II) chloride, titanium tetrachloride, or aluminum chloride either returned unreacted starting material or promoted extensive decomposition of the tetrahalide. Silver salts smoothly facilitated the addition of water to the tetrahalides to produce the dihaloenones in very high yields (Table 1). The hydrolysis of the tetrabromo compounds proceeded at room temperature, whereas the hydrolysis of the tetrachloro compounds required higher temperatures. This is not surprising and can be explained based on the difference between C−Cl and C−Br bond strengths.

TABLE 1. Silver-Promoted Hydrolysis and Alcoholysis of Tetrahalides



halide	Z	X	R	conditions[a]	product	yield (%)[b]
8a	O	Br	H	method A	**9a**	83
8b	O	Br	CH_3	method A	**9b**	85
8c	CH_2	Br	H	method A	**9c**	90
8d	O	Cl	H	method B	**9d**	84
8e	CH_2	Cl	H	method B	**9e**	86
8a	O	Br	H	method C	**10a**	85
8b	O	Br	CH_3	method C	**10b**	87
8c	CH_2	Br	H	method C	**10c**	82

[a] Method A: 2 equiv of $AgNO_3$, 1:1 acetone/water, at 25 °C. Method B: 1 equiv of Ag_2O, 1 equiv of $AgNO_3$, 1:1 dioxane/water, reflux. Method C: 2 equiv of $AgBF_4$, 2 equiv of $(CH_2OH)_2$, CH_2Cl_2, −78 → +25 °C. [b] Isolated yield after chromatography.

In addition to water, silver ion also promoted the addition of diols to the tetrahalides to produce ketals **10a**−**c**, which can function as protected derivatives of the enones. Silver tetrafluoroborate was superior to silver nitrate because of the small amounts of water present in the silver nitrate, which led to a mixture of ketals and enones. The facile addition of the oxygen-based nucleophiles, promoted by silver salts, encouraged an investigation of the addition of the carbon-based nucleophiles to the tetrahalides. We imagined that moderate nucleophiles such as aromatics, heteroaromatics, and allyl/vinylsilanes would easily add to the allylic cation once generated upon treatment with a Lewis acid. These studies began with the attempted addition of an activated arene (anisole) to the tetrabromo adduct **8a**. Traditional Lewis acids such as aluminum chloride, boron trifluoride etherate, or titanium tetrachloride resulted in extensive decomposition of the starting halide. The previous success with silver salts prompted us to examine the reaction of **8a** with anisole and silver tetrafluoroborate. Under these conditions, a complex mixture of products was formed, with some evidence of compounds resulting from multiple arylation of the tetrabromide. There was concern that the extensive decomposition of the materials was related to the production of a strong acid (HBF_4) during the arylation reaction. In an attempt to scavenge the strong acid produced, silver oxide was added to the reaction mixture. Under these new conditions, a clean conversion to a new adduct **11a** was observed (Scheme 4).

The product of this Friedel−Crafts type reaction resulted from the addition of both a molecule of the arene and a molecule of water. Overall, the reaction consumed 2 mol of silver ion, suggesting the sequential generation of the cations from the tetrabromide. A mechanistic

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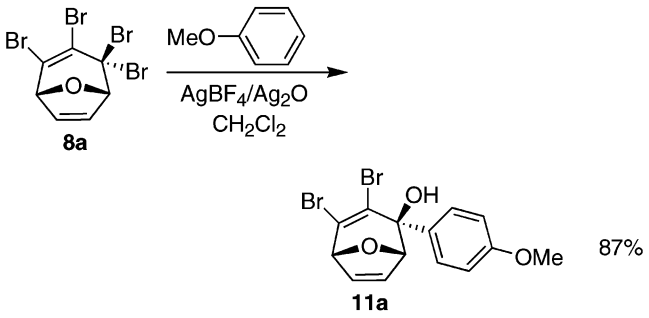
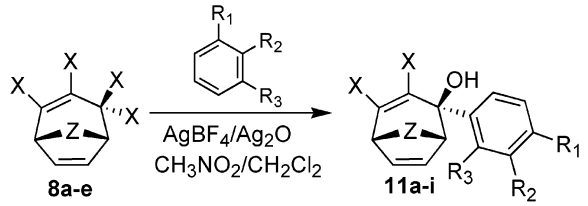
SCHEME 4



proposal for the formation of these adducts rationalizes the stereochemistry of the arylation (Scheme 5).

The initial reaction with silver ion generated the allylic cation **12**, which is attacked by anisole from the less sterically congested exo face to give the transient tribromide **13**. Although not identified, **13** is conceivably one of the products produced in the absence of silver oxide. An equivalent of fluoroboric acid is generated during this process, which reacts with silver oxide to liberate an equivalent of water. A further reaction of **13** with silver ion generated a second allylic cation **14**. It is proposed that bromide **13** is more reactive toward ionization than **8a** because of the extra stabilization in **14** from the pendant aromatic ring. Therefore, if only a single equivalent of silver ion is added to the reaction, a mixture of products would be expected. The allylic cation was preferentially attacked by water (rather than a second molecule of the arene) to produce the tertiary alcohol **11a**. When considering the attack of water on cation **14**, two different outcomes are possible. The attack at position a leads to the observed product **11a**. Alternatively, the attack at the other terminus of the allylic cation at position b would produce bromohydrin **15**, which would be expected to collapse to the enone **16**. Although the enone **16** is the more stable compound (see below), the alcohol forms kinetically, possibly owing to the greater localization of the cationic center at the benzylic position. The ease of the conversion of the tetrabromide to an arylated adduct prompted a study of the reaction utilizing a combination of different tetrahalides and aromatic systems (Table 2).

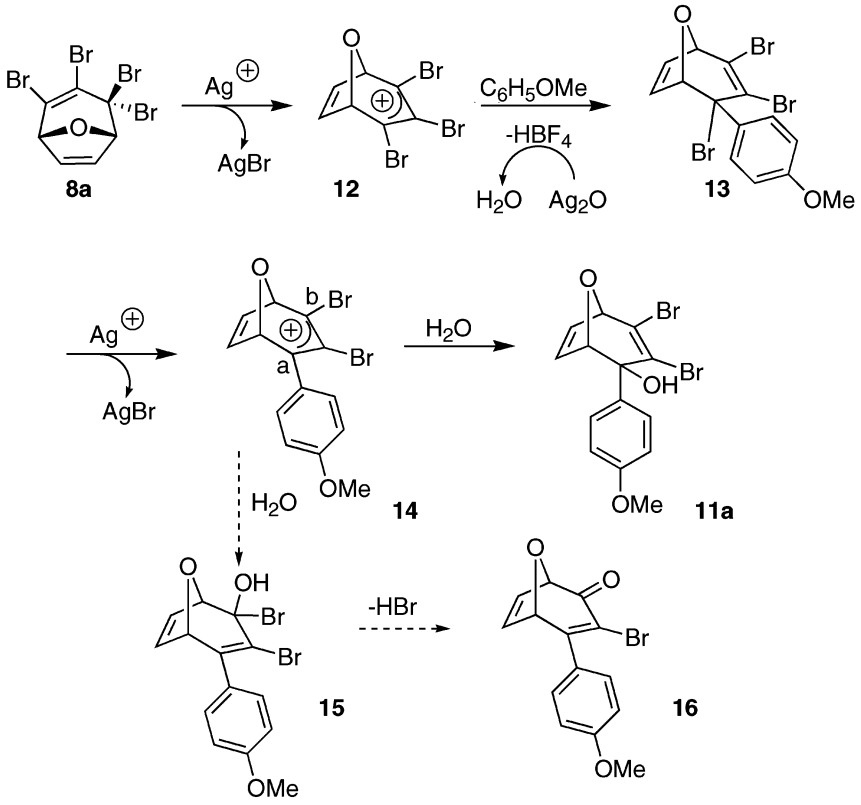
TABLE 2. Silver-Promoted Arylation of Tetrahalides



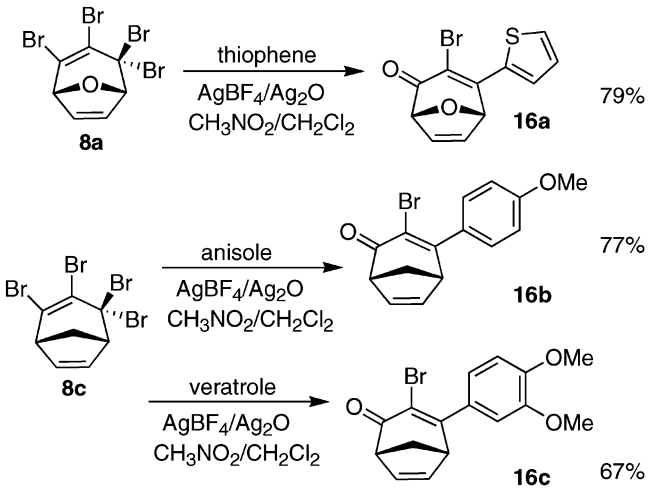
halide[a]	R_1	R_2	R_3	product	yield (%)[b]
8a	OMe	H	H	**11a**	87
8a	OMe	OMe	H	**11b**	75
8a	OMe	Me	H	**11c**	70
8a	OEt	H	H	**11d**	82
8a	OMe	OMe	OMe	**11e**	82
8a	OMe	Br	H	**11f**	80
8a	OMe	I	H	**11g**	35
8d	OMe	H	H	**11h**	68
8d	OMe	OMe	H	**11i**	64

[a] The tetrahalide is treated with 1 equiv of $AgBF_4$, 1 equiv of Ag_2O, and 2 equiv of the aromatic in dichloromethane at −78 °C. [b] Yield refers to the major regioisomer only after purification.

SCHEME 5



SCHEME 6



Examination of the reaction of the furan adduct **8a** with a variety of arene nucleophiles revealed that only arenes with one or more activating groups were sufficiently nucleophilic to undergo this reaction. Attempts to employ arenes of a more moderate nucleophilicity such as benzene, toluene, or naphthalene resulted simply in the production of the unsubstituted ketone **9a**. It is believed that this product resulted from the competitive addition of water to allylic cation **12** with the subsequent collapse of the bromohydrin. It appears that only highly activated aromatic rings add to cation **12** faster than water and lead to the arylated products. The placement of a methoxy group was sufficient to promote the addition, and the arylated products were produced in high yield. The regiochemistry of the arylation was extremely high with products formed from an almost exclusive addition to the position para to the activating group. Although minor amounts of the ortho addition products could be seen in the NMR of the crude material, they were separated by chromatography, giving the pure para compound. The stereochemistry of the tertiary alcohol was confirmed by an X-ray structure of the product derived from the addition of trimethoxybenzene. Interestingly, in some cases, the regioisomeric enones **16a**−**c** were produced (Scheme 6).

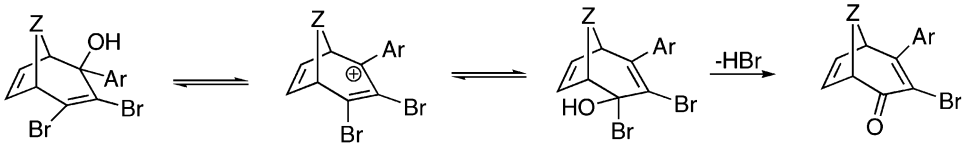
Silver-promoted addition of thiophene to **8a** was observed to initially generate the expected *exo*-alcohol, but upon purification by column chromatography, the compound spontaneously rearranged to the ketone **16a**. Tetrabromide **8c**, which contains a carbon rather than an oxygen bridge, produced the enone derivatives **16b**,**c** directly upon reaction with anisole or veratrole. Although on occasions the tertiary alcohol **17a** did survive chromatography and was characterized, **17b**,**c** have never survived chromatography, but evidence of these compounds has been observed in the crude reaction mixture by GC−MS. This change in product distribution has been attributed to the reversible nature of the addition of water to the allylic cation (Scheme 7).

It is proposed that a catalytic quantity of acid, present either in the reaction mixture or from the silica gel, can promote the reversible dehydration of certain tertiary allylic alcohols to the cations **18a**−**c**. Although kinetic attack occurs at the more substituted carbocation, addition at the other terminus of the allylic cation produces bromohydrins **19a**−**c**. Rapid and likely irreversible loss of hydrobromic acid leads to the thermodynamically favorable aryl enones **16a**−**c**. The ease of this conversion likely depends on the stability of the intermediate carbocations. In the case of the thienyl substituent, the stabilization provided by the sulfur atom helps to promote the ionization of **17a**. The fact that the methylene-bridged compounds appeared to directly produce the enone suggests that the oxabridge in compound **8a** destabilizes the cation, which slows ionization and stabilizes the alcohol. With no such destabilization in **18b**,**c**, the equilibration easily takes place and directly produces the enones. Because this represents a conversion of a kinetic to a thermodynamic product, it was envisioned that more vigorous conditions could be used to promote the conversion of other adducts to cations related to **18** and that other arylated products could be directly converted to the corresponding enones (Scheme 8). This could be demonstrated by reaction of adduct **11a** with trifluoroacetic acid and water in a strongly ionizing solvent to produce enone **16d** in very good yield.

Although the initial halocyclopropene adducts are nonsymmetric, the cation produced by ionization is symmetric and as such attack of the arene on either terminus of the allyl system leads to the same product. If a monosubstituted furan were to be used in the initial cycloaddition reaction, arylation of this adduct could lead to two different isomers. To examine if there would be any influence of a bridgehead substituent on the regioselectivity of the attack of the nucleophile, nonsymmetric adducts **21a** and **21b** were prepared by cycloaddition with 2-methylfuran (**20**) and reacted with a nucleophile under silver-promoted conditions (Scheme 9).

Reaction of 2-methylfuran and tetrabromocyclopropene produced a mixture of regioisomeric cycloadducts **21a** and **21b** in an unassigned 2:1 ratio. Silver-promoted hydrolysis of the adducts produced two enones **22a** and **22b**, again in a 2:1 ratio with **22a**, assigned as the major product by NMR.[11] Attempts were made to separate the two compounds by chromatography without any success. This distribution was interpreted as a slight preference for attack of water at the least-hindered terminus of the

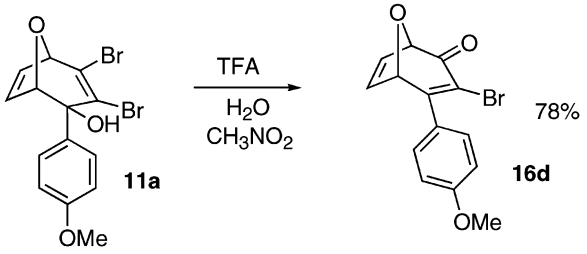
SCHEME 7



17a Z=O, Ar=2 thienyl
17b Z=CH_2, Ar=p-anisyl
17c Z=CH_2, Ar=p-veratryl

18a-c **19a-c** **16a-c**

SCHEME 8



allylic cation and suggested shielding of the allyl system by the bridgehead methyl group. The use of a more demanding nucleophile such as anisole offered much greater levels of selectivity and produced alcohol **23** as the only product, which was assigned by X-ray crystal analysis, thus providing experimental evidence for the degeneracy of the allylic cation (**12**) that is formed from both **21a** and **21b.**

Although the addition of some highly reactive nucleophiles was possible under the silver-promoted additions, it became quite clear that there were severe limitations of this method; i.e., the arenes were limited to only those that were highly activated. In addition, attempts to add other latent nucleophiles such as allyl- and vinylsilanes were unproductive.[12] In an attempt to expand the types of nucleophiles that could be added to these bridged synthons, the addition of more reactive nucleophiles to the readily available ketones **9a**−**c** was examined (Scheme 10).

The dihaloenone derivatives **9a**−**e**, prepared by direct hydrolysis of the tetrahalides, offer several positions for the addition of highly reactive nucleophiles. 1,2 addition would lead to tertiary alcohols **23**, which are diastereomeric to those produced by arylation, while 1,4 addition would produce substituted enones **24** by an addition−elimination mechanism. Little information was available on the addition of powerful nucleophiles such as organometallic reagents to these types of dihaloenones,[13] and there would be concern that competing processes such as metal−halogen exchange[14] might be competitive. Gratifyingly, it was found that 1,2 addition of nucleophiles could be accomplished with the correct choice of the organometallic reagent (Table 3).

Addition of the hydride under Luche conditions[15] exclusively produced the *endo*-alcohols **24a** and **24c**. The reduction of **9b**, however, gave a 1:1 mixture of *exo*- and

SCHEME 9

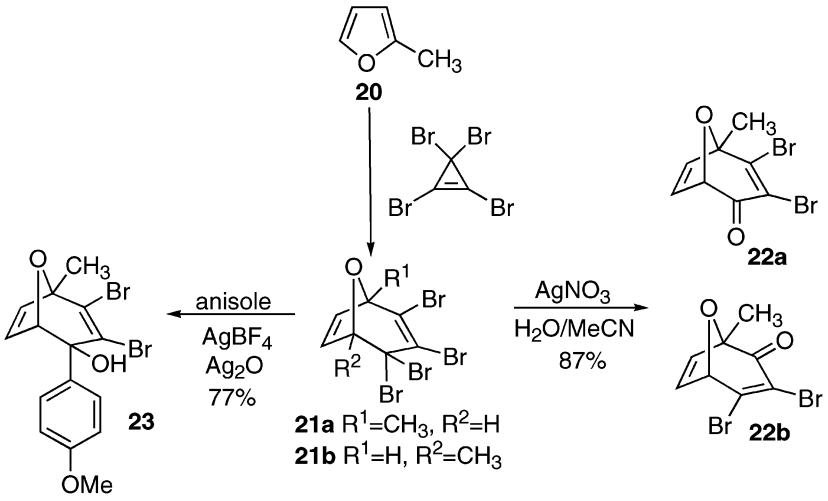
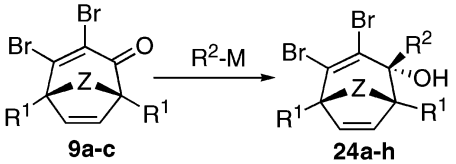
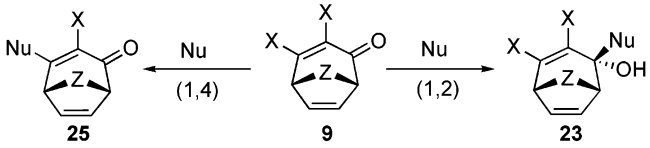


TABLE 3. Addition of Organometallic Agents to Dihaloenones



enone	Z	R^1	reagent	product	R^2	yield (%)
9a	O	H	$NaBH_4$/CeCl	**24a**	H	95
9b	O	CH_3	$NaBH_4/CeCl_3$	**24b** (exo/endo = 1:1)	H	96
9c	CH_2	H	$NaBH_4/CeCl_3$	**24c**	H	97
9a	O	H	^{n}BuLi	decomp	N/A	N/A
9a	O	H	PhLi	decomp	N/A	N/A
9a	O	H	H_2C=CHMgBr	**24d**	H_2C=CH	74
9a	O	H	$H_3CCCMgBr$	**24e**	H_3CCC	92
9a	O	H	C_6H_5MgBr	**24f**	Ph	81
9a	O	H	$C_{10}H_7MgBr$	**24g**	1-naphthyl	89
9a	O	H	C_4H_3SMgBr	**24h**	2-thiophenyl	88
9a	O	H	^{n}BuMgBr	**24a**	H	90
9c	CH_2	H	^{n}BuMgBr	**24c**	H	90

SCHEME 10



SCHEME 11

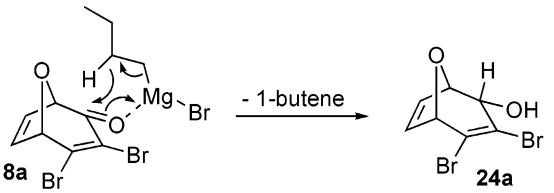
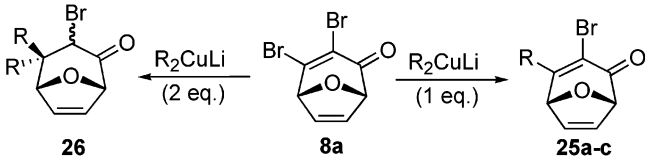


TABLE 4. Addition of Organocuprates to Enone 8a



entry	cuprate	equiv	product	R	yield (%)
1	Me_2CuLi	1	**25a**	CH_3	84
2	Bu_2CuLi	1	**25b**	Bu	88
3	Ph_2CuLi	1	**25c**	Ph	78
4	Me_2CuLi	2	**26**	CH_3	73

endo-alcohols, again demonstrating the shielding effect of the bridgehead methyl group. Attempts to add alkyl groups via the corresponding organolithium reagents led only to the decomposition of the starting enone. This was presumably due to the competitive metal−halogen exchange[16] between the butyl- or phenyllithium reagents utilized and the vinyl bromides. Switching to the Grignard reagents, which are less prone to undergo this type of reaction,[17] successfully led to a clean 1,2 addition of various carbon nucleophiles. Addition of vinyl-, propynyl-, phenyl-, and naphthylmagnesium bromide produced the corresponding *endo*-alcohols **24d**−**h** in good yields. The addition of the organic fragments appears to have occurred exclusively from the exo face as determined by an X-ray crystallographic study of the acetylide addition product **24e**.

Interestingly, the addition of butylmagnesium (or hexylmagnesium) bromide failed to produce the desired tertiary *endo*-alcohol, but instead the secondary *endo*-alcohol **24a** was obtained exclusively. This most likely occurs through a β-hydride transfer from the alkyl Grignard reagent[18] (Scheme 11). A similar reaction was observed with **9c**; again the *endo*-alcohol was obtained exclusively.

To circumvent this facile reduction, we turned to the corresponding cerate derivatives,[19] which have been shown to be less prone to β-hydride reduction. Unfortunately, the addition of the cerate derived from butylmagnesium bromide led only to the alcohol **24a**. With the successful results of the 1,2-addition process, we next examined the addition of organocuprates to the dibromoenone **8a** (Table 4).

Addition of 1 equiv of the Gilman cuprates, derived from methyl-, butyl-, and phenyllithium, effected the clean conversion to the β-substituted enones **25a**−**c** through an addition−elimination sequence. It was also possible to employ 2 equiv of the cuprate to effect the sequential addition of the two methyl groups to the β position of the enone to produce **26** as an approximate 1:1 mixture of *endo*- and *exo*-bromides,[20] resulting from a nonselective protonation of the enolate.

Conclusions

The addition of perhalocyclopropenes to cyclic dienes such as furan and cyclopentadiene provides a direct route to the highly functionalized bicyclo[3.2.1]octene derivatives. It has been shown that these systems can be functionalized through the addition of select nucleophiles to the perhalogenated bridge. The direct generation of cations with silver ion can be followed by the addition of water, alcohols, and activated aromatics. Silver-promoted hydrolysis of the primary adducts gives unusual dihaloenones, which can be substituted directly by the addition of organocopper and organomagnesium reagents. Current efforts are directed toward the preparation of these dihaloenones in homochiral form and their application to the synthesis of natural products containing highly functionalized seven-membered rings.

Experimental Section

2,3,4,4-Tetrabromo-1,5-dimethyl-8-oxabicyclo[3.2.1]octa-2,6-diene (8b). The compound was prepared by refluxing 2,5-dimethylfuran (1.62 g, 0.017 mol) with tetrabromocyclopropene (5.0 g, 0.014 mol) in benzene for 10 h. Benzene was removed under reduced pressure, and the crude brown oil was purified by chromatography on a silica gel column using 10% ethyl acetate in hexane. The product was obtained as a crystalline solid, 5.3 g (81%). Mp: 65−69 °C. ^{1}H NMR (300 MHz, $CDCl_3$)

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δ: 6.50 (d, J = 5.5 Hz, 1H), 6.25 (d, J = 5.5 Hz, 1H), 1.93 (s, 3H), 1.68 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 141.10, 135.5, 133.1, 128.5, 93.2, 89.5, 71.1, 23.9, 22.1. IR (NaCl) ν: 2985, 2935, 1564, 1444, 1377, 1306, 1159, 1090, 942, 869, 758, 726, and 714 cm^{-1}. An analytically pure sample was obtained by sublimation. Anal. Calcd for $C_9H_8Br_4O$: C, 23.93; H, 1.78. Found: C, 24.35; H, 1.75.

General Procedure for the Hydrolysis of the Tetrabromo Adducts (Method A). The 2,3,4,4-tetrabromodienes (**8a**−**c**) were dissolved in 10 mL of 50% aqueous acetone. The resulting solution was then treated with 2.1 equiv of silver nitrate, and the resulting mixture was stirred at room temperature. The mixture turns cloudy over a period of 45 min to 1 h. The reaction was monitored by TLC until all of the starting tetrabromide was consumed. The reaction mixture was then treated with sufficient solid sodium bicarbonate (added in portions) to quench the nitric acid. The mixture was then filtered through Celite to remove the insoluble silver salts and concentrated to remove the acetone. The resulting aqueous layer was then extracted three times with 10 mL of ethyl acetate. The organic layer was washed with water and concentrated to dryness. The product was purified further by column chromatography on silica, using 5% ethyl acetate in hexanes to obtain the corresponding ketones.

3,4-Dibromo-8-oxabicyclo[3.2.1]octa-3,6-dien-2-one (9a). A total of 200 mg of **8a** upon hydrolysis and workup yielded 112 mg of **9a** (83%) as pale yellow crystals. Mp: 86−87 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.02 (dd, J = 5.7 Hz, 1.7H), 6.58 (dd, J = 5.7, 2.0 Hz, 1H), 5.39 (d, J = 1.7 Hz, 1H), 5.17 (d, J = 2.0 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 183.8, 149.4, 138.9, 131.5, 120.3, 87.1, 86.9. IR (NaCl) ν: 3096, 2983, 1704 (very strong), 1558, 1181, 1038, 927, 762, 695, 629, and 550 cm^{-1}. HRMS (EI): M^+ calcd for $C_7H_4Br_2O_2$, 278.8656; found 278.8701. An analytically pure sample was obtained by sublimation. Anal. Calcd for $C_7H_4Br_2O_2$: C, 30.04; H, 1.44. Found: C, 30.07; H, 1.32.

3,4-Dibromo-1, 5-dimethyl-8-oxabicyclo[3.2.1]octa-3,6-dien-2-one (9b). A total of 350 mg of **8b** upon hydrolysis with 290 mg of silver nitrate, followed by workup and column chromatography on silica gel, using 5% ethyl acetate in hexanes gave 201 mg (85%) of **9b** as a colorless semisolid, which slowly crystallized upon standing. Mp: 57−58 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 6.70 (d, J = 5.4 Hz, 1H), 6.20 (d, J = 5.4 Hz, 1H), 1.80 (s, 3H), 1.60 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 186.2, 154.5, 142.5, 135.3, 120.9, 93.0, 91.7, 23.0, 17.9. IR (NaCl) ν: 2987, 2936, 1708 (very strong), 1551, 1376, 1182, 1164, 1120, 942, 878, and 730 cm^{-1}. HRMS (EI): M^+ calcd for $C_9H_8Br_2O_2$, 226.9707; found, 226.9719. An analytically pure sample was obtained by sublimation. Anal. Calcd for $C_9H_8Br_2O_2$: C, 35.10; H, 2.62. Found: C, 35.14; H, 2.62.

3,4-Dibromobicyclo[3.2.1]octa-3,6-dien-2-one (9c). A total of 0.5 g of **8c** upon hydrolysis, workup, and column chromatography on silica gel, using 5% ethyl acetate, gave 300 mg (90%) of **9c** as a white crystalline solid. Mp: 74−75 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 6.84 (dd, J = 4.9, 2.9 Hz, 1H), 6.32 (dd, J = 4.9, 3.6 Hz, 1H), 3.80 (dd, J = 4.7, 3.6 Hz, 1H), 3.65 (m, 1H), 2.72 (d, J = 10.8 Hz, 1H), 2.46 (ddd, J = 10.8, 4.8, 4.7 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 188.5, 153.5, 141.7, 133.6, 121.4, 56.0, 55.5, 50.3. IR (NaCl) ν: 2973, 2945, 1694 (very strong), 1557, 1237, 1212, 1127, 1033, 924, 766, and 708 cm^{-1}. HRMS (EI): M^+ calcd for $C_8H_6Br_2O$, 275.8785; found, 275.8787. An analytically pure sample was obtained by sublimation. Anal. Calcd for $C_8H_6Br_2O$: C, 34.57; H, 2.18. Found: C, 34.68; H, 2.07.

General Procedure for Hydrolysis of the Tetrachloro Adducts (Method B). The hydrolysis of the tetrachloro adducts (**8d**−**e**) (200 mg) was carried out in 10 mL of 50% aqueous dioxane using 1 equiv of silver nitrate and 1 equiv of silver oxide. The reaction mixture was heated to a gentle reflux and monitored by TLC until all of the starting material was consumed. The solid silver salts were removed by filtration through Celite. The dioxane layer was diluted with 20 mL of water and extracted three times with 10 mL of ethyl acetate. The resulting organic layer was dried over anhydrous sodium sulfate and concentrated to dryness. The crude ketone was further purified by column chromatography over silica gel using 5−10% ethyl acetate in hexanes.

3,4-Dichloro-8-oxabicyclo[3.2.1]octa-3,6-dien-2-one (9d).[21] A total of 200 mg of **8d** was dissolved in 10 mL of 50% aqueous dioxane, and the resulting solution was heated to 90 °C with 0.139 g of silver nitrate and 0.202 g of silver oxide. The reaction mixture was worked up as described above to yield 130 mg (84%) of **9d** as a colorless crystalline solid. Mp: 75−76 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.00 (dd, J = 1.9, 5.7 Hz, 1H), 6.60 (dd, J = 2.4, 5.7 Hz, 1H), 5.30 (d, J = 1.9 Hz, 1H), 5.16 (d, J = 1.9 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 184.5, 153.6, 138.8, 131.7, 123.9, 87.1, 85.1. IR (NaCl) ν: 3098, 1713, 1575, 1197, 1059, 928, 885, 771, 702, and 640 cm^{-1}.

3,4-Dichlorobicyclo[3.2.1]octa-3,6-dien-2-one (9e). A total of 200 mg of **8e** was dissolved in 10 mL of 50% aqueous dioxane, and the resulting solution was heated to 90 °C with 0.139 g of silver nitrate and 0.202 g of silver oxide. The reaction mixture was worked up as described above to yield 132 mg (86%) of **9e** as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 6.82 (dd, J = 5.2, 3.0 Hz, 1H), 6.31 (dd, J = 5.2, 3.3 Hz, 1H), 3.63 (m, 2H), 1.08 (m, 1H), 2.5 (ddd, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 189.1, 157.7, 141.6, 133.8, 124.5, 56.3, 52.7, 50.1. IR (film on NaCl plate) ν: 1699, 1572, 1226, 1135, and 770 cm^{-1}. Anal. Calcd for $C_8H_6Cl_2O$: C, 50.83; H, 3.20. Found: C, 50.91; H, 3.28.

Typical Experimental Procedure for the Preparation of Ketals of the Oxabicyclo Systems Using Silver Tetrafluoroborate (Method C). In a glovebox, silver tetrafluoroborate (2 equiv) was weighed and transferred into a 10 mL round-bottom flask containing a magnetic stir bar. The flask was then charged with dry ethylene glycol (2 equiv). The reaction mixture was cooled to −78 °C. In a dry vial, 1 equiv of **8a** was dissolved in about 1.5 mL of dry methylene chloride. The solution of **8a** was then added dropwise with stirring into the flask containing silver tetrafluoroborate and ethylene glycol. The reaction mixture was stirred and allowed to warm to room temperature. The reaction mixture was stirred at room temperature for 10 min and monitored by TLC. Upon complete consumption of the starting material, the reaction mixture was diluted with 10 mL of methylene chloride and quenched with 5 mL of saturated sodium bicarbonate. The silver bromide was filtered through a sintered glass filter. The organic layer was washed with water, dried over anhydrous sodium sulfate, and concentrated to remove the solvent. The residue was subjected to column chromatography using 15% ethyl acetate and 5% triethylamine in hexanes or alternatively passed through a plug of basic alumina.

Spiro[3,4-Dibromo-8-oxabicyclo[3.2.1]octa-3,6-diene-2,2′-dioxolane] (10a). A total of 100 mg of **8a** was dissolved in about 1.5 mL of dry methylene chloride, and the resulting solution was added dropwise to a mixture of 59 mg of dry ethylene glycol and 91.8 mg of silver tetrafluoroborate in about 1.0 mL of dry dichloromethane. The reaction was worked up as given in the typical procedure to obtain 65.5 mg (86%) of **10a**, obtained as a colorless semisolid, which crystallizes over a period of time. Mp: 106−108 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 6.92 (dd, J = 5.9, 1.3 Hz, 1H), 6.34, (dd, J = 5.9, 1.3 Hz, 1H), 4.98 (d, J = 1.3 Hz, 1H), 4.82 (d, J = 1.3 Hz, 1H), 4.40−4.00 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 140.2, 133.6, 131.3, 123.0, 104.7, 84.6, 84.5, 67.2, 65.5. IR (NaCl) ν: 2900, 2895, 1290, 1152, 1067, 1009, 949, 927, and 720 cm^{-1}. HRMS (CI): $M^+ + H$ calcd for $C_9H_8Br_{81}BrO_3$, 324.8947; found, 324.8923. An analytical sample was obtained by recrystallizing the compound from 20% ether in pentanes. Anal. Calcd for $C_9H_8Br_2O_3$: C, 33.37; H, 2.49. Found: C, 33.37; H, 2.49.

Spiro[3,4-dibromo-1,5-dimethyl-8-oxabicyclo[3.2.1]octa-3,6-diene-2,2′-dioxolane] (10b). Reaction of 100 mg of **8b**

(21) Previously reported by Seitz, G.; Van Gammern, R. *Arch. Pharmacol.* **1987**, *320*, 1138.

with 95 mg of silver tetrafluoroborate and 55 mg of ethylene glycol, followed by workup and column chromatography, yields 68 mg (87%) of **10b** as a semisolid. ^{1}H NMR (300 MHz, C_6D_6) δ: 6.14 (d, J = 5.6 Hz, 1H), 5.88 (d, J = 5.6 Hz, 1H), 3.95−3.34 (m, 4H), 1.46 (s, 3H), 1.36 (s, 3H). ^{13}C NMR (75 MHz, C_6D_6) δ: 143.1, 138.5, 136.3, 126.8, 108.2, 91.3, 89.8, 67.24, 67.15, 22.7, 17.9. IR (NaCl) ν: 2983, 2936, 2900, 1587, 1447, 1380, 1205, 1162, 1141, 1118, 1045, 1005, 952, 878, and 734 cm^{-1}. HRMS (CI): $M^+ + H$ calcd for $C_{11}H_{12}Br_2O_3$, 350.9231; found, 350.9194. Anal. Calcd for $C_{11}H_{12}Br_2O_3$: C, 37.53; H, 3.44. Found: C, 37.91; H, 3.35.

Spiro[3,4-dibromobicyclo[3.2.1]octa-3,6-diene-2,2′-dioxolane] (10c). Reaction of 100 mg of **8c** with 101 mg of silver tetrafluororate and 59 mg of dry ethylene glycol after workup and purification afforded 63 mg (82%) of **10c** as a colorless oil. ^{1}H NMR (300 MHz, C_6D_6) δ: 6.33 (dd, J = 5.4, 2.8 Hz, 1H), 5.92 (dd, J = 5.3, 3.0 Hz, 1H), 3.90−3.30 (m, 4H), 2.93 (m, 1H), 2.65 (m, 1H), 2.25 (d, J = 10.6 Hz, 1H), 1.65 (m, 1H). ^{13}C NMR (75 MHz, C_6D_6) δ: 142.5, 136.5, 134.0, 125.1, 109.1, 66.9, 65.6, 52.8, 50.9, 44.8. IR (NaCl) ν: 2950, 2891.5, 1596.5, 1450.4, 1303.3, 1206.1, 1142.6, 1120.0, 1034.0, 1015.4, 964.1, 948.3, 922.1, and 737.5 cm^{-1}. HRMS (EI): M^+ calcd for $C_{10}H_{10}Br_2O_2$, 319.9047; found, 319.9055. Anal. Calcd for $C_{10}H_{10}Br_2O_2$: C, 37.30; H, 3.13. C, 37.63; H, 3.03.

General Experimental Procedure for the Arylation of the Oxabicyclo Systems Using Silver Tetrafluoroborate. In a glovebox, 184 mg (0.94 mmol) of dry silver tetrafluoroborate and 217.4 mg (0.94 mmol) of dry silver oxide were weighed and transferred into a 10 mL round-bottom flask containing a magnetic stir bar. This flask was then taken out of the glovebox and kept under an argon atmosphere. The contents of this flask was then charged with about 1 mL of dry methylene chloride, 1 mL of dry nitromethane, and 1.88 mmol of the desired aromatic compound. The contents of the flask was then cooled to −78 °C. In a dry vial, 200 mg (0.47 mmol) of 2,3,4,4-tetrabromo-8-oxabicyclo[3.2.1]octa-2,6-diene (**8a**) was dissolved in 1.5 mL of dry methylene chloride. This solution was then added dropwise over a period of about 5−10 min to the stirring mixture of silver tetrafluoroborate and silver oxide in the flask. The contents of the flask was kept at −78 °C, stirred for another 1 h, and checked by TLC to confirm the completion of the reaction. After all of the starting material was consumed, the reaction mixture was quenched with 5 mL of a sodium bicarbonate solution and extracted three times with 15 mL of ethyl acetate. The organic layer was washed with water, dried over anhydrous sodium sulfate, and concentrated to dryness. The residual organic material was subjected to column chromatography over silica gel using a gradient of hexanes to 5% ethyl acetate in hexanes.

3,4-Dibromo-2-(4-methoxyphenyl)-8-oxabicyclo[3.2.1]-octa-3,6-dien-2-ol (11a). Reaction of 200 mg of **8a** with anisole affords, after workup and column chromatography with 5% ethyl acetate in hexanes, 126 mg (87%) of **11a** as colorless crystals. Mp: 109−111 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.18 (d, J = 8.4 Hz, 2H), 6.88 (d, J = 8.4 Hz, 2H), 6.82 (dd, J = 6.2, 1.2 Hz, 1H), 5.80 (dd, J = 6.2, 1.2 Hz, 1H), 5.00 (d, J = 1.2 Hz, 1H), 4.89 (d, J = 1.2 Hz, 1H), 3.80 (s, 3H), 3.20 (br s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 159.7, 137.8, 131.1, 130.9, 129.2, 127.8, 113.8, 111.5, 88.7, 84.5, 78.8, 55.5. IR (NaCl) ν: 3446 (br), 2958, 1512, 1301, 1249, 1174, 1032, 907, 835, 734, and 714 cm^{-1}. HRMS: M^+ calcd for $C_{14}H_{12}{}^{81}BrBrO_3$, 387.91343; found, 387.9133. An analytically pure sample was obtained by recrystallizing the compound from 10% ethyl acetate in hexanes. Anal. Calcd for $C_{14}H_{12}Br_2O_3$: C, 43.33; H, 3.12. Found: C, 43.09; H, 3.08.

3,4-Dibromo-2-(3,4-dimethoxyphenyl)-8-oxabicyclo-[3.2.1]octa-3,6-dien-2-ol (11b). A total of 200 mg of **8a** upon reaction with veratrole, followed by workup and column chromatography on silica gel with 5% ethyl acetate in hexanes, afforded 135 mg (75%) of **11b** as pale cream crystals. Mp: 139−140 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 6.90−6.68 (m, 4H), 5.83 (dd, J = 5.8, 1.75 Hz, 1H), 5.02 (d, J = 1.7 Hz, 1H), 4.90 (d, J = 1.7 Hz, 1H), 3.90 (s, 6H), 3.31 (br s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 149.0, 137.6, 131.2, 130.9, 129.5, 128.2, 119.1, 110.9, 109.7, 88.7, 84.5, 78.8, 56.2, 56.1. IR (NaCl) ν: 3446 (br), 2958, 2935, 1601, 1515, 1463, 1415, 1261, 1142, 1029, 918, 860, and 730 cm^{-1}. HRMS: calcd M^+ for $C_{15}H_{14}Br_2O_4$, 415.9259; found, 415.9278. An analytically pure sample was obtained by recrystalizing the compound from 10% ethyl acetate in hexanes. Anal. Calcd for $C_{15}H_{14}Br_2O_4$: C, 43.09; H, 3.38. Found: C, 43.24; H, 3.39.

3,4-Dibromo-2-(4-methoxy-3-methylphenyl)-8-oxabicyclo[3.2.1]octa-3,6-dien-2-ol (11c). A total of 200 mg of **8a** affords, after reaction with 2-methylanisole and purification by column chromatography on silica gel with 5% ethyl acetate, 133 mg (70%) of **11c**. Mp: 115−117 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.04 (s, 1H), 7.02 (d, J = 8.5 Hz, 1H), 6.82 (dd, J = 6.0, 1.7 Hz, 1H), 6.78 (d, J = 8.5 Hz, 1H), 5.83 (dd, J = 6, 1.7 Hz, 1H), 5.05 (d, J = 1.7 Hz, 1H), 4.88 (d, J = 1.7 Hz, 1H), 3.82 (s, 3 H), 3.20 (br s, 1H), 2.22 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 157.8, 137.7, 131.2, 131.0, 128.7, 128.6, 126.8, 125.2, 109.6, 88.7, 84.5, 78.8, 55.5, 16.7. IR (NaCl) ν: 3436, 2956, 2835, 1503, 1251, 1132, 1032, 920, and 734 cm^{-1}. HRMS: exact M^+ calcd for $C_{15}H_{15}Br_2O_3$, 399.9309; found, 399.9356. An analytically pure sample was obtained by recrystallizing the compound from 10% ethyl acetate in hexanes. Anal. Calcd for $C_{15}H_{15}Br_2O_3$: C, 44.81; H, 3.51. Found: C, 44.54; H, 3.50.

3,4-Dibromo-2-(4-ethoxyphenyl)-8-oxabicyclo[3.2.1]octa-3,6-dien-2-ol (11d). A total of 200 mg of **8a** upon arylation with anethole and column chromatography produced 156 mg (82%) of **11d** as a colorless semisolid. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.17 (d, J = 8.8 Hz, 2H), 6.87 (d, J = 8.8 Hz, 2H), 6.84 (dd, J = 1.9, 5.9 Hz, 1H), 5.82 (dd, J = 2.1, 5.9 Hz, 1H), 5.04 (d, J = 1.9 Hz), 4.90 (d, J = 2.1 Hz, 1H), 4.08 (q, J = 7.1 Hz, 2H), 3.20 (br s, 1H), 1.42 (t, J = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 159.1, 137.8, 131.0, 130.9, 129.0, 128.5, 127.8, 114.3, 88.7, 84.5, 78.8, 63.6, 15.0. IR (NaCl) ν: 3440, 2978, 1610, 1511, 1247, 1047, 907, 734, and 601 cm^{-1}. Anal. Calcd for $C_{15}H_{14}Br_2O_3$: C, 44.81; H, 3.61. Found: C, 45.05; H, 3.61.

3,4-Dibromo-2-(2,3,4-trimethoxyphenyl)-8-oxabicyclo-[3.2.1]octa-3,6-dien-2-ol (11e). A total of 200 mg of **8a** upon reaction, followed by workup and column chromatography with 5% ethyl acetate, afforded 155.5 mg (73%) of **11e** as pale cream crystals. Mp: 112−114 °C. (Note: The compound exhibits restricted rotation at the bond connecting the aryl and bicyclic ring system and as a result shows broad peaks at room temperature, and therefore the NMR data is reported for the major rotamer at an elevated temperature.) ^{1}H NMR (300 MHz, DMSO-*d*, 115 °C) δ: 6.92 (d, J = 9 Hz, 1H), 6.64−6.76 (m, 3H), 5.74 (d, J = 5.4 Hz, 1H), 5.00 (s, 1H), 4.88 (s, 1H), 3.82 (s, 3H), 3.80 (s, 3H), 3.72 (s, 3H). ^{13}C NMR (75 MHz, DMSO-*d*, 115 °C) δ: 153.0, 150.7, 135.3, 130.9, 130.7, 128.4, 123.4, 122.2, 106.7, 87.3, 83.0, 76.9, 60.3, 59.6, 55.5. IR (NaCl) ν: 3449 (br), 2942, 2838, 1599, 1494, 1464, 1413, 1298, 1278, 1234, 1101, 1049, 923, and 730 cm^{-1}. HRMS: an exact M^+ calcd for $C_{16}H_{16}Br_2O_5$, 445.9364; found, 445.9366. An analytically pure sample was obtained by recrystallizing the compound from 20% ether in pentanes. Anal. Calcd for $C_{16}H_{16}Br_2O_5$: C, 42.89; H, 3.60. Found: C, 43.17; H, 3.61.

3,4-Dibromo-2-(3-Bromo-4-methoxyphenyl)-8-oxabicyclo[3.2.1]octa-3,6-dien-2-ol (11f). A total of 200 mg of **8a** upon arylation with *o*-bromoanisole produced 176 mg (80%) of **11f** as a colorless amorphous solid. Mp: 90−92 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.56 (d, J = 1.9 Hz, 1H), 7.15 (dd, J = 1.9, 8.5 Hz, 1H), 6.86 (m, 2H), 5.85 (dd, J = 2.0, 5.8 Hz, 1H), 5.05 (d, J = 1.9 Hz, 1H), 4.88 (d, J = 2.1 Hz, 1H), 3.90 (s, 3H), 3.36 (br s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 155.9, 138.3, 131.6, 131.5, 130.7, 130.6, 127.7, 127.0, 111.8, 111.6, 88.6, 84.5, 56.5. IR (NaCl) ν: 3431, 2963, 1600, 1497, 1256, 1055, 912, and 731 cm^{-1}. An analytically pure sample was obtained by recrystallizing the compound from 20% ether in pentanes. Anal. Calcd for $C_{14}H_{11}Br_3O_3$: C, 36.02; H, 2.37. Found: C, 36.28; H, 2.38.

3,4-Dibromo-2-(3-iodo-4-methoxyphenyl)-8-oxabicyclo-[3.2.1]octa-3,6-dien-2-ol (11g). A total of 200 mg of **8a** upon arylation with *o*-iodoanisole produced 77 mg (32%) of **11g** as a colorless amorphous solid. The hydrolysis compound **9a** was also isolated 85 mg (65%) during column chromatography. Mp: 164−165 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.75 (s, 1H), 7.14 (d, J = 8.6 Hz, 1H), 6.86 (d, J = 5.7 Hz, 1H), 6.78 (d, J = 8.6 Hz, 1H), 5.85 (dd, J = 5.7, 1.6 Hz, 1H), 5.05 (d, J = 1.6 Hz, 1H), 4.88 (s, 1H), 3.90 (s, 3H), 3.28 (br s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 158.2, 138.3, 137.52, 131.6, 131.2, 130.6, 130.2, 128.1, 127.7, 110.5, 88.6, 86.0, 84.5, 56.6. IR (NaCl) ν: 3430 (br), 2961, 1598, 1556, 1490, 1253, 1050, 913, 730, and 667 cm^{-1}. An analytically pure sample was obtained by recrystallizing the compound from 20% ether in pentanes. Anal. Calcd for $C_{14}H_{11}Br_2IO_3$: C, 32.72; H, 2.16. Found: C, 32.94; H, 2.27.

3,4-Dichloro-2-(4-methoxyphenyl)-8-oxabicyclo[3.2.1]-octa-3,6-dien-2-ol (11h). A total of 200 mg of **8d** upon arylation with anisole, followed by workup and column chromatography, afforded 157 mg (68%) of **11h** as a colorless amorphous solid. Mp: 130−132 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.18 (d, J = 8.7 Hz, 2H), 6.88 (d, J = 8.7 Hz, 2H), 6.78 (dd, J = 5.8, 1.5 Hz, 1H), 5.80 (dd, J = 5.8, 2 Hz, 1H), 4.94 (d, J = 1.5 Hz, 1H), 4.85 (d, J = 2 Hz, 1H), 3.80 (s, 3H), 3.40 (br s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 159.6, 137.8, 136.9, 130.9, 128.2, 127.9, 121.2, 113.9, 89.2, 82.4, 82.1, 55.4. IR (NaCl) ν: 3449 (br), 2961, 2837, 1611, 1513, 1250, 1176.5, 1041, 910, 760, 735, 719, 649, and 630 cm^{-1}. HRMS (EI): an exact mass calcd for $C_{14}H_{12}Cl_2O_3$, 298.0163; found, 298.0110. An analytically pure sample was obtained by recrystallizing the compound from 20% ethyl acetate in hexanes. Anal. Calcd for $C_{14}H_{12}Cl_2O_3$: C, 56.21; H, 4.04. Found: C, 56.14; H, 4.05.

3,4-Dichloro-2-(3,4-dimethoxyphenyl)-8-oxabicyclo[3.2.1]-octa-3,6-dien-2-ol (11i). A total of 200 mg of **8d** upon arylation with veratrole, followed by workup and column chromatography, afforded 172 mg (64%) of **11i** as a colorless amorphous solid. Mp: 151−152 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 6.90 (d, J = 1.7 Hz, 1H), 6.83 (d, J = 8.2 Hz, 1H), 6.77 (dd, J = 6.0, 1.5 Hz, 1H), 6.71 (dd, J = 8.2, 1.7 Hz, 1H), 5.82 (dd, J = 6, 2 Hz, 1H), 4.95 (d, J = 1.5, 1H), 4.87 (d, J = 2 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 149.0, 137.7, 137.0, 130.9, 130.6, 128.5, 119.2, 110.9, 109.8, 89.18, 82.5, 56.1, 56.0. IR (NaCl) ν: 3452 (br), 2959, 2935, 2837, 1611, 1514, 1416, 1236, 1144, 1028, 877, 758, and 734 cm^{-1}. HRMS (EI): an exact mass calcd for $C_{15}H_{14}Cl_2O_4$, 328.0269; found, 328.0278. An analytically pure sample was obtained by recrystallizing the compound from 20% ethyl acetate in hexanes. Anal. Calcd for $C_{15}H_{14}Cl_2O_4$: C, 54.73; H, 4.29. Found: C, 54.94; H, 4.27.

3-Bromo-4-thiophen-2-yl-8-oxabicyclo[3.2.1]octa-3,6-dien-2-one (16a). A total of 200 mg of **8a** upon arylation with thiophene produced 105 mg (79%) of **16a** as a pale brown semisolid. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.76 (d, J = 5.2 Hz, 1H), 7.72 (d, J = 3.8 Hz, 1H), 7.26 (dd, J = 5.0, 3.8 Hz, 1H), 6.94 (dd, J = 5.5, 1.4 Hz, 1H), 6.60 (dd, J = 5.5, 2 Hz, 1H), 5.88 (d, J = 1.7 Hz, 1H), 5.22 (d, J = 2 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 185.7, 151.8, 138.8, 136.3, 132.9, 131.6, 131.4, 128.0, 112.1, 86.7, 84.0. IR (NaCl) ν: 3100, 1689 (very strong), 1544, 1416, 1254, 1175, 1068, 935, 715, 699. HRMS (EI): an exact M$^+$ calcd for $C_{11}H_7BrO_2S$, 281.9350; found, 281.9353.

3-Bromo-4-(4-methoxyphenyl)bicyclo[3.2.1]octa-3,6-dien-2-one (16b). A total of 200 mg of **8c** upon arylation with anisole, followed by workup and column chromatography, afforded 110 mg (77%) of **16b** as a colorless amorphous solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.45 (d, J = 8.7 Hz, 2H), 6.96 (d, J = 8.7 Hz, 2H), 6.80 (m, 1H), 6.32 (m 1H), 3.86 (s, 3H), 3.66 (m, 2H), 2.72 (d, J = 10.3 Hz, 1H), 2.48−2.58 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 191.2, 163.9, 160.5, 142.9, 133.2, 131.0, 129.5, 115.6, 113.8, 56.2, 55.5, 51.7, 50.2. IR (NaCl) ν: 2966, 2838, 1683 (very strong), 1604, 1507, 1250, 1178, 1027, 832, 773, and 713 cm^{-1}. HRMS: an exact M$^+$ calcd for $C_{15}H_{13}BrO_2$, 304.0099; found, 304.0094. Anal. Calcd for $C_{15}H_{13}BrO_2$: C, 59.04; H, 4.29. Found: C, 58.90; H, 4.29.

3-Bromo-4-(3,4-dimethoxyphenyl)bicyclo[3.2.1]octa-3,6-dien-2-one (16c). A total of 200 mg of **8c** upon arylation with veratrole, followed by workup and column chromatography, afforded 107 mg (67%) of **17** as a colorless amorphous solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.06 (s, 1H), 7.04 (d, J = 8.8 Hz, 1H), 6.92 (d, J = 8.8 Hz, 1H), 6.82 (m, 1H), 6.34 (m, 1H), 3.94 (s, 3H), 3.92 (s, 3H), 3.70−3.64 (m, 2H), 2.74 (d, J = 10.3 Hz, 1H), 2.60−2.50 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 191.1, 163.9, 150.0, 148.5, 142.8, 133.2, 131.2, 120.9, 115.7, 111.4, 110.8, 56.2, 56.1, 51.7, 50.2. IR (NaCl) ν: 2993, 2837, 1683 (very strong), 1599, 1513, 1269, 1169, 1144, 1025, 915, 774, 731, and 714 cm^{-1}. HRMS: an exact M$^+$ calcd for $C_{16}H_{15}BrO_3$, 334.0205; found, 334.0210. Anal. Calcd for $C_{15}H_{13}BrO_2$: C, 57.33; H, 4.51. Found: C, 57.11; H, 4.48.

Acid-Catalyzed Hydrolysis of 11a to 16d. A total of 20 mg of **11a** was dissolved in about 0.5 mL of a mixture of 8:1:1 nitromethane/water/trifluoroacetic acid. The resulting mixture was refluxed until all of the starting material was converted to the product. The reaction mixture was cooled and neutralized with saturated aqueous sodium bicarbonate. The resulting mixture was extracted twice with 5 mL of ethyl acetate. The combined organic layers were washed with water, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The resulting residue was subjected to column chromatography on silica gel. The product **16d** (12 mg, 78%) was eluted with 10% ethyl acetate in hexanes as colorless crystals, which undergo slow decomposition. Mp: 122−123 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.50 (d, J = 8.8 Hz, 2H), 6.98 (d, J = 8.8 Hz, 2H), 6.92 (dd, J = 5.7, 1.6 Hz, 1H), 6.60 (dd, J = 5.7, 2.4 Hz, 1H), 5.49 (d, J = 1.6 Hz, 1H), 5.18 (d, J = 2.4 Hz, 1H), 3.86 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 186.4, 161.3, 160.5, 140.3, 131.1, 130.0, 126.6, 114.3, 113.7, 86.9, 85.1, 55.6. IR (NaCl) ν: 2974, 2839, 1694 (very strong), 1604, 1302, 1253, 1179, 1072, 929, 834, and 697 cm^{-1}. Anal. Calcd for $C_{14}H_{11}BrO_3$: C, 54.75; H, 3.61. Found: C, 54.55; H, 3.65.

2,3,4,4-Tetrabromo-1-methyl-8-oxabicyclo[3.2.1]octa-2,6-diene and 2,3,4,4-Tetrabromo-5-methyl-8-oxabicyclo-[3.2.1]octa-2,6-diene (21a,b). 2-Methylfuran (0.69 g, 8 mmol) was refluxed in about 2 mL of benzene with 1.5 g (4 mmol) of tetrabromocyclopropene. The solvent was removed under reduced pressure and subjected to column chromatography, using 5% ethyl acetate in hexanes, to elute 1.5 g (83%) of a mixture of the two compounds as a colorless semisolid. The spectral data of the major isomer are reported. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 6.76 (dd, J = 5.7, 1.9 Hz, 1H), 6.32 (d, J = 5.7 Hz, 1H), 5.00 (d, J = 1.9 Hz, 1H), 1.94 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 142.5, 137.8, 133.6, 130.4, 91.1, 85.1, 70.3, 23.5. IR (NaCl) ν: 2985, 1581, 1387, 1304, 1075, 752, and 718 cm^{-1}. HRMS: calcd for $C_8H_6Br_4O$, 433.7125; found, 433.7147. Anal. Calcd for $C_8H_6Br_4O$: C, 21.95; H, 1.38. Found: C, 22.16; H, 1.39.

3,4-Dibromo-5-methyl-8-oxabicyclo[3.2.1]octa-3,6-dien-2-one and 3,4-Dibromo-1-methyl-8-oxabicyclo[3.2.1]octa-3,6-dien-2-one (22a,b). A total of 0.2 g of the **21a**,**b** mixture upon hydrolysis, according to method A and followed by workup and column chromatography on silica gel using 10% ethyl acetate, gave 110 mg (81.5%) of a mixture of **22a**,**b** as a pale yellow oil. The spectra of the major compound are reported. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 6.75 (d, J = 5.7 Hz, 1H), 6.49 (dd, J = 2.4, 5.7 Hz, 1H), 5.19 (d, J = 2.4 Hz, 1H), 1.82 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 184.1, 154.3, 142.7, 131.0, 120.8, 91.7, 87.6, 22.7. IR (NaCl) ν: 2988, 1708 (very strong), 1546, 1186, 1083, 850, and 721 cm^{-1}. Anal. Calcd for $C_8H_6Br_2O_2$: C, 32.69; H, 2.06. Found: C, 32.93; H, 2.05.

3,4-Dibromo-2-(4-methoxyphenyl)-5-methyl-8-oxabicyclo[3.2.1]octa-3,6-dien-2-ol (23). Reaction of **21a**,**b** (250 mg) with anisole, as per the general procedure outlined for arylation, afforded, after workup and column chromatography with 5% ethyl acetate in hexanes, 195 mg (85%) of **23** as colorless crystals. Mp: 139−141 °C. (Note: Small amounts of the ortho-substitution product are observed in ^{1}H NMR.) ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.18 (d, J = 8.8 Hz, 2H), 6.88 (d,

J = 8.8 Hz, 2H), 6.56 (d, J = 5.7 Hz, 1H), 5.76 (dd, J = 5.7, 2.1 Hz, 1H), 4.88 (d, J = 2.1 Hz, 1H), 3.81 (s, 3H), 3.19 (s, 1H), 1.73 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 159.7, 141.7, 136.2, 130.4, 129.6, 129.4, 127.9, 113.8, 89.2, 88.5, 79.3, 55.4, 22.5. IR (NaCl) ν: 3442, 2955, 1512, 1250, 1175, 1060, 832, 737, and 623 cm^{-1}. HRMS: calcd for $C_{15}H_{14}Br_2O_3$, 399.9309; found, 399.9296. An analytical sample was obtained by recrystallizing the compound from 20% ether in pentanes. Anal. Calcd for $C_{15}H_{14}Br_2O_3$: C, 44.81; H, 3.51. Found: C, 44.61; H, 3.51.

General Experimental Procedure for the Luche Reduction of Bicyclic Enones (8a−c). The ketones (100 mg) were dissolved in a mixture of 0.2 mL of methylene chloride and 0.8 mL of methanol. The cerium chloride heptahydrate (0.5 equiv) was dissolved in 0.2 mL of water and added to the above solution. The solution was stirred at room temperature, and 1 equiv of sodium borohydride was added and stirred for 5 min. The reaction showed complete conversion of the starting materials to the corresponding products. The reaction mixture was diluted with 1 mL of water and extracted three times with 5 mL of ethyl acetate. The ethyl acetate layers were combined, dried over anhydrous sodium sulfate, and concentrated under reduced pressure to afford the crude product as a pale yellow oil. The compounds were purified by column chromatography on silica gel using 10−15% ethyl acetate in hexanes.

3,4-Dibromo-8-oxabicyclo[3.2.1]octa-3,6-dien-2-ol (24a). The ketone (**9a**, 100 mg) was treated as per the general procedure with 55.7 mg of cerium chloride heptahydrate and 13.5 mg of sodium borohydride. The reaction mixture, upon workup and purification, afforded by column chromatography 96 mg (95%) of **24a** as a colorless oil, which crystallizes upon standing. Mp: 102−103 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 6.90 (dd, J = 1.6, 5.9 Hz, 1H), 6.29 (dd, J = 1.91, 5.9 Hz, 1H), 5.24 (dd, J = 1.9, 5.9 Hz, 1H), 4.87 (d, J = 1.9 Hz, 1H), 4.63 (dd, J = 5.9, 5.7 Hz, 1H), 2.18 (d, J = 5.4 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 139.8, 130.5, 129.7, 124.8, 84.5, 81.8, 70.6. IR (NaCl) ν: 3389, 1601, 1407, 1296, 1090, 1043, 1002, 978, 943, 873, and 720 cm^{-1}. An analytically pure sample was obtained by recrystallizing the compound from 10% ethyl acetate in hexanes. Anal. Calcd for $C_7H_6Br_2O_2$: C, 29.82; H, 2.15. Found: C, 30.12; H, 2.09.

3,4-Dibromo-1,5-dimethyl-8-oxabicyclo[3.2.1]octa-3,6-dien-2-ol (24b). Treatment of 100 mg of **9b** afforded 97 mg (96%) of **24b** (mixture of *exo*- and *endo*-alcohols) as a colorless oil. The spectral data for the major compound are reported. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 6.54 (d, J = 5.7 Hz, 1H), 6.00 (d, J = 5.7 Hz, 1H), 4.24 (s, 1H), 2.44 (s, 1H), 1.61 (s, 3H), 1.60 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 142.5, 133.8, 134.6, 126.8, 88.8, 88.2, 76.5, 22.6, 22.1. IR (NaCl) ν: 3424 (br), 2978, 1590, 1449, 1373, 1296, 1173, 1072, 1049, 937, 879, and 737 cm^{-1}. Anal. Calcd for $C_9H_{10}Br_2O_2$: C, 34.87; H, 3.25. Found: C, 34.44; H, 3.12.

3,4-Dibromobicyclo[3.2.1]octa-3,6-dien-2-ol (24c). Treatment of 100 mg of **9b** afforded 98 mg (97%) of **24c** as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 6.69 (dd, J = 5.7, 2.8 Hz, 1H), 6.1 (dd, J = 5.7, 2.8 Hz, 1H), 4.48 (d, J = 5.4 Hz, 1H), 3.34−3.17 (m, 2H), 2.16−2.10 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 142.2, 133.0, 132.8, 124.8, 74.1, 51.9, 46.5, 44.1. IR (NaCl) ν: 3370, 2942, 2868, 1600, 1109, 1030, and 744 cm^{-1}. Anal. Calcd for $C_8H_8Br_2O$: C, 34.32; H, 2.88. Found: C, 34.56; H, 2.85.

General Experimental Procedure for the Addition of the Grignard Reagents to 3,4-Dibromo-8-oxabicyclo-[3.2.1]octa-3,6-dien-2-one (9a). A total of 100 mg of the dibromoenone **8a** (0.35 mmol) was dissolved in about 2 mL of dry THF. The resulting solution was cooled to 0 °C. The desired Grignard (1.2 equiv, 0.42 mmol) was added dropwise over a period of 5 min. The solution was stirred at 0 °C for about 5−10 min, and the TLC was checked for the completion of the reaction. The reaction mixture was quenched with aqueous sodium bicarbonate and extracted three times with 10 mL of ethyl acetate. The organic layer was dried over anhydrous sodium sulfate and concentrated to dryness. The resulting brown semisolid was purified by column chromatography to afford the 1,2-addition products as crystalline solids.

3,4-Dibromo-2-vinyl-8-oxabicyclo[3.2.1]octa-3,6-dien-2-ol (24d). Reaction of 100 mg of **9a** with 1.2 equiv of vinylmagnesium bromide as described in the general procedure, followed by workup and column chromatography, afforded 80 mg (73%) of the product as colorless crystals. Mp: 67−70 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 6.85 (dd, J = 5.9, 1.6 Hz, 1H), 6.26 (dd, J = 5.9, 2.1 Hz, 1H), 6.10 (m, 1H), 5.36 (m, 2H), 4.90 (d, J = 2.1 Hz, 1H), 4.84 (d, J = 1.7 Hz, 1H), 2.18 (br s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 140.4, 139.9, 131.1, 129.3, 126.8, 116.2, 85.9, 84.4, 76.5. IR (NaCl) ν: 3437 (br, s), 1602, 1035, 921, and 723 cm^{-1}. An analytically pure sample was obtained by recrystallizing the compound from 10% ethyl acetate in hexanes. Anal. Calcd for $C_9H_8Br_2O_2$: C, 35.10; H, 2.62. Found: C, 35.31; H, 2.51.

3,4-Dibromo-2-prop-1-ynyl-8-oxabicyclo[3.2.1]octa-3,6-dien-2-ol (24e). Reaction of 100 mg of **9a** with 1.2 equiv of propynylmagnesium bromide as described in the general procedure, followed by workup and column chromatography, afforded 105 mg (92%) of the product as colorless crystals. Mp: 149−150 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 6.82 (dd, J = 5.9, 1.6 Hz, 1H), 6.22 (dd, J = 5.9, 2.1 Hz, 1H), 5.19 (d, J = 2.1 Hz), 4.85 (d, J = 1.6 Hz), 2.50 (br s, 1H), 1.85 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 139.5, 130.5, 129.2, 125.7, 86.4, 84.4, 82.6, 79.6, 70.2, 4.0. IR (NaCl) ν: 3412, 2966, 2225, 1601, 1278, 1055, 1031, 926, and 732 cm^{-1}. An analytically pure sample was obtained by recrystallizing the compound from 10% ethyl acetate in hexanes. Anal. Calcd for $C_{10}H_8Br_2O_2$: C, 37.54; H, 2.52. Found: C, 37.73; H, 2.79.

3,4-Dibromo-2-phenyl-8-oxabicyclo[3.2.1]octa-3,6-dien-2-ol (24f). Reaction of 100 mg of **9a** with 1.2 equiv of phenylmagnesium bromide as described in the general procedure, followed by workup and column chromatography, afforded 103 mg (81%) of the product as colorless crystals. Mp: 99−100 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.61−7.30 (m, 5H), 6.87 (dd, J = 5.9, 1.7 Hz, 1H), 6.42 (dd, J = 5.9, 1.9 Hz, 1H), 5.00 (d, J = 1.6 Hz, 1H), 4.95 (d, J = 1.9 Hz, 1H), 2.51 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 143.5, 139.6, 131.8, 129.9, 128.7, 128.5, 127.0, 126.1, 87.6, 84.4, 78.5. IR (NaCl) ν: 3432, 3059, 1604, 1493, 1448, 1304, 1058, 1032, 920, 736, 721, and 699 cm^{-1}. An analytically pure sample was obtained by recrystallizing the compound from 20% diethyl ether in pentanes. Anal. Calcd for $C_{13}H_{10}Br_2O_2$: C, 43.61; H, 2.82. Found: C, 43.82; H, 2.72.

3,4-Dibromo-2-naphthalen-1-yl-8-oxabicyclo[3.2.1]octa-3,6-dien-2-ol (24g). Reaction of 100 mg of **9a** with 1.2 equiv of naphthylmagnesium bromide as described in the general procedure, followed by workup and column chromatography, afforded 130.0 mg (89%) of the product as colorless crystals. Mp: 202−204 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.81 (d. J = 3.1 Hz, 1H), 7.82−7.92 (m, 2H), 7.41−7.59 (m, 4H), 6.96 (dd, J = 5.9, 1.7 Hz, 1H), 6.58 (dd, J = 5.9, 1.9 Hz, 1H), 5.66 (d, J = 1.9 Hz, 1H), 4.96 (d, J = 1.7 Hz, 1H), 2.80−2.90 (br s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 139.3, 136.7, 135.3, 131.3, 130.8, 130.4, 130.2, 129.8, 128.5, 127.4, 126.4, 125.9, 125.7, 124.9, 85.9, 84.4, 81.7. IR (NaCl) ν: 3428, 3049, 1597, 1508, 1287, 1057, and 777 cm^{-1}. HRMS: calcd for $C_{17}H_{12}Br_2O_2$, 405.9204; found, 405.9293. An analytically pure sample was obtained by recrystallizing the compound from 10% ethyl acetate in hexanes. Anal. Calcd for $C_{17}H_{12}Br_2O_2$: C, 50.03; H, 2.96. Found: C, 50.27; H, 2.94.

3,4-Dibromo-2-thiophen-2-yl-8-oxabicyclo[3.2.1]octa-3,6-dien-2-ol (24h). A total of 100 mg of **9a** was treated with 1.2 equiv of thiophen-2-ylmagnesium bromide as described above. The resulting solution, upon workup and column chromatography, afforded 115 mg (88%) of the product as pale yellow crystals. Mp: 52−55 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.30 (dd, J = 4.9, 1.2 Hz, 1H), 7.15 (dd, J = 3.6, 1.9 Hz, 1H), 7.00 (dd, J = 4.9, 3.6 Hz, 1H), 6.95 (dd, J = 5.9, 1.6 Hz, 1H), 6.39 (dd, J = 5.9, 2.1 Hz, 1H), 5.13 (d, J = 2.1 Hz, 1H), 4.99

(d, J = 1.9 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 148.0, 140.0, 131.3, 130.4, 127.2, 126.8, 125.9, 125.5, 87.4, 84.4, 76.8. IR (NaCl) ν: 3412, 1603, 1304, 1233, 1104, 1037, 925, 737, and 712 cm^{-1}. HRMS: calcd for $C_{11}H_8O_2BrS$, 361.8611; found, 361.8612. Anal. Calcd for $C_{11}H_8O_2BrS$: C, 36.29; H, 2.21. Found: C, 36.38; H, 2.14.

General Experimental Procedure for the Addition of Cuprates to 3,4-Dibromo-8-oxabicyclo[3.2.1]octa-3,6-dien-2-one (9a). Purified CuI[22] (81.6 mg, 0.43 mmol) was suspended in dry diethyl ether and cooled to −78 °C. The desired alkyl- or aryllithium (0.79 mmol) was added dropwise over a period of 5 min. The resulting solution was warmed and kept at −10 °C for 30 min. The resulting cuprate was then cooled to −78 °C. The dibromoenone (100 mg, 0.35 mmol) was dissolved in about 2 mL of ether, and the resulting solution was added to the cuprate dropwise over a period of 5 min. The resulting solution was stirred at −78 °C and periodically monitored by TLC. Upon completion of the reaction, the solution was warmed to 0 °C and treated with 5 mL of saturated aqueous ammonium chloride. The solution was extracted three times with 10 mL of diethyl ether. The organic layer was dried over anhydrous sodium sulfate and concentrated to dryness. The resulting brown semisolid was purified by column chromatography over silica gel using 5−10% ethyl acetate and hexanes as the solvent.

3-Bromo-4-methyl-8-oxabicyclo[3.2.1]octa-3,6-dien-2-one (25a). A total of 100 mg of **9a** was treated with 1.1 equiv of Me_2CuLi as per the general procedure. The reaction was followed by workup and column-chromatographic purification to afford 65 mg (84%) of the product as a brown semisolid. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 6.92 (dd, J = 2.1, 5.7 Hz, 1H), 6.56 (dd, J = 2.1, 5.2 Hz, 1H), 5.16 (d, J = 2.1 Hz, 1H), 5.12 (d, J = 2.1 Hz, 1H), 2.12 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 185.8, 162.0, 139.4, 131.5, 115.5, 86.8, 84.3, 20.4. IR (NaCl) ν: 2980, 1707 (very strong), 1603, 1240, 1068, 929, 764, 692, and 625 cm^{-1}. HRMS: an exact M^+ calcd for $C_8H_7BrO_2$, 213.9629; found, 213.9619.

3-Bromo-4-butyl-8-oxabicyclo[3.2.1]octa-3,6-dien-2-one (25b). A total of 100 mg of **9a** was treated with 1.1 equiv of Bu_2CuLi as per the general procedure. The reaction was followed by workup and column-chromatographic purification to afford 80 mg (88%) of the product as a brown oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 6.85 (dd, J = 1.9, 5.7 Hz, 1H), 6.54 (dd, J = 2.4, 5.7 Hz, 1H), 5.18 (d, J = 1.9 Hz, 1H), 5.10 (d, J = 2.4 Hz, 1H), 2.56−2.36 (m, 2H), 1.62−1.36 (m, 4H), 0.97 (t, J = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 186.2, 165.3, 140.1, 131.2, 115.2, 83.9, 83.3, 34.3, 28.6, 22.8, 14.0. IR (NaCl) ν: 2959, 1705, 1594, and 1063 cm^{-1}. HRMS: an exact M^+ calcd for $C_{11}H_{13}BrO_2$, 256.0099; found, 256.0103. Anal. Calcd: C, 51.38; H, 5.10. Found: C, 51.49; H, 5.20.

3-Bromo-4-phenyl-8-oxabicyclo[3.2.1]octa-3,6-dien-2-one (25c). A total of 100 mg of **9a** was treated with 1.1 equiv of Ph_2CuLi as per the general procedure. The reaction was followed by workup and column-chromatographic purification to afford 77 mg (78%) of the product as a brown semisolid. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.45 (s, 5H), 6.96 (dd, J = 1.9, 5.7 Hz, 1H), 6.62 (dd, J = 2.4, 5.7 Hz, 1H), 5.46 (d, J = 1.9 Hz, 1H), 5.20 (d, J = 2.4 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 186.3, 161.1, 140.4, 134.7, 131.1, 130.3, 128.9, 127.9, 114.8, 86.9, 85.2. IR (NaCl) ν: 2979, 1699, 1585, 1186, 1072, and 697 cm^{-1}. HRMS: an exact M^+ calcd for $C_8H_7BrO_2$, 275.9786; found, 275.9762. An analytical sample was obtained by recrystallizing the compound from 20% ether in pentanes. Anal. Calcd: C, 56.34; H, 3.27. Found: C, 56.10; H, 3.19.

3-Bromo-4,4-dimethyl-8-oxabicyclo[3.2.1]oct-6-en-2-one (26). A total of 50 mg of **9a** was treated with 2.2 equiv of Me_2CuLi as per the general procedure, monitored by TLC, and worked up. The pale brown semisolids were subjected to column chromatography to afford 30 mg of **26** as a pale brown oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 6.60−6.48 (m, 2H), 4.94 (s, 1H), 4.76 (d, J = 1.9 Hz, 1H), 4.72 (d, J = 1.9 Hz, 1H), 1.35 (s, 3H), 1.08 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 194.2, 134.2, 132.7, 88.4, 85.6, 62.9, 25.4, 23.3. IR (NaCl) ν: 2982, 1710 (very strong), 1587, 1188, 1070, and 702 cm^{-1}. HRMS: an exact M^+ calcd for $C_9H_{10}BrO_2$, 229.9942; found, 299.9960.

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Supporting Information Available: Copies of ^{1}H and ^{13}C NMR spectra for compounds **16a**, **25a**, and **26** and crystallographic information files for compounds **11e**, **23**, and **24e**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(22) CuI was purified as per the procedure given by Dieter, K. R.; Silks, L. A., III; Fishpaugh, J. R.; Kastner, M. E. *J. Am. Chem. Soc.* **1985**, *107*, 4679.