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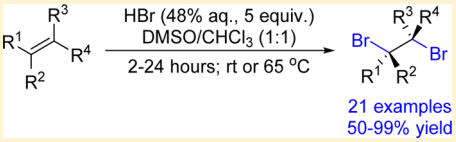
Bromination of Olefins with HBr and DMSO

Megha Karki and Jakob Magolan*

Department of Chemistry, University of Idaho, Moscow, Idaho 83844, United States

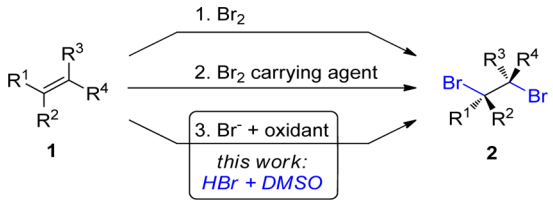
Supporting Information

ABSTRACT: A simple and inexpensive methodology is reported for the conversion of alkenes to 1,2-dibromo alkanes via oxidative bromination using HBr paired with dimethyl sulfoxide, which serves as the oxidant as well as cosolvent. The substrate scope includes 21 olefins brominated in good to excellent yields. Three of six styrene derivatives yielded bromohydrins under the reaction conditions.



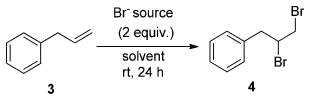
Vicinal dibromoalkanes (**2**) are useful synthetic precursors to cyclopropanes,[1] alkynes,[2] and vinyl bromides of value in cross-coupling chemistry.[2,3] Their various preparations from alkenes (**1**) can be classified into three general approaches: (1) treatment with molecular bromine in halogenated solvent[4] or alternative media,[5] (2) treatment with a bromine carrying agent such as a tribromide salt[6] or analogous reagent,[7] and (3) treatment with bromide in the presence of a stoichiometric oxidant such as Oxone,[8] H_2O_2,[9] O_2,[10] Selectfluor,[11] and others[12] (Scheme 1). The third of these strategies, oxidative bromination, is analogous to the biological solution to electrophilic halogenation which employs haloperoxidase (H_2O_2) or flavin-dependent halogenase (O_2) enzymes to produce X^+ from X^-.[13] In their 2008 comparative review of 24 methods, Eissen and Lenoir concluded that many modern bromination methods that circumvent the use of molecular bromine suffer from significantly higher resource demands and waste production compared to the traditional choice of Br_2 in $CHCl_3$.[14] The authors emphasize the need for continued development in this field and highlight oxidative bromination in general, and the use of H_2O_2/HBr specifically,[9c] as the most favorable of current methods based on a number of environmental, health, and safety factors.

Scheme 1. General Approaches to Bromination of Olefins



Herein we present our discovery of a simple oxidative bromination of olefins using HBr and dimethyl sulfoxide (DMSO). DMSO is a polar aprotic solvent widely used for synthetic applications at all scales.[15] In the presence of various activating reagents, DMSO is a mild oxidant that has been employed primarily for the oxidation of alcohols.[16] DMSO-based oxidations are metal-free, mild, and inexpensive. For these reasons, we are interested in expanding the use of this oxidant. In the present case we sought to test the potential applicability of DMSO in the context of oxidative bromination. We began by treating allylbenzene (**3**) with four bromide reagents in DMSO (Table 1).

Table 1. Reaction Discovery[a]



entry	Br^- source	solvent	yield[b] (%)
1	Bu_4NBr	DMSO	0
2	KBr	DMSO	0
3	NaBr	DMSO	0
4	HBr (48% aq)	DMSO	13
5	HBr (48% aq)	$CHCl_3$	0

[a]Reaction conditions: substrate (0.5 mmol), solvent (0.5 mL), "Br^- source" (2 equiv); reaction workup with Et_2O/H_2O. [b]NMR yield with CH_2Br_2 as internal standard.

Although no reaction occurred with Bu_4NBr, KBr, or NaBr in DMSO, we were pleased to observe that HBr yielded some of the desired 2,3-dibromopropylbenzene (**4**, entry 4). The reaction did not proceed when DMSO was replaced with chloroform (entry 5), in which case trace hydrobromination was observed but most of the substrate remained unreacted.

In previous literature, the pairing of HBr and DMSO has been used for the α oxidation of ketones,[17] bromination of arenes,[18] and benzylic oxidation.[19] In most cases, it was believed that HBr reacts with DMSO to yield bromodimethylsulfonium bromide (BDMS, **5**), a well-established electrophilic bromination reagent that is more commonly prepared from dimethyl sulfide and bromine.[20] BDMS is an orange solid that precipitates from dichloromethane solution upon addition of DMS and Br_2.[21] Most commonly, this reagent has been used to brominate various arenes and carbonyl derivatives.[20] In 2008, Das and co-workers reported bromination of olefins with

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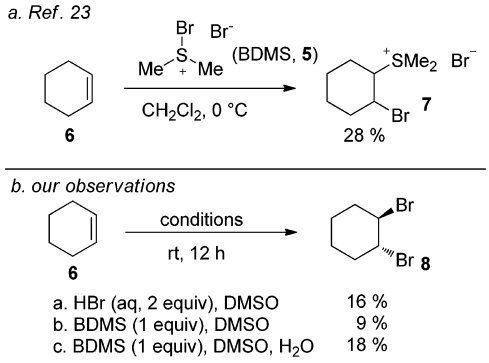
BDMS in acetonitrile.[22] Earlier, similar reaction conditions were employed by Chow and Bakker to form 1-bromo-2-sulfonium bromides, such as **7**, which precipitated in low yields upon treatment of olefins with BDMS in CH_2Cl_2 or CH_3CN at 0 °C (Scheme 2a).[23]

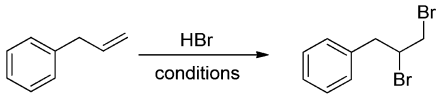
Scheme 2. Work of Chow and Bakker[23] and Our Comparison of HBr with BDMS



We directly compared the reactivity of HBr in DMSO to BDMS in DMSO using cyclohexene as the substrate (Scheme 2b). In neither case was precipitation of sulfonium salts observed but rather exclusive conversion to *trans*-1,2-dibromocyclohexane in low yields after 12 h at room temperature. Upon addition of water to the BDMS/DMSO reaction (intended to mimic the water present in our HBr/DMSO system) the rates of the two processes were similar to 18% and 16% yields, respectively, after 12 h at room temperature. These observations lend support to the notion that the active brominating species in the HBr/DMSO process is BDMS.

We conducted a brief optimization of this reaction (Table 2). The yield of (2,3-dibromopropyl)benzene (**4**) from allylbenzene was improved to 57% and 96% by increasing the amount of HBr to 5 and 10 equiv, respectively, and extending reaction time to 24 h (entries 2 and 3). When the reaction temperature was warmed to 65 °C, a yield of 86% was observed in just 12 h with 5 equiv of HBr (entry 4). A screen of cosolvents identified the two solvent mixtures of DMSO and $CHCl_3$ (1:1) as optimal giving nearly quantitative conversion, and 80% isolated yield, of the desired product after 12 h at 65 °C.

Table 2. Reaction Optimization[a]

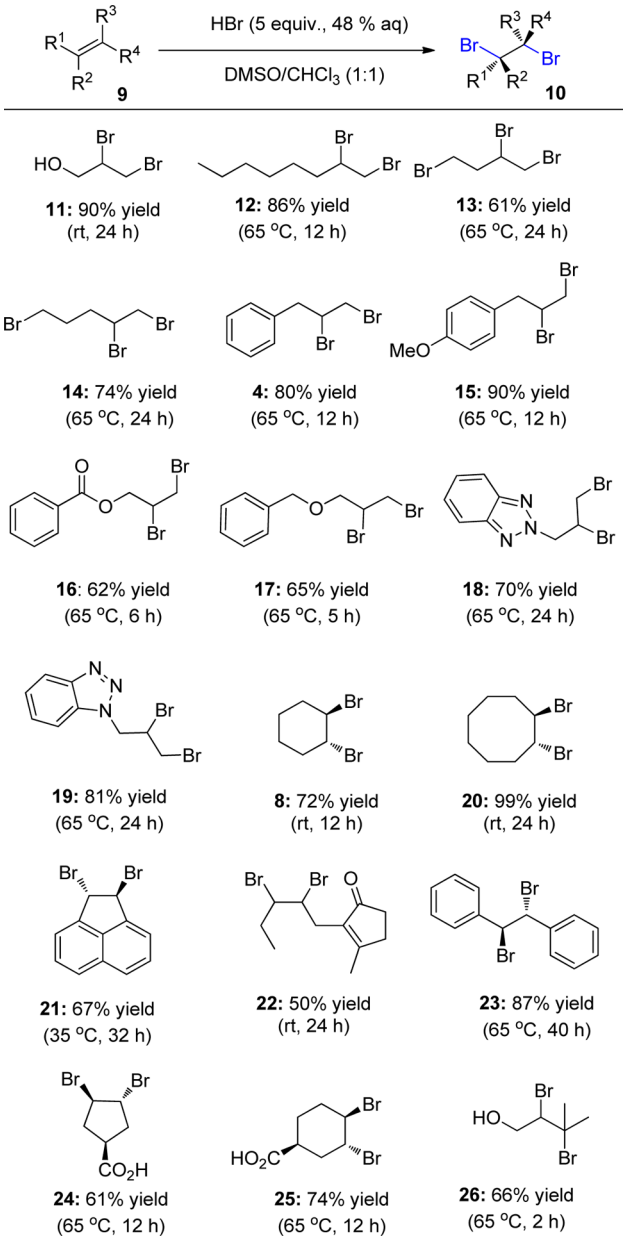


entry	solvent	HBr (equiv)	temp (°C)	time (h)	yield[b] (%)
1	DMSO	2	rt	24	13
2	DMSO	5	rt	24	57
3	DMSO	10	rt	24	96
4	DMSO	5	65	12	86
5	DMSO/$CHCl_3$[c]	5	65	12	98 (80)[d]

[a]Reaction conditions: substrate (0.5 mmol), solvent (0.5 mL). [b]NMR yield with CH_2Br_2 as internal standard. [c]DMSO (0.5 mL) and $CHCl_3$ (0.5 mL). [d]Isolated yield.

The substrate scope of this bromination was evaluated with 10 terminal olefins and 8 polysubstituted olefins (Table 3).

Table 3. Substrate Scope[a]



[a]Reaction conditions: alkene substrate (0.5−1.0 mmol), HBr (48% aq, 5 equiv), DMSO (1 mL per mmol of substrate), $CHCl_3$ (1 mL per mmol of substrate). Reported yields are for isolated products after chromatography.

Allyl alcohol was converted to 2,3-dibromopropan-1-ol (**11**) in 90% yield in 24 h at room temperature. 1-Octene was brominated in 12 h at 65 °C to yield the corresponding dibromooctane **12** in 86% isolated yield. Allylbenzene and *p*-(methoxyallyl)benzene were readily brominated to give bromoalkanes **4** and **15** in 80% and 90% yield, respectively. Reaction of allyl benzoate gave dibromide **16** in 6 h with 62% isolated yield. Longer reaction times resulted in considerable hydrolysis of the ester. *N*-Allyl benzotriazoles gave compounds **18** and **19** in good yields. For cyclohexene, the reaction temperature was lowered to room temperature to avoid loss of

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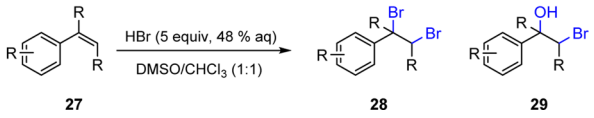
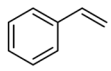
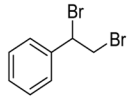
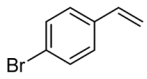
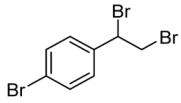
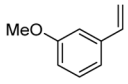
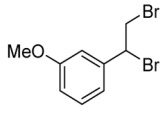
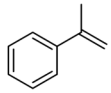
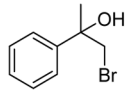
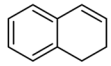
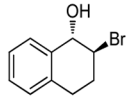
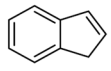
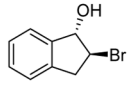
Table 4. Reaction of Styrene Derivatives



27 28 29

Entry	Substrate	Product	Time (h)	Temp (° C)	Isolated Yield (%)
1	 **30**	 **31**	12	65	61
2	 **32**	 **33**	24	65	65
3	 **34**	 **35**	12	65	61
4	 **36**	 **37**	3	65	93
5	 **38**	 **39**	12	65	72
6	 **40**	 **41**	12	65	65

the volatile substrate. The reaction was completed in 12 h giving *trans*-1,2-dibromocyclohexane (**8**) in 72% isolated yield. Conversion of cyclooctene was also complete at room temperature in 24 h to give **20** in 99% yield. The temperature was also lowered for two other substrates, acenaphthylene and *cis*-jasmone, to minimize the formation of unidentified side products. In these cases, the desired dibromoalkanes **21** and **22** were obtained in 67% and 50% yield after 32 and 24 h, respectively. A reaction time of 40 h at 65 °C was required for complete conversion of *trans*-stilbene to the corresponding product (**23**), which was obtained in 87% yield. Carboxylic acids are well tolerated under these reaction conditions with compounds **24** and **25** obtained in good yields. Compound **25** was isolated as a single diastereomer in 74% yield. Finally, 3-methylbut-2-en-1-ol reacted rapidly to give the dibromo alcohol **26** in 66% yield.

We next applied this reaction to a series of styrene derivatives (Table 4). Styrene (**30**), *p*-bromostyrene (**32**), and *m*-methoxystyrene (**34**) behaved as expected, giving the corresponding dibromides in good yields. However, in the case of α-methylstyrene (**36**), we observed nearly exclusive formation of the *trans*-bromohydrin **37** which was isolated in 93% yield. Similarly 1,2-dihydronaphthalene (**38**) and indene (**40**) afforded *trans*-bromohydrins **39** and **41**, respectively, in good isolated yields. In these two cases, a small amount of dibromination was also observed via crude ^{1}H NMR. A control experiment was conducted to determine the potential that bromohydrins **37**, **39**, and **41** are formed via initial bromination and subsequent substitution of −Br with −OH. We subjected 1,2-dibromoindane (prepared via standard Br_2-based bromination of indene) to our HBr/DMSO reaction conditions. We observed complete conversion of 1,2-dibromoindane to bromohydrin **41** in 12 h. Thus, it is possible that substrates **36**, **38**, and **40** undergo initial dibromination before conversion to bromohydrins. The isolated bomohydrins have a *trans* relationship between hydroxyl and bromide groups. Therefore, if a substitution of −Br to −OH occurs, the observed stereochemistry indicates an S_N1 process whereby a carbocation intermediate reacts with water at its less sterically hindered face.

Scheme 3 offers a proposed mechanism for the conversion of DMSO to BDMS followed by subsequent olefin bromination.

This methodology was not suitable for the bromination of α,β-unsaturated carbonyl derivatives. We also attempted to replace HBr with HCl for an analogous chlorination reaction

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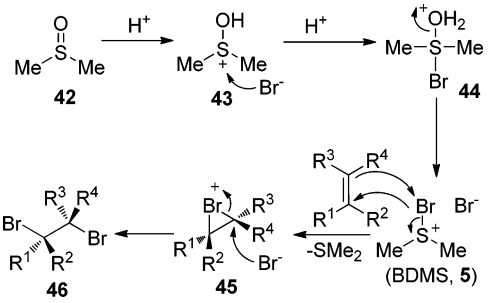
Scheme 3. Proposed Reaction Mechanism



without success. We must report that our work directly contradicts Yusubov et al., who have reported the oxidation of olefins to 1,2-diketones under identical conditions.[24]

In summary, we have described a unique process for dibromination of olefins with HBr and DMSO. This methodology offers a simple, inexpensive, and mild alternative to the use of Br_2 or other more resource-intensive strategies.

EXPERIMENTAL SECTION

General Considerations. Unless otherwise noted, commercially available reagents and solvents were used without further purification. Infrared spectra were obtained on a Thermo Scientific Nicolet 380 FT-IR spectrometer as thin films on ZnSe disks, and peaks are reported in cm^{-1}. ^1H and ^{13}C NMR experiments were performed on a Bruker AVANCE 500 MHz instrument, and samples were obtained in $CDCl_3$ (referenced to 7.26 ppm for ^1H and 77.0 ppm for ^{13}C). Coupling constants (J) are reported in hertz. The multiplicities of the signals are described using the following abbreviations: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad. MALDI-HRMS of compounds were recorded on a Q-TOF mass spectrometer using 2,5-dihydroxybenzoic acid as a matrix and mixture of polyethylene glycol (PEG 600) and (PEG 1000) as internal calibration standards. Elemental analyses were obtained on a CE0440 elemental analyzer (EAI Exeter Analytical). Reaction progress was monitored by thin-layer chromatography (TLC, EMD Chemicals, Inc., silica gel 60 F254), visualized under UV light, and plates were developed using *p*-anisaldehyde or potassium permanganate stains. Flash chromatography was performed using silica gel (Sorbent Technologies, particle size 40−63 μm). Melting points were determined using a Mel-Temp II apparatus and are uncorrected.

General Procedure for Dibromination Reaction. A solution of HBr (48% aq, 5 equiv) in DMSO (1 mL per mmol of substrate) was added to a reaction vial containing a magnetic stir bar and the alkene substrate (0.5−1.0 mmol) in $CHCl_3$ (1 mL per mmol of substrate). The reaction vial was capped and stirred at the specified temperature (rt or 65 °C) until complete disappearance of starting material was observed by TLC or ^1H NMR (TLC plates visualized using *p*-anisaldehyde or potassium permanganate stains). The reaction was transferred to a separatory funnel containing water and extracted with ether (3 × 30 mL). The combined organic extracts were dried over $MgSO_4$, and solvent was removed in vacuo. The residue was purified by flash column chromatography on silica gel (gradient elution with EtOAc and hexanes). *Note: Flash chromatography effectively removes all trace DMSO that may remain after workup.*

(2,3-Dibromopropyl)benzene (4). The standard procedure was used with allylbenzene (132.5 μL, 1.0 mmol), HBr (48% aq, 0.56 mL, 5 mmol), and DMSO (1 mL). After 12 h of stirring at 65 °C, the reaction was worked up and purified as described above to yield compound **4** as an oil (0.223 g, 80% yield): R_f = 0.87 (hexanes/EtOAc 70:30 v/v); ^1H NMR ($CDCl_3$, 500 MHz) δ 7.37−7.27 (m, 5H), 4.41−4.33 (m, 1H), 3.83 (dd, J = 10.5, 4.2 Hz, 1H), 3.64 (dd, J = 10.4, 8.9 Hz, 1H), 3.51 (dd, J = 14.5, 4.8 Hz, 1H), 3.14 (dd, J = 14.5, 7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 136.9, 129.5, 128.5, 127.2, 52.4, 42.0, 36.0. ^1H and ^{13}C NMR spectral data are consistent with previously reported values.[25]

***trans*-1,2-Dibromocyclohexane (8).** The standard procedure was used with cyclohexene (101 μL, 1.0 mmol), HBr (48% aq, 0.56 mL, 5 mmol), and DMSO (1 mL). After 12 h of stirring at room temperature, the reaction was worked up and purified as described above to yield compound **8** as a colorless liquid product (175 mg, 72% yield): R_f = NA; ^1H NMR ($CDCl_3$, 500 MHz) δ 4.45 (s, 2H), 2.57−2.31 (m, 2H), 1.96−1.74 (m, 4H), 1.57−1.46 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 55.2, 32.1, 22.4. ^1H and ^{13}C NMR spectral data are consistent with previously reported values.[5d]

2,3-Dibromopropan-1-ol (11). The standard procedure was used with allyl alcohol (68 μL, 1.0 mmol), HBr (48% aq, 0.56 mL, 5 mmol), and DMSO (1 mL). The reaction was stirred for 24 h at room temperature. After workup and purification as above, compound **11** was obtained as a colorless liquid (196 mg, 90% yield): R_f = 0.62 (Hexanes/EtOAc 70:30 v/v); ^1H NMR ($CDCl_3$, 500 MHz) δ 4.39−4.23 (m, 1H), 4.02 (d, J = 3.9 Hz, 2H), 3.88−3.74 (m, 2H), 1.94 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 64.2, 53.6, 31.5. ^1H and ^{13}C NMR spectral data are consistent with previously reported values.[26]

1,2-Dibromooctane (12). The standard procedure was used with 1-octene (78.5 μL, 0.5 mmol), HBr (48% aq, 0.28 mL, 2.5 mmol), and DMSO (0.5 mL). After 12 h of stirring at 65 °C, the reaction was worked up and purified as described above to yield compound **12** as a colorless liquid product (116.2 mg, 86% yield): R_f = 0.65 (Hexanes/EtOAc 70:30 v/v); ^1H NMR ($CDCl_3$, 500 MHz) δ 4.25−4.08 (m, 1H), 3.85 (dd, J = 10.2, 4.5 Hz, 1H), 3.63 (t, J = 9.9 Hz, 1H), 2.20−2.07 (m, 1H), 1.79 (dddd, J = 14.6, 10.0, 9.0, 4.6 Hz, 1H), 1.64−1.48 (m, 1H), 1.48−1.24 (m, 6H), 0.94−0.86 (m, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 53.2, 36.4, 36.1, 31.6, 28.5, 26.7, 22.5, 14.0. ^1H and ^{13}C NMR spectral data are consistent with previously reported values.[5b]

1,2,4-Tribromobutane (13). The standard procedure was used with 4-bromobut-1-ene (102 μL, 1.0 mmol), HBr (48% aq, 0.56 mL, 5 mmol), and DMSO (1 mL). After 24 h of stirring at 65 °C, the reaction was worked up and purified as described above to yield compound **13** as a clear colorless oil (179 mg, 61% yield): ^1H NMR ($CDCl_3$, 500 MHz) δ 4.38 (tdd, J = 9.8, 4.3, 2.8 Hz, 1H), 3.90 (dd, J = 10.5, 4.2 Hz, 1H), 3.72−3.51 (m, 3H), 2.68 (dddd, J = 15.5, 9.3, 6.4, 2.8 Hz, 1H), 2.26 (dddd, J = 15.5, 10.0, 5.5, 4.3 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 50.3, 39.2, 35.9, 30.4; IR (cm^{-1}): 2923.3, 1462.9, 736.8, 475.43. Anal. Calcd ($C_4H_7Br_3$, 294.81): C, 16.3; H, 2.39. Found: C, 16.73; H, 2.07.

1,2,5-Tribromopentane (14). The standard procedure was used with 5-bromopent-1-ene (118.5 μL, 1.0 mmol), HBr (48% aq, 0.56 mL, 5 mmol), and DMSO (1 mL). After 24 h of stirring at 65 °C, the reaction was worked up and purified as described above to yield compound **14** as an oil (227 mg, 74% yield): R_f = 0.66 (hexanes/EtOAc 90:10 v/v); ^1H NMR ($CDCl_3$, 500 MHz) δ 4.18 (tdd, J = 9.8, 4.4, 3.0 Hz, 1H), 3.87 (dd, J = 10.3, 4.4 Hz, 1H), 3.63 (t, J = 10.1 Hz, 1H), 3.51−3.40 (m, 2H), 2.43−2.33 (m, 1H), 2.24−2.13 (m, 1H), 2.07−1.88 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 51.43, 35.82, 34.71, 32.27, 30.02; IR (cm^{-1}) 2959.7, 1257.0, 1141.0, 563.8. Anal. Calcd ($C_5H_9Br_3$, 308.84): C, 19.45; H, 2.94. Found: C, 19.71; H, 2.84.

1-(2,3-Dibromopropyl)-4-methoxybenzene (15). The standard procedure was used with 1-allyl-4-methoxybenzene (153.4 μL, 1.0 mmol), HBr (48% aq, 0.56 mL, 5 mmol), and DMSO (1 mL). After 12 h of stirring at 65 °C, the reaction was worked up and purified as described above to yield compound **15** as a colorless oil (276.6 mg, 90% yield): R_f = 0.65 (hexanes/EtOAc 90:10 v/v); ^1H NMR ($CDCl_3$, 500 MHz) δ 7.25−7.15 (m, 2H), 6.92−6.83 (m, 2H), 4.33 (dddd, J = 9.0, 7.4, 4.9, 4.2 Hz, 1H), 3.84−3.78 (m, 3H), 3.81 (s, 3H), 3.61 (dd, J = 10.5, 8.9 Hz, 1H), 3.42 (dd, J = 14.6, 4.9 Hz, 1H), 3.10 (dd, J = 14.7, 7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 158.8, 130.6, 128.8, 113.9, 55.2, 52.9, 41.1, 35.9; IR (cm^{-1}) 2929.8, 2833.6, 1610.4, 1509.9, 1463.1, 1430.4, 1242.7, 1176.3, 1031.6, 806.2, 594.5. Anal. Calcd ($C_{10}H_{12}Br_2O$, 308.01): C, 38.99; H, 3.93. Found: C, 39.21; H, 3.84.

2,3-Dibromopropyl benzoate (16). The standard procedure was used with allyl benzoate (154 μL, 1.0 mmol), HBr (48% aq, 0.56 mL, 5 mmol), and DMSO (1 mL). After 6 h of stirring at 65 °C, the reaction was worked up and purified as described above to yield compound **16**

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as a clear colorless oil (182 mg, 62% yield): R_f = 0.35 (hexanes/EtOAc 90:10 v/v); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.11−8.04 (m, 2H), 7.63−7.56 (m, 1H), 7.51−7.45 (m, 2H), 4.77 (dd, J = 12.2, 4.5 Hz, 1H), 4.72 (dd, J = 12.2, 5.3 Hz, 1H), 4.47 (ddt, J = 9.2, 5.3, 4.6 Hz, 1H), 3.88 (dd, J = 10.7, 4.8 Hz, 1H), 3.83 (dd, J = 10.7, 9.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 165.8, 133.4, 129.8, 129.5, 128.5, 65.60, 47.0, 32.1; IR (cm^{-1}) 2950, 1720.6, 1602.1, 1451.92, 1377.2, 1267.7, 725.9, 707.04; APCI-HRMS calcd for $C_{10}H_{11}Br_2O_2$ $(M + H)^+$ 320.9126, found 320.9115.

((2,3-Dibromopropoxy)methyl)benzene (17). The standard procedure was used with ((allyloxy)methyl)benzene (77.6 μL, 0.5 mmol), HBr (48% aq, 0.28 mL, 2.5 mmol), and DMSO (0.5 mL). After 5 h of stirring at 65 °C, the reaction was worked up and purified as described above to yield compound **17** as a clear colorless oil (100 mg, 65% yield): R_f = 0.69 (hexanes/EtOAc 90:10 v/v); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.36 (d, J = 4.8 Hz, 5H), 4.66−4.58 (m, 2H), 4.27 (dd, J = 8.3, 4.9 Hz, 1H), 3.92−3.79 (m, 4H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 137.5, 128.5, 127.9, 127.7, 73.5, 71.1, 49.1, 33.1; IR (cm^{-1}) 3028.9, 2859.7, 1495.3, 1452.4, 1360.0, 1072.6, 695.4, 573.9. ^{1}H and ^{13}C NMR spectral data are consistent with previously reported values.[27]

2-(2,3-Dibromopropyl)-2*H*-benzotriazole (18). The standard procedure was used with 2-allyl-2*H*-benzotriazole (125 mg, 0.79 mmol), HBr (48% aq, 0.44 mL, 3.95 mmol), and DMSO (1 mL). After 24 h of stirring at 65 °C, the reaction was worked up and purified as described above to yield compound **18** as a white solid (175 mg, 70% yield): mp = 81−83 °C; R_f = 0.79 (hexanes/EtOAc 70:30 v/v); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.98−7.79 (m, 2H), 7.41 (dd, J = 6.6, 3.1 Hz, 2H), 5.34 (dd, J = 14.1, 5.4 Hz, 1H), 5.13 (dd, J = 14.1, 7.1 Hz, 1H), 4.87 (tt, J = 7.3, 5.4 Hz, 1H), 3.99−3.77 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 144.6, 126.9, 118.2, 59.9, 47.0, 33.4; IR (cm^{-1}): 3041.2, 2922.59, 1561.2, 1425.4, 1345.9, 1168.2, 751.2; ESI-HRMS calcd for $C_9H_9Br_2N_3$ $(M + H)^+$ 317.9243, found 317.9243.

1-(2,3-Dibromopropyl)-1*H*-benzotriazole (19). The standard procedure was used with 1-allyl-1*H*-benzotriazole (159 mg, 1.0 mmol), HBr (48% aq, 0.56 mL, 5 mmol), and DMSO (1 mL). After 24 h of stirring at 65 °C, the reaction was worked up and purified as described above to yield compound **19** as a white solid (130 mg, 81% yield): R_f = 0.85 (hexanes/EtOAc 90:10 v/v); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.12−8.07 (m, 1H), 7.64 (dt, J = 8.4, 0.9 Hz, 1H), 7.57−7.51 (m, 1H), 7.41 (ddd, J = 8.4, 6.9, 1.0 Hz, 1H), 5.25 (dd, J = 14.9, 5.0 Hz, 1H), 5.05 (dd, J = 14.9, 6.9 Hz, 1H), 4.76 (dddd, J = 8.2, 6.9, 5.1, 4.5 Hz, 1H), 3.89−3.76 (m, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 145.8, 133.6, 127.9, 124.2, 120.3, 109.4, 51.9, 47.8, 33.5, 29.7; IR (cm^{-1}): 2977.3, 1590.5, 1488.0, 1407.2, 1102.47, 728.77; ESI-HRMS calcd for $C_9H_9Br_2N_3$ $(M + H)^+$ 317.9241, found 317.9244.

1,2-Dibromocyclooctane (20). The standard procedure was used with cyclooctene (130 μL, 1.0 mmol), HBr (48% aq, 0.56 mL, 5 mmol), and DMSO (1 mL). After 24 h of stirring at room temperature, the reaction was worked up and purified as described above to yield compound **20** as a colorless liquid product (268 mg, 99% yield): R_f = 0.81 (hexanes/EtOAc 90:10 v/v); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.64−4.51 (m, 1H), 2.41 (dddd, J = 15.8, 8.9, 3.6, 1.3 Hz, 1H), 2.09 (dddd, J = 15.7, 7.8, 5.0, 2.7 Hz, 1H), 1.90−1.79 (m, 1H), 1.72−1.54 (m, 2H), 1.53−1.42 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 61.5, 33.2, 25.9, 25.4. ^{1}H and ^{13}C NMR spectral data are consistent with previously reported values.[28]

***trans*-1,2-Dibromoacenaphthene (21).** The standard procedure was used with acenaphthylene (100 mg, 0.66 mmol), HBr (48% aq, 0.37 mL, 5 mmol), and DMSO (0.5 mL). After 32 h of stirring at 35 °C, the reaction was worked up and purified as described above to yield compound **21** as a light brown solid (138 mg, 67% yield): mp = 111−114 °C; R_f = 0.83 (Hexanes/EtOAc 90:10 v/v); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.82 (dd, J = 7.5, 1.4 Hz, 2H), 7.70−7.56 (m, 4H), 6.01 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 140.5, 134.8, 131.0, 128.8, 125.9, 122.5, 54.9; ^{1}H and ^{13}C NMR spectral data are consistent with previously reported values.[29]

2-(2,3-Dibromobutyl)-3-methylcyclopent-2-enone (22). The standard procedure was used with *cis*-jasmone (170 μL, 1.0 mmol), HBr (48% aq, 0.56 mL, 5 mmol), and DMSO (1 mL). After 24 h of stirring at room temperature, the reaction was worked up and purified as described above to yield compound **22** as a clear oil (151 mg, 50% yield): R_f = 0.72 (hexanes/EtOAc 70:30 v/v); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.57 (td, J = 7.0, 2.3 Hz, 1H), 4.02 (ddd, J = 8.0, 5.5, 2.3 Hz, 1H), 2.88 (d, J = 7.0 Hz, 2H), 2.61−2.51 (m, 2H), 2.44−2.36 (m, 2H), 2.15 (s, 3H), 2.05−1.94 (m, 2H), 1.06 (t, J = 7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 209.2, 173.7, 136.5, 62.0, 56.9, 34.2, 32.0, 32.0, 30.6, 17.8, 12.4; IR (cm^{-1}) 2967.6, 2912.6, 1690.9, 1644.6, 1432.9, 1382.5, 545.91.512.9. Anal. Calcd ($C_{11}H_{16}Br_2O$, 324.06): C, 40.77; H, 4.98. Found: C, 40.95; H, 4.91.

***meso*-1,2-Dibromo-1,2-diphenylethane (23).** The standard procedure was used with *trans*-stilbene (180 mg, 1.0 mmol), HBr (48% aq, 0.56 mL, 5 mmol), and DMSO (1 mL). After 40 h of stirring at 65 °C, the reaction was worked up and purified as described above to yield compound **23** as a white solid (295 mg, 87% yield): mp = 236−238 °C; R_f = 0.78 (hexanes/EtOAc 90:10 v/v); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.55−7.49 (m, 4H), 7.45−7.34 (m, 6H), 5.48 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 140.0, 129.0, 128.8, 127.9, 56.1. Anal. Calcd ($C_{14}H_{12}Br_2$, 340.06): C, 49.45; H, 3.56. Found: C, 49.7; H, 3.37. ^{1}H and ^{13}C NMR spectral data are consistent with previously reported values.[11]

3,4-Dibromocyclopentanecarboxylic Acid (24). The standard procedure was used with cyclopent-3-enecarboxylic acid (103 μL, 1.0 mmol), HBr (48% aq, 0.56 mL, 5 mmol), and DMSO (1 mL). After 12 h of stirring at 65 °C, the reaction was worked up and purified as described above to yield compound **24** as a white powder (167 mg, 61% yield): mp = 111−113 °C; R_f = 0.51 (hexanes/EtOAc 70:30 v/v); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.63 (ddd, J = 4.8, 2.1, 1.2 Hz, 1H), 4.55 (dt, J = 6.2, 1.8 Hz, 1H), 3.45−3.33 (m, 1H), 3.11−2.97 (m, 2H), 2.68−2.57 (m, 1H), 2.49 (ddt, J = 15.0, 8.6, 1.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 179.0, 56.2, 54.3, 40.5, 37.2, 37.1; IR (cm^{-1}) 2920.93, 1686.83, 1315.21, 914.17, 535.45. Anal. Calcd ($C_6H_8Br_2O_2$, 271.94): C, 26.50; H, 2.97. Found: C, 26.31; H, 2.88.

(1*S*,3*R*,4*R*)-3,4-Dibromocyclohexanecarboxylic Acid (25). The standard procedure was used with cyclohex-3-enecarboxylic acid (117 μL, 1.0 mmol), HBr (48% aq, 0.56 mL, 5 mmol), and DMSO (1 mL). After 12 h of stirring at 65 °C, the reaction was worked up and purified as described above to yield compound **25** as a pale yellow solid (211.7 mg, 74% yield): mp = 80−82 °C; R_f = 0.59 (hexanes/EtOAc 70:30 v/v); δ 4.70 (dd, 1H), 4.60 (dd, J = 3.3 Hz, 1H), 3.01−2.92 (m, 1H), 2.67−2.59 (m, 1H), 2.57−2.47 (m, 1H), 2.28−2.20 (m, 1H), 2.08−1.93 (m, 4H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 180.2, 51.9, 51.8, 37.4, 30.7, 28.2, 23.0; IR (cm^{-1}) 2929.89, 2605.09, 1701.33, 1451.40, 1283.43, 1026.09, 928.75, 889.46, 686.92, 541.99. ^{1}H and ^{13}C NMR spectral data are consistent with previously reported values.[30]

2,3-Dibromo-3-methylbutan-1-ol (26). The standard procedure was used with 3-methylbut-2-en-1-ol, (102 μL, 1.0 mmol), HBr (48% aq, 0.56 mL, 5 mmol), and DMSO (1 mL). After 2 h of stirring at 65 °C, the reaction was worked up and purified as described above to yield compound **26** as white crystals (162 mg, 66% yield): mp = 38−39 °C; R_f = 0.59 (hexanes/EtOAc 70:30 v/v); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.42 (dd, J = 8.2, 2.9 Hz, 1 H), 4.33 (d, J = 12.6, 2.9 Hz, 1 H), 3.98 (dd, J = 8.2, 12.5 Hz, 1 H), 1.98 (s, 3 H), 1.84 (s, 3 H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 69.0, 66.1, 64.8, 35.5, 29.7; IR (cm^{-1}) 3243.76, 2972.09, 2953.23, 1376.92, 1093.64, 1067.70, 975.03, 548.19. Anal. Calcd ($C_5H_{10}Br_2O$, 245.94): C, 24.42; H, 4.1. Found: C, 24.81; H, 4.01.

1,2-(Dibromoethyl)benzene (31). The standard procedure was used with styrene (**30**, 57.5 μL, 0.5 mmol), HBr (48% aq, 0.28 mL, 2.5 mmol), and DMSO (0.5 mL). After 12 h of stirring at 65 °C, the reaction was worked up and purified as described above to yield compound **30** as a white solid (80 mg, 61% yield): mp = 71−73 °C; R_f = 0.79 (hexanes/EtOAc 90:10 v/v); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.44−7.32 (m, 3H), 5.15 (dd, J = 10.6, 5.4 Hz, 1H), 4.11−3.99 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 138.7, 129.2, 128.9, 127.7, 50.9, 35.0. ^{1}H and ^{13}C NMR spectral data are consistent with previously reported values.[12f]

1-Bromo-4-(1, 2-bromoethyl)benzene (33). The standard procedure was used with 4-bromostyrene (**32**, 131 μL, 1.0 mmol), HBr (48% aq, 0.56 mL, 5 mmol), and DMSO (1 mL). After 24 h of

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stirring at 65 °C, the reaction was worked up and purified as described above to yield compound **33** as a white solid (222 mg, 65% yield): mp = 56−58 °C; R_f = 0.82 (hexanes/EtOAc 90:10 v/v); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.54−7.50 (m, 2H), 7.30−7.26 (m, 2H), 5.09 (dd, J = 11.0, 5.1 Hz, 1H), 4.06 (dd, J = 10.3, 5.1 Hz, 1H), 3.96 (dd, J = 11.0, 10.3 Hz, 1H);^{13}C NMR ($CDCl_3$, 500 MHz) δ 137.7, 132.1, 129.3, 123.2, 49.6, 34.6. ^{1}H and ^{13}C NMR spectral data are consistent with previously reported values.[31]

1-(1,3-Dibromoethyl)-3-methoxybenzene (35). The standard procedure was used with 3-methoxystyene (**34**, 69.4 μL, 0.5 mmol), HBr (48% aq, 0.28 mL, 2.5 mmol), and DMSO (0.5 mL). After 12 h of stirring at 65 °C, the reaction was worked up and purified as described above to yield compound 35 as white solid (90 mg, 61% yield): mp = 64−66 °C; R_f = 0.61 (hexanes/EtOAc 90:10 v/v); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.30 (t, J = 7.9 Hz, 1H), 6.99 (ddd, J = 7.8, 1.6, 0.8 Hz, 1H), 6.94 (t, J = 2.1 Hz, 1H), 6.88 (ddd, J = 8.3, 2.6, 0.9 Hz, 1H), 5.11 (dd, J = 10.5, 5.4 Hz, 1H), 4.11−3.93 (m, 2H), 3.83 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 159.8, 140.1, 129.9, 119.9, 114.6, 113.5, 55.3, 50.8, 35.0; IR (cm^{-1}) 2917.1, 2833.9, 1600.22, 1490.4, 1462.29, 1434.1, 1047.0, 698.3. Anal. Calcd ($C_9H_{10}Br_2O$, 293.99): C, 36.77; H, 3.43. Found: C, 36.44; H, 3.45.

1-Bromo-2-phenylpropan-2-ol (37). The standard procedure was used with α-methylstyrene (**36**, 65 μL, 0.5 mmol), HBr (48% aq, 0.28 mL, 2.5 mmol), and DMSO (0.5 mL). After 3 h of stirring at 65 °C, the reaction was worked up and purified as described above to yield compound **37** as a colorless oil (100 mg, 93% yield): R_f = 0.76 (hexanes/EtOAc 70:30 v/v); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.49−7.44 (m, 2H), 7.41−7.35 (m, 2H), 7.33−7.27 (m, 1H), 3.82−3.67 (m, 1H), 2.53 (s, 1H), 1.69 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 144.2, 128.4, 127.5, 124.9, 73.1, 46.3, 28.1; IR (cm^{-1}) 3437.57, 2975.72, 1492.64, 1445.88, 1373.48, 1064.98, 696.85. ^{1}H and ^{13}C NMR spectral data are consistent with previously reported values.[32]

***trans*-2-Bromo-1,2,3,4-tetrahydronaphthalen-1-ol (39).** The standard procedure was used with 1,2-dihydronaphthalene (**38**, 65.3 μL, 0.5 mmol), HBr (48% aq, 0.28 mL, 2.5 mmol), and DMSO (0.5 mL). After 12 h of stirring at 65 °C, the reaction was worked up and purified as described above to yield compound **39** as a white powder (82 mg, 72% yield): mp = 108−110 °C; R_f = 0.5 (hexanes/EtOAc 90:10 v/v); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.57−7.48 (m, 1H), 7.26−7.23 (m, 2H), 7.14−7.07 (m, 1H), 4.91 (d, J = 7.0 Hz, 1H), 4.37 (ddd, J = 10.0, 7.0, 3.2 Hz, 1H), 3.09−2.85 (m, 2H), 2.51 (td, J = 5.7, 3.1 Hz, 1H), 2.29 (dddd, J = 13.7, 9.7, 8.4, 6.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 135.4, 135.0, 128.5, 128.03, 126.7, 74.2, 56.2, 29.8, 28.1. ^{1}H and ^{13}C NMR spectral data are consistent with previously reported values.[33]

***trans*-2-Bromo-1-indanol (41).** The standard procedure was used with indene (**40**, 57.8 μL, 0.5 mmol), HBr (48% aq, 0.28 mL, 2.5 mmol), and DMSO (0.5 mL). After 12 h of heating at 65 °C, the reaction was worked up and purified as described above to yield compound **41** as a white powder (69.3 mg, 65% yield): mp = 120−122 °C; R_f = 0.68 (hexanes/EtOAc 70:30 v/v); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.44−7.40 (m, 1H), 7.31−7.28 (m, 2H), 7.25−7.21 (m, 1H), 5.32 (d, J = 5.8 Hz, 1H), 4.29 (td, J = 7.3, 5.8 Hz, 1H), 3.59 (dd, J = 16.2, 7.3 Hz, 1H), 3.28−3.19 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 141.7, 139.7, 129.0, 127.6, 124.6, 124.1, 83.5, 54.5, 40.5; IR (cm^{-1}) 3211.77, 2908.20, 2849.39, 1477.19, 1461.02, 1438.36, 1343.48, 1289.79, 1183.46, 1063.85, 750.17, 729.86. ^{1}H and ^{13}C NMR spectral data are consistent with previously reported values.[8b]

■ ASSOCIATED CONTENT

Supporting Information

^{1}H and ^{13}C NMR spectra are provided. This material is available free of charge via the Internet at http://pubs.acs.org/.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: jmagolan@uidaho.edu.

Notes

The authors declare no competing financial interest.

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■ DEDICATION

We dedicate this manuscript to the memory of the late Dr. Aaron D. Mills.

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