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A Novel Route to Geminal Dibromocyclobutanes: Syntheses of 2-Substituted Cyclobutanone Acetals and Their Reaction with Boron Tribromide

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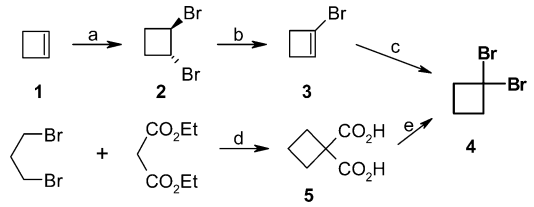
Nine 2-substituted cyclobutanone acetals, in addition to the parent cyclobutanone acetal, were synthesized from their corresponding cyclobutanones and subsequently treated with boron tribromide. The substituents were either alkyl chains or a phenyl and a benzyl group, respectively. The major compounds obtained in these reactions were, in most cases, the geminal dibromocyclobutanes which were obtained in yields between 50 and 73%. A 2-fold excess of BBr_3 and a reaction time of 3 h at −78 °C afforded the best yields. In four cases no dibromide formation was observed at all, and the cyclobutanone acetals were hydrolyzed to the corresponding cyclobutanone. This is probably due to increased steric hindrance of the acetal and BBr_3 in the transition state.

Introduction

Intra- and intermolecular reactions of small-ring carbenes, e.g., cyclopropylidenes and cyclobutylidenes, respectively, continue to be a field of growing interest. These reactive species have been used for the construction of polycyclic compounds such as spiropentanes,[1] spirohexanes,[2] spirohexenes,[3] and tricyclic compounds comprising a three-, four-, and five-membered ring, respectively.[4] For the generation of cyclopropylidenes, the nearly exclusive method in use is the reaction between a readily available *gem*-dihalocyclopropane and alkyllithium at low temperatures (<−50 °C).[1a] To this end, *gem*-dibromocyclopropanes are reacted with methyllithium in diethyl ether at −78 °C. In contrast, for cyclobutylidenes, the method mostly applied is the Bamford−Stevens reaction, where a sodium or lithium salt of a cyclobutanone tosylhydrazone is thermally or photochemically decomposed,[5] or flash-pyrolyzed,[6] to generate the carbene. The drawback of this reaction, however, is the relatively high temperature required (>150 °C). In cases where thermally labile compounds are expected, this method may not be the right choice, and an organometallic route to cyclobutylidenes or the corresponding cyclobutylidenoids is preferred. To date, only two synthetic preparations of geminal dibromocyclobutanes are known. However, the syntheses of *gem*-dibromocyclobutanes published in the literature so far are laborious and/or give low yields (vide infra). This led us to develop a more convenient and general synthesis of such compounds.

SCHEME 1. Previous Syntheses of 1,1-Dibromocyclobutane[a]



[a] Key: (a) Br_2 in $CHCl_3$; (b) KOH, 110 °C; (c) HBr; (d) 50% NaOH in water, TEBA; (e) Br_2, HgO in CH_2Cl_2.

In the first published preparation of 1,1-dibromocyclobutane (**4**), the double bond in cyclobutene (**1**) was brominated to give *trans*-1,2-dibromocyclobutane (**2**), which underwent elimination reaction upon treatment with potassium hydroxide to give 1-bromo-1-cyclobutene (**3**). Addition of hydrogen bromide afforded 1,1-dibromocyclobutane (**4**) in an overall yield of 28% (Scheme 1).[7] Later, **4** was synthesized in a two-step synthesis.[8] Diethyl malonate and 1,3-dibromopropane were reacted in aqueous sodium hydroxide solution with a phase-transfer catalyst (triethylbenzylammonium chloride) yielding 1,1-cyclobutanedicarboxylic acid (**5**), which also is com-

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mercially available.[9] The latter compound was converted to 1,1-dibromocyclobutane by a double Hunsdiecker−Borodin degradation in an overall yield of 11%.

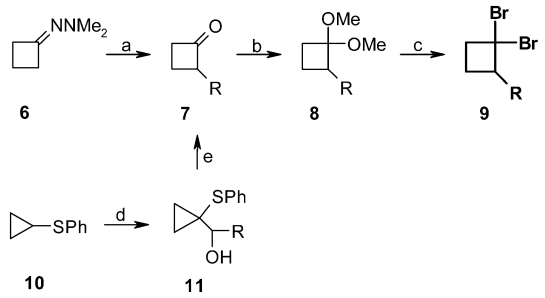
No general synthesis of 2-substituted geminal dibromocyclobutanes has been reported so far. A reinvestigation of the proposed ring enlargement of 1-(1-bromo-1-*p*-tolylmethyl)cyclopropyl bromide to 1,1-dibromo-2-*p*-tolylcyclobutane[10] led only to ring opening to give the (*Z*)- and (*E*)-isomers of 2,4-dibromo-1-*p*-tolyl-1-butene.[11] This was also the case when at C-1 a phenyl group was present instead of a *p*-tolyl group.[11]

As described earlier, the synthesis of geminal dibromocyclopropanes is much simpler than the preparation of geminal dibromocyclobutanes. While dibromocarbenes add to double bonds to give the corresponding geminal dibromocyclopropanes in one step, the dibromo moiety in four-membered rings has to be introduced in a totally different fashion. The reaction of cyclobutanones with phosphorus pentahalide to give geminal dihalocyclobutanes is applicable for geminal dichlorocyclobutanes only.[12] While adamantanone and 7-norbornanone easily are converted to 2,2-dibromoadamantane[13] and 7,7-dibromonorbornane,[14] respectively, the reaction between phosphorus pentabromide and cyclobutanone, however, gave only a 77:23 mixture of 2-bromocyclobutanone and 2,2-dibromocyclobutanone.[15] Moreover, the aforementioned method using substituted cyclobutenes as starting materials cannot be applied when an unsaturated side chain is present. Bromination and subsequent elimination or addition of hydrogen bromide is expected to also brominate the pendant double bond. Therefore, a novel method was sought which allows the introduction of a *gem*-dibromo moiety in a four-membered ring through a replacement of another geminal group.

Results and Discussion

Syntheses of 2-Substituted Cyclobutanones. 2-Substituted cyclobutanones (**7**) are easily available through a number of syntheses.[16] In the study outlined here, two methods were employed. The first procedure consists of a Lewis acid-catalyzed rearrangement of 1-substituted cyclopropyl phenyl sulfides (**11**) (Scheme 2). These compounds were synthesized from cyclopropylphenyl sulfide (**10**), which was reacted with butyllithium to generate the cyclopropyl anion. Addition of the appropriate aldehyde gave sulfides **11**,[17] which upon treatment with acids, preferentially *p*-TsOH in water-saturated benzene, rearranged smoothly to the corresponding cyclobutanones.[18] The rearrangements were successful, but reaction time and choice of the acid proved to be important for optimum yields.

SCHEME 2. Syntheses of 2-Substituted Geminal Dibromocyclobutanes[a]



[a] Key: (a) *n*-BuLi, then RBr in dry THF; (b) trimethyl orthoformate on Montmorillonite K-10 in pentane; (c) BBr_3 in dry CH_2Cl_2, 3 h; (d) *n*-BuLi, then RCHO in dry THF, then H_3O^+; (e) TsOH in water-saturated benzene.

TABLE 1. Isolated Yields (%) of Compounds 7, 8 and 9

entry	R	7	8	9
a	H		95	73
b	hexyl	67[a]	90	70
c	isopropyl	44[b]	98	*c*
d	*tert*-butyl	60[b]	96	*c*
e	isobutyl	45[b]	90	50[d]
f	cyclohexyl	66[b]	93	*c*
g	cyclobutylmethyl	72[a]	91	57
h	cyclohexylmethyl	78[a]	94	62
i	phenyl	45[b]	94	*c*
j	benzyl	65[a]	92	63

[a] General procedure 1. [b] General procedure 2. [c] Only the corresponding cyclobutanone was formed. [d] Cyclobutanone **7e** could be isolated in 19% yield.

Cyclobutanones in entries b, g, h, and j in Table 1 were successfully synthesized via a complementary method. Here, the anion of cyclobutanone *N*,*N*-dimethylhydrazone (**6**) generated by a strong base reacted with an alkyl or aryl bromide to give the desired cyclobutanone directly upon treatment with a weak acid.[19]

Synthesis of Cyclobutanone Acetals. A plethora of methods has been published for the synthesis of acetals from the corresponding ketones.[20] We chose to use the version developed by Taylor and Chiang, since the experiments can been done at room temperature and also require a short reaction time.[21] Trimethyl orthoformate was applied on a clay, Montmorillonite K-10, and addition of the cyclobutanone afforded the corresponding cyclobutanone acetals (**8**) in uniformly high yields of 90−98% (Table 1).

Boron Tribromide-Induced Cleavage of Cyclobutanone Acetals. It is known that boron tribromide has been used for cleavage of alkyl ethers to alkyl bromides and alcohols.[22] Methyl ethers of secondary or tertiary alchohols give methanol and secondary or tertiary alkyl

(9) CAS registry number provided by the author: 5445-51-2.
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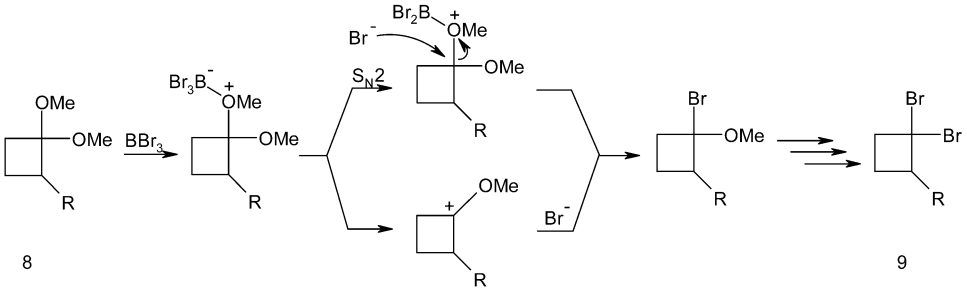
SCHEME 3. Boron Tribromide-Induced Cleavage of Cyclobutanone Acetals



bromides, respectively, in the reaction with BBr_3.[23] However, only few examples for the cleavage of alkanone acetals to *gem*-dibromoalkanes have been reported in the literature.[24] The boron tribromide-induced cleavage of cyclobutanone acetals was performed in dichloromethane at −78 °C for 3 h (Scheme 2), and the geminal dibromocyclobutanes (**9**) were isolated in 50−73% yields (Table 1). Characteristic in the ^{1}H NMR spectra of **9** is the absorption of the tertiary proton at C-2 in the range of δ 3.25−3.52 ppm, while in the ^{13}C NMR spectra the corresponding carbon atoms all resonate between 62.6 and 65.0 ppm. Furthermore, the quaternary carbons with the geminal dibromo substituents, with the exception of the parent system (δ 57.3 ppm), absorb in the area of δ 38.9 and 40.0 ppm. The first step of the reaction mechanism probably consists of an attack of the reagent's boron atom at the ether oxygen in the cyclobutanone acetal to form an ylide (Scheme 3). Loss of bromide leads to an oxonium ion that either loses dibromomethoxyborane and the resulting carbocation recombines with the bromide ion or the bromide ion attacks the oxonium ion in a S_N2 reaction to give 1-bromo-1-methoxycyclobutane. Repetition of these steps will lead to the geminal dibromocyclobutanes directly. Dibromomethoxyborane is hydrolyzed ultimately to methanol and boric acid upon treatment with water.

Nevertheless, in entries c, d, f, and i the geminal dibromocyclobutanes **9** could not be observed at all. This is probably due to the steric hindrance the substituents at C-2 introduce to the molecule, thereby precluding attack of the boron atom in boron tribromide at the oxygen atom of one of the methoxy groups. Moreover, the best molar ratio was found to be a 2-fold excess of boron tribromide, while an equimolar addition of BBr_3 or less afforded only the ketone. It was also necessary to keep the temperature at −78 °C for at least 3 h. A shorter reaction time favored the cyclobutanone formation.[25] The cyclobutanones (**7**) obtained in the reaction probably stem from acid-induced acetal cleavage of **8**, but only in entry e some cyclobutanone could be detected besides the geminal dibromocyclobutane. To prevent hydrolysis of the dibromocyclobutane, before workup with water and sodium bicarbonate, pentane was added to the reaction mixture. The geminal dibromocyclobutanes were isolated using flash chromatography or bulb-to-bulb distillation, and turned out to be stable at room temperature. Their reaction with methyllithium will be part of a forthcoming publication.

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Experimental Section

General Information. Trimethyl orthoformate, Montmorillonite K-10, and boron tribromide were used as purchased. Dichloromethane was distilled from CaH_2 prior to use. FT NMR spectra were recorded on a DRX-400 or a DPX-250 spectrometer at the following Larmor frequencies: $\nu_o(^1H)$ = 400 and 250 MHz, respectively, and ν_o (^{13}C) = 100 and 62.9 MHz, respectively. IR absorption spectra were recorded on an IR spectrometer by pressing a drop of neat liquid between two NaCl plates. MS assays were performed on a MAT 900 spectrometer. Analytical GC analyses were conducted using a GC instrument outfitted with a 30 m poly(dimethylsiloxane) capillary column (PE−1, 0.32 mm i.d., and 0.25 μm film thickness) and a flame-ionization detector. The following condition and temperature program was used: $T_{oven,i}$ = 50 °C (10 min), ramp + 5 °C/min, $T_{oven,f}$ = 100 °C, ramp +15 °C/min, $T_{oven,f}$ = 250 °C (10 min), $T_{injector}$ = 220 °C, T_{FID} = 250 °C, and flow = 2.1 mL of He/min. GC−MS analyses were conducted using a GC instrument outfitted with a 30 m poly(methylphenylsiloxane) capillary column (HP-5MS (95% dimethyl and 5% diphenyl), 0.25 mm i.d., and a 0.25 μm film thickness). Flash chromatography was performed with use of silica gel 60 (230−400 mesh) and hexanes as eluent. Microanalyses were performed by the Mikroanalytisches Laboratorium am Institut für Physikalische Chemie der Universität Wien, Austria. Bulb-to-bulb distillation was performed using a Kugelrohr apparatus.

Synthesis of Sulfides (11): General Procedure. To a solution of cyclopropyl phenyl sulfide (20 mmol) in dry THF (30 mL) at 0 °C was added *n*-BuLi (25 mmol). After 2 h, the aldehyde was added. The mixture was allowed to reach room temperature, and after 2 h, water (5 mL) and diethyl ether (100 mL) were added. The organic layer was separated, washed with brine, and dried ($MgSO_4$), and the solvents were removed in vacuo. Bulb-to-bulb distillation afforded the desired compound.

1-(1-Phenylthiocyclopropyl)-2-methyl-1-propanol (11c). Yield: 87%. t_R = 26.60 min. Bp: 85 °C/0.01 Torr. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.90 (d, 3H, J = 6.6 Hz), 0.98 (d, 3H, J = 6.6 Hz), 0.98−1.02 (m, 3H), 1.09−1.13 (m, 1H), 1.54 (d, 1H, J = 7.1 Hz), 2.10−2.21 (m, 1H), 2.77 (t, 1H, J = 7.3 Hz), 7.15−7.19 (m, 1H), 7.24−2.27 (m, 2H), 7.50−7.52 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.6, 16.3, 18.6, 19.9, 30.2, 33.4, 83.2, 126.3, 128.7, 130.2, 136.4. IR (neat): ν 3443, 3060, 3005, 2959, 2930, 2872, 1584, 1479, 1439, 1387, 1366, 1245, 1089, 1026, 982, 739, 692 cm^{-1}. MS (m/z): 222 (67, M^+), 179 (55), 161 (52), 151 (33), 150 (46), 149 (54), 135 (33), 118 (20), 117 (100), 116 (20), 110 (42), 109 (35), 91 (61), 77 (28), 73 (28), 71 (20), 69 (22), 65 (21), 55 (23), 51 (22).

1-(1-Phenylthiocyclopropyl)-2,2-dimethyl-1-propanol (11d). Yield: 66%. t_R = 27.15 min. Bp: 100 °C/0.01 Torr. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.89−1.21 (m, 4H), 1.10 (s, 9H), 1.76 (d, 1H, J = 8.1 Hz), 2.76 (d, 1H, J = 7.8 Hz),

7.15−7.20 (m, 1H), 7.24−7.30 (m, 2H), 7.52−7.57 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.9, 18.1, 27.4, 29.3, 37.5, 86.1, 126.1, 128.7, 129.7, 126.9. IR (neat): ν 3473, 3060, 2954, 2905, 2869, 1584, 1480, 1439, 1396, 1364, 1240, 1050, 1026, 1012, 976, 739, 692 cm^{-1}. MS (*m*/*z*): 236 (36, M^+), 180 (30), 179 (199), 161 (32), 151 (20), 149 (21), 135 (24), 117 (57), 110 (29), 109 (21), 91 (49), 73 (29), 57 (73). HRMS: calcd for $C_{14}H_{20}OS$ 236.1235, found 236.1228. Anal. Calcd for $C_{14}H_{20}OS$: C, 71.14; H, 8.52. Found: C, 70.92; H, 8.30.

1-(1-Phenylthiocyclopropyl)-3-methyl-1-butanol (11e). Yield: 84%. t_R = 27.15 min. Bp: 100 °C/0.01 Torr. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.84 (d, 3H, J = 6.6 Hz), 0.90 (d, 3H, J = 6.6 Hz), 0.96−1.02 (m, 2H), 1.02−1.09 (m, 2H), 1.36−1.43 (m, 1H), 1.46−1.54 (m, 1H), 1.74 (d, 1H, J = 6.8 Hz), 3.36 (s, 1H), 7.13−7.19 (m, 1H), 7.23−7.30 (m, 2H), 7.44−7.49 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.9, 14.5, 21.7, 23.6, 24.6, 31.9, 44.2, 74.6, 126.0, 128.7, 129.2, 136.5. IR (neat): ν 3422, 3060, 2956, 2929, 2869, 1584, 1480, 1439, 1385, 1367, 1070, 1026, 991, 738, 692 cm^{-1}. MS (*m*/*z*): 236 (32, M^+), 180 (23), 151 (24), 150 (80), 149 (54), 135 (55), 117 (100), 110 (30), 109 (28), 105 (22), 91 (35). HRMS: calcd for $C_{14}H_{20}OS$ 236.1235, found 236.1237. Anal. Calcd for $C_{14}H_{20}OS$: C, 71.14; H, 8.52. Found: C, 70.85; H, 8.73.

1-(1-Phenylthiocyclopropyl)cyclohexylmethanol (11g). Yield: 78%. t_R = 29.55 min. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.92−1.06 (m, 5H), 1.10−1.27 (m, 4H), 1.60−1.78 (m, 5H), 1.81−1.89 (m, 1H), 2.06 (d, 1H, J = 12.9 Hz), 2.78 (s, 1H), 7.18−7.23 (m, 1H), 7.26−7.31 (m, 2H), 7.55−7.58 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.6, 16.5, 25.9, 26.0, 26.4, 29.2, 30.0, 30.1, 43.1, 82.8, 126.4, 128.7, 130.4, 136.4. IR (neat): ν 3463, 2925, 2853, 1479, 1467, 1450, 1395, 1364, 1099, 1085, 985, 759 cm^{-1}. MS (*m*/*z*): 262 (77, M^+), 180 (35), 179 (59), 161 (41), 151 (53), 150 (88), 149 (53), 135 (34), 117 (100), 111 (21), 110 (50), 109 (38), 95 (36), 91 (64), 83 (66), 79 (21), 77 (30), 73 (23), 69 (21), 67 (24), 65 (24), 55 (78), 51 (21).

1-(1-Phenylthiocyclopropyl)phenylmethanol (11i). Yield: 74%. t_R = 29.35 min. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.94−1.02 (m, 2H), 1.06−1.15 (m, 2H), 2.67 (s, 1H), 4.83 (s, 1H), 7.20−7.45 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.5, 14.7, 32.1, 75.9, 126.2, 127.0, 127.8, 128.0, 128.8, 129.2, 135.7, 149.4. IR (neat): ν 3416, 3061, 3029, 2956, 2931, 2871, 1584, 1479, 1453, 1439, 1041, 1027, 739, 701 cm^{-1}. MS (*m*/*z*): 256 (94, M^+), 151 (20), 150 (87), 149 (100), 135 (29), 134 (41), 117 (85), 116 (42), 115 (36), 110 (25), 109 (23), 107 (58), 105 (58), 91 (37), 79 (43), 77 (52), 51 (25).

Synthesis of Cyclobutanones: General Procedure 1. Under an argon atmosphere at −10 °C, cyclobutanone *N*,*N*-dimethylhydrazone **6** (10.0 mmol) was dissolved in dry THF (50 mL) and *n*-BuLi in hexane (11.0 mmol) was added. After the mixture was stirred at this temperature for 1 h, a solution of alkyl bromide (10.0 mmol) in dry THF (8.0 mL) was slowly added, and the mixture was stirred at room temperature. After 20 h, 2 M HCl (20 mL) was added, and the stirring was continued for 1 h. The reaction mixture was extracted with EtOAc (3 × 30 mL), the organic layers were collected, washed with brine (10 mL), and dried ($MgSO_4$), and the solvents were removed in vacuo. Bulb-to-bulb distillation afforded the desired compound. The cyclobutanones **7** in entries b, g, h, and j were synthesized according to this procedure.

Synthesis of Cyclobutanones: General Procedure 2. The sulfide **11** (50 mmol) and *p*-TsOH (25 mmol) were dissolved in water-saturated benzene (100 mL), refluxed for 2 h, and then cooled to room temperature. Water (10 mL) and dichloromethane (100 mL) were added. The layers were separated, and the organic layers washed once with aqueous bicarbonate solution (20 mL) and brine (20 mL) and dried ($MgSO_4$). Removal of the solvents in vacuo followed by bulb-to-bulb distillation provided the desired compound. The cyclobutanones **7** in entries c, d, e, f, and i were synthesized according to this procedure.

2-Hexylcyclobutanone (7b). t_R = 21.16 min. Bp: 50 °C/0.2 Torr. ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.88 (t, 3H), 1.20−1.35 (m, 8H), 1.43−1.58 (m, 1H), 1.60−1.75 (m, 2H), 2.10−2.25 (m, 1H), 2.82−3.12 (m, 2H), 3.20−3.35 (m, 1H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 14.0, 16.9, 22.5, 27.0, 29.1, 29.5, 31.6, 44.3, 60.6, 212.5. IR (neat): ν 2957, 2927, 2856, 1782, 1466, 1395, 1379, 1093, 1069, 757, 723 cm^{-1}. MS (*m*/*z*): 154 (4, M^+), 126 (5), 111 (8), 98 (100), 97 (18), 84 (38), 83 (27), 82 (27), 70 (43), 69 (35), 68 (10), 67 (12), 58 (16), 57 (18), 56 (58), 55 (97), 54 (12), 53 (11).

2-Isopropylcyclobutanone (7c). t_R = 5.60 min. Bp: 150 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.89 (d, 3H, J = 6.8 Hz), 0.99 (d, 3H, J = 6.6 Hz), 1.66−1.75 (m, 1H), 1.82−1.90 (m, 1H), 2.01−2.11 (m, 1H), 2.77−2.86 (m, 1H), 2.88−2.98 (m, 1H), 3.01−3.09 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.5, 19.8, 20.2, 28.9, 44.1, 67.4, 211.8. IR (neat): ν 2960, 2874, 1779, 1468, 1386, 1367, 1087 cm^{-1}. MS (*m*/*z*): 112 (18, M^+), 94 (18), 84 (30), 70 (21), 69 (100), 56 (44), 55 (74).

2-*tert*-Butylcyclobutanone (7d). t_R = 7.55 min. Bp: 70 °C/12 Torr. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.96 (s, 9H), 1.77−1.87 (m, 1H), 1.96−2.06 (m, 1H), 2.71−2.81 (m, 1H), 2.87−2.97 (m, 1H), 3.11−3.18 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.9, 27.1, 31.9, 44.3, 71.3, 212.0. MS (*m*/*z*): 126 (20, M^+), 98 (21), 84 (13), 83 (100), 70 (33), 69 (84), 57 (16), 55 (34).

2-Isobutylcyclobutanone (7e). t_R = 11.25 min. Bp: 100 °C/12 Torr. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (d, 3H, J = 6.3 Hz), 0.91 (d, 3H, J = 6.6 Hz), 1.32−1.40 (m, 1H), 1.59−1.75 (m, 3H), 2.17−2.26 (m, 1H), 2.87−2.97 (m, 1H), 2.98−3.09 (m, 1H), 3.28−3.38 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.8, 22.3, 22.7, 26.5, 38.6, 44.5, 59.2, 212.5. IR (neat): ν 2957, 2928, 2871, 1780, 1468, 1386, 1368, 1095, 1067 cm^{-1}. MS (*m*/*z*): 126 (13, M^+), 98 (42), 83 (11), 82 (33), 70 (25), 69 (61), 56 (72), 55 (100). HRMS: calcd for $C_8H_{14}O$ 126.1045, found 126.1041. Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 76.35; H, 10.90.

2-Cyclohexylcyclobutanone (7f). t_R = 21.90 min. Bp: 65 °C/0.5 Torr. ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.91−1.08 (m, 2H), 1.10−1.31 (m, 3H), 1.50−1.80 (m, 6H), 1.85−1.96 (m, 1H), 1.96−2.11 (m, 1H), 2.74−2.97 (m, 2H), 3.01−3.14 (m, 1H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 14.4, 25.8, 25.9, 26.3, 30.3, 30.9, 38.5, 44.2, 66.4, 211.8. IR (neat): ν 2925, 2853, 1777, 1480, 1449, 1178, 1084, 1025, 739, 691 cm^{-1}. MS (*m*/*z*): 152 (6, M^+), 150 (17), 135 (15), 134 (33), 124 (32), 117 (22), 95 (18), 85 (10), 83 (12), 82 (34), 80 (100), 68 (23), 67 (45), 55 (27), 54 (22), 53 (11).

2-Cyclobutylmethylcyclobutanone (7g). t_R = 18.60 min. Bp: 50 °C/0.2 Torr. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.54−1.68 (m, 4H), 1.76−1.89 (m, 3H), 1.99−2.07 (m, 2H), 2.10−2.20 (m, 1H), 2.32−2.44 (m, 1H), 2.86−2.95 (m, 1H), 2.96−3.06 (m, 1H), 3.17−3.26 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.0, 18.4, 28.2, 28.3, 34.0, 36.5, 44.6, 58.9, 212.4. IR (neat): ν 2957, 2929, 2864, 1780, 1444, 1395, 1325, 1243, 1087, 756 cm^{-1}. MS (*m*/*z*): 138 (7, M^+), 110 (58), 95 (11), 82 (41), 81 (23), 71 (24), 69 (15), 68 (72), 67 (100), 66 (11), 55 (61), 54 (46), 53 (18). HRMS: calcd for $C_9H_{14}O$ 138.1045, found 138.1047. Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.13; H, 10.47.

2-Cyclohexylmethylcyclobutanone (7h). t_R = 23.55 min. Bp: 50−52 °C/0.03 Torr. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.79−0.97 (m, 3H), 1.10−1.29 (m, 3H), 1.30−1.41 (m, 2H), 1.58−1.74 (m, 6H), 2.15−2.24 (m, 1H), 2.86−2.95 (m, 1H), 2.96−3.07 (m, 1H), 3.29−3.39 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.9, 26.1, 26.2, 26.4, 33.0, 33.5, 35.9, 37.4, 44.5, 58.7, 212.6. IR (neat): ν 2923, 2852, 1778, 1449, 1082, 757 cm^{-1}. MS (*m*/*z*): 166 (11, M^+), 148 (12), 138 (37), 122 (16), 109 (14), 96 (26), 95 (19), 94 (96), 93 (17), 84 (15), 83 (87), 82 (45), 81 (34), 71 (19), 67 (37), 55 (100), 54 (11). HRMS: calcd for $C_{11}H_{18}O$ 166.1358, found 166.1354. Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.23; H, 10.97.

2-Phenylcyclobutanone (7i). t_R = 22.50 min. Bp: 75−80 °C/0.5 Torr. ^{1}H NMR (250 MHz, $CDCl_3$): δ 2.17−2.32 (m, 1H), 2.47−2.61 (m, 1H), 2.97−3.11 (m, 1H), 3.16−3.31 (m, 1H), 4.51−4.59 (m, 1H), 7.25−7.37 (m, 5H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 17.6, 44.8, 64.5, 126.9, 128.5, 128.6, 136.5. 208.1.

IR (neat): ν 3060, 3028, 2963, 2926, 1782, 1686, 1602, 1496, 1449, 1393, 1201, 1072, 736, 698 cm^{-1}. MS (*m*/*z*): 146 (9, M$^+$), 120 (10), 118 (7), 105 (30), 104 (100), 78 (10), 77 (18).

2-Benzylcyclobutanone (7j). t_R = 23.30 min. Bp: 50 °C/0.05 Torr. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.69−1.78 (m, 1 H), 2.11−2.20 (m, 1 H), 2.77−2.84 (m, 1 H), 2.87−2.90 (m, 1 H), 2.98−3.07 (m, 2 H), 3.54−3.64 (m, 1 H), 7.16−7.40 (m, 5 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 16.6, 35.2, 44.5, 61.2, 126.3, 128.5, 128.7, 138.8, 210.9. IR (neat): ν 3062, 3028, 2990, 2950, 2925, 1778, 1603, 1496, 1454, 1394, 1228, 1205, 1082, 1030, 743, 700 cm^{-1}. MS (*m*/*z*): 160 (38, M$^+$), 131 (17), 118 (48), 117 (50), 104 (18), 91 (100), 65 (15).

Synthesis of Cyclobutanone Acetals 8: General Procedure. Trimethyl orthoformate (3.0 mL) and Montmorillonite K-10 (2.0 g) were stirred for 15 min, and then filtered. The wet filter cake, hexane (20 mL) and the cyclobutanone (10 mmol) were stirred at room temperature until GC analysis showed completition of the reaction. The mixture was filtered, water (5 mL) was added, and the organic layer separated, washed with $NaHCO_3$ (10%, 5 mL), and dried ($MgSO_4$). Removal of the solvent in vacuo followed by flash chromatography (hexane) on silica gel, or bulb-to-bulb distillation, provided the desired compounds as colorless oils.

1,1-Dimethoxycyclobutane (8a). t_R = 3.85 min. Bp: 112 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.60−1.77 (m, 2 H), 2.13 (t, 4 H, J = 8.0 Hz), 3.15 (s, 6 H). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 11.3, 31.5, 48.3, 102.9. IR (neat): ν 2996, 2948, 2830, 1459, 1274, 1235, 1153, 1144, 1111, 1043, 846 cm^{-1}. MS (*m*/*z*): 116 (0.1, M$^+$), 88 (100), 85 (54), 58 (39), 57 (35), 55 (10), 53 (12).

2-Hexyl-1,1-dimethoxycyclobutane (8b). t_R = 23.20 min. Bp: 65 °C/0.1 Torr. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.87 (t, 3H, J = 7.1 Hz), 1.15−1.35 (m, 8H), 1.35−1.45 (m, 2H), 1.50−1.62 (m, 1H), 1.77−1.94 (m, 2H), 2.09−2.16 (m, 1H), 2.30−2.40 (m, 1H), 3.14 (s, 3H), 3.16 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.0, 18.4, 22.6, 27.2, 28.8, 29.4, 30.1, 31.8, 44.7, 48.4, 48.5, 103.6. IR (neat): ν 2989, 2930, 2857, 2830, 1744, 1458, 1262, 1229, 1158, 1125, 1043, 857 cm^{-1}. MS (*m*/*z*): 200 (0.4, M$^+$), 172 (20), 169 (15), 137 (12), 135 (13), 101 (71), 98 (32), 97 (27), 89 (13), 88 (100), 85 (21), 84 (15), 70 (10), 69 (14), 58 (44), 57 (14), 56 (18), 55 (37). HRMS: calcd for $C_{12}H_{24}O_2$ 200.1776, found 200.1773. Anal. Calcd for $C_{12}H_{24}O_2$: C, 71.95; H, 12.07. Found: C, 72.14; H, 11.71.

1,1-Dimethoxy-2-isopropylcyclobutane (8c). t_R = 13.90 min. Bp: 40 °C/0.6 Torr. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.82 (d, 3H, J = 6.8 Hz), 0.98 (d, 3H, J = 6.6 Hz), 1.31−1.40 (m, 1H), 1.70−1.84 (m, 2H), 1.86−1.93 (m, 1H), 2.02−2.09 (m, 1H), 2.11−2.17 (m, 1H), 3.15 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.8, 19.8, 22.8, 28.5, 28.8, 48.1, 48.6, 51.7, 104.1. IR (neat): ν 2989, 2953, 2870, 2831, 1463, 1382, 1364, 1267, 1227, 1158, 1136, 1114, 1046, 856, 759 cm^{-1}. MS (*m*/*z*): 158 (0.1, M$^+$), 143 (1.6), 130 (15), 127 (11), 115 (62), 95 (13), 88 (100), 69 (12), 58 (26), 55 (11). HRMS: calcd for M$^+$ − CH_3 143.1072, found 143.1074. Anal. Calcd for $C_9H_{18}O_2$: C, 68.31; H, 11.46. Found: C, 68.58; H, 11.18.

1,1-Dimethoxy-2-*tert*-butylcyclobutane (8d). t_R = 15.70 min. Bp: 50 °C/1 Torr. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.95 (s, 9H), 1.45−1.54 (m, 1H), 1.69−1.79 (m, 1H), 1.90−1.97 (m, 1H), 2.03−2.11 (m, 1H), 2.17−2.22 (m, 1H), 3.10 (s, 3H), 3.15 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.2, 27.7, 30.5, 44.3, 47.4, 48.0, 53.6, 104.4. IR (neat): ν 2990, 2954, 2870, 2831, 1467, 1362, 1274, 1216, 1155, 1115, 1037, 909, 856, 760, 736 cm^{-1}. MS (*m*/*z*): 157 (5, M$^+$ − CH_3), 141 (11), 129 (55), 125 (14), 88 (100), 83 (11), 69 (14), 58 (26), 55 (10). HRMS: molecular peak not found. Anal. Calcd for $C_{10}H_{20}O_2$: C, 69.72; H, 11.70. Found: C, 69.97; H, 11.39.

1,1-Dimethoxy-2-isobutylcyclobutane (8e). t_R = 17.55 min. Bp: 60 °C/0.7 Torr. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.86 (d, 3H, J = 6.6 Hz), 0.90 (d, 3H, J = 6.6 Hz), 1.23−1.33 (m, 1H), 1.38−1.43 (m, 2H), 1.49−1.59 (m, 1H), 1.79−1.96 (m, 2H), 2.11−2.18 (m, 1H), 2.42−2.51 (m, 1H), 3.16 (s, 3H), 3.18 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.9, 22.2, 23.5, 26.0, 28.9, 39.1, 43.0, 48.5, 48.6, 103.8. IR (neat): ν 2990, 2953, 2870, 2830, 1467, 1384, 1367, 1259, 1226, 1156, 1123, 1042, 853, 758 cm^{-1}. MS (*m*/*z*): 140 (7, M$^+$ − CH_4O), 126 (18), 98 (48), 97 (32), 91 (12), 84 (10), 83 (17), 82 (37), 70 (29), 69 (66), 67 (12), 57 (10), 56 (73), 55 (100). HMRS: Calcd for M$^+$ − CH_4O 140.1201, found 140.1197. Anal. Calcd for $C_{10}H_{20}O_2$: C, 69.72; H, 11.70. Found: C, 70.01; H, 11.32.

2-Cyclohexyl-1,1-dimethoxycyclobutane (8f). t_R = 23.85 min. Bp: 50 °C/0.05 Torr. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.74 (dq, 1H, J = 12 Hz, J = 3.6 Hz), 0.88 (dq, 1H, J = 12.4 Hz, J = 3.8 Hz), 1.08−1.31 (m, 3H), 1.34−1.48 (m, 2H), 1.60−1.72 (m, 4H), 1.75−1.81 (m, 1H), 1.84−1.92 (m, 1H), 1.93−2.00 (m, 1H), 2.04−2.16 (m, 2H), 3.13 (s, 3H), 3.14 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 16.5, 26.2, 26.4, 26.7, 28.7, 29.9, 33.5, 37.9, 48.1, 48.8, 50.4, 104.3. IR (neat): ν 2988, 2923, 2851, 2830, 1448, 1266, 1158, 1126, 1046, 854 cm^{-1}. MS (*m*/*z*): 170 (22, M$^+$), 127 (15), 89 (11), 88 (100), 58 (16), 57 (19), 56 (14). HRMS: calcd for $C_{12}H_{22}O_2$ 170.1307, found 170.1310. Anal. Calcd for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18. Found: C, 72.59; H, 11.02.

2-Cyclobutylmethyl-1,1-dimethoxycyclobutane (8g). t_R = 22.05 min. Bp: 50 °C/0.1 Torr. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.22−1.32 (m, 1H), 1.48−1.71 (m, 4H), 1.74−1.85 (m, 3H), 1.86−1.94 (m, 1H), 1.97−2.06 (m, 2H), 2.10−2.18 (m, 1H), 2.22−2.37 (m, 2H), 3.15 (s, 3H), 3.17 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.5, 18.6, 28.4, 28.7, 29.0, 34.2, 37.5, 42.7, 48.4, 48.5, 103.7. IR (neat): ν 2948, 2857, 2830, 1444, 1260, 1241, 1158, 1125, 1042, 861, 758 cm^{-1}. MS (*m*/*z*): 152 (30, M$^+$ − CH_4O), 123 (18), 110 (12), 109 (21), 98 (12), 97 (100), 92 (14), 91 (34), 85 (15), 84 (15), 82 (10), 81 (11), 79 (17), 71 (27), 68 (16), 67 (39), 65 (10), 60 (10), 57 (48), 57 (29), 55 (34), 54 (14), 53 (13), 50 (15). HMRS: calcd for M$^+$ − CH_4O 152.1201, found 152.1198. Anal. Calcd for $C_{11}H_{20}O_2$: C, 71.70; H, 10.94. Found: C, 71.99; H, 11.09.

2-Cyclohexylmethyl-1,1-dimethoxycyclobutane (8h). t_R = 24.85 min. Bp: 50 °C/0.01 Torr. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.78−0.99 (m, 2H), 1.13−1.33 (m, 5H), 1.35−1.48 (m, 2H), 1.60−1.75 (m, 5H), 1.78−1.95 (m, 2H), 2.11−2.18 (m, 1H), 2.44−2.53 (m, 1H), 3.14 (s, 3H), 3.18 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.0, 26.3, 26.4, 26.7, 28.9, 33.0, 34.3, 35.6, 37.7, 42.4, 48.5, 48.6, 103.8. IR (neat): ν 2989, 2923, 2852, 2830, 1448, 1266, 1230, 1159, 1123, 1043, 860, 758 cm^{-1}. MS (*m*/*z*): 184 (5, M$^+$ − C_2H_4), 101 (47), 97 (17), 88 (100), 85 (18), 83 (28), 71 (62), 67 (12), 58 (19), 55 (17). HRMS: calcd for M$^+$ − C_2H_4 184.1463, found 184.1458. Anal. Calcd for $C_{13}H_{24}O_2$: C, 73.54; H, 11.39. Found: C, 73.55; H, 11.25.

1,1-Dimethoxy-2-phenylcyclobutane (8i). t_R = 23.90 min. Bp: 70−75 °C/0.3 Torr. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.93−2.03 (m, 1H), 2.08−2.19 (m, 2H), 2.25−2.33 (m, 1H), 3.01 (s, 3H), 3.20 (s, 3H), 3.62 (t, 1H, J = 8.6 Hz), 7.21−7.36 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.2, 29.5, 48.7, 48.9, 51.0, 104.0, 126.4, 128.0, 128.9, 139.6. IR (neat): ν 3061, 3027, 2993, 2950, 2831, 1603, 1497, 1458, 1259, 1163, 1117, 1036, 861, 759, 698 cm^{-1}. MS (*m*/*z*): 192 (6, M$^+$), 164 (12), 129 (9), 104 (7), 91 (10), 89 (7), 88 (100), 58 (27). HRMS: calcd for $C_{12}H_{16}O_2$ 192.1150, found 192.1147. Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.96; H, 8.39. Found: C, 74.90; H, 8.52.

2-Benzyl-1,1-dimethoxycyclobutane (8j). t_R = 24.75 min. Bp: 75 °C/0.01 Torr. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.27−1.37 (m, 1H), 1.64−1.74 (m, 1H), 1.80−1.89 (m, 1H), 2.08−2.16 (m, 1H), 2.56−2.66 (m, 2H), 2.85−2.94 (m, 1H), 3.01 (s, 3H), 3.14 (s, 3H), 7.06−7.13 (m, 3H), 7.16−7.21 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.4, 28.6, 36.3, 45.8, 48.5, 48.7, 103.4, 125.7, 128.2, 128.8, 140.9. IR (neat): ν 3062, 3027, 2990, 2948, 2830, 1782, 1603, 1496, 1453, 1260, 1222, 1160, 1121, 959, 855, 747, 728, 700 cm^{-1}. MS (*m*/*z*): 206 (1, M$^+$), 178 (8), 175 (12), 174 (43), 173 (25), 143 (23), 142 (13), 141 (23), 131 (10), 129 (12), 128 (13), 118 (11), 117 (21), 115 (19), 103 (10), 91 (42), 89 (13), 88 (100), 77 (10), 65 (14), 58 (24), 55 (13), 51 (12). HRMS: calcd for $C_{13}H_{18}O_2$ 206.1307, found 206.1311. Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.79. Found: C, 75.85; H, 8.59.

Synthesis of Geminal Dibromocyclobutanes: General Procedure. Boron tribromide (1.94 mL, 5.05 g, 20.2 mmol)

was added dropwise to the cyclobutanone acetal **8** (10 mmol) dissolved in dry CH_2Cl_2 (25 mL) at −78 °C. After 3 h, the dry ice/acetone was replaced by an ice bath, and the reaction was allowed to reach 0 °C. Pentane (100 mL) was added, and the mixture was quenched with $NaHCO_3$ (10%, 10 mL). The organic layer was separated, washed with brine (5 mL), and dried ($MgSO_4$). Removal of the solvent in vacuo followed by flash chromatography (hexane) on silica gel or bulb-to-bulb distillation provided the desired compounds as colorless oils.

1,1-Dibromocyclobutane (9a). t_R = 18.65 min; ^{1}H NMR (250 MHz, $CDCl_3$): δ 2.20 (dt, 2H, J = 7.5 Hz), 3.24 (t, 4H, J = 7.4 Hz). ^{13}C NMR (62.9 MHz, $CDCl_3$): δ 18.2, 50.0, 57.3. IR (neat): ν 2999, 2957, 2871, 1436, 1422, 1247, 1096, 1033, 840, 706 cm^{-1}. MS (*m*/*z*): 216 (2), 214 (4, M^+), 212 (2), 188 (22), 186 (48), 184 (25), 135 (82), 133 (80), 107 (13), 105 (14), 85 (50), 84 (13), 83 (83), 70 (10), 53 (100), 51 (20), 50 (16), 49 (25).

1,1-Dibromo-2-hexylcyclobutane (9b). t_R = 25.20 min. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88−0.93 (m, 3H), 0.97−1.04 (m, 1H), 1.19−1.16 (m, 1H), 1.25−1.38 (m, 7H), 1.40−1.50 (m, 1H), 1.50−1.60 (m, 2H), 2.06 ("q", 2H, J = 8.1 Hz), 3.40 (t, 1H, J = 6.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.0, 18.8, 21.0, 22.5, 27.7, 28.7, 31.6, 38.9, 39.5 (CBr_2), 65.0. IR (neat): ν 2955, 2927, 2857, 1466, 1207, 1156, 1029, 913, 693, 614 cm^{-1}. MS (*m*/*z*): 300 (7), 298 (15, M^+), 296 (8), 219 (5), 163 (12), 161 (13), 138 (11), 137 (100), 135 (13), 133 (12), 95 (78), 84 (14), 83 (31), 82 (10), 81 (87), 79 (12), 71 (10), 69 (59), 67 (52), 66 (11), 65 (18), 57 (15), 56 (28), 55 (61). HRMS: calcd for $C_{10}H_{18}{}^{79}Br_2$ 295.9775, found 295.9782. Anal. Calcd for $C_{10}H_{18}Br_2$: C, 40.29; H, 6.08. Found: C, 40.23; H, 5.82.

1,1-Dibromo-2-isobutylcyclobutane (9e). t_R = 22.10 min. Bp: 70−72 °C/0.5 Torr.^{1}H NMR (400 MHz, $CDCl_3$): δ 0.90 (d, J = 6.6 Hz, 3H), 0.97 (d, J = 6.6 Hz, 3H), 1.01−1.13 (m, 2H), 1.32−1.38 (m, 1H), 1.50−1.55 (m, 1H), 1.73−1.80 (m, 1H), 1.85−1.95 (m, 1H), 2.02−2.10 (m, 1H), 3.43−3.48 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.1, 20.7, 21.5, 22.8, 25.9, 40.0, 47.4, 63.2. IR (neat): ν 2958, 2870, 1466, 1424, 1386, 1260, 1235, 1166, 1028, 917, 872, 692, 617 cm^{-1}. MS (*m*/*z*): 272 (2), 270 (4, M^+), 268 (2), 191 (10), 189 (10), 109 (100), 69 (35), 67 (44), 65 (11), 56 (45), 55 (18), 53 (14). HRMS: calcd for $C_8H_{14}{}^{79}Br_2$ 267.9462, found 267.9471. Anal. Calcd for $C_8H_{14}Br_2$: C, 35.59; H, 5.23. Found: C, 35.85; H, 5.05.

1,1-Dibromo-2-cyclobutylmethylcyclobutane (9g). t_R = 24.45 min; ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.95−1.02 (m, 1H), 1.05−1.12 (m, 1H), 1.30−1.36 (m, 1H), 1.49−1.57 (m, 1H), 1.58−1.64 (m, 1H), 1.65−1.75 (m, 1H), 1.78−1.96 (m, 2H), 2.04−2.13 (m, 2H), 2.14−2.22 (m, 2H), 2.56 (sept, 1H, J = 7.8 Hz), 3.27−3.33 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.4, 18.9, 20.9, 28.0 (two carbons), 33.9, 39.5, 45.8, 62.8. MS (*m*/*z*): 284 (0.5), 282 (1, M^+), 280 (0.5), 256 (2), 254 (4), 252 (2), 203 (11), 201 (13), 175 (17), 173 (17), 121 (47), 94 (14), 93 (100), 91 (25), 85 (39), 83 (52), 81 (44), 79 (56), 77 (30), 69 (13), 68 (15), 67 (59), 65 (17), 55 (70), 53 (28), 51 (12). HRMS: calcd for $C_9H_{14}{}^{79}Br_2$ 279.9462, found 279.9465. Anal. Calcd for $C_9H_{14}Br_2$: C, 38.33; H, 5.00. Found: C, 38.59; H, 4.79.

1,1-Dibromo-2-cyclohexylmethylcyclobutane (9h). t_R = 26.55 min. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.78−0.91 (m, 2H), 0.94−1.11 (m, 3H), 1.19−1.23 (m, 1H), 1.24−1.30 (m, 2H), 1.31−1.38 (m, 1H), 1.49−1.60 (m, 2H), 1.63−1.76 (m, 4H), 1.77−1.85 (m, 1H), 1.99−2.07 (m, 1H), 3.47−3.52 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.1, 20.7, 26.0, 26.1, 26.4, 32.3, 33.5, 35.1, 40.0, 46.0, 62.6. IR (neat): ν 2923, 2851, 1448, 1423, 1217, 1163, 1028, 935, 890, 692, 620 cm^{-1}. MS (*m*/*z*): 312 (1.5), 310 (3, M^+), 308 (1.5), 233 (3), 231 (6), 229 (3), 149 (61), 109 (24), 96 (14), 95 (17), 87 (11), 85 (66), 84 (16), 83 (100), 82 (25), 81 (23), 69 (16), 67 (42), 56 (15), 55 (64), 53 (10). HRMS: calcd for $C_{11}H_{18}{}^{79}Br_2$ 307.9779, found 307.9778. Anal. Calcd for $C_{11}H_{18}Br_2$: C, 42.60; H, 5.85. Found: C, 42.85; H, 6.02.

1,1-Dibromo-2-benzylcyclobutane (9j). t_R = 26.40 min. Bp: 100 °C/0.001 Torr. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.62−0.68 (m, 1 H), 0.80−0.86 (m, 1 H), 1.16−1.29 (m, 2 H), 3.21−3.26 (m, 1 H), 3.38−3.44 (m, 1 H), 3.51 (t, 1 H, J = 7.3 Hz), 7.16−7.27 (m, 5 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.3, 21.2, 38.9, 44.8, 64.6, 127.2, 128.5, 129.4, 138.0. IR (neat): ν 3063, 3028, 2935, 1603, 1494, 1454, 1424, 1265, 1218, 1154, 1030, 941, 897, 748, 704, 688 cm^{-1}. MS (*m*/*z*): 306 (0.1), 304 (0.2, M^+), 302 (0.1), 148 (11), 92 (32), 91 (100), 65 (10). HRMS: calcd for $C_{11}H_{12}{}^{79}Br_2$ 301.9306, found 301.9316. Anal. Calcd for $C_{11}H_{12}Br_2$: C, 43.46; H, 3.98. Found: C, 43.65; H, 3.98.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra of **8c**,**g**, **9b**,**e**,**g**,**h**,**j**. This material is available free of charge via the Internet at http://pubs.acs.org.

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