δ 0.15 (s, 9 H), 0.97-2.00 (m, 12 H), 1.16 (d, 3 H, J = 6.8 Hz), 2.61-2.72 (m, 1 H), 3.33 (br s, 1 H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 109.6, 86.2, 78.0, 40.1, 30.8, 29.6, 27.7, 26.4, 26.3, 26.0, 15.0, 0.1.

2-(3-Butynyl)-1-cyclohexanol (23). Reaction of cyclohexanone (0.097 g, 0.99 mmol) with titanium tetrachloride (0.206 g, 1.08 mmol) and 3-methyl-1-(trimethylsilyl)allene (0.172 g, 1.36 mmol) in 4 mL of methylene chloride at -78 °C for 1 h, -78 °C to 25 °C over 0.5 h, and at 25 °C for 1 h according to general procedure B gave 0.217 g of an orange oil. Subsequent reaction of this material with anhydrous potassium fluoride (0.145 g, 2.50 mmol) in 4 mL of Me_2SO at 25 °C for 14 h afforded 0.145 g of an orange oil. Column chromatography on silica gel (elution with tetrahydrofuran-hexane) furnished 0.116 g (77%) of 2-(3-butynyl)-1-cyclohexanol (**23**) as a colorless oil: IR (film) 3450, 3300, 2980, 2930, 2850, 2100, 1450, 1380, 1240, 1150, 1040, 1000, 960, 925, 900, 840, 760 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.20 (d, 3 H, J = 7.0 Hz), 1.14-1.73 (m, 11 H), 2.14 (d, 1 H, J = 2.4 Hz), 2.51 (dq, 1 H, J = 7.0, 2.4 Hz); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 86.2, 72.0, 70.9, 37.5, 35.1, 33.7, 25.7, 21.9, 21.8, 14.6; MS, m/e 109 (M^+ - 43). Anal. Calcd for $C_{10}H_{16}O$: C, 78.90; H, 10.60. Found: C, 78.61; H, 10.42.

Acknowledgment. We thank Eli Lilly and Company, Firmenich SA, and the National Science Foundation for generous financial support.

Registry No. **2**, 74542-82-8; **3**, 71320-96-2; **6**, 14657-22-8; **7**, 74542-81-7; **8**, 590-19-2; **9**, 14583-74-5; **10**, 81435-37-2; **11**, 74542-86-2; **12**, 74542-85-1; **13**, 74542-87-3; **14**, 74552-19-5; **15**, 74552-18-4; **16**, 36185-09-8; **17**, 36185-12-3; **18**, 19135-08-1; **19**, 74542-84-0; **20**, 74552-17-3; **21a**, 103934-05-0; **21b**, 103934-12-9; **22a**, 103934-06-1; **22b**, 104051-34-5; **23**, 103934-07-2; **24**, 103934-08-3; **25**, 77494-37-2; **26**, 103934-09-4; **27**, 103934-10-7; **28a**, 103934-11-8; **28b**, 103934-13-0; **29**, 104011-57-6; **30**, 92945-17-0; **31**, 75643-02-6; **32a**, 81435-59-8; **32b**, 81435-48-5; cyclohexanecarboxaldehyde, 2043-61-0; 3-phenylpropionaldehyde, 104-53-0; 3-methyl-2-butanone, 563-80-4; cyclohexanone, 108-94-1; 1-phenyl-2-propanone, 103-79-7; acetone, 67-64-1.

New Methods of Formation of Meta-Substituted Aromatic Compounds

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The addition of organolithium reagents to the oxa tricyclic ketone 1 occurs stereospecifically to produce the corresponding tertiary carbinols **2a-d**. When the alcohols **2a-d** are treated with $TiCl_4$, ring fragmentation and dehydration occur to produce good yields of 5,6-dihydrobenzaldehydes **3a-d**. Oxidation of aldehydes **3a-d** then leads to the corresponding meta-substituted benzaldehydes **4a-d**. Alternatively, use of the Lewis acid Me_2BBr did not stop at the dihydrobenzaldehyde stage. Tautomerization of the diene aldehydes **3a-d** produced meta-substituted benzyl alcohols **7a-d** or benzyl bromides **8a-d** under prolonged reaction times. The addition of silica gel to the reactions accelerated the formation of the benzyl bromides.

The formation of strained bridged polycyclic ring systems may provide synthetically useful reactive synthons that may be induced to undergo selective ring-fragmentation reactions. The advantages of such processes can allow for flexibility in the placement of functional substituents as well as the control of stereochemical elements in accordance with the geometric contraints of small rings. The chemical literature contains numerous examples of this approach,[1] and of particular interest to us were tricyclic ring systems containing a highly strained cyclopropane unit.

We recently described[2] the synthesis and reactivity of the oxa tricyclic ketone **1**, conveniently prepared from commercially available sodium 3,4-dihydro-2*H*-pyran-2-carboxylate (Scheme I). The cyclopropyl ring could be fragmented under mild-acid conditions to produce oxabicyclo[2.2.2]octanones. Among the reaction described with **1** was the stereospecific addition of organolithium agents to the ketone (from the less hindered face), to produce the corresponding tertiary alcohols **2**.

We undertook the reactivity study of these oxa tricyclic alcohols **2** employing acid catalysis to effect ring fragmentations. This paper describes the novel discovery that these alcohols undergo sequential cleavage of the cyclopropyl ring followed by regiospecific opening of the ether

Scheme I. Synthesis of Oxa Tricyclic Ketone

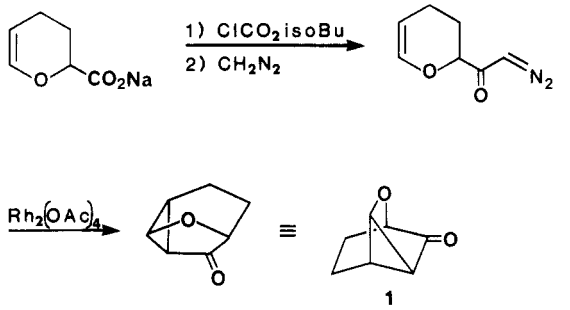
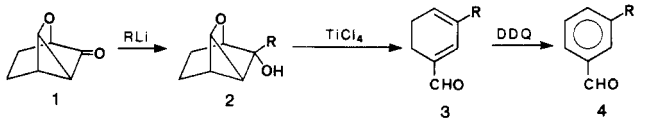


Table I



	R	% yield 2	3	4
a	Me	76	69[a,b]	30
b	*t*-Bu	73	100[b]	90[c]
c	Ph	79	100[d]	88
d	2-thienyl	80	62[a,d]	63[e]

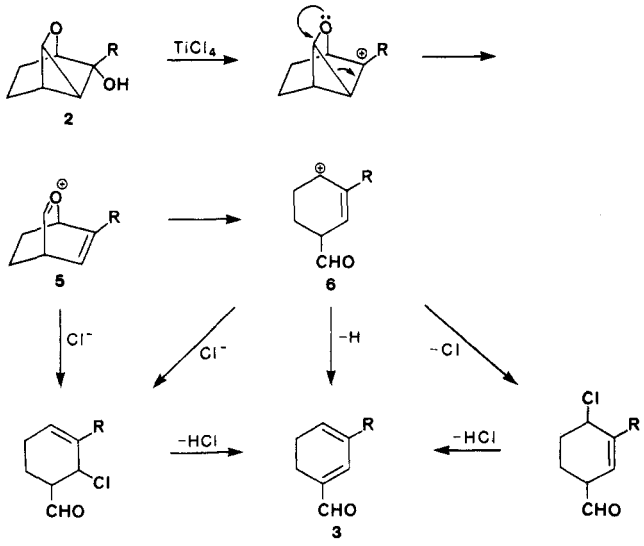
[a] Diene aldehyde unstable. [b] 5 equiv of $TiCl_4$/1.1 equiv of Et_3N. [c] Reaction time 2 days. [d] 0.2 equiv of $TiCl_4$, no Et_3N. [e] Yield from oxatricyclanol **2d** without isolation of **3d**.

cycle to form cyclohexadiene aldehydes and meta-substituted benzaldehydes, benzyl alcohols, or benzyl bromides,

(1) An early example of this approach appears in Woodward's reserpine synthesis. The synthesis and stereochemistry of the E ring are controlled through strained policyclic ring formation and fragmentation: Kornfeld, E. C.; Fornefeld, E. J.; Kline, G. B.; Mann, M. J.; Morrison, D. E.; Jones, R. G.; Woodward, R. B. *J. Am. Chem. Soc.* **1956**, *78*, 3087.
(2) Adams, J.; Belley M. *Tetrahedron Lett.* **1986**, *27*, 2075.

0022-3263/86/1951-3878$01.50/0

Scheme II. Proposed Mechanism for $TiCl_4$ Catalysis



depending upon the reaction conditions.

Results and Discussion

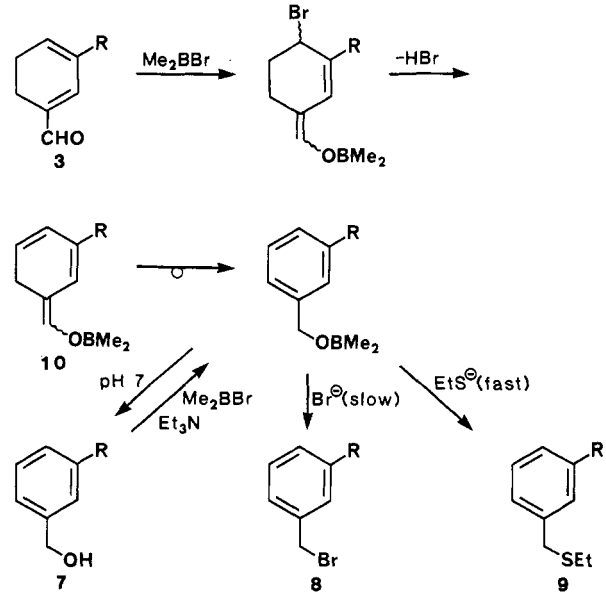
A variety of Lewis and Brønsted acids (vide infra) in organic media were capable of converting oxa tricyclic alcohols **2a–d** to their corresponding diene aldehydes **3a–d**. In many cases this process afforded rather low yields and was accompanied by decomposition of the substrate. Nevertheless, it was discovered that the use of $TiCl_4$ (5 equiv) and Et_3N (1 equiv) produced good yields of cyclohexadiene aldehydes **3** (Table I). The reaction appears to be general for a variety of alkyl and aryl substituents. In cases of aryl substitution (**2c,d** → **3c,d**) even a catalytic amount of $TiCl_4$ without Et_3N effected this conversion. $AlCl_3$ could be used for the rapid conversion of **2c** to **3c**, and ZnI_2 also produced good results but this reaction was very slow at room temperature. Even concentrated HCl in THF produced **3c** in 1 h, but none of these catalysts appeared as effective as $TiCl_4$.

In general, dihydrobenzaldehydes tend not to be stable. Both **3a** and **3d** decompose on standing at room temperature either by redox disproportionation or as a result of dimerization reactions. In the case of the 2-thienyl compound **3d** a Diels–Alder dimer was isolated.[3] The decomposition of the diene aldehydes could be retarded by storage in dilute solution under an inert atmosphere at 0 °C.

In a synthetically useful reaction, the dihydrobenzaldehydes **3a–d** could be efficiently converted to their corresponding meta-substituted benzaldehydes **4a–d** (see Table I) by oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). The oxidation reaction of **3b** (R = *t*-Bu) is slow but produces excellent yields. The conversion of **3a** to **4a** (R = Me) gave a disappointing yield presumably due to the instability of the diene aldehyde.

The following mechanism (Scheme II) is proposed to account for the observed conversion of tertiary alcohols **2** to diene aldehydes **3**. First, a complex is formed between the alcohol and the Lewis acid ($TiCl_4$). The cleavage of the tertiary C–O bond leads to a tertiary carbocation. The cyclic ether oxygen then participates in the cleavage of the cyclopropyl ring with concomitant olefin formation, to produce an oxonium ion intermediate **5**.[4] The oxonium ion **5** can then be cleaved to releave ring strain, leading to the allylic carbocation **6** that loses a proton to give the product **3**. Alternatively, chloride ion (from $TiCl_4$) can displace the oxonium ion **5** in an S_N2' fashion (less hindered attack) or directly attack cation **6** followed by elimination of HCl to arrive at the same product.

Scheme III. Proposed Mechanism for Me_2BBr Catalysis



Unique among the Lewis acids examined in the rearrangement of oxa tricyclic alcohols was dimethylboron bromide. This reagent has been found to be a very mild and selective agent for the cleavage of ethers and acetals.[5] It was anticipated that the reaction with Me_2BBr would produce similar results to $TiCl_4$. However, treatment of the tertiary alcohol **2a** with Me_2BBr (5 equiv) and Et_3N (2 equiv) produced an intermediate that was converted directly to the meta-substituted benzyl alcohol **7a** (Scheme III).

In addition, it was found that, under prolonged reaction times, the benzyl alcohol **7a** itself was transformed to its corresponding benzyl bromide **8a**. The reaction was followed by TLC, and it was demonstrated that the first intermediate formed coeluted with diene aldehyde **3a**. Early quenching of the reaction permitted the isolation of small amounts of diene aldehyde **3a** that could be resubmitted to Me_2BBr/Et_3N treatment to produce benzyl alcohol **7a**. In a single experiment with alcohol **2a** ethanethiol was added in addition to Me_2BBr/Et_3N, and a modest yield (37%) of 3-[(ethylthio)methyl]toluene (**9**; R = Me) was produced.

The formation of the benzyl bromide **8a** could be markedly accelerated by the addition of silica gel to the reaction. The role of silica gel in the reaction at first glance appeared to be solely to generate HBr in situ. However, if HBr(aq) is added to the reaction, only decomposition products are observed. We surmise that silica gel serves to moderate the acidity of the HBr generated and produces a much cleaner reaction, leading to a moderate yield of the benzyl bromide **8a**. The results of all the Me_2BBr experiments to produce benzyl alcohols **7a–d** and benzyl

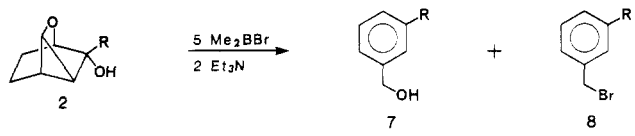
(3) The dimer was identified by its mass spectrum (M^+), but no further characterization was obtained.

(4) A similar oxonium ion was observed by: Bégué, J. P.; Charpantier-Morize, M.; Bonnet-Delpon, D.; Sansoulet, J. *J. Org. Chem.* **1980**, *102*, 7798.

(5) (a) Guindon, Y.; Yoakim, C.; Morton, H. E. *Tetrahedron Lett.* **1983**, *24*, 2969. (b) Guindon, Y.; Yoakim, C.; Morton, H. E. *J. Org. Chem.* **1984**, *49*, 3912 (see ref 32).

(6) Gouesnard, J. P.; Martin, G. J. *Tetrahedron* **1974**, *30*, 151.

Table II



	R	reactn conditions[a]	% yield 7	% yield 8
a	Me	16 h	40	
		SiO_2,[b] 16 h	10	43
b	*t*-Bu	SiO_2, 2 h	50	10
		SiO_2, 16 h		64
c	Ph	reflux, 24 h	56	
		SiO_2, 40 h		52
d	2-thienyl	SiO_2, 16 h	36	24
		SiO_2, 40 h		30

[a] In CH_2Cl_2; started at −78 °C, then for the indicated times at room temperature. [b] Silica gel for flash chromatography.

bromides **8a–d** are summarized in Table II.

Since the diene aldehyde **3a** is detected as a discrete intermediate in experiments with Me_2BBr, the proposed mechanism to that point of the reaction remains similar to the course suggested for $TiCl_4$ catalysis. We reason that the diene aldehydes **3a** react further in the presence of Me_2BBr due to the enhanced electrophilicity of the unsaturated aldehyde once complexed to the boron,[5b] together with the increased nucleophilicity of bromide ion (relative to Cl^- in $TiCl_4$). Elimination of HBr produces intermediate **10**, which is prone to tautomerization to the aromatic benzyl boronate. Scheme III depicts the possible routes to benzyl alcohols, bromide, and ethylthio compounds.

Conclusion

The work presented here represents a general route to the preparation of meta-substituted alkyl- and arylbenzaldehydes, benzyl alcohols, and benzyl bromides via the rearrangement of a strained tricyclic skeleton. Although four steps are involved, the sequence described herein provides unique access to benzene derivatives with carbon substituents located meta to each other. In the most widely used method of introducing a second carbon substituent into a monosubstituted benzene, the Friedel–Crafts reaction, carbon electrophiles generally give unsatisfactory yields of 1,3-disubstituted benzenes.[7] Other syntheses of meta-substituted aromatic compounds used as aryl Grignard condensation (made from the corresponding meta-bromo-substituted aromatic) with dimethylformamide to yield the benzaldehyde[8,10] or formaldehyde to give the benzyl alcohol.[11,12]

The similar acid-catalyzed rearrangement of aryl-8-oxabicyclo[3.2.1]octenones to produce meta-substituted arylbenzaldehydes was recently reported by Mann and co-workers, and their proposed mechanism complements the work described here.[15] Furthermore, by using $TiCl_4$ as the catalyst we also have access to dihydrobenzaldehydes, compounds that due to their instability are difficult to prepare.[6]

We are currently expanding the methodology to include more highly substituted aromatic systems, by beginning with different substitution patterns on the initial dihydropyrancarboxylate.

Experimental Section

General Procedures. Nuclear magnetic resonance spectra (^1H NMR and ^{13}C NMR) were recorded on a Bruker AM 250-MHz FT spectrometer. Infrared spectra were obtained on a Perkin-Elmer Model 681 instrument. High-resolution mass spectra were obtained at the McGill University mass spectrometry unit on a ZAB-HS spectrometer. Elemental analyses were performed by Galbraith Laboratories, Knoxville TN. Melting points were obtained on a Buchi 510 melting point apparatus and are uncorrected. Purifications by flash chromatography employed 200–400-mesh silica gel supplied by E. Merck.

2-Oxatricyclo[2.2.2.0^{3,5}]octan-6-one (1). To a suspension of 18.822 g (125 mmol) of sodium 3,4-dihydro-2*H*-pyran-2-carboxylate in 150 mL of anhydrous THF were added 2.0 mL (0.1 equiv) of triethylamine and 0.6 mL (0.05 equiv) of dimethylformamide followed by dropwise addition of 17.1 mL (1.05 equiv) of isobutyl chloroformate. After 1.5 h of stirring (room temperature), the formation of the mixed anhydride was complete (the yield determined by NMR, using 1 mL of reaction mixture, after filtration and evaporation, was about 95%).

To this solution was added, at −78 °C, 800 mL of ether containing diazomethane (from 60 g of *N*-(nitrosomethyl)urea). The temperature was raised to room temperature and the reaction mixture concentrated to about 400 mL. The salts were removed by filtration on Celite, and the diazo ketone was purified by filtration on 500 g of silica gel using dichloromethane as eluant. After concentration to 100 mL, the solution was added dropwise to a suspension of 0.8 g (0.015 equiv) of rhodium acetate dimer in 50 mL of dichloromethane. When the addition was complete, the reaction was stirred for another 30 min and then was washed (2×) with 5% aqueous sodium carbonate and filtered on silica gel. Finally, the oxatricyclanone **1** was purified by flash chromatography on silica gel with 20% EtOAc/hexane containing 2% Et_3N to yield 9.119 g (58%). The ketone **1** could also be purified by distillation: bp 90 °C (12 mmHg); IR (neat) ν 2940, 1740, 1190, 1040, 1020 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.81 (1 H, m, J = 9.3 Hz), 1.92 (1 H, m, J = 0.7 Hz), 2.04 (1 H, ddd, J = 0.7, 3.7, 9.3 Hz), 2.15–2.36 (3 H, m), 3.89 (1 H, ddd, J = 0.7, 0.7, 4.1 Hz), 4.81 (1 H, dd, J = 3.7, 3.7 Hz); ^{13}C NMR ($CDCl_3$) δ 14.8 (t, C-8), 26.7 (d, C-4), 27.6 (d, C-5), 29.3 (t, C-7), 66.0 (d, C-3), 74.8 (d, C-1), 210.7 (s, C-6); exact mass calcd for $C_7H_8O_2$ 124.0524, found 124.0524. Anal. Calcd for $C_7H_8O_2$: C, 67.73; H, 6.50. Found: C, 67.26; H, 6.41.

6-Phenyl-2-oxatricyclo[2.2.2.0^{3,5}]octan-6-ol (2c). To 2.30 g (18.5 mol) of 2-oxatricyclo[2.2.2.0^{3,5}]octan-6-one (**1**) in 20 mL of THF at −78 °C was slowly added 12 mL (24 mmol) of phenyllithium (2.0 M) in cyclohexane. The reaction mixture was allowed to warm to room temperature for 10 min. After hydrolysis with 25% aqueous ammonium acetate, extraction with ether, and chromatography on silica gel (15% EtOAc/hexane), 2.94 g (79% yield) of the oxatricyclanol **2c** was obtained: mp 83–84 °C; IR (neat) 3410, 2935, 1490, 1445, 1052, 1029 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.05 (1 H, m), 1.73 (1 H, m), 1.84 (1 H, m), 2.01–2.21 (2 H, m), 2.29 (1 H, m), 2.36 (1 H, s), 3.81 (1 H, m), 4.21 (1 H, dd, J = 5.0, 5.0 Hz), 7.26–7.43 (3 H, m), 7.59–7.65 (2 H, m); MS, m/e (relative intensity) 202 (M^+, 2), 184 (9), 146 (91), 105 (86), 77 (100), 55 (100); exact mass calcd for $C_{13}H_{14}O_2$ 202.0994, found 202.0996. Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.06; H, 6.95.

The following compounds were prepared similarly:

6-Methyl-2-oxatricyclo[2.2.2.0^{3,5}]octan-6-ol (2a): IR (neat) 3440, 2970, 2940, 1153, 1138, 1060, 1035, 998 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.78 (1 H, m), 1.38 (1 H, m), 1.40 (3 H, s), 1.64 (1 H,

(7) For a discussion of such reactions with leading references see: March J. *Advanced Organic Chemistry*, 3rd ed.; Wiley: New York, 1985; pp 481, 485.
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(9) Commercially available from Aldrich Chemical Co.
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(13) Plummer, E. L. U.S. Patent 4 426 524, 1984; *Chem. Abstr.* **1984**, *100*, 192112*r*.
(14) Grovenstein, E., Jr.; Wentworth, G. *J. Am. Chem. Soc.* **1967**, *89*, 2348.
(15) Mann, J.; Wilde, P. D.; Finch, M. W. *J. Chem. Soc., Chem. Commun.* **1985**, 1543.

s), 1.71 (1 H, m), 1.85 (1 H, m), 1.97–2.16 (2 H, m), 3.50 (1 H, m) 3.93 (1 H, dd, J = 5.4, 5.4 Hz); MS, m/e 140 (M^+), 97, 84, 71, 69.

6-*tert*-Butyl-2-oxatricyclo[2.2.2.0^{3,5}]octan-6-ol (2b): IR (neat) 3445, 2980, 2950, 1060, 1045, 1010 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.86 (1 H, m), 1.02 (9 H, s), 1.56 (1 H, dd, J = 5.0, 8.3 Hz), 1.74 (1 H, m), 1.84 (1 H, s), 1.85 (1 H, m), 1.97–2.17 (2 H, m), 3.88–3.95 (2 H, m); MS, m/e (relative intensity) 182 (M^+, 0.5), 125 (18), 57 (100); exact mass calcd for $C_{11}H_{18}O_2$ 182.1307, found 182.1287;

6-(2-Thienyl)-2-oxatricyclo[2.2.2.0^{3,5}]octan-6-ol (2d): IR (neat) 3390, 2930, 1231, 1097, 1052, 1028, 998 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.03 (1 H, m), 1.75–1.90 (2 H, m), 1.98–2.34 (4 H, m), 3.84 (1 H, m), 4.18 (1 H, dd, J = 5.6, 5.6 Hz), 6.99 (1 H, dd, J = 3.8, 4.5 Hz), 7.09 (1 H, dd, J = 1.5, 3.8 Hz), 7.24 (1 H, dd, J = 1.5, 4.5 Hz); MS, m/e (relative intensity) 208 (M^+, 2), 152 (74), 139 (58), 111 (77), 55 (100); exact mass calcd for $C_{11}H_{12}O_2S$ 208.0558, found 208.0544.

3-Phenyl-5,6-dihydrobenzaldehyde (3c). To 100.6 mg (497 μmol) of 6-phenyl-2-oxatricyclo[2.2.2.0^{3,5}]octan-6-ol (**2c**) in 3 mL of CH_2Cl_2 was added 22 μL (0.4 equiv) of titanium tetrachloride. After 5 h, the reaction mixture was hydrolyzed (25% NH_4OAc), extracted with ethyl acetate, washed with brine, dried over sodium sulfate, and filtered through silica gel with ethyl acetate to yield 92 mg (100% yield) of the desired compound **3c**: ^{1}H NMR ($CDCl_3$) δ 2.42 (4 H, s), 6.46 (1 H, br s), 7.09 (1 H, s), 7.25–7.36 (5 H, m), 9.56 (1 H, s); exact mass calcd for $C_{13}H_{12}O$ 184.0888, found 184.0876.

The following compounds were prepared similarly:

3-Methyl-5,6-dihydrobenzaldehyde (3a)[6] and 3-*tert*-butyl-5,6-dihydrobenzaldehyde (3b): IR (neat) 2958, 1673, 1572 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.13 (9 H, s), 2.20–2.40 (4 H, m), 6.07 (1 H, m), 6.95 (1 H, s), 9.55 (1 H, s); MS, m/e (relative intensity) 164 (M^+, 5), 163 (27), 147 (100), 137 (35), 125 (34); exact mass calcd for $C_{11}H_{16}O$ 164.1201, found 164.1189;

3-(2-Thienyl)-5,6-dihydrobenzaldehyde (3d): ^{1}H NMR (CD_2Cl_2) δ 2.44 (4 H, s), 6.58 (1 H, br s), 7.04 (1 H, dd, J = 4.4, 5.3 Hz), 7.14 (2 H, m), 7.23 (1 H, d, J = 5.3 Hz), 9.62 (1 H, s).

1,1′-Biphenyl-3-carboxaldehyde (4c).[8] To 53 mg (288 μmol) of 3-phenyl-5,6-dihydrobenzaldehyde (**3c**) in 1.2 mL of CH_2Cl_2 was added 200 mg (3 equiv) of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone. After 30 min, the reaction mixture was poured on silica gel and eluted with 10% ethyl acetate in hexane to yield 46 mg (88%) of the title compound **4c**.

Similarly were prepared **tolualdehyde (4a)**,[9] **3-*tert*-butylbenzaldehyde (4b)**[10] **and 3-(2-thienyl)benzaldehyde (4d).**

Data for **4d**: IR (neat) 2830, 2720, 1700, 1598, 1582, 1477 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.13 (1 H, dd, J = 4.0, 5.0 Hz), 7.35 (1 H, d, J = 5.0 Hz), 7.40 (1 H, d, J = 4.0 Hz), 7.55 (1 H, dd, J = 8.0, 8.0 Hz), 7.78 (1 H, d, J = 8.0 Hz), 7.86 (1 H, d, J = 8.0 Hz), 8.11 (1 H, s), 10.06 (1 H, s); MS, m/e (relative intensity) 188 (M^+, 100), 187 (44), 159 (33), 115 (37), 69 (31); exact mass calcd for $C_{11}H_8OS$ 188.0296, found 188.0297.

3-(Hydroxymethyl)-1,1′-biphenyl (7c).[11] To 41 mg (203 μmol) of 6-phenyl-2-oxatricyclo[2.2.2.0^{3,5}]octan-6-ol (**2c**) in 1.5 mL of CH_2Cl_2 at −78 °C were added 95 μL (3 equiv) of triethylamine and 700 μL (5 equiv) of dimethylboron bromide (1.70 M in CH_2Cl_2). The reaction mixture was allowed to warm to room temperature and heated to reflux 24 h. After hydrolysis with 25% aqueous ammonium acetate, extraction with ethyl acetate, and chromatography on silica gel (25% EtOAc/hexane), 21 mg (56%) of the alcohol **7c** was obtained.

Similarly were prepared **3-methylbenzyl alcohol (7a)**,[9] **3-*tert*-butylbenzyl alcohol (7b)**[12] [exact mass calcd for $C_{11}H_{16}O$ 164.1201, found 164.1200], and **3-(2-thienyl)benzyl alcohol (7d)**[13] [exact mass calcd for $C_{11}H_{10}OS$ 190.0452, found 190.0449].

3-(Bromomethyl)-1,1′-biphenyl (8c).[14] To 96 mg (475 μmol) of 6-phenyl-2-oxatricyclo[2.2.2.0^{3,5}]octan-6-ol (**2c**) in 2 mL of CH_2Cl_2 at −78 °C were added 132 μL (2 equiv) of triethylamine, 1.3 mL (5 equiv) of dimethylboron bromide 1.80 M in CH_2Cl_2, and 200 mg of silica gel (for flash chromatography). The mixture was allowed to warm to room temperature and stirred 40 h. After filtration and hydrolysis with 25% aqueous ammonium acetate, extraction with ethyl acetate, and chromatography on silica with hexane, 61 mg (52% yield) of the bromide **8c** was obtained.

Similarly were prepared **3-methylbenzyl bromide (8a)**,[8] **3-*tert*-butylbenzyl bromide (8b)** [IR (neat) 2960, 1603, 1589, 1479 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.28 (9 H, s), 4.45 (2 H, s), 7.17 (1 H, ddd, J = 1.7, 1.7, 7.3 Hz), 7.22 (1 H, dd, J = 7.3, 7.3 Hz), 7.28 (1 H, ddd, J = 1.7, 1.7, 7.3 Hz), 7.33 (1 H, br s); MS, m/e (relative intensity) 147 (M − Br, 15), 58 (10), 43 (100); exact mass calcd for $C_{11}H_{15}$ (M − Br) 147.1174, found 147.1182], and **3-(2-thienyl)benzyl bromide (8d)**[13] [exact mass calcd for $C_{11}H_9BrS$ 251.9608, found 251.9600.

3-[(Ethylthio)methyl]toluene (9). To a cooled solution (−78 °C) of 23.8 mg of 6-methyl-2-oxatricyclo[2.2.2.0^{3,5}]octan-6-ol (**2a**) in 1 mL of CH_2Cl_2 were added 14 μL (1.1 equiv) of ethanethiol, 52 μL (2.2 equiv) of triethylamine, and 200 μL (2.2 equiv) of dimethylboron bromide 1.83 M in CH_2Cl_2. The reaction mixture was then allowed to warm to room temperature and was stirred 30 min before hydrolysis with 25% aqueous ammonium acetate. Extraction with ethyl acetate and chromatography on silica with hexane yielded 10 mg (35%) of the title compound **9**: IR (neat) 2965, 2920, 1610, 1591 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.25 (3 H, t, J = 7.2 Hz), 2.35 (3 H, s), 2.44 (2 H, q, J = 7.2 Hz), 3.69 (2 H, s), 7.03–7.24 (4 H, m); MS, m/e (relative intensity) 166 (M^+, 4), 105 (36), 69 (100); exact mass calcd for $C_{10}H_{14}S$ 166.0816, found 166.0808.

Registry No. 1, 103668-90-2; **2a**, 103668-92-4; **2b**, 103668-93-5; **2c**, 103668-94-6; **2d**, 103668-95-7; **3a**, 52866-48-5; **3b**, 103668-96-8; **3c**, 103668-97-9; **3d**, 103668-98-0; **4a**, 620-23-5; **4b**, 23039-28-3; **4c**, 1204-60-0; **4d**, 103668-99-1; **7a**, 587-03-1; **7b**, 51503-09-4; **7c**, 69605-90-9; **7d**, 103669-00-7; **8a**, 620-13-3; **8b**, 102405-32-3; **8c**, 14704-31-5; **8d**, 85553-44-2; **9a**, 103669-01-8; MeLi, 917-54-4; *t*-BuLi, 594-19-4; PhLi, 591-51-5; 2-thienyl Li, 2786-07-4; 3,4-dihydro-2*H*-pyran-2-carboxylic acid sodium salt, 16698-52-5; 2-diazo-1-(2-(3,4-dihydro-2*H*-pyranyl))ethanone, 103668-91-3.