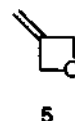
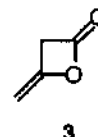
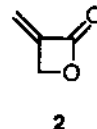


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Table 1. Synthesis of 2,2-Disubstituted 3-Methyleneoxetanes **10**

Entry	Allylsilane 8	Yield (%) ^a	Yield(%) ^a		3-Methylene- oxetane 10	Yield (%)
			(9)	(11)		
a		63	98	—		91
b		33	88	—		73
c		54	85(38) ^b	—		76
d		38	88	—		73
e		48	59	32		77
f		78	73(49) ^b	21(49) ^b		92
g		61	74	20	—	—
h		62	71	27	—	—



Synthesis of 2,2-Disubstituted 3-Methyleneoxetanes

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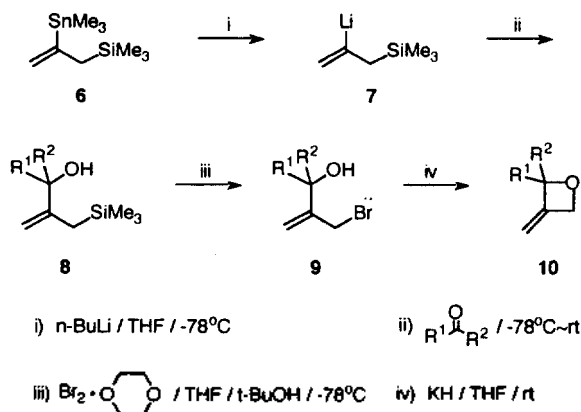
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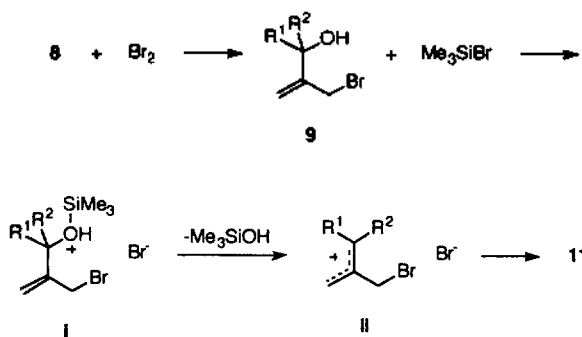
Strained small oxacycles containing an exocyclic methylene group, methylene oxirane (allene oxide) **1**, α -methylene- β -lactone **2** and diketene **3** have been studied intensively by theoretical and synthetic chemists. Surprisingly, however, studies on methyleneoxetanes **4** and **5** have quite been ignored. Only the parent 3-methyleneoxetane **5** was synthesized from the retro Diels-Alder reaction of an anthracene ad-

duct⁵ and the interaction between the endocyclic oxygen and the methylene group of it was investigated by ultraviolet photoelectron spectra and molecular orbital calculations.⁶

In continuation of our studies on exploring synthetic application of 2-trialkylstannyl-3-trimethylsilylpropene **6**,⁷ we found a facile method for the synthesis of 2,2-disubstituted 3-methyleneoxetanes. Transmetalation of **6** with *n*-butyllithium provided 2-lithio-3-trimethylsilylpropene **7**, which reacted smoothly at -78°C with carbonyl compounds to produce 2-[(trimethylsilyl)methyl]allyl alcohols **8** in moderate yields. This route revealed much improved yield of **8a** compared to the reaction of the vinyl lithium intermediate **7** generated from lithium halogen exchange of 2-bromoallylsilane by *t*-butyllithium with cyclohexanone⁸ (18%, cf. Table 1, entry a). When allyl alcohols **8a-d** were treated with a 10% excess



of dioxane dibromide in tetrahydrofuran-*t*-butyl alcohol (10–15 equiv) at -78°C , 2-(bromomethyl)allyl alcohol **9a-d** were obtained in high yields.⁹ When the reaction was performed in the absence of *t*-butyl alcohol, the yield became lower (entry c). On the contrary, the reactions of alcohols **8e-h** where R^1 and/or R^2 is an aryl group with dioxane dibromide provided 2-(bromomethyl)allyl alcohols **9e-h** along with 3-bromo-2-(bromomethyl)propenes **11e-h**. By adding *t*-butyl alcohol the formation ratio of monobromide over dibromide was improved, although dibromide was still produced (entry f). The formation of dibromides **11** could be explained as follows. 2-[(Trimethylsilyl)methyl]allyl alcohols **8** react with bromine to yield allyl bromides **9** and bromotrimethylsilane. The bromotrimethylsilane formed reacts further with the products **9** to afford **11**. In the reactions of allyl alcohols **8a-d**, the generated bromotrimethylsilane could be removed by the reaction of it with *t*-butyl alcohol.¹⁰ However, in the reactions of alcohols **8e-h**, the formations of dibromides **11e-h** could not be completely suppressed by *t*-butyl alcohol. The difference would come from the stability of the carbocations **ii**.



When 0.02 M THF solution of 2-(bromomethyl)allyl alcohols **9b-f** were treated with potassium hydride at room temperature for 5 min, 3-methyleneoxetanes **10b-f** were produced in high yields. In case of **9a**, the reaction proceeded rapidly and completely by adding a small amount of HMPA to afford **10a**. The infrared absorption for the exocyclic carbon-carbon double bonds in **10** were appeared at high frequency (1688 cm^{-1} - 1698 cm^{-1}) due to the small ring size effect.¹² Unfortunately, the reactions of **9f** and **9g** where R^1 is a hydrogen with potassium hydride did not yield 2-mono-substituted 3-methyleneoxetanes **10f** and **10g**, but a mixture of unidentified products.

In conclusion the route should be useful for the synthesis of 2,2-disubstituted 3-methyleneoxetanes, although it is not applicable for the synthesis of 2-mono-substituted 3-methyleneoxetanes.¹¹ The reason for this difference would be interesting but not clear at the present.

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- Spectral data for the selected products are given below. **8e**: ^1H NMR (300 MHz, CDCl_3) δ 0.05 (9H, s), 1.46 (2H, s), 4.92 (1H, s), 5.23 (1H, s), 7.30-7.55 (5H, m); ^{13}C NMR δ -0.77, 21.4, 29.1, 77.6, 108.6, 125.4, 126.8, 128.3, 146.3, 151.8, **9e**: ^1H NMR δ 1.78 (3H, s), 2.16 (1H, s), 3.85 (1H, d, $J=11.1$ Hz), 3.95 (1H, d, $J=11.1$ Hz), 5.52 (1H, s), 5.53 (1H, s), 7.20-7.47 (5H, m); ^{13}C NMR δ 29.9, 31.8, 76.9, 117.6, 125.2, 127.2, 128.3, 145.2, 150.2. **11e**: ^1H NMR δ 2.13 (3H, s), 4.04 (2H, s), 4.34 (2H, s), 7.26-7.39 (5H, m); ^{13}C NMR δ 21.5, 30.5, 33.4, 127.0, 127.7, 128.4, 129.2, 141.7, 143.7. **10a**: ^1H NMR (500 MHz) δ 1.35-1.86 (10H, m), 4.72-4.73 (1H, m), 4.89-4.90 (1H, m), 4.98-5.00 (2H, m); ^{13}C NMR δ 22.1, 25.0, 36.7, 72.7, 93.9, 101.7, 153.0; MS m/z 138 (M^+ , 5), 94 (49), 81 (30), 67 (28), 55 (100%); IR (neat) ν_{max} 1697 (C=C) cm^{-1} ; **10b**: ^1H NMR (300

MHz) δ 1.50-2.10 (12H, m), 4.68-4.69 (1H, m), 4.84-4.85 (1H, m), 4.95-4.98 (2H, m); ^{13}C NMR δ 21.5, 29.0, 40.0, 72.6, 97.2, 101.0, 155.0; MS m/z 152 (M^+ , 11), 134 (10), 119 (42), 91 (72), 84 (100), 79 (55), 67 (41%); IR ν_{max} 1697 cm^{-1} . **10c**: ^1H NMR δ 1.46-2.26 (14H, m), 4.68-4.69 (1H, m), 4.83-4.85 (1H, m), 4.96-4.98 (2H, m); ^{13}C NMR δ 21.0, 24.4, 28.0, 35.3, 72.5, 96.7, 101.2, 154.1; MS m/z 166 (M^+ , 11), 133 (11), 119 (12), 105 (21), 91 (34), 86 (75), 84 (100), 79 (41), 67 (25%); IR ν_{max} 1697 cm^{-1} . **10d**: ^1H NMR δ 1.50-2.20 (14H, m), 4.79-4.80 (1H, m), 4.92-4.94 (2H, m), 5.06-5.08 (1H, m); ^{13}C NMR δ 26.47, 26.54, 32.3, 33.7, 37.1, 72.4, 97.7, 103.5, 153.1; MS m/z 190 (M^+ , 37), 175 (37), 150 (43), 133 (42), 117 (33), 105 (29), 91 (64), 84 (100), 79 (96), 67 (33), 55 (60%); IR ν_{max} 1688 cm^{-1} . **10e**: ^1H NMR δ 1.81 (3H, s), 4.83-4.86 (1H, m), 4.98-5.01 (1H, m), 5.05-5.18 (2H, m), 7.24-7.51 (5H, m); ^{13}C NMR δ 28.5, 73.7, 94.2, 103.3, 124.0, 127.2, 128.3, 144.8, 152.4; MS m/z 160 (M^+ , 21), 159 (27), 145 (99), 129 (57), 115 (85), 105 (100), 77 (96%); IR ν_{max} 1692 cm^{-1} . **10f**: ^1H NMR δ 5.08-5.09 (1H, m), 5.14-5.15 (1H, m), 5.15-5.19 (2H, m), 7.13-7.47 (10H, m); ^{13}C NMR δ 74.1, 96.9, 106.2, 125.2, 127.6, 127.8, 143.7, 150.5; MS m/z 222 (M^+ , 11), 206 (100), 191 (72), 165 (23), 128 (14), 105 (18), 84 (17%); IR ν_{max} 1698 cm^{-1} .

The Ring Structure and Barrier to Planarity of Oxetane

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Conformations of 4-membered ring systems have been extensively investigated by a variety of experimental and theoretical methods.¹ Cyclobutane is stable in a puckered conformation with the puckering angle of *ca.* 30° and the barrier

to planarity of 1.5 kcal/mol.¹⁻³ Although planar conformation is favorable in terms of ring strain, the cyclobutane ring structure may alleviate unfavorable eclipsed interactions between vicinal hydrogens by tilting the CH_2 groups in the opposite direction.² Thus, the degree of puckering in 4-membered ring systems is generally accepted as a compromise between ring strain and torsional strain.

The introduction of heteroatom in the cyclic compounds usually changes the equilibrium conformation.⁴ In oxetane, replacement of CH_2 group by O atom can substantially reduce the number of unfavorable eclipsed interactions between vicinal hydrogen. This may cause oxetane to be flatter than cyclobutane. Far-IR⁵ and microwave (MW)⁶ studies have provided that the ring structure of oxetane is planar. However, the planar conformation of oxetane is not the minimum of the puckering potential energy function (PPEF) but is attributed to a rapid equilibrium between two puckered conformers through a small energy barrier. X-ray results at low temperature (90 K and 140 K) have furnished that the oxetane ring exists in a puckered conformation with the puckering angle with *ca.* 10°.⁷ The NMR analyses⁸ using dipolar coupling constants have agreed to the X-ray data. Since both experiments, X-ray and NMR, have been carried out in the condensed phases, the equilibrium conformation may differ from the one in the gas-phase.

Ab initio methods have been applied to oxetane with the modest basis sets,^{9,10} *i.e.* 3-21G and 4-21G. All the calculations have concluded that the planar form is the equilibrium conformation. Earlier semi-empirical MINDO/2' results have estimated the geometry of oxetane poorly and a zero puckering potential.¹¹ Laane and coworkers have utilized the molecular mechanics (MM2) to examine the PPEF for oxetane.¹² MM2 has deduced that the ring structure of oxetane is planar and, of course, with no puckering potential.

In order to better understand the conformational nature of oxetane, *ab initio* and semi-empirical molecular orbital calculations were performed using the GAUSSIAN 92¹² series of programs on a CRAY Y-MP computer. The equilibrium geometries were fully optimized at four different levels of theories - PM3,¹³ HF/3-21G,¹⁴ HF/6-31G*,¹⁵ and MP2/6-31G*.¹⁶ Semi-empirical method was applied to assess the performance of PM3 hamiltonian for our future studies on highly substituted oxetane derivatives.¹⁷

Table 1 summarizes the geometric parameters optimized

Table 1. Calculated and Observed Geometries^a of Oxetane

	PM3	HF/3-21G	HF/6-31G*	MP2/6-31G*	MW ^b	X-ray ^c
CO	1.453	1.476	1.419	1.451	1.449(2)	1.460(1)
CC	1.544	1.558	1.537	1.533	1.549(3)	1.534(2)
C_αH	1.099	1.079	1.082	1.087	1.091(2)	0.97(2)
C_βH	1.099	1.078	1.084	1.092	1.100(3)	0.97(2)
$\angle\text{COC}$	92.60	92.10	92.78	90.08	91.59(70)	90.18(8)
$\angle\text{CCO}$	90.82	90.95	91.66	91.45	91.44(30)	91.99(7)
$\angle\text{CCC}$	85.76	86.00	83.90	84.13	84.55(10)	84.79(9)
$\angle\text{HC}_\alpha\text{H}$	107.31	110.26	109.26	109.66	110.18(10)	
$\angle\text{HC}_\beta\text{H}$	109.20	110.74	109.04	109.31	110.44(30)	
Ring puckering angle ^d	0.00	0.00	0.00	17.85	0.00	10.7(1)

^aLengths in Å, and angles in degrees. ^bFrom the rotational constants, ref. 6b. ^cAt 90 K, ref. 7. ^dsee Figure 1 for the definition.