0.26 0.28 and 0.29 respectively, which is shown in Figure 6. The energy transferred into phonons increases as the incident collision energy is increased. In the low lenergy region, *i.e.*, less than 400 meV, the rate of energy transfer sharply increases while in the high energy region, the rate is reduced.

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References

1. C. J. Mogab, *in VLSI Technology*, edited by S. M. Sze (McGraw-Hill, New York, 1983) Chapter 8, 303-346.
2. J. C. Tully, *Ann. Rev. Phys. Chem.*, **31**, 319 (1980).
3. J. P. Toennies, *in Dynamics of Gas-Surface Interaction*, edited by G. Benedek and U. Valbusa (Springer, Berlin, 1982) pp. 208-226.
4. G. A. Somorjai, *Chemistry in Two Dimensions: Surface* (Cornell University, New York, 1981), Chapter 7, pp. 331-380.
5. D. Eichenauer and J. P. Toennies, *J. Chem. Phys.*, **85**, 532 (1986).
6. J. J. Lander and J. Morrison, *J. Chem. Phys.*, **37**, 729 (1962).
7. E. T. Gawlinski and J. D. Guton, Phys. Rev., **B36**, 4774 (1987).
8. F. F. Abraham and J. Q. Broughton, *Phys. Rev. Lett.*, **56**, 734 (1986).
9. R. J. Hamers, R. M. Tromp, and J. E. Demuth, *Phys. Rev.*, **B34**, 5347 (1986).
10. R. A. Stansfield, K. Broomfield, and D. C. Clary, *Phys. Rev.*, **B39**, 7680 (1989).
11. R. Biwas and D. R. Hamann, *Phys. Rev. Lett.*, **55**, 2001 (1985).
12. R. Lampinen, R. M. Nieminen, and K. Kasaki, *Surf. Sci.*, **203**, 201 (1988).
13. F. F. Abraham and I. P. Batra, *Surf. Sci.*, **163**, L752 (1985).
14. S. C. Park and J. M. Bowman, *J. Chem. Phys.*, **81**, 6277 (1984).
15. B. C. Choi and R. T. Poe, *J. Chem. Phys.*, **83**, 1330 (1985).
16. B. C. Choi and R. T. Poe, *J. Chem. Phys.*, **83**, 1334 (1985).
17. L. M. Hubbard and W. H. Miller, *J. Chem. Phys.*, **80**, 5827 (1984).
18. G. D. Billing, *Chem. Phys.*, **86**, 349 (1984).
19. C. B. Smith and L. M. Raff, *J. Chem. Phys.*, **83**, 1411 (1985).
20. H.-D. Meyer, *Surf. Sci.*, **104**, 117 (1981).
21. R. R. Lucchese and J. C. Tully, *Surf. Sci.*, **137**, 570 (1984).
22. R. R. Lucchese and J. C. Tully, *J. Chem. Phys.*, **80**, 3451 (1984).
23. S. C. Park and D. C. Clary, *J. Appl. Phys.*, **60**, 1183 (1986).
24. S. C. Park and J. M. Bowman, *J. Chem. Phys.*, **80**, 3845 (1984).
25. S. A. Adelman and J. M. Doll, *J. Chem. Phys.*, **61**, 4242 (1974).
26. W. R. Gentry and C. F. Giese, *J. Chem. Phys.*, **63**, 3144 (1975).
27. H.-D. Meyer, *Chem. Phys.*, **61**, 365 (1981).
28. R. P. Feynman and A. R. Hibbs, *Quantum Mechanics and Path Integrals* (McGrawHill, New York, 1965), Chapter 8, pp. 232-234.
29. R. Tubino, L. Piseri, and G. Zerbi, *J. Chem. Phys.* **56**, 1022 (1972).
30. W. A. Steele, *The Interaction of Gases with Solid Surfaces* (Pergamon, Oxford, 1974).

Formal Synthesis of Isocomene

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A stereocontrolled synthesis of (±)-isocomene (**1**) *via* selective monoketalization of tricyclo[6.3.0.0^{1,5}]undeca-4,7-dione (**13**) was reported. Grignard reaction of bicyclic enone **10**, which was prepared from 2-methyl-1,3-cyclopentadione, gave the 1,4-addition product **11**. The subsequent aldol condensation product **12** was converted to mesyl derivative **13**. Transformation from **13** to the desired product **19** was achieved by a series of reactions, *i.e.*, the selective monoketalization at C-4 carbonyl group, the elimination of a mesyl group, Birch alkylation, methylation at C-6, the reduction of carbonyl group, the dehydration of alcohol **18**, and hydrolysis of the ketal group.

Introduction

The tricyclic sesquiterpene isocomene (**1**) has the unique framework of tricyclo[6.3.0.0^{1,5}]undeca-4,7-dione which comprises a variety of the polyquinanes. Since the first isolation of the tricyclic sesquiterpene isocomeme (**1**) in 1977 from

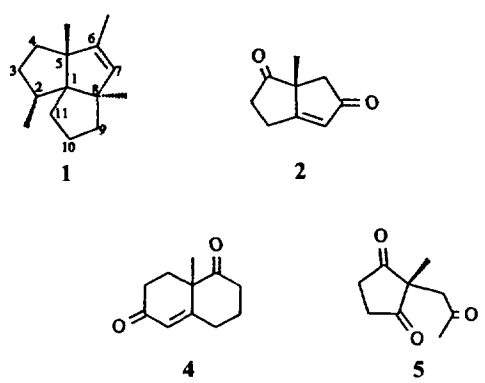


Figure 1.

Isocoma wrightii and Berkheya radula by Zalkow and Bohlmann, respectively.[1,2] Isocomene (**1**) has been attracting the attention of synthetic chemists because of its unique structural feature of three contiguous, quaternary chiral centers.[3]

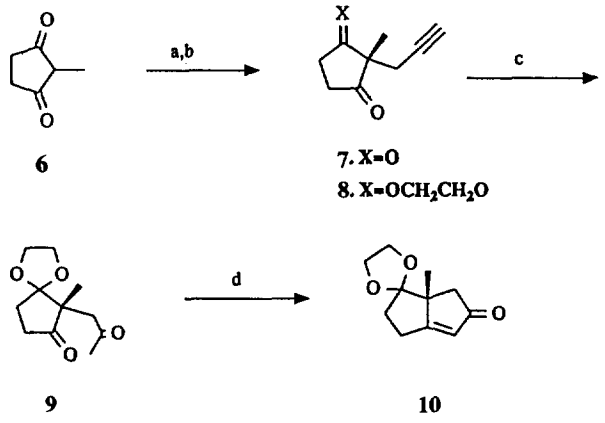
In previous communication,[4] we have briefly described the synthesis of isocomene and herein, we report the details concerning to this synthesis. Our synthetic strategy of isocomene was based on the conjecture that bicyclo[3.3.0]octenone **2** can serve as an intermediate leading to tricyclic skeleton such as tricyclo[6.3.0.$0^{1,5}$]undecane **3**. The structural similarity of bicyclo[3.3.0]octenone to the Wieland-Miescher ketone (**4**) known as a building block for the fused six-membered rings[5] indicates its usefulness as a building block, because the Michael addition to this enedione can provide an extra ring and thus lead to various products of polyquinanes such as coriolin and gymnomitrol.[6,7] Recently optically active bicyclo[3.3.0]octenones have been prepared. In spite of this resourcefulness, however, up to date, only one example of the construction of tricyclo[6.3.0.$0^{1,5}$]undecane ring system from bicyclo[3.3.0]octenones has been reported.[8] We herein described another application of bicyclo[3.3.0]octenone **2** to isocomene (**1**).

Results and Discussion

In general, the synthesis of bicyclo[3.3.0]octenones have not been well pursued toward tricyclic system, since it was reported that triketone **5** did not give a product of bicyclo[3.3.0]octenone under a variety of conditions of aldol condensations[9] and this fact might have limited its usefulness as a synthetic intermediate. In order to circumvent this difficulty associated with triketone **5**, the preparation of the ketal of **5** from 2,2-dimethylpropan-1,3-diol was reported.[10] But no further utilization has been explored at all. As for the synthesis of isocomene, we decided to exploit monoketal derivative of **8** from ethylene glycol instead of 2,2-dimethylpropan-1,3-diol, because it simplifies the synthesis.

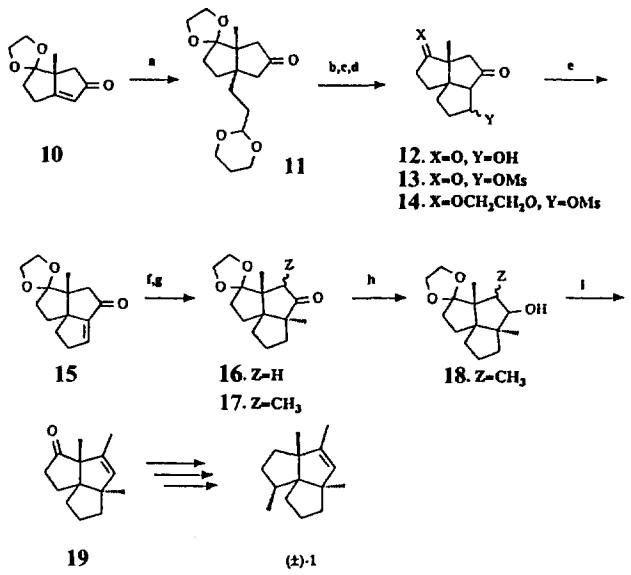
In our synthetic plan, 2-methylcyclopetadione (**6**) was alkylated with propargyl bromide and $NaHCO_3$ in water in 90% yield in order to prepare the bicyclic system. The resulting diketone **7** was easily transformed into the monoketal **8** in 82% yield by treating with ethylene glycol in the presence of a catalytic amount of p-toluenesulfonic acid (See Scheme 1).

The terminal acetylene group of **8** was converted to the acetyl group. The treatment of **8** with mercuric acetate in pyridine at refluxing temperature lead to methyl ketone **9** in 76% yield. The aldol reaction of this ketone treating with 5% ethanolic KOH provided the bicyclic enone **10** in 83% yield.



Reagents:
(a) $NaHCO_3$, $HC\equiv CCH_2Br$, 100℃, 5 h (b) $HOCH_2CH_2OH$, *p*-TsOH, Benzene, reflux, 3 h (c) $Hg(OAc)_2$, pyridine, EtOH, 4 h, H_2S (d) 5% Methanolic KOH, reflux, 1 h.

Scheme 1.



Reagents:
(a) BrMg  , $CuBr\cdot Me_2S$, THF, 0℃→RT (b) 3% HCl, THF, reflux, 4 h (c) MsCl, Et_3N, DCM, 0℃ (d) $TMSOCH_2CH_2OTMS$, TMSOTf, DCM, −20℃, 24 h (e) DBU, DCM, RT (f) *liq* NH_3, Li, THF, *t*-BuOH, CH_3I, −78℃→RT (g) LDA, THF, CH_3I, −78℃→RT (h) LAH, THF, 0℃, 3 h (i) $POCl_3$, pyridine, 48 h; 5% HCl, THF.

Scheme 2.

In order to constitute tricyclic system upon this bicyclic enone, the intermolecular Michael addition was needed as the next step. Therefore, in the presence of the complex cuprous bromide-methyl sulfide, the Grignard reagent derived from 2-(2-bromoethyl)-1,3-dioxolane at room temperature furnished 92% yield of 1,4-conjugate addition product **11** from **10**[11] (See Scheme 2). In contrast, the Grignard reagent

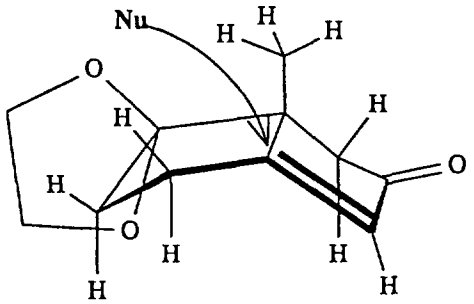


Figure 2.

from 2-(2-bromoethyl)-1,3-dioxane was found to give poor yield and furthermore, it needed lower reaction temperature such as −78℃. The newly formed bond has exclusively a *cis* configuration relative to the angular methyl group, because the Grignard reagent could approach from sterically less crowded convex side of bicyclic enone system as shown in Figure 2.[3a]

The next step was the aldol condensation between the ketone and the aldehyde to introduce an extra ring. In the course of deprotection, we found that the selective deprotection between the ketal and the acetal of **11** was dependent on the acidic conditions. Under the treatment with oxalic acid in aqueous THF at room temperature, the acetal group was removed. But under the condition of 1% HCl in THF at room temperature the ketal group was removed. In contrast, when the condition of refluxing in 3% aqueous HCl was employed, ketone **11** was converted to hyroxydiketone **12** in 73% yield *via* consecutive deprotection of the ketal and the acetal followed by the aldol condensation. The next step in the reaction sequence was the elimination of an aldolic hydroxyl group to obtain enone **15a**. Therefore, the compound **12** was mesylated to obtain **13** by treating with methane sulfonyl chloride and triethylamine in dichloromethane and the subsequent elimination utilizing DBU gave smoothly enone **15a** in 95% yield.

Now it became necessary to introduce a methyl group at α-position of α,β-unsaturated ketone fragment by quenching of the Birch reduction intermediate of the enone with a methylating agent such as methyl iodide. Accordingly, we had to protect the carbonyl group at C-4 adjacent to the angular methyl in order to introduce the methyl group at C-8 postion. Without any protection of this carbonyl group, it would be difficult to obtain selective methylation at the position next to C-4 carbonyl group. When we tried chemoselective monoketalization of the endione **3** utilizing both conventional method and transketalization,[12] we could not obtain the desirable result because of either poor selectivity or decomposition during reaction. After suffering from this difficult result, we found that the recourse for the success was the selective mono-ketalization prior to the elimination reaction of the mesylate derivative **13**. Althoulgh, in the planar projection, it seems that the angular methyl group at C-5 gives more steric hindrance at C-4 carbonyl group, the examination of the three dimensional molecular models of diketone **12** by molecular mechanics (MMII) calculation reveals that the carbonyl group at C-4 position has almost same steric constrain as that of the carbonyl group at C-7 position. In addition, if a bulky methane sulfonate group was introduced at hydroxyl group, this would bring in further steric congestion to the carbonyl group at C-7. From this supposition, the compound **12** was transformed into the mesylate derivative **13** in 93% yield by treating with methane sulfonylchloride and triethylamine in dichloromethane at 0℃ and indeed, this derivative was successfully monoketalized at the C-4 carbonyl group in 85% yield by employing a mild treatment with 1,2-bis(trimethylsilyloxy)ethane in the presence of TMSOTf at −20℃.[13] Then, the mesyl group of **14** was eliminated by treating with DBU in dichloromethane to obtain the corresponding enone **15b** in 89% yield. The following Birch reduction of enone **15b** by lithium and *t*-BuOH in liquid ammonia and the quenching of the intermediate with methyl iodide gave 84% yield of **16**. In order to attach a methyl group at C-6, **16** was reacted with LDA and methyl iodide to furnish 81% yield of the methylated ketone **17**. The remaining transformations in the synthesis were the reduction of a ketone group to the hydroxyl group and subsequent elimination of this group. But the methylated ketone **17** was found to be resistive toward the reduction with sodium borohydride because of increased steric hindrance due to the attached methyl group. Nevertheless, this problem was overcome by utilizing a stronger reducing agent of lithium aluminum hydride to obtain the desired product **18** in 84% yield. Upon the subjection of standard dehydration condition by using phosphoroxyl chloride and pyridine for 48 hours, the compound **18** gave the elimination product in 82% yield, of which ketal was finally deprotected under acidic condition of 5% HCl in THF to the desired product **19** in 95% yield. Finally, this work constitutes a formal total synthesis of isocomene, because ketone **19** was already transformed to racemic isocomene.[3a,d]

Experimental

General Comments. Melting points were determined on a Thomas-Hoover Uni-Melt apparatus in capillary tubes and are uncorrected. Infrared (IR) spectra were recorded on a Shimadzu IR-435 spectrophotometer. ^{1}H-NMR spectra were attained on Bruker AM-300 NMR, Varian 360 EM, and Varian FX 80 spectrometers and measured in $CDCl_3$ solution, unless otherwise stated, relative to Me_4Si, as an internal standard ($\delta = 0.00$). Mass spectra were obtained on a Schimadzu GCMS-QP 1000 at 70 eV and recorded herein (relative intensity and assignment). High resolution mass spectra (HRMS) were recorded on Joel JMS-DX303 mass spectrometer. Elemental analyses were taken on Perkin-Elmer 240C elemental analyzer in our laboratories. Unless otherwise indicated in a specific experiment, all of the chemicals used were reagent grade and no additional purification has been done. CH_2Cl_2 was distilled over P_2O_5 or CaH_2. *t*-Butyl alcohol was distilled over CaH_2 and stored over molecular sieves. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl immediately prior to use. Thin layer chromatography (TLC) was performed on Merck 60 F-254 glass plates without activation. Column chromatography procedures utilized silica gel (Merck, silica gel 60, 70-230 mesh).

2-Methyl-2-(2-propynyl)-1,3-cyclopentadione (7). To a solution of 2-methyl-1,3-cyclopentadione (**6**) (5.56 g, 50 mmol) and $NaHCO_3$ (4.2 g, 50 mmol) in H_2O was added propargyl bromide (11 m*l*, 60 mmol) at room temperature. The reaction mixture was warmed to 100℃ for 4 h. After

cooling the reaction mixture was extracted with dichloromethane (2×50 m*l*), dried over $MgSO_4$, and evaporated under reduced pressure to give crude product, which was recrystallized in hexane-ethyl acetate (2:1) to yield a colorless solid **7** (6.75 g, 90%), mp 71-72℃ (lit.[10], 70-72℃); ^{1}H-NMR (60 MHz; $CDCl_3$) δ 1.03 (brs, CH_3, 3H), 2.00 (brs, C≡CH, 1H), 2.50 (brs, C≡CCH_2, 2H), 2.85 (brs, $COCH_2$, 4H); m/e 150 (M^+, 15.3%), 66 (47.4), 57 (20.2), 41 (100).

2-Methyl-2-(2-propynyl)-3,3-ethylenedioxy-1-cyclopentanone (8). To a solution of **7** (7.5 g, 50 mmol) in benzene (150 m*l*) were added ethylene glycol (9.61 g, 100 mmol) and a catalytic amount of *p*-TsOH (960 mg, 5 mmol) with stirring at room temperature. The mixture was refluxed for 3 h. After cooling to room temperature, saturated aq. $NaHCO_3$ was added to the reaction mixture. The benzene layer was separated and washed with water and brine. The organic extract was dried over $MgSO_4$ and the solvent was evaporated *in vacuo* to give a crude product, which was purified by column chromatography (silica gel, hexane: ethyl acetate=2:1) to provide the ketal **8** (8.0 g, 82%), mp 84~85℃; IR (KBr) 2924, 1725 cm^{-1}; ^{1}H NMR (60 MHz, $CDCl_3$) δ 1.22 (s, CH_3, 3H), 1.90-2.50 (m, CH_2, 6H), 4.00 (brs, OCH_2CH_2O, 4H); *m/e* 194 (M^+, 13.6%), 123 (15.4), 99 (100), 86 (48.3), 56 (28.9), 45 (18.4), 41 (36.5); Anal. Calcd for $C_{11}H_{14}O_3$: C, 68.02; H, 7.26. Found: C, 67.84; H, 7.27.

2-Methyl-2-(2-oxopropyl)-3,3-ethylendioxy-1-cyclopentanone (9). To a solution of ketal **8** (9.00 g, 46.0 mmol) in ethanol (200 m*l*) were added $Hg(OAc)_2$ (29.4 g, 92.0 mmol) and pyridine (7.30 g, 92.0 mmol). The solution was refluxed for 4 h. After cooling to room temperature, the reaction mixture was saturated with H_2S gas. Then the solution was filtered though Celite 545 to remove black precipitates of HgS. The solvent was evaporated to give a crude product, which was purified by column chromatography (silica gel, hexane: ethyl acetate=1:1) to provide syrupy **9**: (7.34 g, 75%); IR (KBr) 2940, 1732, 1709 cm^{-1}; ^{1}H-NMR (60 MHz; $CDCl_3$) δ 1.11 (s, CH_3, 3H), 1.80-2.60 (m, CH_2, 6H), 2.08 (s, CH_3CO, 3H), 3.90 (brs, OCH_2CH_2O, 4H); *m/e* 212 (M^+, 2.3%), 169 (99.1), 113.0 (29.5), 69 (36.9), 55 (20.7), 43 (100).

5-Methyl-6,6-ethylenedioxy-bicyclo[3.3.0]oct-1-en-3-one (10). A solution of **9** (7.50 g, 62.5 mmol) in 5% ethanolic KOH solution (20 m*l*) was refluxed for 1 h. The reaction mixture was cooled to room temperature, neutralized with 10% aqueous HCl, extracted with dichloromethane (2× 100 m*l*), and dried over $MgSO_4$. The solvent was evaporated to give a crude product, which was purified by column chromatography (silica gel, hexane: ethyl acetate=1:1) to afford a slightly yellow syrup **10** (5.35 g, 78%); IR (KBr) 2940, 1732, 1702, and 1138 cm^{-1}; ^{1}H NMR (60 MHz, $CDCl_3$) δ 1.29 (s, CH_3, 3H), 2.0-2.2 (m, CH_2, 2H), 2.3-2.8 (m, CH_2, 4H), 3.88 (brs, OCH_2CH_2O, 4H), 5.70 (brs, =CH, 1H); *m/e* 195 (M+1, 15.9%), 194 (M^+, 83.5), 86 (100), 85 (36.4), 83 (55.3), 79 (43.9), 43 (59.8); HRMS *m/e* Calcd for $C_{11}H_{14}O_3$: 194.0943. Found: 194.0953.

1-[(3,3-Propylenedioxy)propyl]-6,6-(ethylenedioxy)-5-methylbycyclo-[3.3.0]octa-3-one (11). To a suspension of Mg (1.04 g, 42.8 mmol) in anhydrous THF (2 m*l*) was added bromoethyl-1,3-dioxane (5.83 m*l*, 42.8 mmol) *via* hyperdermic syringe under nitrogen. After stirring for 2 h, the solution was added to a mixture of the diene **10** (4.15 g, 21.4 mmol) and CuBr-Me_2S (1.10 g, 5.35 mmol) in Me_2S (5 m*l*) and THF (20 m*l*) *via* syringe dropwise under nitrogen at 0℃. The color of solution was changed to black and then the solution was quenched with saturated aqueous NH_4Cl and ammonia water. The solution was extracted with dichloromethane (3×50 m*l*) and dried over $MgSO_4$. The solvent was evaporated to give a crude product, which was purified by column chromatography (silica gel, hexane: ethyl acetate=1:2) to furnish **11** as a solid (6.1 g, 92%), mp 72-73℃; IR (KBr) 2930, 1730, 1138 cm^{-1}; ^{1}H NMR (80 MHz, $CDCl_3$) δ 1.05 (s, CH_3, 3H), 1.30-2.65 (m, CH_2, 14H), 3.87 (brs, OCH_2 CH_2O, 4H), 3.55-4.20 (m, $OCH_2CH_2CH_2O$, 4H), 4.45 (m, CH, 1H); *m/e* 310 (M^+, 0.9%), 113 (28.4), 100 (20.7), 99 (100), 87 (10.7); Anal. Calcd for $C_{17}H_{26}O_5$: C, 65.78; H, 8.44. Found: C, 65.94; H, 8.52.

9-Hydroxy-5-methyltricyclo[6.3.0.0^{1,5}]undeca-4,7-dione (12). To a solution of **11** (615 mg, 1.99 mmol) in THF (10 m*l*) was added 3% HCl (10 m*l*) and the solution was refluxed for 4 h. Afther the cooling, the solution was neutralized with a saturated aqueous $NaHCO_3$ and extracted with dichloromethane (2×10 m*l*) and dried over anhydrous $MgSO_4$. The solvent was evaporated under the reduced pressure to obtain the crude product which was purified by column chromatography (silica gel, hexane: ethyl acetate=1:1) to provide **12** as a colorless solid: (280 mg, 68%), mp 48-49℃ (hexane); IR (KBr) 3290, 2950, 1750 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.14 (s, CH_3, 3H), 1.62-2.77 (m, CH and CH_2's, 11H), 4.54 (m, CHOH, 1H): *m/e* 208 (M^+, 6.8%), 190 (M^+-H_2O, 11.3), 111 (16.6), 109 (20.3), 83 (13.7), 80 (100), 79 (22.6), 43 (22.7), 41 (17.3); HRMS *m/e* Calcd for $C_{12}H_{16}O_3$ 208.1099. Found: 208.1097.

9-α-methanesulfonyloxy-5-methyltricyclo[6.3.0.0^{1,5}] undeca-4,7-dione (13). To a solution of **12** (1.04 g, 5.0 mmol) and triethylamine (695 μ*l*, 5.0 mmol) in dichloromethane (10 m*l*) was added methanesulfonyl chloride (464 μ*l*, 6.0 mmol) at 0℃. After stirring for 3 h, water (2 m*l*) was added to the solution and the organic layer was separated. The extract was dried over anhydrous $MgSO_4$ and evaporated to dryness to obtain a crude product, which was triturated with hexane: ethyl acetate=3:1 to furnish **13** as a white solid (1.19 g, 83%); mp 140-141.5℃ (decomp.); IR (KBr) 2960, 1700, 1348, 1180, 850 cm^{-1}; ^{1}HNMR (300 MHz, $CDCl_3$) δ 1.17 (s, CH_3, 3H), 1.76-2.74 (m, CH_2 and CH, 11H), 2.99 (s, OSO_2CH_3, 3H), 5.28 (m, CH, 1H); *m/e* 207 (M^+-79, 0.8%), 163 (11.1), 107 (20.8), 93 (11.4), 91 (18.5), 80 (100), 79 (49.5), 55 (15.3), 43 (45.9) 41.0 (33.6); Anal. Calcd for $C_{13}H_{18}O_5S$: C, 54.53; H, 6.33; S, 11.19. Found: C, 54.47; H, 6.02; S, 11.14.

4,4-Ethylenedioxy-9-methanesulfonyloxy-5-methyltricyclo[6.3.0.0^{1,5}]-undeca-7-one (14). To a solution of **13** (286 mg, 1 mmol) and 1,2-bis(triethylsilyloxy)ethane (490 μ*l*, 2 mmol) in dichloromethane (10 m*l*) was added a catalytic amount of trimethylsilyl trifluoromethanesulfonate at −22℃ under argon atmosphere. The resulting solution was stirred for 24 h with maintaining the temperature around −20℃. After the reaction was quenched with a few drops of pyridine, organic layer was separated by adding water (5 m*l*). The organic layer was dried over anhydrous $MgSO_4$ and the solvent was evaporated *in vacuo* to give a crude product, which was triturated with hexane: ethyl acetate=3:1 to provide **14** as a white solid (260 mg, 79%), mp 106-108℃; IR (KBr) 2950, 1740, 1350, 1170, and 890 cm^{-1}; ^{1}H-NMR (60 MHz, $CDCl_3$) δ 1.15 (s, CH_3, 3H), 1.60-2.55 (m, CH_2, 11H),

2.92 (s, SO_2CH_3, 3H), 3.80 (m, OCH_2CH_2O, 4H), 5.18 (dd, CH, 1H); m/e 251 (M^+-79, 44%), 100 (15.2), 99 (100), 79 (15.8), 55 (14.9), 41.0 (15.2); HRMS *m/e* Calcd for $C_{15}H_{22}O_6S$: 330.1138. Found: 330.1138.

4,4-Ethylenedioxy-5-methyltricyclo[6.3.0.0^{1,5}]undece-11-en-7-one (15). To a solution of **14** (620 mg, 1.88 mmol) in dichloromethane (5 m*l*) was added 1,5-diazabicyclo [5.4.0]undecene (562 μ*l*, 3.76 mmol) at room temperature and the reaction mixture was stirred for 3 h. The reaction solution was washed with water and the organic layer was separated, dried over anhydrous $MgSO_4$, and evaporated to dryness under the reduced pressure to provide a crude product. Purification by column ctromatography (silica gel, hexane: ethyl acetate=2:1) furnished the pure white solid product 15 (389 mg, 89%), mp. 102-103℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.96 (s, CH_3, 3H), 1.77~2.25 (m, CH_2, 6H), 2.31 (d, CH, J=9.5 Hz, 1H), 2.93 (d, CH, J=9.5 Hz, 1H), 3.95 (m, OCH_2CH_2O, 4H), 6.47 (dd, =CH, J=1.2, 3.5 Hz, 1H); *m/e* 234 (M^+, 1.0%), 100 (24.7), 99 (100).

4,4-Ethylenedioxy-5,8-dimethyltricyclo[6.3.0.0^{1,5}]undeca-7-one (16). A solution of lithium in NH_3(liquid) was prepared by addition of freshly cut lithium wire (25.4 mg, 3.65 mmol) to anhydrous NH_3 (25 m*l*) at −78℃ and the solution was stirred for 15 min. A THF solution of **15** (389 mg, 1.66 mmol) and *t*-BuOH (141 μ*l*, 1.58 mmol) was added *via* syringe over 5 min to this solution. The resulting reaction mixture was stirred for 10 min and excess methyl iodide (516 μ*l*, 8.3 mmol) in THF (10 m*l*) was added dropwise over 5 min. The temperature of the solution was raised to room temperature to evaporate liquid ammonia. After the removal of liquid ammonia, THF solution was partitioned between ether and water. The organic layer was separated, washed with water, dried over $MgSO_4$, and evaporated to give a crude product which was purified by column chromatography (silica gel, hexane: ethyl acetate=2:1) to give a white solid **16** (353 mg, 85%), mp 49-50℃; IR (KBr) 2950, 2900, 1712 cm^{-1}; ^{1}H NMR (80 MHz, $CDCl_3$) δ 1.11 (s, CH_3, 3H), 1.40-2.65 (m, CH_2, 12H), 3.88 (brs, OCH_2CH_2O, 4H); *m/e* 250.0 (M^+, 2.1%), 100 (8.1), 99 (100); Anal. Calcd for $C_{15}H_{22}O_3$: C, 71.96; H, 8.86. Found: C, 71.96; H, 8.95.

4,4-Ethylenedioxy-5,6,8-trimethyltricyclo[6.3.0.0^{1,5}]undeca-7-one (17). In order to prepare lithium diisopropylamide, to a solution of diisopropylamine (0.316 m*l*, 2.25 mmol) in THF (5 m*l*) at −78℃ was added 1.74 M n-BuLi (1.30 m*l*, 2.26 mmol) dropwise *via* syringe under argon atmosphere. After stirring for 15 min, the temperature was raised to 0℃ and the stirring was continued for 30 min. To a solution of **16** (513 mg, 2.05 mmol) in THF (5 m*l*) at −78℃, was added lithium diisopropylamide in THF *via* cannula under argon atmosphere. After 30 min methyl iodide (135 μ*l*, 2.13 mmol) was added to this reaction mixture. Stirring was continued overnight and then reaction was quenched with saturated ammonium chloride. The aqueous layer was extracted with Et_2O (3×10 m*l*) and the organic layers were combined, dried over anhydrous $MgSO_4$, and evaporated *in vacuo*. The residue was chromatographed on silica gel column by eluting with hexane: ethyl acetate=4:1 to get the product **17** (330 mg, 61%) and recovered starting material (152 mg); ^{1}H NMR (80 MHz, $CDCl_3$) δ 0.79 (s, CH_3, 3H), 0.98 (d, CH_3, J=6.5 Hz, 3H), 1.11 (s, CH_3, 3H), 1.13-2.25 (m, CH_2, 10H), 2.70 (q, CH, 1H), 3.92 (brs, OCH_2CH_2O, 4H); *m/e* 264 (M^+, 0.8%), 100 (8.4), 99 (100.0), 55 (5.9), 41.0 (6.2).

4,4-Ethylenedioxy-5,6,8-trimethyltricyclo[6.3.0.0^{1,5}]undecan-7-ol (18). To a suspension of lithium aluminium hydride (33.2 mg, 0.878 mmol) in THF (5 m*l*) was added a solution of ketone **17** (116 mg, 0.439 mmol) in THF (5 m*l*) at 0℃. The mixture was stirred at 0-5℃ and then was warmed to room temperature for 3 h. The reaction solution was quenched with water (0.1 m*l*) and 10% NaOH solution (0.3 m*l*). The resulting suspension was removed by filtration and clean filtrate was dried over Na_2SO_4. The solvent was removed *in vacuo* to provide the crude product, which was chromatographed on silica gel column by eluting with hexane: ethyl acetate=3:1 to get the pure alcohol **18** (74.3 mg, 64%) and the recovered starting material **17** (28.1 mg); ^{1}H NMR (80 MHz, $CDCl_3$) δ 0.79 (s, CH_3, 3H), 0.95 (s, CH_3, 3H), 1.00 (d, CH_3, J=6.5 Hz, 3H), 1.10-2.10 (m, CH_2, 10H), 2.52 (q, $CH_3CHCHOH$, 1H), 3.18 (brd, CHOH, 1H), 3.85 (brs, OCH_2CH_2O, 4H); *m/e* 266 (M^+, 2.0%), 100 (10.8), 99 (100), 55 (9.1); HRMS *m/e* Calcd for $C_{16}H_{26}O_3$: 266.1883. Found: 266.1890.

5,6,8-Trimethyltricyclo[6.3.0.0^{1,5}]undec-6-en-4-one (19). To a solution of alcohol **18** (50 mg, 0.188 mmol) in anhydrous pyridine (3 m*l*) was added phosphoxychloride (24 μ*l*, 0.263 mmol) at 0℃. After stirring for 48 h at room temperature, water was added and the solution was extracted with ether (2×5 m*l*). The ether extracts were dried over anhydrous $MgSO_4$ and the solvent was removed *in vacuo* to give a crude product (38 mg). This product was used next step without any further purification; ^{1}H-NMR (60 MHz, $CDCl_3$) δ 0.99 (s, CH_3, 3H), 1.07 (s, CH_3, 3H), 1.69 (s, CH_3, 3H), 1.13-2.14 (m, CH_2, 10H), 3.90 (brs, OCH_2CH_2O, 4H), 5.13 (m, =CH, 1H); *m/e* 248 (M^+, 7.1%), 149 (22.8), 148 (20.0), 119 (11.6), 99 (100.0), 55 (10.8), 51 (11.0), 49.0 (35.7), 42.0 (10.6). To a solution of the crude ketal (38 mg, 0.153 mmol) in THF (5 m*l*) was added 10% aqueous HCl solution (5 m*l*). The solution was stirred for 1 h and neutralized with saturated aqueous $NaHCO_3$, washed with water, and dried over anhydrous $MgSO_4$. The solvent was evaporated under reduced pressure to give a crude product, which was chromatographed on silica gel column by eluting with hexane: ether= 4:1 to get the pure product **19** (27 mg, 86%); IR (KBr) 2997, 1727, 1457, 1062, 843 cm^{-1}; ^{1}HNMR (300 MHz, $CDCl_3$) δ 1.06 (s, CH_3, 3H), 1.17 (s, CH_3, 3H), 1.21-1.66 (m, CH_2, 6H), 1.61 (d, CH_3, J=1.3 Hz, 3H), 1.85-1.91 (m, CH, 1H), 2.03-2.17 (m, CH_2, 2H), 2.37-2.54 (m, CH, 1H), 5.09 (brs, =CH, 1H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 12.41, 15.46, 22.34, 23.92, 28.67, 37.04, 38.53, 42.13, 56.52, 59.78, 65.33, 136.18, 138.44, 220.35; *m/e* 206 (M+2, 4.0%), 205 (M+1, 30.0), 204 (M^+, 37.7), 149 (40.0), 148 (100), 147 (24.0), 133 (35.0), 120 (65.8), 119 (30.7), 105 (33.4), 91 (19.1), 41 (25.9).

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References

1. L. H. Zalkow, R. N. Harris, D. Van Derveer, and J. A. Bertrand, *J. Chem. Soc., Chem. Commun.*, 456 (1977).
2. F. Bohlmann, N. Le Van, and J. Pickardt, *Chem. Ber.*, **110**, 3777 (1977).
3. (a) L. A. Paquette and Y. K. Han, *J. Org. Chem.*, **44**, 4014 (1979); *J. Am. Chem. Soc.*, **103**, 1835 (1981); (b) W. Oppolzer, K. Battig, and T. Hudlicky, *Helv. Chim. Acta*, **62**,

1493 (1979); *Tetrahedron*, **37**, 1359 (1981); (c) M. C. Pirrung, *J. Am. Chem. Soc.*, **101**, 7130 (1979); *ibid.*, **103**, 82 (1981); (d) W. G. Dauben and D. M. Walker, *J. Org. Chem.*, **46**, 1103 (1981); (e) P. A. Wender and G. B. Dreyer, *Tetrahedron*, **37**, 4445 (1981); (f) E. Wenkert and T. S. Arrhenius, *J. Am. Chem. Soc.*, **105**, 2030 (1983); (g) B. C. Ranu, M. Kavka, L. A. Higgs, and T. Hudlicky, *Tetrahedron Lett.*, **25**, 2447 (1984); (h) Y. Tobe, T. Yamashita, K. Kakiuchi, and Y. Odaira, *J. Chem. Soc., Chem. Commun.*, 898 (1985); (i) G. G. G. Manzardo, M. Karpf, and A. S. Dreiding, *Helv. Chim. Acta*, **69**, 659 (1986).
4. H. W. Lee and I.-Y. C. Lee, *Bull. Korean Chem. Soc.*, **11**, 273 (1990).
5. (a) G. Stork, *Pure Appl. Chem.*, **9**, 131 (1964); (b) R. E. Ireland, P. A. Aristoff, and C. F. Hoyng, *J. Org. Chem.*, **44**, 4318 (1979).
6. S. Danishefsky, R. Zamboli, M. Kahn, and S. J. Etheredge, *J. Am. Chem. Soc.*, **102**, 2097 (1980).
7. S. C. Welch and S. Chayabunjonglerd, *J. Am. Chem. Soc.*, **101**, 6768 (1979).
8. A. Leon-Bay and L. A. Paquette, *J. Org. Chem.*, **46**, 4173 (1982).
9. B. M. Trost and D. P. Curran, *J. Am. Chem. Soc.*, **103**, 7380 (1981).
10 G. Geetha, N. Raju, K. Rajagopalan, and S. Swaminathan, *Ind. J. Chem.*, **B20**, 238 (1981).
11 J. C. Stowell, *J. Org. Chem.*, **41**, 560 (1976).
12 G. Bauduin and Y. Pietrasanta, *Tetrahedron*, 4225 (1973).
13 T. Tsunoda, M. Suzuki, and R. Noyori, *Tetrahedron Lett.*, 1357 (1980).

Effects of van der Waals Bonding on the Collisional Dissociation of a Highly Excited Chemical Bond

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Dissociation of a highly excited diatomic molecule in the $Ar+Ar\cdots O_2$ and $Ar+O_2$ collisions is studied using trajectory dynamics procedures in the collision energy range of 0.050 to 1.0 eV. Between 0.050 and 0.2 eV, dissociation probabilities are very large for the complexed system compared to the uncomplexed system. This efficient dissociation of O_2 in $Ar\cdots O_2$ is attributed to the ready flow of energy from the incident atom to the large-amplitude vibrational motion of the excited O_2 *via* the van der Waals bond. Thermal-averaged dissociation probabilites of O_2 in $Ar+Ar\cdots O_2$ near room temperature are nearly two orders of magnitude larger than those of O_2 in $Ar+O_2$.

Introduction

In recent studies on the collision dynamics of van der Waals (vdW) complexes, we have shown that excitation of vdW complexes is very efficient and that the energy initially present in a high-frequency chemical bond remains when the collision is over.[1,2] When a heavy mass barrier is present between vdW bonds, energy flow from one vdW bond to another becomes seriously hindered and energy localizes in one of the weak bonds.[3,4] Energy flow blockage in molecular systems by heavy atoms or multiple bonds has been investigated by many researchers in recent years.[4-15] In a vdW complex involving diatomic and rare gas atom units, the chemical bond essentially conserves its individuality and experiences weak dynamical coupling with the vdW bond because of the large disparity in oscillator frequencies. Energy transfer to the chemical bond is, therefore, inefficient and the energy initially present in the bond remains when the collision is over. However, a new situation arises when the chemical bond is highly excited, especially to near the dissociation thereshold. At such excitation, the chemical bond becomes seriously weakened and undergoes a low-frequency vibrational motion, which may even be comparable to that of the vdW bond. In the complex with such a highly excited bond, a weak coupling between the vdW and chemical bonds can become sufficient to induce efficient intramolecular energy flow, thus causing the molecular unit to gain enough energy for dissociation.

The purpose of this paper is to study the effects of vdW bonding on the dissociation of O_2 in $Ar\cdots O_2$, in which the chemical bond is in a highly excited state. Such a complexed state is particularly important in the studies of thermal dissociation of O_2 dispersed in the argon gas or in the argon matrix.[16] In this model system, another Ar atom is incident on the complex to perturb its internal state. This collision-induced intramolecular dynamics will be treated in classical mechanics by sampling a sufficiently large number of trajectories in the collision energy range of 0.050 to 1.0 eV. The result will then be compared with that of $Ar+O_2$ to discuss the effects of vdW bonding on the dissociation of O_2 in the complex. In both the complexed and uncomplexed systems, O_2 is initially either in the ground state or in a highly excited state with the vibrational energy equal to 99% of the dissociation energy.

Interaction Model

For the incident Ar approaching the linear complex $Ar\cdots O_2$