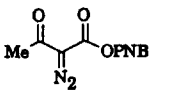
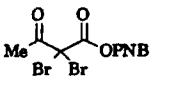
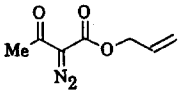
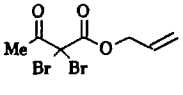
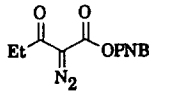
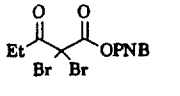
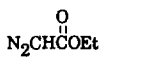
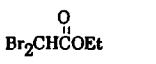
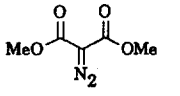
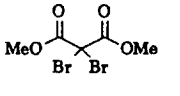
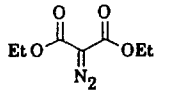
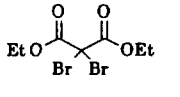
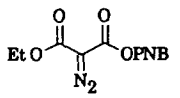
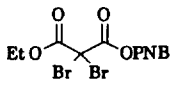
Table 1. *gem*-Dibromination of Diazo Compounds

Entry	Reactant(1)[a]	Product(2)[b]	Yield(%)[c]
A[d]			87
B			85
C			90
D			75
E	Ph_2CN_2	Ph_2CBr_2	73
F			85
G			85
H			89

[a] see ref. 12. [b] all compounds were characterized by IR, MS, and NMR spectra. [c] isolated yields. [d] PNB = *p*-nitrobenzyl.

rough aqueous work up. Allyl acetoacetate was obtained by alcoholysis of diketene. Ethyl PNB malonate was prepared by the treatment of mono-potassium salt of ethyl hydrogen malonate[13] with *p*-nitrobenzyl bromide in the presence of catalytic amount of 18-crown-6. Commercially available ethyl diazoacetate (1D) was used and diphenyl diazomethane (1E) was prepared by oxidation of benzophenone hydrazone with yellow mercuric oxide[14].

A general procedure is as follows. To a solution of 1A (0.51 g, 1.93 mmol) in CH_2Cl_2 (20 m*l*) was added dropwise a solution of Br_2 (0.21 m*l*, 4.24 mmol) in CH_2Cl_2 (5 m*l*) at room temperature for 5 min. The reaction mixture gave the evolution of N_2. The mixture was additionally stirred for 30 min at the same temperature. The resulting solution was successively washed with 5% $NaHSO_3$ solution and water, and dried over anhydrous $MgSO_4$. Evaporation of the solvent *in vacuo* gave 2A (0.67 g, 87%) in oil.

Using the procedure described above, various diazo compounds were brominated to afford the corresponding dibromides. The results are shown in Table 1. As shown in the table, this pathway is quite general for the synthesis of dibromides from carbonyl or active methylene compounds containing diazo group, and applicable to synthesis of many heterocyclic compounds and hydrocarbons.

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11. IR(neat): ν = 1720, 1610, 1520, 1350 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ = 2.64 (s, 3H), 5.43 (s, 2H), 7.58 (d, 2H, J = 8.8 Hz), 8.26 (d, 2H, J = 9.0 Hz). ^{13}C-NMR ($CDCl_3$): δ = 23.1, 58.4, 123.5, 128.1, 141.0, 147.5, 162.9, 190.9. MS (70 eV): *m/z* (relative intensity) = 394 (1.2), 396 (1.9), 398 (1.1). Anal. Calcd for $C_{11}H_9NO_5Br_2$: C, 33.4; H, 2.30; N, 3.50. Found: C, 34.4; H, 2.30; N, 3.70.
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A Synthetic Approach to Hydrindanes *via* the Homologous Michael Addition to Tricyclo[4.3.0.0^{1,5}]nonanes

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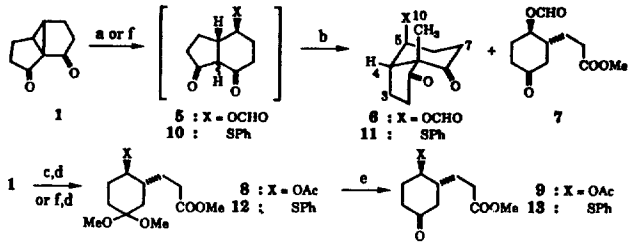
Since several efficient ways have been developed to synthesize cyclopropanes,[1] their transitory formation has been often employed in terpene synthesis.[2] Furthermore, recent advances in asymmetric cyclopropanations provide chiral cyclopropanes,[1,3] which can be appropriately transformed into chiral complex molecules. The most versatile chemistry of cyclopropanes certainly stems from their nucleophilic cleavage, which is known to occur in the presence of one or more electron-withdrawing groups on the ring. Since the nucleo-



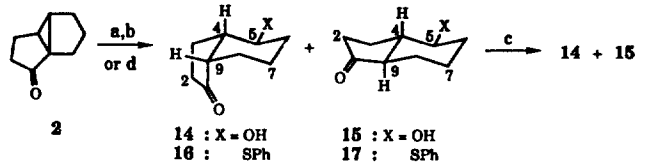
Reagents: a. HCOOH/RT. b. MeI/K_2CO_3THE/50℃. c. HOAc (10 eq.)/$ZnCl_2$ (cat.)/CH_2Cl_2/RT. d. $CH(OMe)_3$/CSA (cat.)/MeOH/35℃ e. PPTS (cat)/acetone/RT. f. PhSH (10 eq.)/$ZnCl_2$(cat.)/CH_2Cl_2/RT.

Scheme 1.

philic cleavage is the homologous (or 1, 5) version of the classical Michael addition,[4] it results in not only introducing a functional group to γ-position of the electron-withdrawing group but also achieving a form of umpolung synthesis. Although either of two bonds adjacent to the electron-withdrawing group can be cleaved in unsymmetrical cyclopropanes, their regioselective openings seem to be guided by stereoelectronic effect when the electron-withdrawing group is contained in another ring. In accordance with the effect, cyclopropylketones are opened by the bond cleavage perpendicular to the carbonyl group, and acid-mediated ring openings of cyclopropylcarbinols are expected to occur by the bond cleavage (anti)parallel to the C-OH bond. Thereby the effect controls the stereoselective introduction of nucleophiles. In order to investigate the feasibility of the above theme in terpene synthesis, we synthesized tricyclo[4.3.0.$0^{1,5}$]nonanes **1-4**,[5] regarded as activated cyclopropanes. In this paper we wish to describe tricylclo[4.3.0.$0^{1,5}$]nonanes **1-4** to produce several hydrindanes which may be otherwise synthetically difficultly obtained.

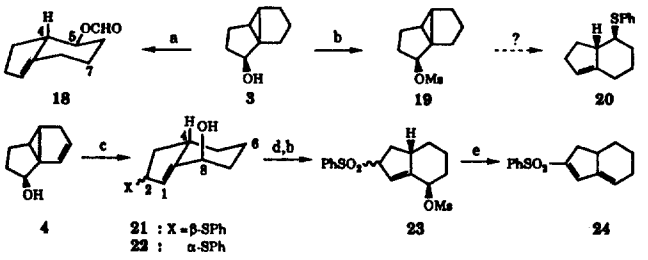
Solvolysis of tricyclic dione **1** in formic acid furnished bicyclic dione **5**, which was treated with methyl iodide in THF in the presence of potassium carbonate to give methylated bicyclic dione **6** in 88% yield along with a few percent of cyclohexanone derivative **7** (Scheme 1).[6] Ketone **7** was evidently formed *via* retroaldol reaction by water contained in potassium carbonate.[7] The relative stereochemistry of **6** was corroborated by nOe difference experiments e.g., irradiation at H_3-C (10) showed enhancements at H-C (4) and H-C (7), irradiation at H-C (5) showed enhancements at H_2-C (3), and $J_{H\text{-}C(4),\ H\text{-}C(5)}$=6.2 Hz, which imply that both methyl and formate substituents occupy the axial positions. Dione **1** reacted with acetic acid in dichloromethane in the presence of zinc chloride to provide probably bicyclo[4.3.0]nonanedione derivative. The crude product was treated with trimethyl orthoformate in methanol in the presence of (±)-camphorsulfonic acid (CSA) in order to obtain methyl enol ether. However, only the retroaldol product **8** could be isolated in 75% yield.[6] Deprotection of ketal **8** in acetone in the presence of pyridinium p-toluenesulfonate (PPTS) provided ketone **9** in 92% yield,[7] of which NMR spectroscopic data were closely related to those of the corresponding formate **7**.

Since it is also merit introducing sulfur nucleophile, **1** was subjected to thiophenol in dichloromethane in the presence of zinc chloride to yield bicyclic dione **10**. The crude dione



Reagents: a. HCOOH/45℃. b.K_2CO_3(cat.)/MeOH/RT. c. t-BuOK or DBU(cat.)/THF/RT. d. PhSNa/Zn(OTf)$_2$/THF/RT.

Scheme 2.



Reagents: a. HCOOH/RT. b. MsCl/DMAP(cat.)/Et_3N/CH_2Cl_2/RT. c. PhSH/AIBN(cat.)/PhH/70℃. d. OXONE®MeOH/THF/H_2O/RT. e. CD_3ONa/CD_3OD/RT.

Scheme 3.

10 reacted with methyl iodide in THF in the presence of potassium carbonate to produce methylated bicyclic dione **11** in 80% yield.[6] The relative sterochemistry assigned to **11** followed from nOe difference experiments, of which the results were interpreted similarly to those of **6**. On the other hand, treatment of **10** with trimethyl orthoformate in methanol in the presence of CSA afforded the retroaldol products, ketal **12** and ketone **13** in 40% and 12% yield respectively.[6] Ketal **12** was confirmed by deprotection in acetone in the presence of PPTS to furnish ketone **13** in 95% yield.

Sovolytic cleavage of tricyclic ketone **2** in formic acid induced the expected opening of cyclopropane to form an isomeric mixture of bicyclic formates (Scheme 2). For the feasible separation, the crude formates reacted with potassium carbonate in methanol to give a 4 : 1 mixtureof the corresponding alcohols **14** and **15** in 94% overall yield.[6] After chromatographic separation, each alcohol was isomerized by potassium t-butoxide or DBU in THF to result in a 3 : 1 mixture of the identical isomeric alcohols **14** and **15**. Their relative stereochemistries were determined by nOe difference experiments e.g. **14**: irradiation at H-C (5) showed enhancement at H-C (7) [no effects between H-C (5) and H-C (9), and between H-C (7) and H-C (9)] and $J_{H\text{-}C(4),\ H\text{-}C(5)}$=9.8 Hz, and **15**: irradiation at H-C (5) showed enhancements at H-C (7) and H-C (9). Although treatment of **2** with thiophenol under various acidic conditions failed to open its cyclopropane ring cleanly, **2** reacted with sodium thiophenoxide in THF in the presence of zinc triflate[8] to provide an isomeric mixture of ketones **16** and **17** in 95% yield, which could not be separated completely due to the rapid isomerization on silica gel. After their equilibration on silica gel, the ratio of **16** and **17** turned out to be 3 to 1 by proton NMR spectroscopic data. The relative stereochemistries were concluded from nOe difference experiments of pure **16**,[6] analogous to those of **14**, and from correlation of spectroscopic data with

those of **14** and **15**.

Tricyclic alcohol **3** was readily solvolyzed in formic acid to produce bicyclic olefin **18** in 97% yield (Scheme 3).[6] Its relative stereochemistry was deduced from nOe difference experiments e.g., irradiation at H-C (5) showed enhancement at H-C (7) and $J_{H\text{-}C(4),\ H\text{-}C(5)}=10.4$ Hz. The attempt to afford bicyclic thiophenyl ether **20** from **3** was unsuccessful using thiophenol or sodium thiophenoxide under various acidic conditions. In addition, substitution reaction of mesylate **19** by sodium thiophenoxide did not give any productive result probably due to poor interactions between the involved orbitals. Solvolytic and nucleophilic cleavage of tricyclic olefinic alcohol **4** under various acidic conditions failed to furnish any promising outcome. Since **4** was considered as a vinylcyclopropane derivative.[9] the desired transformation was intended using radical process. Treatment of **4** with thiophenol in benzene in the presence of AIBN provided a 1 : 1 isomeric mixture of thiophenyl ethers **21** and **22** in 55% yield.[6] of which the isomeric relationship was proved by the following chemical conversions. After the mixture of **21** and **22** was oxidized by OXONE®,[10] the resulting sulfones were subjected to methanesulfonyl chloride to yield mesylates **23**. Since the eliminated product **24** was unstable during purification, **23** was eliminated with sodium methoxide-d_3 in methanol-d_4 to produce an isomerically pure diene **24**, which was identified by direct measurement of NMR spectra of the reaction mixture [two vinyl protons at δ 5.89 (br s) and 6.97 (s)]. The relative sterochemistries of **21** and **22** were unambiguously settled by nOe difference experiments e.g., **21**: irradiation at H-C (1) showed enhancement at H-C (8) and irradiation at H-C (4) showed enhancement at H-C (6), and **22**: irradiation at H-C (1) showed enhancement at H-C (8), and irradiation at H-C (4) showed enhancements at H-C (2) and H-C (6).

We have demonstrated that tricyclo[4.3.0.0^{1,5}]nonane systems can be efficiently converted into several hydrindane derivatives under acidic conditions *via* the homologous Michael addition. Work is now in progress to extend this approach to other bicyclic carbon skeletons.

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6. 2-D COSY experiments and DEPT experiments were carried out to assign the structures of all new compounds. Selected NMR data are reported below. **6**: ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.39 (3H, s), 1.76-1.87 (1H, m), 2.05-2.22 (2H, m), 2.22-2.40 (3H, m), 2.42-2.48 (1H, m), 2.48-2.59 (1H, m), 2.68-2.80 (1H, m), 5.19 (1H, dt, J=2.6 & 6.2 Hz), 8.16 (1H, s). ^{13}C-NMR (75.5 MHz, $CDCl_3$) δ 19.74, 22.58, 28.18, 34.30, 34.89, 50.49, 69.89, 160.21, 205.72, 213.04. **14**: ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.10-1.33 (2H, m), 1.35-1.43 (1H, m), 1.58-1.65 (2H, m), 1.83-1.96 (2H, m), 2.03-2.09 (1H, m), 2.16-2.33 (3H, m), 2.36-2.42 (1H, m), 3.22 (1H, dt, J=3.8 & 9.8 Hz), ^{13}C-NMR (75.5 MHz, $CDCl_3$) δ 21.35, 21.98, 22.17, 33.94, 34.57, 44.84, 49.97, 70.12, 218.89. **18**: ^{1}H-NMR (300 MHz, $CDCl_3$) δ 1.26-1.50 (2H, m), 1.52-1.65 (1H, m), 1.78-1.94 (2H, m), 2.01-2.19 (2H, m), 2.26-2.37 (2H, m), 2.38-2.48 (1H, m), 2.57-2,68 (1H, m), 4.55 (1H, dt, J=4.0 & 10.4 Hz), 5.37-5.41 (1H, m), 8.10 (1H, s). ^{13}C-NMR (75.5 MHz, $CDCl_3$) δ 24.31, 27.57, 27.84, 31.16, 31.50, 51.04, 79.36, 123.61, 142.15, 160.95. **21**: ^{1}H-NMR (300 MHz, $CDCl_3$) δ 0.89 (1H, dq, J=4.0 & 12.6 Hz), 1.35-1.43 (1H, m), 1.44-1.58 (1H, m), 1.69-1.76 (1H, m), 1.88-2.03 (3H, m), 2.31 (1H, ddd, J=1.9, 7.8 & 14.0 Hz), 2.66-2.80 (1H, m), 4.18 (1H, qd, J=2.3 & 7.5 Hz), 4.50 (1H, t, J=2.8 Hz), 5.58 (1H, t, J=2.2 Hz), 7.24-7.34 (3H, m), 7.39-7.45 (2H, m). ^{13}C-NMR (75.5 MHz, $CDCl_3$) δ 19.56, 33.29, 35.18, 39.61, 39.92, 51.42, 66.06, 124.36, 126.93, 128.64, 132.21, 135.49, 150.57.
7. Without drying potassium carbonate, **7** was obtained in about 15% yield.
8. Using zinc chloride (or zinc bromide) instead of zinc triflate produced a mixture of **16, 17** and the corresponding chlorides (or bromides).
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