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# RING OPENING OF CYCLOPROPANE IN TRICYCLO[4.3.0.0$^{2,9}$]NONAN-3-ONE WITH ELECTROPHILE-NUCLEOPHILE REAGENTS

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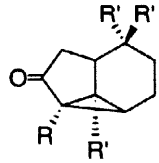
***Abstract***: Four tricyclo[4.3.0.0$^{2,9}$]nonan-3-one systems were treated with TBDMSI, TMSTFA and TMSTFA/NaSPh, affording different cyclopropane cleavage products, depending on the location of the substituent and the nature of the reagent. 

Over the past few years we have been working on project aimed at the synthesis of limonoid model compounds with insect antifeedant activity.[1] As part of this project, we focused our attention on the synthesis of C-12 oxygenated derivatives of havanensin limonoids,[1b] which are potential precursors of C-seco limonoids, such as azadirachtin, considered to be the most active insect antifeedant of the limonoid family.[2] We planned a procedure based on the cleavage of cyclopropyl ketones. A first attempt at this was described in a previous work,[1a] but was clearly insufficient to evaluate the scope of the plan. This prompted us to study the cleavage of several tricyclo[4.3.0.0$^{2,9}$]nonan-3-ones, employing reagents which combine nucleophilic and electrophilic components of varying strengths, to know its scope and potential applicability.

The cyclopropyl ketones **6,13-16** (Scheme 1 and figure 1), whose cleavage is studied here, are related to the CD or CDE structural fragment of havanensin limonoids; however they are of general interest as regards reported cleavage studies of tricyclo[3.3.0.0$^{2,8}$]octan-3-ones.[3]




**6** R' = R = H
**13** R' = H, R = Ph
**14** R' = H, R =Thienyl
**15** R' = $CH_3$, R = H
**16** R' = $CH_3$, R =Furyl

**Figure 1**

Synthesis of the cyclopropyl ketones **6**, **13** and **14** was carried out by the simple procedures depicted in scheme 1. The cyclohexenol acetate **1** was made to react with sodium malonate[4] in THF in the presence of Pd(0) to give exclusively the diester **2**, which was decarboxylated[5] to the monoester **3** by treatment with lithium chloride and $H_2O$/DMSO at 160 °C. Saponification of **3** with KOH in EtOH/$H_2O$ followed by

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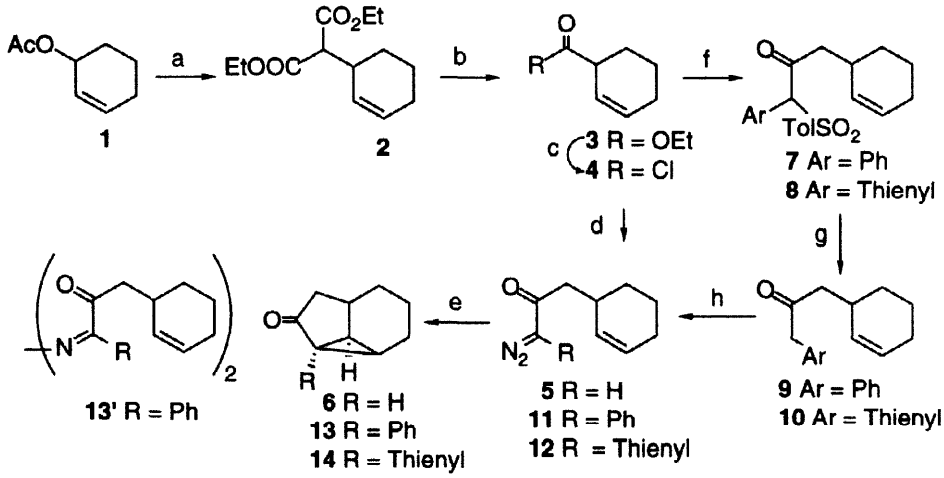
reaction of the dry carboxylic sodium salt with oxalyl chloride[6] afforded the acid chloride **4** in 61 % overall yield from the starting acetate **1**.

Treatment of the acid chloride **4** with an ethereal solution of diazomethane gave the diazoketone **5**, which after reaction with dirhodium tetraacetate[6] was converted into the cyclopropyl ketone **6**.



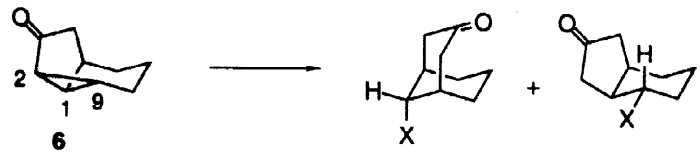

a) $CH_2(CO_2Et)_2$, NaH, $Pd(PPh_3)_4$, THF, reflux; b) LiCl, $H_2O$, DMSO, 160 °C; c) (i) KOH, EtOH-$H_2O$, reflux; (ii) (ClCO)2, benzene, 0 °C; d) $CH_2N_2$, ether, 0 °C; e) $Rh_2(OAc)_4$, $CH_2Cl_2$, rt; f) $TolSO_2CH_2Ar$, BuLi, THF, -35 °C; g) Al-Hg, THF-$H_2O$, 25 °C; h) N-acetylsulfanilyl azide, DBU, $CH_3CN$, 0 °C.

**Scheme 1**

The aryl cyclopropyl ketones **13** and **14** were prepared from the acid chloride **4** in a four step sequence. Condensation of **4** with the appropriate sulfone dianion[7] (Ar = Ph, Thienyl) in THF at -30 °C afforded the corresponding keto sulfones **7** (Ar = Ph) and **8** (Ar = Thienyl) in good yield. The sulfones employed for the condensation were obtained by nucleophilic displacement of the corresponding bromides with sodium-p-toluenesulfinate[8] in DME at 80 °C in 90% yield. Desulfonylation[9] of **7** and **8** was accomplished by treatment with aluminum amalgam in THF/$H_2O$ to give the unsaturated ketones **9** and **10**. Diazo transfer to **9**, **10** was effected with N-acetylsulfanilyl azide.[10] Cyclopropanation was attempted with dirhodium tetraacetate; the phenyl diazo ketone **11** derivative was transformed into the cyclopropyl ketone **13** and the azine **13'** in 62% and 38% yield, respectively; while the thienyl diazo ketone **12** was only obtained in 11% yield. Changing the catalyst to the more electrophilic copper (II) bis-(t-butylsalicyladimidate), the thienyl cyclopropyl ketone **14** was obtained in 32% yield. The cyclopropyl ketones **15** and **16** were obtained by the procedure described by us elsewhere.[1a]

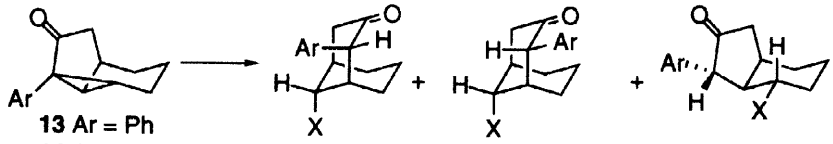
We chose *tert*-butyldimethylsilyl iodide to start the cleavage study (Figure 2). The reagent was prepared "in situ" from *tert*-butyldimethylsilyl chloride and sodium iodide.[3b,3c] Treatment of cyclopropyl ketone **6** with TBDMSI in methylene chloride at 25 °C for 5 hours afforded exclusively the iodo ketone **17** in quantitative yield.[12] The structure of **17** was assigned on the basis of the simplicity of its $^{13}C$ NMR spectrum, with only six signals. The chemical displacement of the carbonyl carbon at 208.9 ppm corresponds to a cyclohexanone; the singlet signal at 4.97 ppm in the $^1H$ NMR indicates an $H_{eq}$-$H_{eq}$ coupling for the geminal iodine hydrogen and its situation on the deshielding cone of the carbonyl group.

**Figure 2**



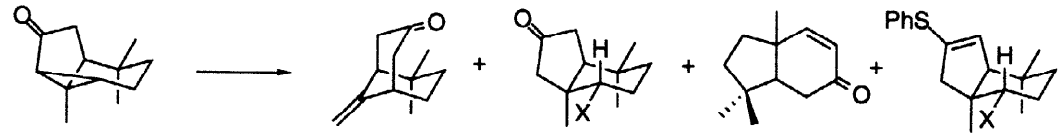
**6**

| Reagent | X | | |
|---|---|---|---|
| TBDMSI | I | **17** | - |
| TMS-TFA | TFA | **27** (1)[a] | **26** (1) |
| TMSTFA/NaSPh | TFA | **27** (3) | **26** (2) |
| | PhS | **32** (2) | **31** (1) |



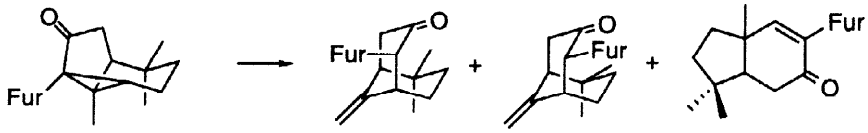
**13** Ar = Ph
**14** Ar = Thienyl

| Reagent | X | | | |
|---|---|---|---|---|
| **Ar = Ph** | | | | |
| TBDMSI | I | **18a** (1) | **18b** (1) | **19** (3) |
| TMSTFA | TFA | -- | -- | **28** |
| **Ar = Thienyl** | | | | |
| TBDMSI | I | **20a** (1) | **20b** (1) | **21** (3) |
| TMSTFA | TFA | -- | -- | **29** |



**15**

| Reagents | X | | | | |
|---|---|---|---|---|---|
| TBDMSI | I | **22** (2) | **23** (1) | -- | -- |
| TMSTFA | TFA | **22** (1) | -- | **30** (2) | -- |
| TMSTFA/NaSPh | SPh | **22** (1) | -- | **30** (1) | **33** (8) |



**16**

| Reagents | X | | | |
|---|---|---|---|---|
| TBDMSI | | **24a** (24) | **24b** (16) | **25** (60) |
| TMS-TFA | | - | - | **25** |
| TMS-TFA/NaSPh | | - | - | **25** |

(a) Relative amounts in parentheses

Cleavage of the [4.3.0.0$^{2,9}$] system is therefore regioselectively inverse compared to the [3.3.0.0$^{2,8}$] system reported by Demuth,[3a] which was shown as a $S_N2$ type of nucleophilic cleavage (Figure 3 and table I). The result of our experiment is similar to that reported by C. Iwata[3c] for a 7,7-dimethyl derivative of the [3.3.0.0$^{2,8}$] system, which is described as the first example of predominant $C_1$-$C_2$ bond cleavage of a tricyclo[3.3.0.0$^{2,8}$]octan-3-one ring system. The regioselectivity in the Iwata example is justified by the steric hindrance of carbon $C_8$ to nucleophilic attack.

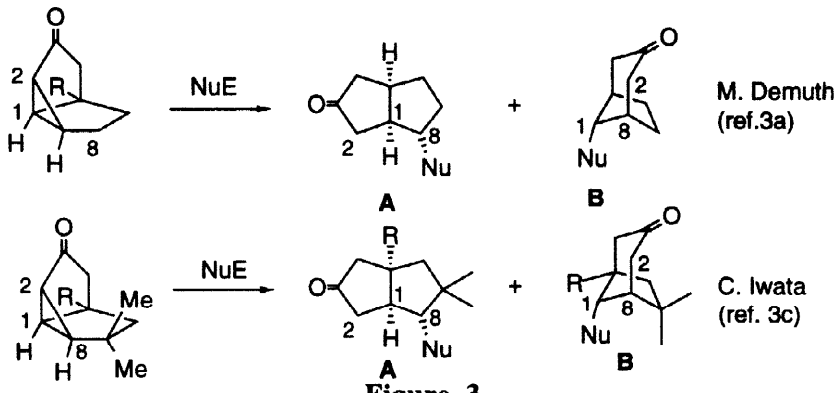



**Figure 3**

Our next cyclopropyl ketone **13** afforded a different result with respect to **6** when treated with TBDMSI. A 1:1:3 mixture of three iodoketones **18a**, **18b** and **19** was obtained. The most significant differences in $^1$H NMR of **18a** and **18b** were the signal assigned to the benzylic hydrogen: a singlet for **18a** (3.83 ppm, $H_{eq}$-$H_{eq}$ coupling ) and a doublet for **18b** (3.92 ppm, J = 5 Hz, $H_{eq}$-$H_{ax}$ coupling). The iodine geminal hydrogen appeared at 5.13 and 5.21 ppm in **18a** and **18b**, respectively. The major cleavage product was identified as the iodo indanone **19**; a signal in the $^{13}$C NMR at 215.7 ppm unequivocally indicates a carbonyl group in the cyclopentane ring. The quartet signal at 4.60 ppm J = 4 Hz and J' = 8 Hz in the $^1$H NMR enssure an equatorial orientation of the iodine and the high coupling constant J = 11 Hz observed for the benzylic hydrogen at 3.32 ppm a *trans* relationship between $H_1$-$H_{7a}$.

Practically the same result was obtained in the treatment of thienyl cyclopropyl ketone **14** with TBDMSI. For substrates **13** and **14**, the $S_N2$ type of nucleophilic cleavage, e.i. $C_9$-$C_2$ bond cleavage, predominates over $C_1$-$C_2$ bond cleavage in a 3/2 ratio.

With TBDMSI the trimethyl cyclopropyl ketone **15** afforded a 2:1 mixture of the unsaturated ketone **22** and the iodoketone **23**; this result parallels previous findings reported by us elsewhere[1a] in the treatment of **15** with TMSI. The $C_1$-$C_2$ bond cleavage predominates over the $C_9$-$C_2$ bond cleavage in a 7/3 ratio.

The final compound studied in the first set of cleavage experiments with TBDMSI was the furyl trimethyl cyclopropyl ketone **16**. Unexpectedly, the result obtained here did not parallel those reported for **16** with TMSI. A 24/16 mixture of the ketones **24a** and **24b**, respectively and ketone **25** was obtained; the epimers **24a** and **24b** have been reported by us.[1a] Structure **25** was assigned to the third ketone on the basis of their spectroscopic data.

Our next cleavage reagent was trimethylsilyl trifluoracetate (TMSTFA), a combination of a strong electrophile and a weak nucleophile. When **6** was treated with TMSTFA without solvent at 60°C a 1:1 mixture of **26** and **27** was formed. A remarkable increase in the $C_9$-$C_2$ bond cleavage against the $C_1$-$C_2$

bond cleavage to afford the bicyclic system [4.3.0] occurred in comparison with TBDMSI, in agreement with the findings of M. Demuth. The behaviour of the phenyl and thienyl cyclopropyl ketones **13** and **14** when reacting with TMSTFA was the same. An absolute regioselective nucleophile addition was achieved, affording the keto esters with the bicyclic system [4.3.0] **28** and **29**, respectively, as the sole product.

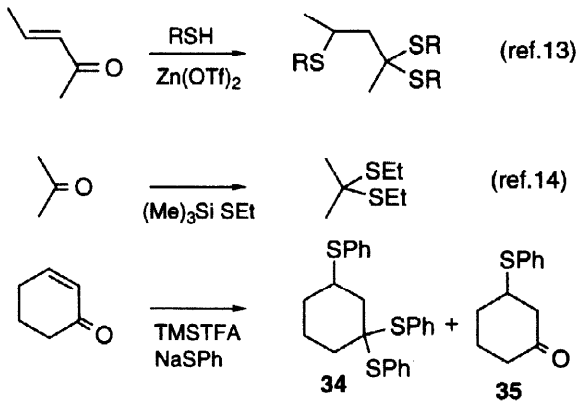
This selective result could find application in the synthesis of demethylated CDE "molecular fragments" of limonoids with a functionalized C ring.

The trimethyl cyclopropyl ketone **15** does not afford any compound originated from the $C_9$-$C_2$ bond cleavage in the reaction with TMSTFA. Instead, a 1:2 mixture of the unsaturated ketones **22** and **30** was obtained. With regard to stereocontrol, an absolutely selective result was reached from the furyl trimethyl cyclopropyl ketone **16**, which with TMSTFA gave the indenone **25** exclusively.

To amplify the cleavage study of the tricyclic system [4.3.0.$0^{2,9}$], we decided to investigate its behaviour with a TMSTFA/NaSPh mixture, composed of a strong electrophile and two nucleophiles, one weak and another strong one. The cyclopropyl ketone **6** afforded a four compound mixture: **26/27** in a 2/3 ratio (22 % yield) and **31/32** in a 1/2 ratio (33% yield).

Again from this reaction the predominance in the mixture of the [3.3.1] system over the [4.3.0] one, which shows preference for $C_1$-$C_2$ bond cleavage is clear. Another interesting feature is the competence of the two nucleophiles, which lies slightly in favour of $PhS^-$.

The reaction of TMSTFA/NaSPh with the trimethyl cyclopropyl ketone **15** afforded a very unexpected result. The crude product consists of a 1:1:8 mixture of the unsaturated ketones **22** and **30** and the disulfide **33**, respectively. The structure of the disulfide **33** was elucidated by spectroscopic means and was confirmed by H-C correlations. The reaction which afforded the major product is analogous to those reported by E.J. Corey[13] and D.A. Evans.[14]




We found that the reaction of TMSTFA/NaSPh with cyclohexenone afforded a mixture of the trisulfide **34** and the ketosulfide **35** in at 1:2.5 ratio.

Unlike the cleavages described above, the cyclopropyl ketone **15** shows a clear preference for the $C_9$-$C_2$ bond rupture. Finally, reaction of the furyl trimethyl cyclopropyl ketone **16** with the mixture TMSTFA/NaSPh afforded excusively one compound, which was identified as the unsaturated ketone **25**. Again the $C_1$-$C_2$ bond cleavage with further rearrangement predominates.

The results of the three sets of cleavage experiments, including some reported by Demuth and Iwata are shown in table 1.

**Table 1**

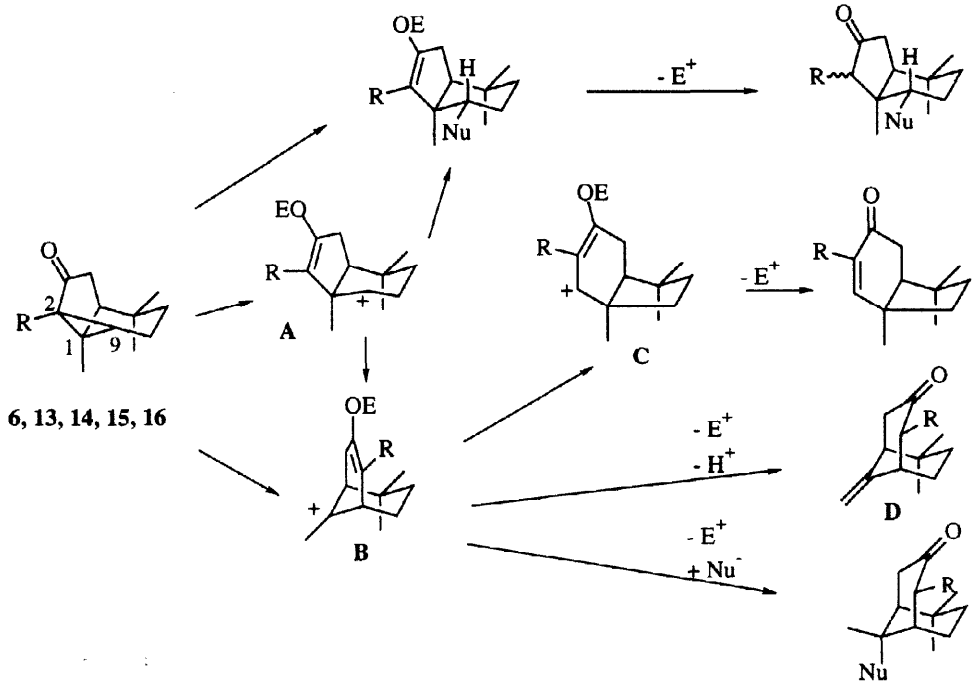
| | TBDMSI | | | | TMSTFA | | | | TMSTFA/NaSPh | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Yield % | A[a] | B[b] | C[c] | Yield % | A[a] | B[b] | C[c] | Yield % | A[a] | B[b] | C[c] |
| Demuth | 84 | 83[d] | 17[e] | | 85 | 100[d] | | | | | | |
| Iwata | 76 | 8[d] | 92[e] | | | | | | | | | |
| 6 | 100 | | 100 | | 93 | 50 | 50 | | 77 | 37 | 63 | |
| 13 | 72 | 58 | 42 | | 74 | 100 | | | | | | |
| 14 | 83 | 62 | 38 | | 71 | 100 | | | | | | |
| 15 | 98 | 35 | 65 | | 76 | | 33 | 67 | 99 | 89 | 10 | 10 |
| 16 | 93 | | 39 | 61 | 73 | | | 100 | 100 | | | 100 |

a) Products of $C_9$-$C_2$ bond cleavage. d) Products of $C_8$-$C_2$ bond cleavage in tricyclo[3.3.0.$0^{2,8}$]octan-3-one.

b) Products of $C_1$-$C_2$ bond cleavage. e) Products of $C_1$-$C_2$ bond cleavage in tricyclo[3.3.0.$0^{2,8}$]octan-3-one.

c) Products of $C_9$-$C_2$ bond cleavage with rearrangement.

The cleavage reactions can be understood in terms of the pathway shown in scheme 2. Initial cleavage of the cyclopropyl ring leads to **A**, initially favored by stereoselectronic effects. In some cases, the cationic intermediate **A** could be trapped by nucleophiles, by exo attack, to afford the bicyclic [4.3.0] compounds **19**, **21**, **23**, **26**, **28**, **29**, **31** and **33**, or rearranged to cation **B**. This intermediate could be trapped by nucleophiles (only secondary cations) to **17**, **18**, **20**, **27**, **32**; deprotonated to afford methylene derivatives (**22**, **24**) or in turn rearranged to cation **C**, which further affords compounds **25** and **30**.




**Scheme 2**

Some conclusions may be drawn. The simplest tricyclo[4.3.0.$0^{2,9}$]octan-3-one has a strong tendency to $C_1$-$C_2$ bond cleavage. This behaviour is the opposite of that shown by the lower homologue [3.3.0.$0^{2,8}$] against reagents which combine strong electrophiles and weak nucleophiles.

The introduction of a phenyl (or thienyl) substituent in $C_2$ shows the normal expected tendency to $C_9$-$C_2$ bond cleavage. The introduction of a methyl substituent in $C_1$ preferently directs the cleavage to the formation of the more stable cationic intermediate **B**, which deprotonates to **D** or rearranges to **C**. However, in the presence of a strong nucleophile such NaSPh the $S_N2$ mechanism seems to operate. Finally, the introduction of a furan ring in $C_2$ as well as a methyl group in $C_1$ direct the cleavage exclusively at $C_1$-$C_2$ bond cleavage. A plausible explanation for this result could be the severe steric hindrance of the nucleophilic attack at the $C_9$ position.

## Experimental

**General methods.** Commercial reagents were used as received. Dichloromethane, chloroform and dimethylsulfoxide were distilled under nitrogen over calcium hydride. Benzene, diethyl ether, tetrahydrofuran and toluene were distilled from sodium. Acetone, ethanol, acetonitrile and methanol were distilled before use. $^1H$ and $^{13}C$ NMR spectra were recorded in $CDCl_3$ solution at 200 and 50 MHz respectively. IR spectra were obtained as thin films. All reactions were carried out under an atmosphere of argon in glassware dried overnight and cooled under argon. Reactions were monitored by TLC. Flash column chromatographies were carried out using silica gel 60 (0.040-0.063 mm Merck). Organic extracts were dried with anhydrous $Na_2SO_4$ and concentrated under reduced pressure with the aid of a rotary evaporator.

**Diethyl 2-cyclohex-2-enyl-malonate 2.**- Cyclohexenol acetate **1** (10 g, 71.4 mmol), triphenylphosphine (1.72 g, 6.59 mmol) and tetrakis-triphenylphosphine palladium (180 mg, 0.15 mmol, 0.22 %M) in dry THF (110 mL) were stirred for 15 min. A solution of the sodium salt of diethyl malonate in dry THF (50 mL), generated from diethyl malonate (39.8 g, 248 mmol) and sodium hydride (68 % mineral oil, 7.94 g, 225 mmol) at 0 °C, was added all at once and the resultant mixture refluxed for 15 h. The reaction mixture was acidified with 2N HCl and extracted with diethyl ether. The organic layer was washed with water and brine, dried, filtered and concentrated under reduced pressure. The crude product was chromatographed (9:1, hexane-diethyl ether) to afford a mixture (26 g) of diester **2** and diethyl malonate which was used without further purification.

**Ethyl cyclohex-2-enyl-acetate 3.-** To a solution of the mixture of diester **2** and diethyl malonate (26 g) in DMSO (25 mL) were added water (1.8 mL, 104 mmol) and LiCl (4.4 g, 104 mmol) and the reaction mixture was heated to 170 °C for 24 h. The mixture was cooled to room temperature, and poured into ethyl acetate. This solution was washed with brine, dried and evaporated. The residue was chromatographed (9:1, hexane-diethyl ether) to afford **3** (7.3 g, 61 % from **1**), as a colourless oil: IR 2936, 1738, 1240 $cm^{-1}$; $^1H$ NMR δ 1.25 (t, 3H, J=7 Hz), 1.2-1.9 (m, 4H), 1.97 (m, 2H), 2.25 (d, 1H, J=3 Hz), 2.29 (d, 1H, J=3 Hz), 2.59 (m, 1H), 4.13 (c, 2H, J=7 Hz), 5.54 (m, 1H), 5.71 (m, 1H) ppm; Anal. Calcd. for $C_{10}H_{16}O_2$: C, 71.39; H, 9.58. Found: C, 71.45; H, 9.52.

**Cyclohex-2-en-acetyl chloride 4.**- A solution of unsaturated ester **3** (3.02 g, 17.8 mmol) and potassium hydroxide (1.03 g, 17.8 mmol) in a mixture of 1:1 ethanol-water (12 mL) was heated under reflux for 5 h. The reaction mixture was evaporated under reduced pressure. A suspension of the dry salt in benzene (15 mL) was teated with oxalyl chloride (4.67 mL, 53 mmol) at 0 °C for 1 h. The reaction mixture

was filtered and the solvent and excess of oxalyl chloride were evaporated under reduced presure. Acid chloride **4** was obtained (2.82 g) in quantitative yield, as a colourless oil: IR 2930, 1802 $cm^{-1}$.

**1-Diazo-3-(cyclohex-2-enyl)propan-2-one 5.-** A solution of acid chloride **4** (360 mg, 2.27 mmol) in diethyl ether (2 mL) was added to a solution of freshly prepared diazomethane (19 mL, 28 mmol, 1.5 M) in diethyl ether at 0 °C, and the mixture was allowed to warm to room temperature overnight. The mixture was filtered and the filtrate was evaporated under reduced pressure. α-Diazo ketone **5** (335 mg, 90%) was used in the next reaction without further purification: IR 2924, 2104, 1640, 1368 $cm^{-1}$; $^1H$ NMR δ 1.2-1.9 (m, 4H), 1.98 (m, 2H), 2.29 (m, 1H), 2.42 (m, 2H), 5.22 (s, 1H), 5.51 (m, 1H), 5.69 (m, 1H) ppm.

**Tricyclo[3.4.0.$0^{2,9}$]nonan-3-one 6.-** A solution of the diazoketone **5** (335 mg, 2.04 mmol) in anhydrous $CH_2Cl_2$ (150 mL) was added dropwise to a suspension of dirhodium tetraacetate (17 mg) in anhydrous $CH_2Cl_2$ (50 mL). The mixture was stirred for 45 min at room temperature, and evaporated under vacuo. Chromatography (9:1, hexane-diethyl ether) of the residue afforded cyclopropyl ketone **6** (153 mg, 55%), as a colourless liquid: IR 2934, 1721 $cm^{-1}$; $^1H$ NMR δ 1.0-2.0 (m, 9H), 2.22 (m, 1H), 2.68 (m, 2H) ppm; $^{13}C$ NMR δ 15.7, 20.3, 23.5, 26.3, 26.5, 26.7, 33.9, 48.6, 216.0 ppm; MS m/z (relative intensity) 136 (7, $M^+$), 121 (3), 108 (12), 94 (32), 79 (100), 66 (42), 53 (67); Anal. Calcd. for $C_9H_{12}O$: C, 79.37; H, 8.88. Found: C, 79.23; H, 8.93.

**1-(Cyclohex-2-enyl)-3-phenyl-3-(toluene-4-sulfonyl)propan-2-one 7.-** Butyllithium (5.1 mL, 8.12 mmol, 1.6 M in hexane) was added slowly with efficient stirring, to a solution of phenyl-*p*-toluenesulfonyl methane (0.95 g, 4.06 mmol) in THF (15 mL) at -30 °C. After 30 min acid chloride **4** (0.64 g, 4.05 mmol) in THF (3 mL) was slowly added by syringe and stirred for 15 min. Subsequently, the reaction mixture was poured into a saturated $NH_4Cl$ solution, stirred and gradually warmed to room temperature. The mixture was extracted with diethyl ether and the organic phase was washed with brine, dried and evaporated. Chromatography of the residue (8:2, hexane/diethyl ether) afforded the keto sulfone **7** (1.42 g, 95%), as a brown, amorphous solid: IR 2980, 1720, 1313 $cm^{-1}$; $^1H$ NMR δ 1.6-2.0 (m, 7H), 2.61 (m, 2H), 2.39 (s, 3H), 5.20 (s, 1H), 5.50 (m, 2H), 7.15-7.51 (m, 9H) ppm; Anal. Calcd. for $C_{22}H_{24}SO_3$: C, 71.71; H, 6.56. Found: C, 71.79; H, 6.52.

**1-(Cyclohex-2-enyl)-3-(3-thienyl)-3-(toluen-4-sulfonyl)propan-2-one 8.-** Butyllithium (5.9 mL, 9.50 mmol, 1.6 M in hexane) was added slowly with efficient stirring, to a solution of 3-(3-thienyl)-*p*-toluenesulfonyl methane (1.19 g, 4.73 mmol) in THF (15 mL) at -30 °C. After 30 min acid chloride **4** (0.75 g, 4.73 mmol) in THF (3 mL) was slowly added by syringe and stirred for 15 min. Subsequently, the reaction mixture was poured into a saturated $NH_4Cl$ solution, stirred and allowed to reach room temperature. The mixture was extracted with diethyl ether and the organic phase was washed with brine, dried, filtered and evaporated. Chromatography of the residue (8:2, hexane/diethyl ether) afforded the keto sulfone **8** (1.50 g, 85%), as a brown, amorphous solid: IR 2990, 1716, 1370 $cm^{-1}$; $^1H$ NMR δ 1.2-2.1 (m, 7H), 2.41 (s, 3H), 2.75 (m, 2H), 5.43 (s, 1H), 5.61 (m, 2H), 7.20 (m, 7H) ppm; Anal. Calcd. for $C_{20}H_{22}S_2O_3$: C, 64.14; H, 5.92. Found: C, 64.19; H, 5.98.

**1-(Cyclohex-2-enyl)-3-phenylpropan-2-one 9.-** Aluminum amalgam (2.1 g) was added onto a solution of β-keto sulfone **7** (0.63 g, 1.70 mmol) in a 9:1 mixture of THF/$H_2O$ (38 ml). The mixture was vigorously stirred at room temperature. After 5 h the mixture was diluted with a 1:1 mixture of ethyl acetate-hexane. The organic layer was washed with 5% sodium bicarbonate solution, dried and evaporated. Chromatography of the residue afforded ketone **9** (0.32 g, 88%), as a viscous, colourless liquid: IR 3021,

2926, 1713 $cm^{-1}$; $^1H$ NMR δ 1.1-1.9 (m, 6H), 2.39 (d, 2H, J=7 Hz), 2.60 (m, 1H), 3.63 (s, 2H), 5.41 (m, 1H), 5.62 (m, 1H), 7.25 (m, 5H) ppm; $^{13}C$ NMR δ 20.6, 24.7, 28.5, 30.6, 47.8, 50.2, 126.5, 127.3, 128.2 (2), 129.0 (2), 130.2, 133.9, 206.4 ppm; Anal. Calcd. for $C_{15}H_{18}O$: C, 84.07; H, 8.46. Found: C, 84.01; H, 8.44.

**1-(Cyclohex-2-enyl)-3-(3-thienyl)propan-2-one 10.-** Aluminum amalgam (3.0 g) was added onto a solution of β-keto sulfone **8** (0.90 g, 2.40 mmol) in a 9:1 mixture of THF/$H_2O$ (54 ml). The mixture was vigorously stirred at room temperature. After 5 h the mixture was diluted with a 1:1 mixture of ethyl acetate-hexane. The organic layer was washed with 5% sodium bicarbonate solution, dried and evaporated. Chromatography of the residue afforded ketone **10** (0.45 g, 85%), as a viscous, colourless liquid: IR 3105, 2930, 1715 $cm^{-1}$; $^1H$ NMR δ 1.5-1.8 (m, 4H), 1.95 (m, 2H), 2.43 (d, 2H, J=7 Hz), 2.65 (m, 1H), 3.71 (s, 2H), 5.45 (m, 1H), 5.69 (m, 1H), 6.96 (d, 1H, J=5 Hz), 7.10 (s, 1H), 7.30 (m, 1H) ppm; $^{13}C$ NMR δ 21.1, 25.1, 28.9, 31.1, 44.6, 48.1, 122.8, 125.7, 127.9, 128.6, 130.9, 134.2, 206.1 ppm; Anal. Calcd. for $C_{13}H_{16}OS$: C, 70.87; H, 7.32. Found: C, 70.82; H, 7.38.

**1-(Cyclohex-2-enyl)-3-diazo-3-phenylpropan-2-one 11.-** A solution of ketone **9** (300 mg, 1.40 mmol), N-acetyl-sulfanilyl azide (437 mg, 1.82 mmol) and DBU (0.27 mL, 1.82 mmol) in dry acetonitrile (7 ml) was stirred at 0 °C protected of light for 1h. The mixture was filtered through a pad of Florisil eluting with a mixture of 9:1 hexane-diethyl ether. Removal under vacuo of the solvent afforded α-diazo ketone **11** (279 mg, 83%), as a viscous, yellow oil: IR 2924, 2072, 1730, 1657 $cm^{-1}$; $^1H$ NMR δ 1.2-2.0 (m, 7H), 2.55 (d, 1H, J=2 Hz), 2.58 (s, 1H), 5.72 (m, 2H), 7.24-7.54 (m, 5H) ppm.

**1-(Cyclohex-2-enyl)-3-diazo-3-(3-thienyl)propan-2-one 12.-** A solution of ketone **10** (0.40 g, 1.82 mmol), N-acetyl-sulfanilyl azide (0.57 g, 2.36 mmol) and DBU (0.35 mL, 2.36 mmol) in dry acetonitrile (9 mL) was stirred at 0 °C protected of light for 1h. The mixture was filtered through a pad of Florisil eluting with a mixture of 9:1 hexane-diethyl ether. Removal under vacuo of the solvent afforded α-diazo ketone **12** (380 mg, 85%), as a viscous, yellow oil: IR 3108, 2928, 2076, 1647 $cm^{-1}$; $^1H$ NMR δ 1.6-2.0 (m, 7H), 2.53 (d, 1H, J=2 Hz), 2.56 (s, 1H), 5.57 (m, 1H), 5.73 (m, 1H), 7.05 (m, 1H), 7.40 (m, 2H) ppm.

**2-Phenyl-tricyclo[3.4.0.$0^{2,9}$]nonan-3-one 13.-** A solution of diazoketone **11** (160 mg, 0.66 mmol) in anhydrous $CH_2Cl_2$ (50 mL) was added dropwise to a suspension of dirhodium tetraacetate (10 mg) in anhydrous $CH_2Cl_2$ (16 mL). The mixture was stirred for 2h at room temperature, and evaporated under vacuo. Chromatography (9:1, hexane-diethyl ether) of the residue afforded azine **13'** (58 mg, 38%), followed by cyclopropyl ketone **13** (88 mg, 62 %), as a colourless liquid.

**13'**: IR 3046, 1701 $cm^{-1}$; $^1H$ NMR δ 1.2-2.0 (m, 6H), 2.79 (m, 1H), 2.86 (s, 1H), 2.90 (d, 1H, J=1 Hz), 5.58 (m, 1H), 5.71 (m, 1H), 7.56 (m, 5H). Anal. Calcd. for $C_{30}H_{32}O_2N_2$: C, 79.59; H, 7.12; N, 6.21. Found: C, 79.45; H, 7.18; N, 6.17.

**13**: IR 3027, 2934, 1717 $cm^{-1}$; $^1H$ NMR δ 0.9-2.0 (m, 8H), 2.18 (d, 1H, J=18 Hz), 2.59 (t, 1H, J=7.5 Hz), 2.84 (dd, 1H, J=11 and 18 Hz), 7.25 (m, 5H) ppm; $^{13}C$ NMR δ 15.4, 19.9, 24.5, 26.2, 31.6, 32.7, 46.1, 49.3, 126.5, 127.5 (2), 128.2 (2), 138.9, 213.5 ppm; MS m/z (relative intensity): 212 (44, $M^+$), 194 (27), 170 (38), 141 (72), 115 (68), 103 (100), 91 (46), 77 (58), 51 (60); Anal. Calcd. for $C_{15}H_{16}O$: C, 84.86; H, 7.59. Found: C, 84.74; H, 7.47.

**2-(3-Thienyl)-tricyclo[3.4.0.$0^{2,9}$]nonan-3-one 14.-** A solution of diazoketone **12** (177 mg, 0.72 mmol) in dry toluene (30 mL) was added dropwise to a solution of bis-(N-*t*-butyl-salicyladiminate) copper

(II) (5 mg) in dry toluene (25 mL) under reflux. After 15 h the solvent was evaporated under reduced pressure and the residue was chromatographed (9:1, hexane-diethyl ether) to afford cyclopropyl ketone **14** (50 mg, 32 %), as a colourless oil: IR 3108, 2934, 1715 $cm^{-1}$; $^1H$ NMR δ 0.8-2.0 (m, 8H), 2.17 (d, 1H, J=18 Hz), 2.57 (t, 1H, J=7 Hz), 2.83 (dd, 1H, J=18 and 3 Hz), 6.95 (m, 1H), 7.25 (m, 2H) ppm; $^{13}C$ NMR δ 15.4, 19.7, 25.1, 26.1, 33.0, 34.5, 42.5, 48.9, 119.9, 125.1, 126.0, 139.6, 213.2 ppm; MS m/z (relative intensity) 218 (62, $M^+$), 189 (25), 176 (32), 161 (31), 147 (58), 135 (49), 115 (39), 109 (86), 91 (55), 45 (100); Anal. Calcd. for $C_{13}H_{14}OS$: C, 71.52; H, 6.46. Found: C, 71.67; H, 6.38.

**General procedure. Reaction of cyclopropyl ketones with TBDMSI.-** To a mixture of *t*-butyldimethylchloro silane (1.83 mmol) and NaI (2.1 mmol) in $CHCl_3$ (2 mL), cyclopropyl ketones (1 mmol) in $CHCl_3$ (1 mL) were added and the reaction mixture was stirred at room temperature. After filtration the solvent was removed under reduced pressure and the residue was taken up in diethyl ether and water; after shaking, the organic layer was separated, dried and evaporated. Chromatography (9:1 hexane-diethyl ether) of the residue afforded bicyclic ketones.

**Reaction of cyclopropyl ketone 6.-** According to the general procedure cyclopropyl ketone **6** (30 mg, 0.22 mmol) yielded 9-iodo-bicyclo[3.3.1]nonan-3-one **17** (58 mg, 100%), as a colourless oil: IR 2983, 1710 $cm^{-1}$; $^1H$ NMR δ 1.4-2.4 (m, 8H), 2.46 (d, 2H, J=16 Hz), 2.74 (dd, 2H, J=6 and 16 Hz), 4.97 (s, 1H) ppm; $^{13}C$ NMR δ 17.4, 27.5 (2), 36.2, 38.6 (2), 47.9 (2), 208.9 ppm; MS m/z (relative intensity) 137 (30, $M^+$-I), 127 (13), 119 (16), 95 (58), 79 (33), 67 (100), 55 (75); Anal. Calcd. for $C_9H_{13}OI$: C, 40.93; H, 4.96. Found: C, 40.75; H, 5.15.

**Reaction of cyclopropyl ketone 13.-** According to the general procedure cyclopropyl ketone **13** (25 mg, 0.12 mmol) yielded 9-iodo-2-phenyl-bicyclo[3.3.1]nonan-3-one **18a** (6 mg, 15%), as a colourless oil, followed by 4-iodo-3-phenyl-octahydro-indan-2-one **19** (17 mg, 42%), as a colourless oil, and finally 9-iodo-2-phenyl-bicyclo[3.3.1]nonan-3-one **18b** (6 mg, 15%), as a colourless oil.

**18a**: IR 2926, 1707 $cm^{-1}$; $^1H$ NMR δ 1.6-1.9 (m, 8H), 2.60 (m, 1H), 2.89 (m, 1H), 3.83 (s, 1H), 5.13 (s, 1H), 7.27 (m, 5H) ppm; MS m/z (relative intensity) 213 (10, $M^+$-I), 185 (19), 127 (11), 91 (100), 77 (20), 53 (22); Anal. Calcd. for $C_{15}H_{17}OI$: C, 52.96; H, 5.04. Found: C, 52.76; H, 5.13.

**19**: IR 2976, 1740 $cm^{-1}$; $^1H$ NMR δ 0.8-2.1 (m, 6H), 2.32 (dd, 1H, J=1 and 19 Hz), 2.53 (dd, 1H, J=7 and 19 Hz), 2.81 (m, 1H), 2.91 (m, 1H), 3.32 (d, 1H, J=11 Hz), 4.60 (dd, 1H, J=4 and 8 Hz), 7.09 (m, 2H), 7.30 (m, 3H) ppm; $^{13}C$ NMR δ 21.9, 27.8, 31.4, 31.6, 32.6, 45.0, 54.1, 57.9, 127.4, 128.4 (2), 128.9 (2), 137.1, 215.7 ppm; MS m/z (relative intensity) 213 (16, $M^+$-I), 185 (15), 129 (36), 115 (32), 91 (100), 81 (32), 65 (23), 51 (30); Anal. Calcd. for $C_{15}H_{17}OI$: C, 52.96; H, 5.04. Found: C, 52.82; H, 5.28.

**18b**: IR 2975, 1720 $cm^{-1}$; $^1H$ NMR δ 1.6-2.6 (m, 8H), 2.67 (dd, 1H, J=2 and 19 Hz), 2.93 (dd, 1H, J=7 and 19 Hz), 3.92 (d, 1H, J=5 Hz), 5.21 (s, 1H), 7.2-7.4 (m, 5H) ppm; MS m/z (relative intensity) 213 (6, $M^+$-I), 129 (10), 115 (15), 97 (100), 77 (12), 55 (30); Anal. Calcd. for $C_{15}H_{17}OI$: C, 52.96; H, 5.04. Found: C, 51.89; H, 4.96.

**Reaction of cyclopropyl ketone 14.-** According to the general procedure cyclopropyl ketone **14** (20 mg, 0.09 mmol) yielded 9-iodo-2-(3-thienyl)-bicyclo[3.3.1]nonan-3-one **20a** (5 mg, 16%), as a colourless oil, followed by 4-iodo-3-(3-thienyl)-octahydro-indan-2-one **21** (16 mg, 51%), as a colourless oil, and finally 9-iodo-2-(3-thienyl)-bicyclo[3.3.1]nonan-3-one **20b** (5 mg, 16%), as a colourless oil.

**20a**: IR 2980, 1710 $cm^{-1}$; $^1H$ NMR δ 1.3-2.4 (m, 8H), 2.48 (d, 1H, J=16.5 Hz), 2.90 (m, 1H), 3.79 (s, 1H), 5.15 (s, 1H), 6.97 (d, 1H, J=5 Hz), 7.02 (s, 1H), 7.34 (m, 1H) ppm; $^{13}C$ NMR δ ppm; MS m/z (relative intensity) 346 (2, $M^+$), 219 (14), 177 (15), 135 (12), 97 (100), 81 (35), 65 (19), 45 (57); Anal. Calcd. for $C_{13}H_{15}OSI$: C, 45.10; H, 4.37. Found: C, 45.23; H, 4.58.

**21**: IR 3015, 1748 $cm^{-1}$; $^1H$ NMR δ 1.8-2.4 (m, 7H), 2.69 (m, 1H), 2.80 (m, 1H), 2.93 (m, 2H), 3.50 (d, 1H, J=10 Hz), 4.60 (m, 1H), 6.95 (m, 1H), 7.03 (d, 1H, J=3 Hz), 7.34 (m, 1H) ppm; $^{13}C$ NMR δ 22.0, 27.6, 31.8, 32.7 (2), 44.0, 32.9, 53.7, 121.9, 126.5, 126.9, 136.8, 214.8 ppm; MS m/z (relative intensity) 219 (21, $M^+$-I), 177 (21), 135 (19), 123 (12), 97 (100), 79 (32), 65 (22); Anal. Calcd. for $C_{13}H_{15}OSI$: C, 45.10; H, 4.37. Found: C, 45.03; H, 4.22.

**20b**: IR 2980, 1705 $cm^{-1}$; $^1H$ NMR δ 1.0-2.5 (m, 8H), 2.62 (m, 1H), 2.89 (m, 1H), 4.11 (d, 1H, J=6 Hz), 5.17 (s, 1H), 6.95 (d, 1H, J=5 Hz), 7.27 (m, 2H) ppm; MS m/z (relative intensity) 219 (16, $M^+$-I), 177 (18), 135 (10), 97 (100), 81 (31), 65 (30); Anal. Calcd. for $C_{13}H_{15}OSI$: C, 45.10; H, 4.37. Found: C, 45.19; H, 4.18.

**Reaction of trimethyl cyclopropyl ketone 15**.- According to the general procedure cyclopropyl ketone **15** (50 mg, 0.28 mmol) yielded 6,6-dimethyl-9-methylene-bicyclo[3.3.1]nonan-3-one **22** (32 mg, 64%), as a colourless oil, followed by 4-iodo-3a,7,7-trimethyl-octahydro-indan-2-one **23** (29 mg, 34%) as a colourless oil.

**22**: IR 2980, 1717 $cm^{-1}$; $^1H$ NMR δ 0.90 (s, 3H), 0.94 (s, 3H), 2.42 (m, 4H), 4.78 (d, 1H, J=2 Hz), 4.89 (d, 1H, J=2 Hz) ppm; $^{13}C$ NMR δ 27.0, 29.9, 29.9, 31.2, 35.5, 38.9, 45.3, 44.8, 50.8, 108.0, 150.6, 211.2 ppm; MS m/z (relative intensity) 178 (8, $M^+$), 167 (34), 149 (92), 137 (8), 123 (11), 112 (22), 97 (22), 83 (84), 71 (65), 57 (100); Anal. Calcd. for $C_{12}H_{18}O$: C, 80.85; H, 10.17. Found: C, 80.73; H, 10.03.

**23**: IR 3067, 1740 $cm^{-1}$; $^1H$ NMR δ 0.82 (s, 3H), 1.17 (s, 3H), 1.43 (s, 3H), 2.05 (d, 1H, J=19 Hz), 2.49 (d, 1H, J=19 Hz), 4.14 (dd, 1H, J=13 and 4 Hz) ppm; $^{13}C$ NMR δ 28.1, 28.7, 30.9, 32.2, 33.4, 36.5, 40.8, 42.7, 44.4, 52.4, 56.6, 215.0 ppm; MS m/z (relative intensity) 306 (8, $M^+$), 279 (31), 264 (10), 167 (60), 149 (100), 112 (38), 97 (30), 83 (45), 71 (78); Anal. Calcd. for $C_{12}H_{19}OI$: C, 47.07; H, 6.25. Found: C, 47.21; H, 6.38.

**Reaction of furyltrimethylcyclopropyl ketone 16**.- According to the general procedure cyclopropyl ketone **16** (30 mg, 0.12 mmol) yielded a 24:16 mixture of 2-(3-furyl)-6,6-dimetyhl-9-methylene-bicyclo[3.3.1]nonan-3-ones **24a** and **24b** (11 mg, 36%), and 6-(3-furyl)-3,3,7a-trimethyl-1,2,3,3a,4,7a-hexahydro-inden-5-one **25** (17 mg, 57%), as a colourless oil.

**24a/24b**: IR 2980, 1720 $cm^{-1}$; $^1H$ NMR δ 0.95 (s, 3H'), 0.96 (s, 3H), 0.99 (s, 3H-3H'), 2.50 (m, 2H-2H'), 3.45 (d, 1H, J=2 Hz), 3.70 (d, 1H', J=4 Hz), 4.93 (d, 1H, J=2 Hz), 4.87 (d, 1H', J=2 Hz), 4.95 (d, 1H, J=2 Hz), 4.99 (d, 1H', J=2 Hz), 6.32 (m, 1H), 6.37 (m, 1H'), 7.31 (m, 1H), 7.38 (m, 1H), 7.39 (m, 1H'), 7.60 (m, 1H') ppm; $^{13}C$ NMR δ 24.7, 27.1, 28.4, 29.9', 31.1, 31.4', 35.7, 42.2, 44.7, 45.0', 46.4', 51.5, 51.6', 52.7, 54.2', 108.2, 110.0, 110.5', 110.7', 119.9, 128.8', 139.4, 141.3', 142.2, 142.7', 150.6, 206.7, 210.7' ppm; MS m/z (relative intensity) 244 (50, M+), 167 (34), 149 (100), 128 (28), 121 (70), 107 (64), 95 (80), 84 (45), 69 (72), 57 (82); Anal. Calcd. for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25. Found: C, 78.45; H, 8.08.

**25**: IR 3021, 2980, 1678 $cm^{-1}$; $^1H$ NMR δ 0.79 (s, 3H), 1.02 (s, 3H), 1.30 (s, 3H), 1.5-2.0 (m, 5H), 2.57 (d, 1H, J=16 Hz), 2.68 (dd, 1H, J=16 and 7 Hz), 6.51 (s, 1H), 6.72 (s, 1H), 7.37 (s, 1H), 8.05 (s, 1H) ppm; $^{13}C$ NMR δ 24.1, 27.8, 29.9, 35.9, 38.8, 39.6, 42.7, 43.5, 53.6, 107.9, 119.5, 128.0, 141.9, 142.2, 152.5, 197.4 ppm; MS m/z (relative intensity) 244 (62, $M^+$), 229 (14), 215 (6), 187 (18), 174 (24), 160 (31), 145 (30), 135 (44), 107 (100), 91 (48), 77 (39), 55 (65); Anal. Calcd. for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25. Found: C, 78.77; H, 8.29.

**General procedure. Reaction of cyclopropyl ketones with TMSTFA.-** Cyclopropyl ketones (2 mmol) were heated in TMSTFA (1 mL) to 60 °C for 24 h. Excess of TMSTFA was removed under reduced pressure and the residue was taken up in diethyl ether and water; after shaking, the organic layer was separated, dried, and evaporated. Chromatography of the residue and elution with 9:1, hexane-diethyl ether yielded bicyclic ketones.

**Reaction of cyclopropyl ketone 6**.- According to the general procedure cyclopropyl ketone **6** (20 mg, 0.15 mmol) afforded a mixture of acid 2-oxo-octahydro-indan-4-yl trifluoroacetate **26** (17 mg, 45%) as a colourless oil, and 3-oxo-bicyclo[3.3.1]nonan-9-yl trifluoracetate **27** (18 mg, 48%), as a colourless oil.

**26**: IR 3010, 1780, 1740, 1350 $cm^{-1}$; $^1H$ NMR δ 1.4-2.0 (m, 7H), 2.22 (m, 5H), 5.04 (br s, 1H) ppm; $^{13}C$ NMR δ 18.6, 26.3, 26.6, 33.9, 39.6, 39.9, 43.6, 76.7, 216.4 ppm; MS m/z (relative intensity) 154 (13, $M^+$-$COCF_3$), 108 (6), 94 (37), 79 (60), 67 (61), 55 (100); Anal. Calcd. for $C_{11}H_{13}O_3F_3$: C, 52.80; H, 5.23. Found: C, 52.71; H, 5.35.

**27**: IR 3025, 1780, 1710, 1390 $cm^{-1}$; $^1H$ NMR δ 1.4-2.0 (m, 6H), 2.58 (m, 6H), 5.40 (br s, 1H) ppm; $^{13}C$ NMR δ 16.6, 25.5 (2), 32.5 (2), 45.2 (2), 77.1, 208.6 ppm; MS m/z (relative intensity) 154 (5, $M^+$-$COCF_3$), 112 (9), 94 (40), 83 (56), 67 (57), 55 (100); Anal. Calcd. for $C_{11}H_{13}O_3F_3$: C, 52.80; H, 5.23. Found: C, 52.97; H, 5.41.

**Reaction of cyclopropyl ketone 13**.- According to the general procedure, cyclopropyl ketone **13** (36 mg, 0.17 mmol) afforded 4-hydroxy-3-phenyl-octahydro-indan-2-one **28** (41 mg, 74%), as a colourless oil: IR 2980, 1778, 1750, 1355 $cm^{-1}$; $^1H$ NMR δ 1.25-1.75 (m, 7H), 2.30 (m, 2H), 2.59 (m, 1H), 3.33 (d, 1H, J=11 Hz), 3.78 (br s, 1H), 7.05 (d, 2H, J=3 Hz), 7.18 (d, 1H, J=3 Hz), 7.25 (m, 2H) ppm; $^{13}C$ NMR δ 18.6, 27.7, 29.2, 30.8, 45.2, 50.5, 55.9, 67.0, 127.1, 128.4 (2), 128.7 (2), 137.9, 217.6 ppm; MS m/z (relative intensity) 230 (2, $M^+$-$COCF_3$), 184 (5), 170 (3), 156 (5), 134 (55), 115 (63), 104 (46), 91 (100), 77 (74), 65 (35), 55 (91); Anal. Calcd. for $C_{17}H_{17}O_3F_3$: C, 62.57; H, 5.25. Found: C, 62.69; H, 5.69.

**Reaction of cyclopropyl ketone 14**.- According to the general procedure, cyclopropyl ketone **14** (40 mg, 0.18 mmol) afforded 4-hydroxy-3-(3-thienyl)-octahydro-indan-2-one **29** (43 mg, 71%), as a colourless oil: IR 2980, 1780, 1740, 1350 $cm^{-1}$; $^1H$ NMR δ 1.2-2.0 (m, 7H), 2.44 (m, 2H), 2.70 (m, 1H), 3.44 (d, 1H, J=12 Hz), 5.25 (br s, 1H), 7.03 (m, 1H), 7.18 (m, 1H), 7.34 (m, 1H) ppm; $^{13}C$ NMR δ 18.7, 25.0, 27.3, 30.6, 44.8, 45.4, 49.7, 75.6, 122.1, 126.5, 126.9, 135.7, 214.0 ppm; MS m/z (relative intensity) 236 (13, $M^+$-$COCF_3$), 140 (41), 110 (49), 97 (100), 77 (24), 65 (26), 55 (70); Anal. Calcd. for $C_{15}H_{15}O_3SF_3$: C, 54.21; H, 4.55. Found: C, 54.21; H, 4.99.

**Reaction of trimethyl cyclopropyl ketone 15**.- According to the general procedure, cyclopropyl ketone **15** (47 mg, 0.26 mmol) afforded unsaturated ketone **22** (12 mg, 25%) and 3,3,7a,-timethyl-1,2,3,3a,4,7a-hexahydro-inden-5-one **30** (24 mg, 51%), as a colourless oil: IR 2830, 1722, 1660 $cm^{-1}$;

$^1$H NMR δ: 0.77 (s, 3H), 0.98 (s, 3H), 1.24 (s, 3H), 1.4-1.8 (m, 5H), 2.42 (d, 1H, J=11 Hz), 2.53 (dd, 1H, J=11 and 7 Hz), 5.84 (d, 1H, J=10 Hz), 6.60 (d, 1H, J=10 Hz) ppm; $^{13}$C NMR δ 23.9, 27.7, 29.8, 34.7, 38.1, 39.5, 42.7, 43.0, 53.7, 126.3, 158.6, 199.4 ppm; **MS m/z (relative intensity) 178 (26, M$^+$), 150 (14), 121 (36), 109 (38), 95 (53), 79 (89), 69 (100), 55 (61); Anal. Calcd. for $C_{12}H_{18}O$: C, 80.85; H,** 10.17. Found: C, 80.79; H, 10.23.

**Reaction of furyl trimethyl cyclopropyl ketone 16.**- According to the general procedure, cyclopropyl ketone **16** (40 mg, 0.16 mmol) afforded unsaturated ketone **25** (29 mg, 73%).

**General procedure. Reaction of cyclopropyl ketones with TMSTFA/NaSPh.**- Cyclopropyl ketones (1 mmol) and NaSPh (2 mmol) were heated in TMSTFA (2 mmol) to 60 °C for 24 h. Excess of TMSTFA was removed under reduced pressure and the residue was taken up in diethyl ether and water; the organic layer was dried and evaporated. Chromatography of the residue and elution with 9:1, hexane-diethyl ether yielded bicyclic ketones.

**Reaction of cyclopropyl ketone 6.**- According to the general procedure, cyclopropyl ketone **6** (50 mg, 0.36 mmol) afforded a 2:3 mixture of trifluoroacetates **26** and **27** (28 mg, 31%), and a 2.5:5 mixture of 4-phenylsulfanyl-octahydro-indan-2-one **31** and 9-phenylsulfanyl-bicyclo[3.3.1]nonan-3-one **32** (41 mg, 46%), as a colourless oil.

**31**: IR 3015, 1745 cm$^{-1}$; $^1$H NMR δ 1.3-2.7 (m, 12H), 3.48 (s, 1H), 7.37 (m, 5H) ppm; $^{13}$C NMR δ 20.2, 26.6 (2), 34.9, 40.6, 41.8, 43.8, 51.2, 127.7, 128.8 (2), 132.6 (2), 134.1, 210.8 ppm; MS m/z (relative intensity) 246 (28, M$^+$), 137 (15), 119 (14), 110 (88), 95 (68), 77 (44), 67 (100), 55 (95); Anal. Calcd. for $C_{15}H_{18}OS$: C, 73.12; H, 7.36. Found: C, 73.25; H, 7.44.

**32**: IR 2990, 1710 cm$^{-1}$; $^1$H NMR δ 1.3-2.7 (m, 12H), 3.70 (bs, 1H), 7.37 (m, 5H) ppm; $^{13}$C NMR δ 17.5, 26.2 (2), 34.2 (2), 47.9 (2), 51.2, 127.1, 129.1 (2), 131.7 (2), 135.2, 210.9 ppm; MS m/z (relative intensity) 246 (28, M$^+$), 137 (15), 119 (14), 110 (88), 95 (68), 77 (44), 67 (100), 55 (95); Anal. Calcd. for $C_{15}H_{18}OS$: C, 73.12; H, 7.36. Found: C, 73.21; H, 7.40.

**Reaction of cyclopropyl ketone 15.**- According to the general procedure, cyclopropyl ketone **15** (100 mg, 0.56 mmol) and NaSPh (222 mg, 1.68 mmol) were treated with TMSTFA (0.3 mL, 1.68 mmol) for 32 h. Work-up and chromatography (hexane-diethyl ether 98:2) of the residue afforded 4,4,7a-trimethyl-2,7-phenylsulfanyl-3a,4,5,6,7,7a-hexahydro-1H-indene **33** (168 mg, 79%), as a colourless oil, unsaturated ketone **22** (10 mg, 10%) and finally, ketone **30** (10 mg, 10%).

**33**: IR 3071, 2953, 1584, 1478, 1439 cm$^{-1}$; $^1$H NMR δ 0.94 (s, 3H), 1.13 (s, 3H), 1.14 (s, 3H), 1.5-2.2 (m, 5H), 2.46 (dd, 2H, J=9 and 2 Hz), 3.23 (t, 1H, J=8 Hz), 6.07 (m, 1H), 7.1-7.4 (m, 10H) ppm; $^{13}$C NMR δ: 23.9, 25.0, 29.9, 35.3, 38.0, 40.2, 42.7, 44.1, 55.6, 61.6, 126.4, 126.5, 126.8, 127.2, 127.9, 128.5, 128.7, 129.0, 130.3, 131.1, 131.7, 135.0, 136.5, 137.3 ppm; MS m/z (relative intensity) 380 (13, M$^+$), 341 (3), 271 (39), 253 (20), 135 (20), 123 (29), 109 (42), 91 (46), 73 (87); Anal. Calcd. for $C_{24}H_{28}S_2$: C, 75.73; H, 7.41. Found: C, 75.68; H, 7.49.

**Reaction of trimethyl cyclopropyl ketone 16.**- According to the general procedure, cyclopropyl ketone **16** (30 mg, 0.12 mmol) afforded ketone **25** (30 mg, 100%).

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## References and Notes

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