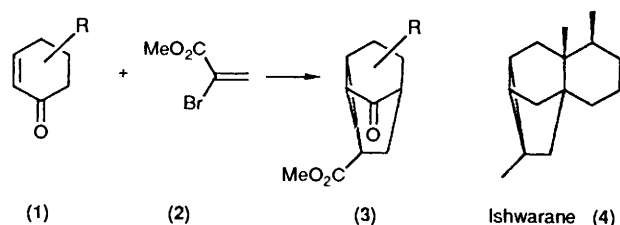# One-pot Annulation to Tricyclo[5.3.1.0^{3,8}]undecane-2,6-diones by Sequential Three-fold Michael Reactions. A Formal Synthesis of (±)-Seychellene

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Lewis acid-assisted triple Michael reactions yield tricyclo[5.3.1.0^{3,8}]undecane-2,6-dione derivatives from the trimethylsilyl enol ethers of cyclohex-2-enones and divinyl ketone. The application of this reaction allowed a formal synthesis of (±)-seychellene.
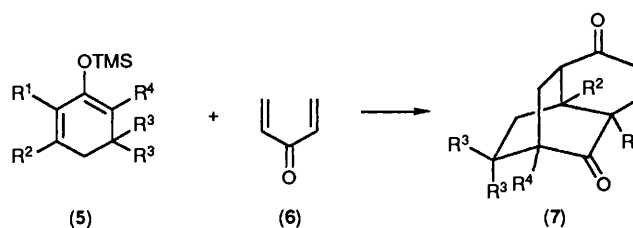
One-pot annulation by multiple C–C bond formation has potential for the construction of polycarbocyclic systems from simpler molecules,[1] and the Michael reaction is an example of this. Thus, the carbanion species generated by the first Michael process still has the possibility of undergoing a successive nucleophilic reaction such as a Michael reaction, an aldol condensation, nucleophilic substitution, a Dieckmann-type condensation, a Wittig condensation, and so on. Although interest in such strategies has been growing, attempts to drive successive carbanionic reactions in one direction often encounters difficulties since the Michael reaction is essentially reversible and a Michael acceptor is usually easy to polymerize. In order to suppress side reactions, various ways of terminating successive reactions have been devised. Successful results were obtained by designing a thermodynamically more stable target molecule under aprotic conditions, or by the participation of an irreversible reaction such as a nucleophilic substitution, elimination, *etc.*[2] to control the reaction at the desired stage. As a part of such efforts, we previously reported the one-pot bicycloannulation of the kinetic enolates of cyclohex-2-enones (1) with methyl α-bromoacrylate (2) to give tricyclo[3.2.1.0^{2,7}]octan-6-ones (3). These were constructed by aprotic base-induced successive Michael-Michael-alkylation reactions and in this way the total synthesis of the tetracyclic sesquiterpene hydrocarbon, (±)-ishwarane (4),[3] was achieved.

(5)   **(6)**   **(7)**

a; R^1 = R^2 = Me, R^3 = R^4 = H
b; R^1 = R^4 = H, R^2 = R^3 = Me
c; R^1 = R^2 = R^3 = R^4 = H
d; R^1 = Me, R^2 = R^3 = R^4 = H
e; R^1 = R^3 = R^4 = H, R^2 = Me
f; R^1 = R^4 = Me, R^2 = R^3 = H
g; R^1 = Me, R^2 = R^4 = H, R^3 = H, isopropenyl

Scheme 2.

Seychellene (8)   Patchouli alcohol (9)

(1)   **(2)**   **(3)**   Ishwarane **(4)**
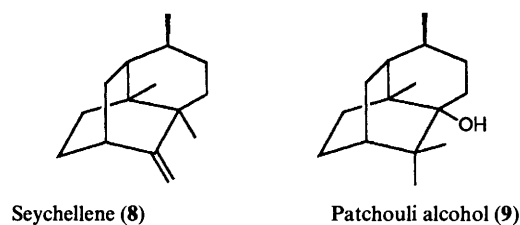
Scheme 1.

Our ongoing interest in the application of sequential Michael reactions to natural product synthesis[4] prompts us to report our results concerning the synthesis of tricyclo[5.3.1.0^{3,8}]undecane-2,6-diones (7) through three successive Michael reactions[5,6] between the trimethylsilyl enol ethers of cyclohex-2-enones (5) and divinyl ketone (6). The tricyclo[5.3.1.0^{3,8}]undecane skeleton is the fundamental carbon framework of several polycyclic natural products such as seychellene (8) or patchouli alcohol (9).

The idea of the three-fold Michael reaction was originally described by Spitzner,[7] who obtained a single Michael product (11a) in 18% yield from the reaction of divinyl ketone (6) with the kinetic enolate (10a) of 2,3-dimethylcyclohex-2-enone generated by lithium di-isopropylamide. Our initial attempts
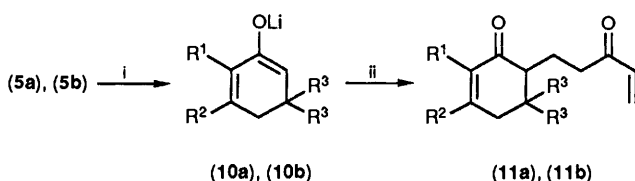
on the three-fold Michael reaction followed the work described by Spitzner and gave results similar to his. The reaction of the kinetic enolate (10a), generated by the cleavage of the trimethylsilyl enol ether (5a) with methyl-lithium,[8] with divinyl ketone (6) then resulted in the formation of a very small amount of the desired tricyclic compound (7a) (1–2%). Quenching the reaction at low temperature gave exclusively the single Michael product (11a) in 49% yield in the presence of HMPA. The kinetic enolate of isophorone (10b), generated in the same way, also gave the single Michael adduct (11b) in 41% yield. On the other hand, the kinetic enolates of other cyclic enones such as 2-phenylthiocyclohex-2-enone or 3-methylcyclopent-2-enone gave no Michael products. These results may be attributable to the instability of divinyl ketone (6) in the strongly basic aprotic media, to the retro-Michael reactions of the double and triple Michael adducts, or to the easy intra- and/or inter-molecular proton transfers between the ketone functionalities.

Toward this end, we turned our attention to the aprotic, Lewis acid-promoted Michael reactions in methylene dichloride which have been extensively developed by Mukaiyama and his co-workers.[9] Under such reaction conditions unnecessary proton transfers are suppressed and give a restricted reaction path. At first, reaction of the trimethylsilyl enol ether (5b) of isophorone with divinyl ketone (6) was investigated as a probe

Scheme 3. *Reagents and conditions:* i, MeLi, THF, $-80\,°C$; ii, (6).

Table 1. Lewis acid-promoted three-fold Michael reaction of the trimethylsilyl enol ether (5b) of isophorone and divinyl ketone[a]

Entry	Lewis acid[b] (ratio)	Amount of metal to the silyl enol ether (5b) (equiv.)	Yield (%)			
			(7b)	(13)	(11b)	(14)[h]
1	$AlCl_3$–$Al(OPr^i)_3$ (1:2)	3	1	27		
2	$TiCl_4$–$Ti(OPr^i)_4$ (1:1)[c]	4	6			27
3	(1:1)[d]	1	8	28		
4	(1:1)	4	8			19
5	(1:1)	2	19			29
6	(1:1)[e]	2		35	30	
7	(1:1)[f]	1		30	10	
8	(0.8:1)	3.6	30			16
9	$TiBr_4$–$Ti(OPr^i)_4$					
10	(1:1)	4	25			
11	Et_2AlCl	2	34			
	Et_2AlCl^g	2	34			

[a] For representative experimental conditions, see Experimental section. [b] A small amount of isophorone was recovered by $TiCl_4$, $TiCl_4$–$Ti(OPr^i)_4$ (1:3), Cp_2TiCl_2, $SnCl_4$, or BCl_3–$B(OPr^i)_3$. [c] A mixture of CH_2Cl_2 and 1,2-dichloroethane (1:1) was used. [d] THF was added at room temperature after overnight reaction ($THF:CH_2Cl_2 = 1:3$). [e] The reaction was quenched at $-75\,°C$ in 1 h. [f] The reaction mixture was stirred at room temperature for 68 h. [g] Divinyl ketone was added to the mixture of Lewis acid and the silyl enol ether (5b). [h] Yields are based on (5b) consumed.

to seek optimum reaction conditions. The trimethylsilyl enol ethers (5) of cyclohex-2-enones were prepared according to the procedure by House *et al.*[10] Divinyl ketone (6) was prepared by a known procedure.[11] Rapid vacuum distillation of 1,5-dichloropentan-3-one and quinoline from a pre-heated oil-bath was crucial to obtain a satisfactory yield of divinyl ketone (6). The results are listed in Table 1. Not all reactions were fruitful when $TiCl_4$, $TiCl_4$–$Ti(OPr^i)_4$ (1:3), Cp_2TiCl_2, $SnCl_4$, or BCl_3–$B(OPr^i)_3$ were employed as Lewis acid promoters, since isophorone was also partially recovered. In reactions 1,3,6, and 7, the double Michael adduct, the bicyclo[2.2.2]octanedione derivative (13) was also isolated, whilst in reactions 6 and 7 the single Michael adduct (11b) was a by-product. The desired tricyclic compound (7b) was obtained in 30% yield by employing $TiCl_4$–$Ti(OPr^i)_4$ (0.8:1) as the catalyst in methylene dichloride (entry 8). Since the third C–C bond-forming step seemed to be sluggish, as indicated by monitoring of the progress of the reaction by TLC and also by the quenching at $-75\,°C$ (entry 6), the reaction initiated at $-80\,°C$ was allowed to stand overnight with gradual warming to room temperature. The reactions catalysed by titanium(IV) were found to be sensitive to minor change of the reaction conditions as seen in entries 2–8. Attempts to change the solvent properties by the addition of a more polar or more co-ordinating solvent such as 1,2-dichloroethane (entry 2), or tetrahydrofuran (entry 3), failed to influence the reaction. In the $TiCl_4$-mediated

reactions, a bicyclic triketone (14) was isolated in *ca.* 20% yield (entries 2, 4, 5, and 8) along with a small amount of a bis-bicyclic triketone (15), which has a symmetrical structure as deducted from the simple ^1H and ^{13}C NMR spectra (see Experimental section). On the other hand, the use of Et_2AlCl as a catalyst gave the desired tricyclic adduct (7b) in an acceptable yield (34%) (entry 10); the average yield for each of the three C–C bond-forming steps was 70%. Among other Lewis acids, the oxyphilic character of aluminium might play an important role for the reaction (*vide infra*). The yield of (7b) was reproducible and independent upon the order of the addition of Et_2AlCl or the substrate (entry 11).

Based on the results cited above, the reactions of other trimethylsilyl enol ethers (5c–g) of cyclohex-2-enones were examined (Scheme 2) and the results are listed in Table 2. The process is a general one for other cyclohex-2-enones, giving moderate yields of the tricyclic compounds (7c–g) in the one-pot operation (entries 1–8). In these reactions, no bicyclo[2.2.2]octane or single Michael adduct were isolated. Although the tricyclic compound (7g) was a single isomer, the configuration of the isopropenyl group has not been determined. The reaction of 1,5-diphenylpenta-1,4-dien-3-one instead of divinyl ketone (6) with the silyl enol ethers (5a) and (5c) proceeded similarly giving rise to the single tricyclic compound (16) (entries 9, 10); the orientation of the phenyl groups remains unknown. Similarly, the trimethylsilyl enol ether of cyclohept-2-enone gave the tricyclic diketone (17) (entry 11). The trimethylsilyl enol ether of 2-benzyloxy- or 2-benzoyloxy-3-methylcyclohex-2-enone gave no Michael products.
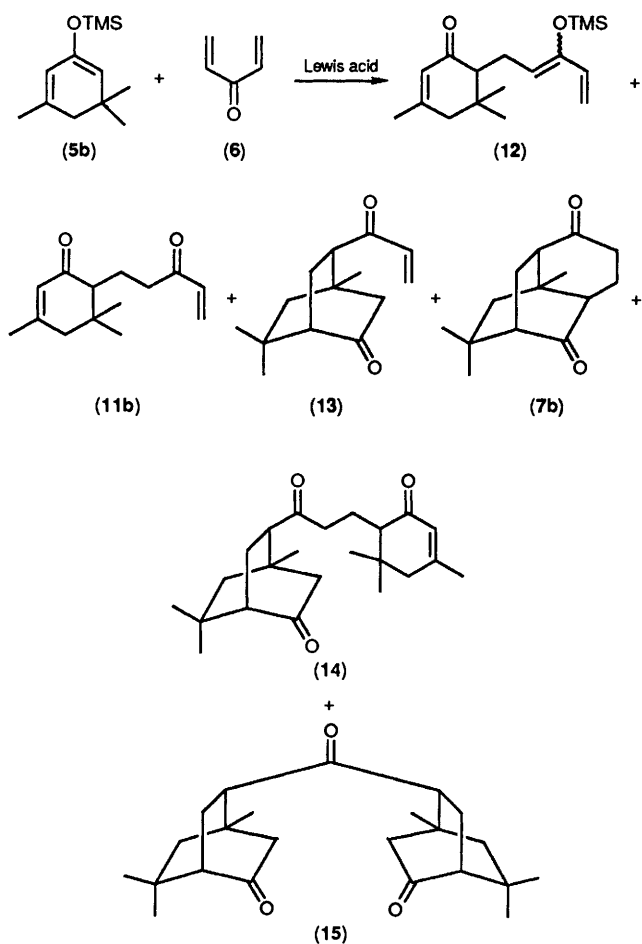

(16a), (16c)   (17)
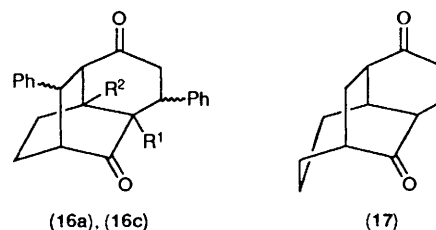
There are two possibilities for the reaction pathway leading to the tricyclic compounds (7) and (16): the first is a three-fold Michael reaction path [path a, $\longrightarrow$ (18) $\longrightarrow$ (19) $\longrightarrow$, Scheme 5] and the second a Diels–Alder–Michael reaction path (path b, $\longrightarrow$ (20) $\longrightarrow$, Scheme 5). When the reaction of (5b) and divinyl ketone (6) was quenched at $-75\,°C$ after 1 h using titanium(IV) (entry 6, Table 1), the single Michael product (11b) and the two-fold Michael product (13) were isolated in 30 and 35% yields, respectively. When Et_2AlCl was used as a Lewis acid and the reaction was quenched at $-80\,°C$, a small amount of the unstable trimethylsilyl enol ether of the single Michael adduct (12), the single Michael adduct (11b), the double Michael adduct (13), and the triple Michael adduct (7b) were isolated along with a small amount of unchanged isophorone. The bicyclo[2.2.2]octanedione (13) was a single isomer as indicated by its NMR spectrum, the orientation of the pendant propenoyl group being tentatively assigned to be *endo* to the 6-membered ring carbonyl as depicted in structure (13). It was thought that longer reactions time might bring about rearrangement of the propenoyl group to give the thermodynamically more stable *endo* configuration, chelation of two oxygen functionalities with a metal probably facilitating such a configuration. No reaction was observed when (13) was treated with $TiCl_4$–$Ti(OPr)_4$, (13) being recovered unchanged. The progress of the reaction was followed (TLC) by disappearance of the spots due to the single and the two-fold Michael products, (11b) and (13), and the appearance of the three-fold Michael

Table 2. Three-fold Michael reaction of the trimethylsilyl enol ethers of cyclohex-2-enones (5c–g) and divinyl ketones.

Entry	Substrate	Lewis acid used [a]	Yield (%) of (7)
1	(5c)	A	trace
2	(5d)	A	5
3		B	13
4	(5e)	A	3
5		B	13
6	(5f)	C	5
7	(5g)	A	4[b]
8		B	8
9	(5b)[c]	C	5 (16a)
10	(5c)[c]	C	10 (16c)
11	[d]	C	9 (17)

[a] A: A mixture of TiCl₄ (1.6 equiv.) and Ti(OPrⁱ)₄ (2 equiv.) was used. B: 2 Equiv. of Et₂AlCl was used. C: 3 Equiv. of Et₂AlCl was used. [b] A single isomer was obtained. [c] 1,5-Diphenylpenta-1,4-dien-3-one was used. [d] The trimethylsilyl enol ether of cyclohept-2-enone was used.

Table 3. Three-fold Michael reaction of the trimethylsilyl enol ether (5a) of 2,3-dimethylcyclohex-2-enone and divinyl ketone.

Entry	Lewis acid	Equiv.	Yield (%) of (7a)
1	TiCl₄–Ti(OPrⁱ)₄		
	(1:1)	4	9
2	(0.8:1)	3.6	20
3	Et₂AlCl	1	2
4		2	8[a]
5		2	17[b]
6		2	34
7		3	37[c]
8		3	43[d]

[a] The amount of divinyl ketone was 2 equiv. [b] The amount of divinyl ketone was 0.8 equiv. [c] The triethylsilyl enol ether was used. [d] The amount of divinyl ketone was 1.2 equiv.

with 1.2 equiv. of divinyl ketone (6) (entry 8). Since Et₂AlCl is a good proton scavenger,[13] excess of Et₂AlCl played some role in improving the yield by ensuring a clean reaction. Since the tricyclic diketone (7a) has previously been transformed into (±)-seychellene (8) by Jung and co-workers,[14] the present work constitutes a formal synthesis of naturally occurring tricyclic sesquiterpene (8).[15] The spectral data for (7a) (¹H and ¹³C NMR, IR, and mass) were identical with those of an authentic specimen.

Scheme 4.

product (7b). These results support a sequential three-fold Michael pathway (path a, Scheme 5) for the reaction.
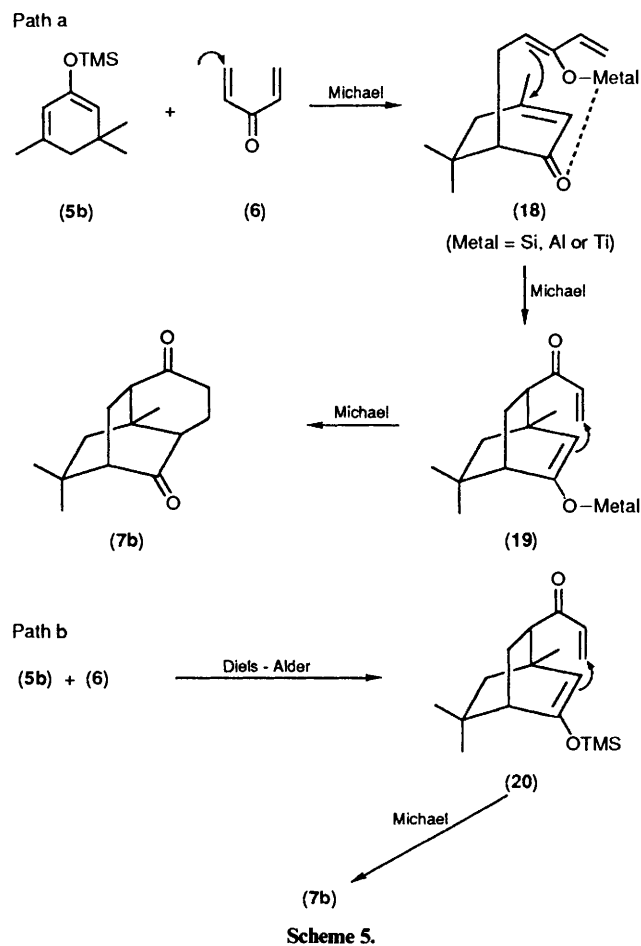
Since (−)-seychellene (8), isolated from patchouli oil (*Pogostemon*, Benth.),[12] is a plant sesquiterpene possessing a unique tricyclo[5.3.1.0³,⁸]undecane framework, its formal synthesis via a three-fold Michael reaction was attempted (Scheme 6). The results of the reaction of the trimethylsilyl enol ether (5a) of 2,3-dimethylcyclohex-2-enone with divinyl ketone (6) are listed in Table 3. The best yield (43%) of the tricyclic ketone (7a) was obtained when 3 equiv. of Et₂AlCl were used

Scheme 5.

Thus, we have demonstrated that a number of the trimethylsilyl enol ether (5) of cyclohex-2-enones react with divinyl ketone (6) to produce various tricyclo[5.3.1.0³,⁸]undecane-2,6-

dione derivatives (7) by a three-fold Michael pathway, enabling the formation of three new bonds and two new six-membered rings at a one-step; the reaction has been applied to the formal total synthesis of $(\pm)$-seychellene (8).

(5a)   (6)   (7a)   Seychellene (8)
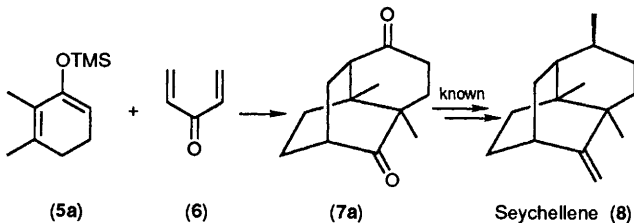
Scheme 6.

Experimental

IR spectra were recorded for solutions in carbon tetrachloride on a JASCO A-3 spectrophotometer. ^{1}H and ^{13}C NMR spectra were obtained for solutions in deuteriochloroform with a JEOL PMX-60 (60 MHz), FX-90Q (22.5 MHz) or PS-100 (100 MHz) instrument with tetramethylsilane as internal standard. Mass spectra were obtained on a JEOL JMS-DX 300 spectrometer with a JMA-3500 data system. Preparative medium-pressure liquid chromatography (MPLC) were carried out on a JASCO PRC-50 instrument. Microanalyses were carried out in the microanalytical laboratory of this Institute. Ether for extractions refers to the use of diethyl ether. Light petroleum has a b.p. range of 30–50 °C. Et$_2$AlCl was used as 1M solution in hexane. Other Lewis acids were used as 1M solution in CH$_2$Cl$_2$.

General Procedure for a Lewis Acid-assisted Three-fold Michael Reaction.—To a stirred solution of Lewis acid in anhydrous methylene dichloride was added successively a solution of divinyl ketone (6) (1.1–1.2 equiv.) and the trimethylsilyl enol ether in anhydrous methylene dichloride at −85 °C under nitrogen. After being stirred for 2 h at −80 °C, the resulting solution was allowed to warm to room temperature in 3–4 h and stand at that temperature overnight (12–18 h). The reaction was quenched by addition of aqueous potassium carbonate and the resulting suspension was filtered through a bed of Celite. The water layer was extracted with ether (2 × 30 ml), and the combined organic layers were washed with water and brine. After evaporation of the solvent, the residue was passed through a short column of silica gel with the aid of hexane–ethyl acetate (2:1), and then, the products were separated by MPLC.

3,8-Dimethyltricyclo[5.3.1.0^{3,8}]undecane-2,6-dione (7a). M.p. 148–149 °C (from light petroleum) (lit.,^{14} 120 °C); ν_{max} 1 720 cm^{-1}; δ_H 0.87 (3 H, s), 1.09 (3 H, s), and 1.2–2.5 (12 H, m); δ_C(22.5 MHz) 19.0, 20.0, 22.9, 25.9, 28.8, 31.6, 34.7, 40.1, 40.8, 49.2, 54.1, and 212.7; m/z 206 (M^+, 100), 178 (25), 163 (33), 138 (59), 123 (35), 111 (43), 110 (42), 107 (39), 97 (41), 96 (53), 95 (50), 93 (42), 79 (54), and 55 (62) (Found: C, 75.9; H, 8.8. C$_{13}$H$_{18}$O$_2$ requires C, 75.7; H, 8.8%).

8,10,10-Trimethyltricyclo[5.3.1.0^{3,8}]undecane-2,6-dione (7b). M.p. 94–95 °C (from light petroleum); ν_{max} 1 725 and 1 710 cm^{-1}; δ 0.94 (3 H, s), 1.01 (3 H, s), 1.11 (3 H, s), 1.2–2.6 (11 H, m); m/z 220 (M^+, 59), 109 (35), 96 (100), and 55 (31) (Found: C, 76.6; H, 9.3. C$_{14}$H$_{20}$O$_2$ requires C, 76.3; H, 9.2).

Tricyclo[5.3.1.0^{3,8}]undecane-2,6-dione (7c). ν_{max} 1 725 and 1 710 cm^{-1}; m/z 178 (M^+, 100), 150 (49), 122 (42), 96 (44), 79 (57), and 55 (51) (Found: M, m/z 178.098 94. C$_{11}$H$_{14}$O$_2$ requires M, 178.099 34).

3-Methyltricyclo[5.3.1.0^{3,8}]undecane-2,6-dione (7d). ν_{max} 1 720, 1 710, and 1 455 cm^{-1}; δ 1.18 (3 H, s) and 1.3–3.0 (13 H, m); m/z 191 (M^+ − 1, 100), 163 (70), 135 (40), 122 (65), 110 (75),

107 (66), 96 (62), 95 (54), 93 (56), 81 (69), 80 (73), 79 (75), and 55 (60) (Found: M, m/z 192.115 48. C$_{12}$H$_{16}$O$_2$ requires M, 192.115 01).

8-Methyltricyclo[5.3.1.0^{3,8}]undecane-2,6-dione (7e). M.p. 120–121 °C (from hexane); ν_{max} 1 725 and 1 710 cm^{-1}; δ 0.94 (3 H, s) and 1.4–2.7 (13 H, m); m/z 191 (M^+ − 1, 84), 163 (51), 135 (77), 123 (100), 121 (57), 109 (62), 107 (63), 100 (57), 96 (61), 95 (97), 94 (78), 93 (72), 92 (54), 82 (51), and 55 (63) (Found: M, 192.114 31. C$_{12}$H$_{16}$O$_2$ requires M, 192.115 01).

1,3-Dimethyltricyclo[5.3.1.0^{3,8}]undecane-2,6-dione (7f). ν_{max} 1 720, 1 460, and 1 380 cm^{-1}; δ 1.00 (3 H, s), 1.17 (3 H, s), and 1.2–3.0 (12 H, m).

10-Isopropenyl-3-methyltricyclo[5.3.1.0^{3,8}]undecane-2,6-dione (7g). ν_{max} 1 720, 1 650, and 1 455 cm^{-1}; δ 1.08 (3 H, s), 1.78 (3 H, s), 0.7–2.9 (12 H, m), and 4.78 (2 H, br s); m/z 232 (M^+, 12), 231 (64), 109 (100), 108 (37), and 55 (31) (Found: 232.146 66. C$_{15}$H$_{20}$O$_2$ requires 232.146 36).

6-(3-Oxopent-4-enyl)-3,5,5-trimethylcyclohex-2-enone (11b). ν_{max} 1 700, 1 670, 1 620, and 1 380 cm^{-1}; δ 0.98 (3 H, s), 1.07 (3 H, s), 1.5–2.5 (6 H, m), 2.20 (2 H, s), 2.5–2.9 (2 H, m), 5.7–5.9 (2 H, m), and 6.0–6.6 (2 H, m); m/z 220 (M^+, 7), 205 (28), 135 (75), 123 (98), 83 (39), 82 (100), and 55 (81) (Found: M, m/z 220.146 21. C$_{14}$H$_{20}$O$_2$ requires M, 220.146 21).

6-(3-Trimethylsiloxypenta-2,4-dienyl)-3,5,5-trimethylcyclohex-2-enone (12). δ 0.20 (9 H, s), 0.96 (3 H, s), 1.05 (3 H, s), 1.90 (3 H, s), 2.0–2.53 (5 H, m), 4.70–5.13 (3 H, m), 5.20 (1 H, br d, J 17), 5.82 (1 H, br s), and 6.17 (1 H, dd, J 17, 10 Hz).

4,6,6-Trimethyl-2-oxobicyclo[2.2.2]octan-8-yl vinyl ketone (13). M.p. 57–58 °C (from light petroleum); ν_{max} 3 100, 1 720, 1 695, 1 670, 1 640, 1 615, and 915 cm^{-1}; δ(100 MHz) 0.94 (3 H, s), 1.13 (3 H, s), 1.25–3.05 (8 H, m), 5.78 (1 H, dd, J 9.5, 2.0 Hz), 6.19 (1 H, dd, J 16.6, 2.0 Hz), and 6.44 (1 H, dd, J 16.6, 9.5 Hz); m/z 220 (M^+, 12), 138 (22), 137 (29), 123 (59), 55 (100), and 41 (60) (Found: C, 75.9; H, 9.15. C$_{14}$H$_{20}$O$_2$ requires C, 76.3; H, 9.15%).

{4,6,6-Trimethyl-2-oxobicyclo[2.2.2]octan-8-yl} [3,5,5-trimethyl-1-oxocyclohex-2-en-6-yl] *ketone* (14). M.p. 102–103 °C (from hexane); ν_{max} 1 730, 1 715, 1 670, 1 460, 1 380, 1 375, and 1 090 cm^{-1}; δ 0.92 (3 H, s), 0.93 (3 H, s), 0.95 (3 H, s), 1.03 (3 H, s), 1.2–3.13 (13 H, m), 1.90 (3 H, br s), 2.17 (2 H, br s), and 5.73 (1 H, br s); m/z 359 (M^+ + 1, 29); 358 (M^+, 22), 221 (64), 193 (59), 165 (54), 138 (55), 123 (100), 121 (30), 69 (34), and 55 (43) (Found: 358.251 15. C$_{23}$H$_{34}$O$_3$ requires 358.250 75).

Bis{4,6,6-trimethyl-2-oxobicyclo[2.2.2]octan-8-yl} *Ketone* (15). M.p. 181–182 °C (crystallized spontaneously); ν_{max} 1 720, 1 465, 1 380, 1 080, and 860 cm^{-1}; δ_H 0.93 (3 H × 2, s), 1.02 (3 H × 2, s), 1.12 (3 H × 2, s), and 1.22–3.13 (8 H × 2, m); δ_C 24.1, 24.4, 28.7, 31.2, 31.7, 37.1, 44.2, 50.8, 51.2, 54.0, and 214.5; m/z 359 (M^+ + 1, 32), 358 (M^+, 32), 221 (59), 165 (87), 138 (68), 123 (90), 121 (100), 95 (47), 81 (41), 69 (49), 55 (48), and 41 (46) (Found: 358.250 52. C$_{23}$H$_{34}$O$_3$ requires 358.250 75).

3,8-Dimethyl-4,11-diphenyltricyclo[5.3.1.0^{3,8}]undecane-2,6-dione (16a). M.p. 204–205 ° (from ether); ν_{max} 1 720 sh, 1 715, 1 660, 1 605, 1 500, and 1 458 cm^{-1}; δ 0.83 (3 H, s), 1.23 (3 H, s), 1.4–2.1 (5 H, m), 2.5–2.8 (1 H, m), 2.93 (2 H, t, J 3.5 Hz), 3.2–3.4 (1 H, m), 3.87 (1 H, dd, J 7, 3 Hz), 7.33 (10 H, s); m/z 358 (M^+, 100), 226 (98), 196 (57), 105 (32), 104 (59), and 91 (43).

4,11-Diphenyltricyclo[5.3.1.0^{3,8}]undecane-2,6-dione (16c). ν_{max} 1 720, 1 715 sh, 1 605, 1 495, and 1 455 cm^{-1}; δ 1.75 (4 H, br s), 2.2–2.7 (3 H, m), 2.7–3.0 (2 H, m), 3.18 (2 H, br s), 3.9–4.3 (1 H, m), 7.27 (5 H, s), and 7.29 (5 H, s); m/z 330 (M^+, 4), 226 (27), 135 (100), 131 (29), and 124 (32) (Found: 330.161 88. C$_{23}$H$_{22}$O$_2$ requires 330.161 88).

Tricyclo[5.4.1.0^{3,8}]dodecane-2,6-dione (17). M.p. 60–61 °C; ν_{max} 1 710, 1 455, and 1 235 cm^{-1}; δ 1.3–2.1 (9 H, m) and 2.2–3.1 (7 H, m); m/z 192 (M^+, 10), 191 (88), 163 (34), 125 (100), 95 (39), 79 (63), and 55 (69) (Found: 192.115 19. C$_{12}$H$_{16}$O$_2$ requires 192.115 01).

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