Intramolecular Diels–Alder reaction of cyclopenta-1,3-diene derivatives generated *in situ* from 4-(pent-4-enyl)cyclopent-2-enone ethylene ketals

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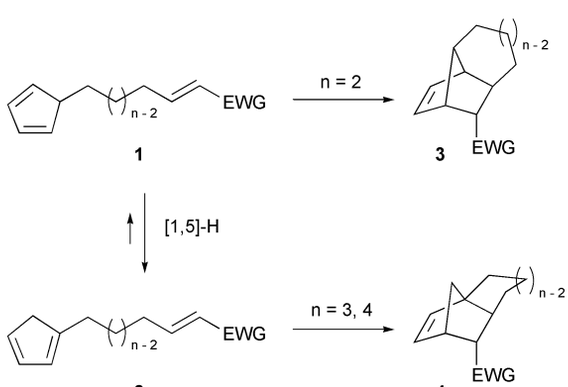
Intramolecular Diels–Alder reaction of cyclopenta-1,3-diene derivatives **16** generated *in situ* from the corresponding 4-(pent-4-enyl)cyclopent-2-enone ethylene ketals **15** is investigated. 4-[(*E*)-5-(Ethoxycarbonyl)pent-4-enyl]cyclopent-2-enone ethylene ketal **15a** and 4-(5,5-dicyanopent-4-enyl)cyclopent-2-enone ethylene ketal **15b** were prepared in 5 steps from cyclopent-2-enone ethylene ketal **5**. Upon heating at 120 °C, compound **15a** undergoes intramolecular Diels–Alder reaction *via* the 4-substituted cyclopenta-1,3-dien-2-yl enol ether **17a** to produce tricyclo[5.2.1.$0^{1,5}$]decan-8-one derivative **19a** as the sole product. On the other hand, **15b** undergoes intramolecular Diels–Alder reaction at the same temperature *via* the 5-substituted cyclopenta-1,3-dien-2-yl enol ether **16b** to give tricyclo[4.4.0.$0^{2,8}$]decan-10-one derivative **18b** as the major product. The molecular structures of these cyclization products are unequivocally elucidated by X-ray crystallographic analyses. The latter reaction represents, to our knowledge, the first direct trapping of 5-substituted cyclopenta-1,3-diene derivative having a simple three-carbon tether by Diels–Alder cyclization prior to isomerization by 1,5-hydrogen migration.

Introduction

The intramolecular Diels–Alder reaction is an attractive synthetic method which is capable of constructing polycyclic ring systems in a single operation.[1] This reaction has indeed played an important role in the recent advances of synthetic organic chemistry and has been successfully exploited in the syntheses of a variety of interesting polycyclic species including many natural products.[2] However, when cyclopenta-1,3-diene derivatives are used as a diene component, the reaction course is complicated by the readily occurring 1,5-sigmatropic rearrangement in this system.[3,4] It has been well documented that the intramolecular Diels–Alder cycloaddition of alkenylcyclopenta-1,3-dienes gives two types of tricyclic cycloadducts, **3** or **4**, depending on the carbon-chain length (Scheme 1).[5] A chain

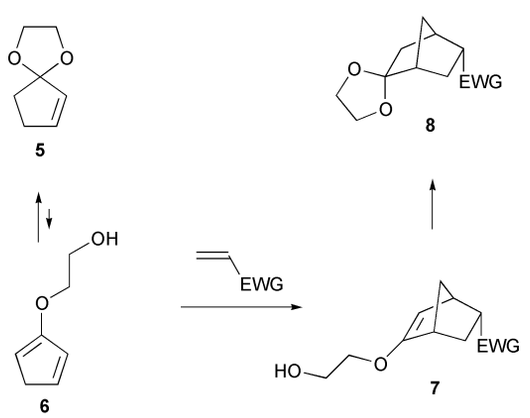


EWG = electron withdrawing group

Scheme 1

length of 2 gives exclusively **3** *via* the 5-alkenyl isomer **1** whereas a chain length of 3 or 4 leads specifically to **4** *via* the 1-alkenyl isomer **2**.

Incidentally, we have previously demonstrated that 2-(2-hydroxyethoxy)cyclopenta-1,3-diene **6** is generated reversibly from cyclopent-2-enone ethylene ketal **5** under mild heating conditions (50–100 °C) and can be intercepted with a variety of dienophiles ultimately to give trinorbornan-2-one ethylene ketals **8** through recyclization of the initial adducts **7** (Scheme 2).[6]



EWG = electron withdrawing group

Scheme 2

This reaction is highly regioselective and not complicated by the formation of isomeric adducts resulting either from 1,4-elimination in **5** or from 1,5-hydrogen migration in the cyclopenta-1,3-diene system of **6**, as demonstrated by the regioselective reactions of methyl-substituted derivatives of **5**. Thus, the reaction of the 2- and 5-methyl-substituted derivatives **9** and **10** with dienophiles led to the exclusive production of the corresponding trinorbornan-2-one ethylene ketals **13** and **14**, respectively, through the additions of the dienophile to the cyclopenta-1,3-dien-2-yl enol ether intermediates **11** and **12** (Scheme 3).[6] Scrambling of the cycloadducts **13** and **14** through possible interconversion of the intermediates **11** and **12** by 1,5-hydrogen migration was not observed.

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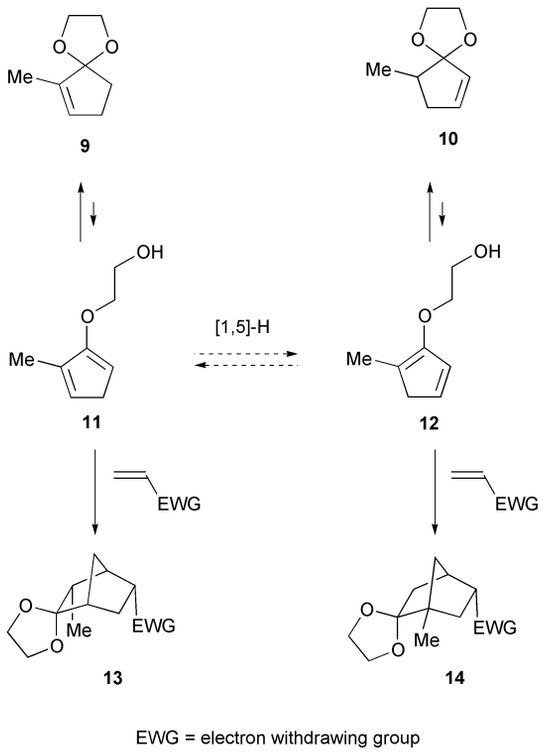
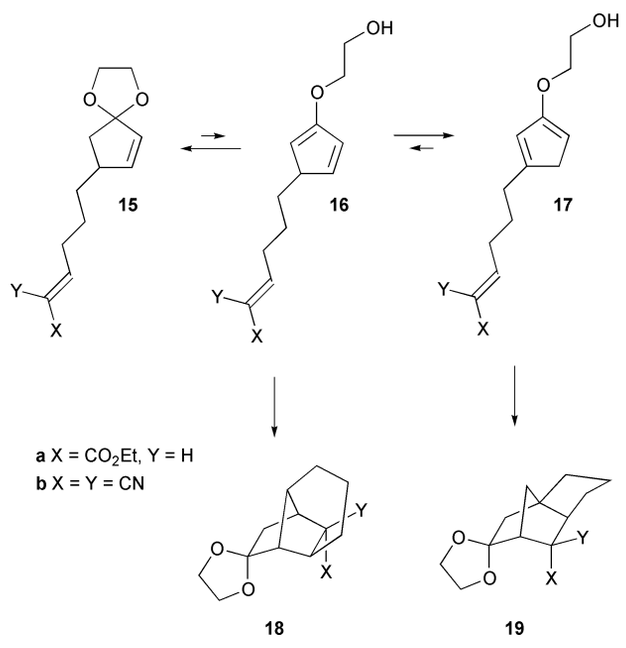


Scheme 3

To explore the scope of our *in situ*-generated dienol ether methodology, we were interested in extending this process to the intramolecular version, especially the reaction of cyclopent-2-enone ethylene ketals **15** having a simple three-carbon tether at the 4-position. Particularly interesting is the possibility that 5-substituted cyclopenta-1,3-diene derivatives **16**, kinetically generated from **15** *via* 1,2-elimination, may be directly incorporated in Diels–Alder cyclization prior to isomerization by 1,5-hydrogen migration (Scheme 4). In fact, we found that this



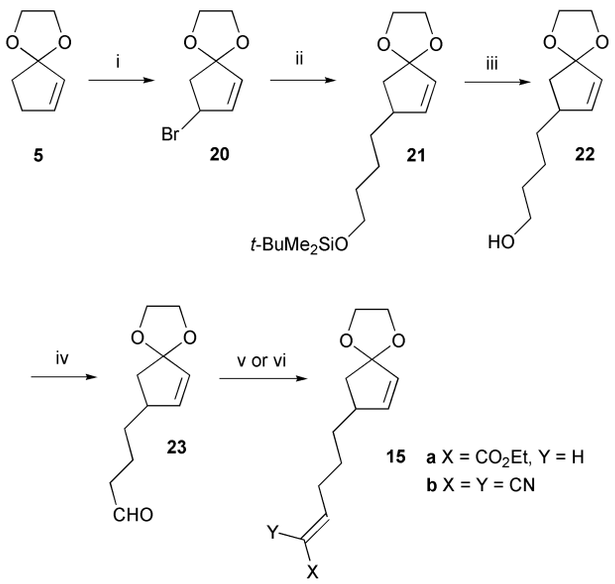
Scheme 4

was realized with dicyano compound **15b**, although less activated monoester **15a** gave the cycloadduct **19a** after isomerization by 1,5-hydrogen migration. In this paper, we report the details of the syntheses and thermal reactions of **15a** and **15b**, together with the X-ray molecular structure analyses of their reaction products.

Results and discussion

Preparation of 15a and 15b

The syntheses of the cycloaddition substrates **15a** and **15b** are illustrated in Scheme 5. Allylic bromination of commercially

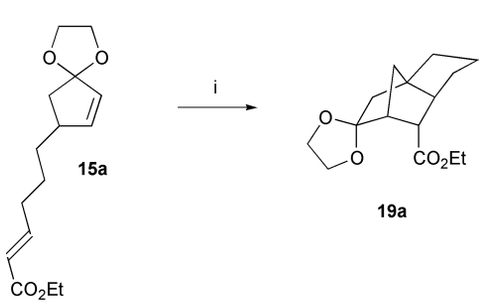


Scheme 5 *Reagents and conditions (and yields)*: i, *hv*, NBS, AIBN, 2,6-lutidine, CCl_4 (74%); ii, $TBDMSO(CH_2)_4I$, *t*-BuLi, Et_2O–hexane, −78 °C (24%); iii, Bu_4NF, THF, 0 °C, (98%); iv, PCC, NH_4OAc, MS4A, CH_2Cl_2, room temp. (63%); v, $(EtO)_2P(O)CH_2CO_2Et$, NaH, THF, 0 °C (92%); vi, $CH_2(CN)_2$, piperidinium acetate (56%).

available **5**[7] with *N*-bromosuccinimide (NBS) gave bromide **20**,[8] which was alkylated with 4-(*tert*-butyldimethylsilyloxy)butyllithium, prepared from the corresponding iodide and *tert*-butyllithium, to afford silyl ether **21**. Desilylation of **21** using tetrabutylammonium fluoride (TBAF) followed by pyridinium chlorochromate (PCC) oxidation of the resultant alcohol **22** provided aldehyde **23**. Horner–Emmons reaction of **23** with ethyl diethoxyphosphorylacetate produced (*E*)-unsaturated ester **15a**, while Knoevenagel condensation of **23** with malononitrile gave the dicyanomethylene **15b**.

Thermal reactions of 15a and 15b

The thermal reaction of **15a** was examined by heating an acetonitrile solution of **15a** (1.9×10^{-3} M) in a sealed tube. Upon heating the sample at 120 °C (37% conversion after 10 days) or at 150 °C (47% conversion after 5 days), slow consumption of **15a** together with the quantitative formation of a single product was observed (Scheme 6). At 80 °C, no consumption of



Scheme 6 *Reagents and conditions (and yield)*: i, MeCN, 120 °C, 10 days (37% conversion) or 150 °C, 5 days, (47% conversion) (94%).

the starting material **15a** was observed even after a prolonged reaction period. The product was isolated by preparative GLC in 94% yield (*vs* conversion of **15a**) and unequivocally identified as **19a** by X-ray crystallographic analysis (Fig. 1). The exclusive

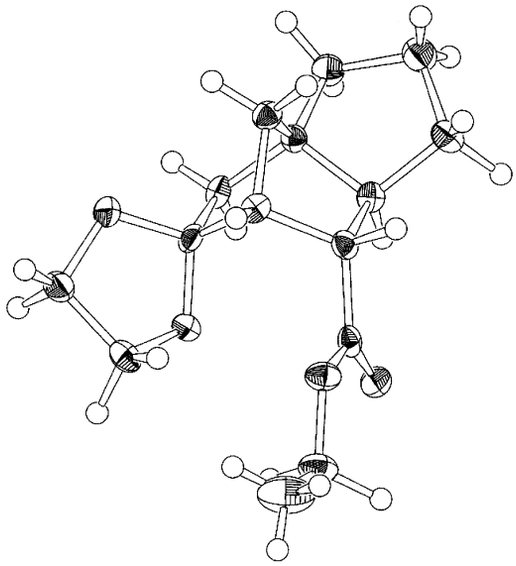
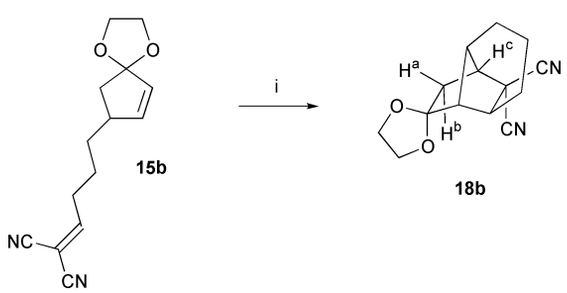


Fig. 1 X-Ray molecular structure of **19a**.

formation of **19a** can be rationalized in terms of an intramolecular Diels–Alder cycloaddition of **17a** after the isomerization of **16a** by 1,5-hydrogen migration.

The cyclopenta-1,3-diene intermediate **16a**, initially generated from **15a** *via* 1,2-elimination, would undergo three competitive intramolecular processes; recyclization to the ketal form **15a**, isomerization to **17a** by 1,5-hydrogen migration, and intramolecular Diels–Alder cyclization to **18a** (Scheme 4). In this respect, it is interesting to note the fact that only oligomeric products resulting from the intermolecular reactions were produced when the thermal reaction of **15a** was conducted under more concentrated conditions (1.9×10^{-2} M) at 120 °C. This indicates effective generation but inefficient trapping of the cyclopenta-1,3-diene intermediate **16a** by intramolecular Diels–Alder cyclization to afford **18a**. Accordingly, we next turned our attention to the reaction of **15b** having a doubly activated dienophile moiety.

Heating of an acetonitrile solution of **15b** (1.1×10^{-3} M) in a sealed tube at 120 °C for 4 days led to the complete consumption of **15b** accompanied by the predominant formation of a single major product (64% yield) which showed many different features compared with **19a** in the ^{1}H and ^{13}C NMR spectra (Scheme 7). For example, in the ^{1}H NMR spectrum, the *exo*-



Scheme 7 *Reagents and conditions (and yield)*: i, MeCN, 120 °C, 4 days (64%).

methylene proton H^a adjacent to the ketal moiety exhibits characteristic vicinal coupling (J 4.4 Hz) with the bridgehead proton H^c while no long-range coupling is observed between the *endo*-methylene proton H^b and the *anti* methylene-bridge proton.[9] Moreover, the ^{13}C NMR spectrum of the product displayed only two quaternary carbon signals, at δ_C 39.59 and 115.95. These features are consistent with structure **18b** and excluded the another possible structure **19b**. Finally, the structure of product **18b** was unambiguously determined by X-ray crystallographic study as shown in Fig. 2. The formation of **18b** can be

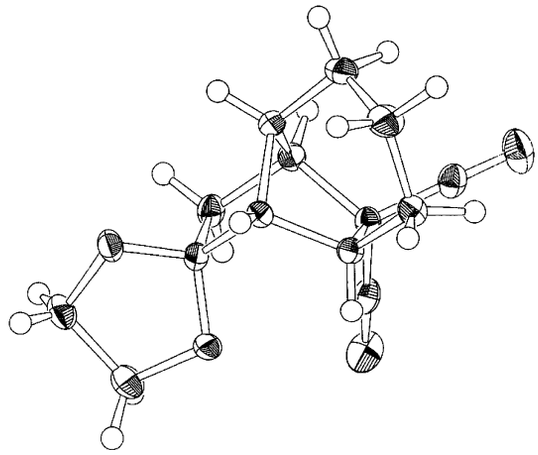


Fig. 2 X-Ray molecular structure of **18b**.

reasonably rationalized in terms of the intramolecular Diels–Alder cycloaddition of **16b** generated *in situ* from **15b** *via* 1,2-elimination (Scheme 4). It is noteworthy that the formation of **18b** represents, to our knowledge, the first direct trapping of a 5-substituted cyclopenta-1,3-diene derivative having a simple three-carbon tether in Diels–Alder cycloaddition prior to isomerization by 1,5-hydrogen migration.[3,5]

Conclusions

The intramolecular Diels–Alder reaction of cyclopenta-1,3-diene derivatives **16** generated *in situ* from the corresponding 4-(pent-4-enyl)cyclopent-2-enone ethylene ketals **15** was found to produce two types of tricyclic cycloadduct, depending on the activity of the dienophile moiety. Thus, simple α,β-unsaturated ester **15a** underwent intramolecular Diels–Alder reaction *via* the 4-substituted cyclopenta-1,3-dien-2-yl enol ether **17a**, after 1,5-hydrogen migration, to produce tricyclo[5.2.1.0^{1,5}]decan-8-one derivative **19a** whereas the more activated dicyanomethylene derivative **15b** underwent intramolecular Diels–Alder reaction directly *via* the 5-substituted cyclopenta-1,3-dien-2-yl enol ether **16b** to give tricyclo[4.4.0.0^{2,8}]decan-10-one derivative **18b**. The present results demonstrate that the intramolecular Diels–Alder reaction based on our *in situ*-generated dienol ether strategy provides a unique and direct route to functionalized tricyclic ring systems in a regio- and stereoselective manner, even overcoming the 1,5-hydrogen migration problem in substituted cyclopenta-1,3-diene derivatives.

Experimental

General methods

Melting points are uncorrected. Elemental analyses were performed by the Center for Instrumental Analysis of Hokkaido University. IR spectra were taken on a Hitachi 270–30 spectrometer. ^{1}H NMR spectra were recorded for samples in $CDCl_3$ on Hitachi R-1900 and JEOL EX-400 spectrometers at 90 and 400 MHz, respectively; chemical shifts are given in δ/ppm using tetramethylsilane as the reference. ^{13}C NMR spectra were recorded on a JEOL EX-400 spectrometer for samples in $CDCl_3$ at 100 MHz; chemical shifts are given in δ_C/ppm using solvent peak as the reference. Mass spectra were recorded at an ionizing voltage of 70 eV. GLC was done on an Hitachi 163 gas chromatograph. Preparative chromatography was performed on Merck Kieselgel 60 (70–230 mesh). Reagents and solvents were obtained from commercial sources and purified prior to use.

4-Bromocyclopent-2-enone ethylene ketal 20

Compound **20** was prepared according to the reported method.[8] Although **20** has not been isolated in the literature

because of its instability, it could be isolated by chromatography on silica gel as a colorless oil (74% yield) and characterized spectroscopically; ν_{max} (neat)/cm^{-1} 2956, 2884, 1362, 1266, 1150, 1090, 1046, 1016, 996 and 948; δ_H (90 MHz) 2.48 (1 H, dd, *J* 15.3 and 3.3 Hz), 2.78 (1 H, dd, *J* 15.3 and 6.8 Hz), 3.97 (4 H, br s), (1 H, dddd, *J* 6.8, 3.3, 2.4 and 0.9 Hz), 5.86 (1 H, dd, *J* 5.5 and 0.9 Hz) and 6.19 (1 H, dd, *J* 5.5 and 2.4 Hz); δ_C 46.27, 47.98, 64.86, 65.29, 111.70, 133.54 138.17; *m*/*z* (EI) 206 (M$^+$ + 2, 1%), 204 (M$^+$, 1), 125 (100), 81 (57), 53 (62).

4-[4-(*tert*-Butyldimethylsilyloxy)butyl]cyclopent-2-enone ethylene ketal 21

To a solution of 4-(*tert*-butyldimethylsilyloxy)butyl iodide[10] (3.0 g, 9.5 mmol) in dry diethyl ether (8 mL) was added a solution of *t*-BuLi in hexane (2.17 M; 8.75 mL, 19.0 mmol) under argon at −78 °C over a period of 30 min. After the mixture had been stirred for an additional 30 min at the same temperature, a solution of **20** (2.05 g, 10.0 mmol) in dry diethyl ether (6 mL) was added to it over a period of 20 min. The mixture was stirred for an additional 2 h at −78 °C, allowed to warm to room temperature, poured into water (20 mL), and extracted with diethyl ether (3 × 20 mL). The extracts were combined, washed successively with 5% aq. $NaHCO_3$ (30 mL) and brine (30 mL), dried with Na_2SO_4, and concentrated. The residue was purified by chromatography on silica gel (hexane 97%, diethyl ether 3%) to give **21** as a colorless oil (0.75 g, 24%) (Found: M$^+$, 312.2101. $C_{17}H_{32}O_3Si$ requires *M*, 312.2121); ν_{max} (neat)/cm^{-1} 2932, 2860, 1474, 1464, 1370, 1256, 1158, 1102, 836 and 776; δ_H (400 MHz) 0.04 (6 H, s), 0.89 (9 H, s), 1.36 (2 H, m), 1.51 (2 H, m), 1.30–1.55 (2 H, m), 1.67 (1 H, dd, *J* 13.9 and 4.6 Hz), 2.26 (1 H, dd, *J* 13.9 and 7.6 Hz), 2.66–2.74 (1 H, m), 3.60 (2 H, t, *J* 6.4 Hz), 3.92–3.97 (4 H, m), 5.68 (1 H, dd, *J* 5.6 and 2.2 Hz) and 6.03 (1 H, dd, *J* 5.6 and 2.2 Hz); δ_C −5.25, 18.36, 24.07, 25.99, 32.88, 35.63, 41.41, 42.63, 63.10, 64.58, 64.81, 119.71, 129.63 and 141.64; *m*/*z* (EI) 312 (M$^+$, 4%), 211 (83), 125 (33), 119 (24), 91 (20), 75 (100) and 73 (32).

4-(4-Hydroxybutyl)cyclopent-2-enone ethylene ketal 22

To a solution of **21** (493 mg, 1.58 mmol) in dry THF (55 mL) was added a solution of Bu_4NF in THF (1.0 M; 2.0 mL, 2.0 mmol) under argon at 0 °C over a period of 5 min. After stirring at room temperature for 3 h, the mixture was evaporated, diluted with water (100 mL), and extracted with dichloromethane (3 × 100 mL). The organic extracts were combined, washed with brine (2 × 100 mL), dried with Na_2SO_4, and concentrated. The residue was purified by chromatography on silica gel (hexane 50%, diethyl ether 50%) to give **22** as a colorless oil (307 mg, 98%) (Found: M$^+$, 198.1270. $C_{11}H_{18}O_3$ requires *M*, 198.1256); ν_{max} (neat)/cm^{-1} 3400, 3064, 2936, 1620, 1372, 1268, 1158, 1076, 1030 and 950; δ_H (400 MHz) 1.39 (2 H, m), 1.30–1.53 (2 H, m), 1.57 (2 H, m), 1.68 (1 H, dd, *J* 13.9 and 4.6 Hz), 2.27 (1 H, dd, *J* 13.9 and 7.8 Hz), 2.68–2.76 (1 H, m), 3.64 (2 H, t, *J* 6.4 Hz), 3.93–3.97 (4 H, m), 5.69 (1 H, dd, *J* 5.6 and 2.2 Hz) and 6.04 (1 H, dd, *J* 5.6 and 2.2 Hz); δ_C 23.96, 32.83, 35.57, 41.37, 42.58, 62.88, 64.59, 64.83, 119.70, 129.77 and 141.50; *m*/*z* (EI) 198 (M$^+$, 13%), 139 (20), 125 (100), 99 (21), 86 (26) and 81 (23).

4-(3-Formylpropyl)cyclopent-2-enone ethylene ketal 23

To a mixture of PCC (339 mg, 1.57 mmol), ammonium acetate (215 mg, 2.62 mmol) and molecular sieves 4Å (610 mg) in dichloromethane (33 mL) was added a solution of **22** (208 mg, 1.05 mmol) in dichloromethane (14 mL) under argon at 0 °C over a period of 10 min. After the mixture had been stirred at room temperature for 3 h, diethyl ether (200 mL) was added and the mixture was filtered through a short pad of Florisil. The filtrate was washed successively with water (100 mL) and brine (100 mL), dried with Na_2SO_4, and concentrated. The residue was purified by chromatography on silica gel (hexane 70%, diethyl ether 30%) followed by distillation to give **23** as a colorless oil (132 mg, 63%), bp 60–65 °C (0.003 Torr) (Found: M$^+$, 196.1080. $C_{11}H_{16}O_3$ requires *M*, 196.1100); ν_{max} (neat)/cm^{-1} 2936, 2884, 2724, 1724, 1372, 1270, 1158, 1104, 1078, 1030 and 948; δ_H (400 MHz) 1.30–1.53 (2 H, m), 1.66 (2 H, m), 1.67 (1 H, dd, *J* 13.9 and 4.6 Hz), 2.27 (1 H, dd, *J* 13.9 and 7.8 Hz), 2.43 (2 H, td, *J* 7.3 and 1.5 Hz), 2.67–2.75 (1 H, m), 3.91–3.96 (4 H, m), 5.69 (1 H, dd, *J* 5.6 and 2.2 Hz), 6.01 (1 H, dd, *J* 5.6 and 2.2 Hz) and 9.75 (1 H, t, *J* 1.5 Hz); δ_C 20.21, 35.17, 41.22, 42.32, 43.86, 64.61, 64.83, 119.53, 130.18, 140.84 and 202.27; *m*/*z* (EI) 196 (M$^+$, 2%), 125 (100), 99 (20), 86 (36), 67 (21), 53 (25), 41 (24) and 39 (20).

4-[(*E*)-5-(Ethoxycarbonyl)pent-4-enyl]cyclopent-2-enone ethylene ketal 15a

To a suspension of NaH (13 mg, 0.54 mmol) in dry THF (2.5 mL) was added a solution of ethyl diethoxyphosphorylacetate (125 mg, 0.58 mmol) in dry THF (2.5 mL) under argon at 0 °C over a period of 5 min and the mixture was stirred for an additional 10 min at the same temperature. A solution of **23** (73 mg, 0.37 mmol) in dry THF (4 mL) was then added and the mixture was stirred at room temperature for 1 h before being evaporated, diluted with water (20 mL), and extracted with diethyl ether (3 × 30 mL). The extracts were combined, washed with brine (40 mL), dried with Na_2SO_4, and concentrated. The residue was purified by chromatography on silica gel (hexane 90%, diethyl ether 10%) followed by distillation to give **15a** as a colorless oil (90 mg, 92%), bp 90–95 °C (0.004 Torr) (Found: M$^+$, 266.1501. $C_{15}H_{22}O_4$ requires *M*, 266.1518); ν_{max} (neat)/cm^{-1} 2980, 2932, 1722, 1656, 1462, 1448, 1370, 1268, 1184, 1152, 1098, 1044 and 988; δ_H (400 MHz) 1.29 (3 H, t, *J* 7.3 Hz), 1.50 (2 H, m), 1.32–1.54 (2 H, m), 1.67 (1 H, dd, *J* 13.9 and 4.6 Hz), 2.21 (2 H, m), 2.27 (1 H, dd, *J* 13.9 and 7.6 Hz), 2.67–2.74 (1 H, m), 3.92–3.96 (4 H, m), 4.18 (2 H, q, *J* 7.3 Hz), 5.70 (1 H, dd, *J* 5.6 and 2.2 Hz), 5.81 (1 H, td, *J* 15.6 and 2.0 Hz), 6.02 (1 H, dd, *J* 5.6 and 2.2 Hz) and 6.94 (1 H, dd, *J* 15.6 and 6.8 Hz); δ_C 14.27, 26.15, 32.17, 35.19, 41.28, 42.34, 60.15, 64.59, 64.83, 119.59, 121.54, 129.99, 141.11, 148.81 and 166.66; *m*/*z* (EI) 266 (M$^+$, 5%), 193 (25), 125 (100), 112 (29), 99 (46), 87 (29), 86 (82), 81 (50), 79 (20), 67 (28), 55 (27), 53 (37), 41 (32) and 39 (23).

4-(5,5-Dicyanopent-4-enyl)cyclopent-2-enone ethylene ketal 15b

To a solution of **23** (30 mg, 0.15 mmol) and malononitrile (15 mg, 0.23 mmol) in dry benzene (6 mL) was added piperidinium acetate (4 mg, 0.03 mmol) under argon at 5 °C and the mixture was stirred at room temperature for 1 h before being diluted with dichloromethane (100 mL), washed successively with 5% aq. $NaHCO_3$ (3 × 30 mL) and brine (30 mL), dried with Na_2SO_4, and concentrated. The residue was purified by chromatography on silica gel (hexane 70%, diethyl ether 30%) to give **15b** as a colorless oil (21 mg, 56%) (Found: M$^+$, 244.1212. $C_{14}H_{16}N_2O_2$ requires *M*, 244.1199); ν_{max} (neat)/cm^{-1} 2932, 2880, 2230, 1608, 1370, 1158, 1098, 1024 and 948; δ_H (400 MHz) 1.40–1.70 (4 H, m), 1.67 (1 H, dd, *J* 13.8 and 4.4 Hz), 2.29 (1 H, dd, *J* 13.8 and 7.7 Hz), 2.61 (2 H, m), 2.75 (1 H, m), 3.95 (4 H, m), 5.74 (1 H, dd, *J* 5.8 and 2.0 Hz), 5.99 (1 H, dd, *J* 5.8 and 2.2 Hz) and 7.32 (1 H, t, *J* 7.8 Hz); δ_C 25.64, 32.87, 34.96, 41.09, 42.04, 64.71, 64.90, 90.26, 110.44, 119.40, 130.77, 140.10 and 169.02; *m*/*z* (EI) 244 (M$^+$, 4%), 139 (26), 125 (93), 86 (100), 81 (34) and 53 (23).

6-(Ethoxycarbonyl)tricyclo[5.2.1.0^{1,5}]decan-8-one ethylene ketal 19a

A solution of **15a** (25 mg, 0.09 mmol) in acetonitrile (50 mL) was heated at 150 °C for 5 days in a glass ampoule. GLC analysis of the reaction mixture showed 47% conversion of the starting material. The mixture was concentrated and the residue was purified by chromatography on silica gel (hexane 90%,

diethyl ether 10%) followed by preparative GLC (10% DC550; 1 m; 190 °C) to give **19a** as a colorless oil (11 mg, 94% *vs* conversion), which was crystallized from hexane at −20 °C to give colorless rods, mp 44–45 °C (Found: M^+, 266.1496. $C_{15}H_{22}O_4$ requires *M*, 266.1518); ν_{max} (neat)/cm^{-1} 2952, 2872, 1738, 1338, 1202, 1120, 1078 1040; δ_H (400 MHz) 1.18–1.29 (1 H, m), 1.27 (3 H, t, *J* 7.3 Hz), 1.48 (2 H, m), 1.50–1.70 (2 H, m), 1.67 (1 H, dd, *J* 13.2 and 2.9 Hz), 1.83 (2 H, m), 2.00 (1 H, d, *J* 13.2 Hz), 2.07 (1 H, m), 2.27 (1 H, tdd, *J* 9.0, 5.9 and 1.0 Hz), 2.46 (1 H, dd, *J* 5.9 and 3.4 Hz), 2.65 (1 H, dt, *J* 3.4 and 2.0 Hz), 3.85 (4 H, m) and 4.13 (2 H, q, *J* 7.3 Hz); δ_C 14.28, 26.32, 28.93, 32.83, 41.88, 47.53, 47.61, 50.55, 52.01, 55.30, 60.10, 64.10, 64.92, 115.75 and 174.07; *m*/*z* (EI) 266 (M^+, 56%), 223 (21), 193 (100), 107 (21) and 79 (26).

7,7-Dicyanotricyclo[4.4.0.0^{2,8}]decan-10-one ethylene ketal 18b

A solution of **15b** (11 mg, 0.045 mmol) in acetonitrile (40 mL) was heated at 120 °C for 4 days in a glass ampoule. GLC analysis of the reaction mixture showed complete consumption of the starting material. The mixture was concentrated and the residue was purified by chromatography on silica gel (hexane 50%, diethyl ether 50%) followed by preparative GLC (10% DC550; 1 m; 190 °C) to give **18b** as a colorless solid (6 mg, 64%). Recrystallization from ethyl acetate afforded single crystals of **18b** suitable for X-ray study, mp 134–135 °C (Found: M^+, 244.1189. $C_{14}H_{16}N_2O_2$ requires *M*, 244.1212); ν_{max} (neat)/cm^{-1} 2960, 2244, 1342, 1106, 1054 and 1014; δ_H (400 MHz) 1.42 (1 H, ddddd, *J* 14.6, 11.2, 9.3, 8.8 and 7.3 Hz), 1.72 (1 H, dddt, *J* 14.6, 8.8, 6.3 and 2.4 Hz), 1.78 (1 H, dddd, *J* 15.1, 11.2, 6.3 and 2.4 Hz), 1.90 (1 H, dddd, *J* 15.1, 9.8, 7.8 and 2.4 Hz), 1.96 (1 H, dd, *J* 14.6 and 4.4 Hz), 2.01 (1 H, dddd, *J* 15.1, 9.3, 6.3 and 2.4 Hz), 2.15 (1 H, dt, *J* 15.1 and 8.8 Hz), 2.17 (1 H, dd, *J* 2.0 and 1.0 Hz), 2.24 (1 H, dd, *J* 14.6 and 0.5 Hz), 2.56 (1 H, ddddd, *J* 9.8, 2.4, 2.2, 2.0 and 1.0 Hz), 2.74 (1 H, dddd, *J* 4.4, 1.5, 1.0 and 0.5 Hz), 2.92 (1 H, ddd, *J* 6.3, 2.2 and 1.5 Hz) and 3.78–4.00 (4 H, m); δ_C 15.22, 20.96, 26.79, 39.59, 41.99, 43.58, 45.06, 48.46, 50.86, 64.38, 65.11, 115.95, 112.47 and 116.39; *m*/*z* (EI) 244 (M^+, 3%), 163 (76), 125 (57) and 86 (100).

X-Ray structure determinations †

Crystal data for 19a. Colorless rod (0.3 × 0.1 × 0.05 mm), $C_{15}H_{22}O_4$, *M* = 266, monoclinic, space group $P2_1/n$, *a* = 6.477(4), *b* = 11.026(6), *c* = 19.42(1) Å, β = 100.121(10)°, *V* = 1365(1) Å^3, *Z* = 4, D_{calc} = 1.295 g cm^{-3}, *T* = 153 K, μ = 0.93 cm^{-1}, *F*(000) = 576. Measurements were made on a Rigaku MSC Mercury CCD diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.710 70 Å). A total of 3095 unique reflections ($2\theta_{max}$ = 55.0°) were collected, of which 1412 observed reflections [$I > 3\sigma(I)$] were used in the structure solution (direct methods) and refinement (full-matrix least-squares with 172 parameters) to give final *R* = 0.044 and *wR* = 0.048. Residual electron density was 0.25 e Å^{-3}.

Crystal data for 18b. Colorless plate (0.6 × 0.6 × 0.2 mm), $C_{14}H_{16}N_2O_2$, *M* = 244, monoclinic, space group $P2_1/n$, *a* = 6.536(3), *b* = 11.364(5), *c* = 16.594(8) Å, β = 106.196(7)°, *V* = 1183(1) Å^3, *Z* = 4, D_{calc} = 1.371 g cm^{-3}, *T* = 173 K, μ = 0.93 cm^{-1}, *F*(000) = 520. Measurements were made on a Rigaku MSC Mercury CCD diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.710 70 Å). A total of 2666 unique reflections ($2\theta_{max}$ = 55.0°) were collected, of which 1914 observed reflections [$I > 3\sigma(I)$] were used in the structure solution (direct methods) and refinement (full-matrix least-squares with 163 parameters) to give final *R* = 0.043 and *wR* = 0.056. Residual electron density was 0.24 e Å^3.

† CCDC reference number(s) 173682–173683. See http://www.rsc.org/suppdata/p1/b1/b109614a/ for crystallographic files in .cif or other electronic format.

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