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Tandem Diels-Alder Reaction of 4-Oxo-2-Cyclopentenyl Acetate. A Facile One-Pot Synthesis of Hydrofluorenones[1].

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Abstract: 4-Oxo-2-cyclopentenyl acetate has been shown to behave as a conjunctive reagent for Tandem Diels-Alder Reaction under aluminum chloride catalysis. This methodology represents a mild and convenient elaboration of hydrofluorenones. Structure analysis of the reaction products by NMR spectroscopy is discussed.

Development of methods for the synthesis of polycarbocyclic compounds by efficient, short routes is an interesting challenge and provides useful ground for the testing of new synthetic strategies. Continuing our study on the Diels-Alder reaction of cycloalkenones[2], we investigated on a new approach to rapidly synthesize polycarbocyclic molecules by multiple Diels-Alder methodology[3]. We observed that under $AlCl_3$ catalysis, the primary cycloadducts, obtained by reaction of 4-oxo-2-cyclopentenyl acetate (**1**)[4] with cyclic or acyclic dienes, eliminated acetic acid quickly and then, the new enone generated *in situ*, underwent a subsequent cycloaddition leading to hydrofluorenones. While our study was in progress, Zwanenburg et al.[5] published an interesting paper on the Lewis acid catalyzed [4+2] cycloadditions of acetoxy ketone **1**. These authors reported that when the reaction was performed under $AlCl_3$ catalysis, acetic acid was eliminated from the primary cycloadducts, thus showing that 4-oxo-2-cyclopentenyl acetate (**1**) behaved as a synthetic equivalent of cyclopentadienone[6]. However, they did not mention any product obtained by Tandem Diels-Alder reaction. We report herein that 4-oxo-2-cyclopentenyl acetate (4-acetyl-2-cyclopenten-1-one) (**1**) behaves as a conjunctive reagent for a mild, efficient one-pot Tandem Diels-Alder Reaction, thus providing promising prospect for building up hydrofluorenones rapidly. Since acetoxy ketone **1** is available in (+) and (-) forms[7], this method provides a convenient entry to optically active substituted hydrofluorenones which are useful intermediates[8] for the synthesis of biologically interesting compounds such as gibberellins, D-homosteroids, norditerpenoids and HFA analogues. The results of the study of the $AlCl_3$ catalyzed cycloadditions of 4-oxo-2-cyclopentenyl acetate (**1**) with 1,3-butadiene, 2,3-dimethyl-1,3-butadiene, (E)-piperylene, (E)-1-methoxy-1,3-butadiene and cyclopentadiene are herein reported.

Results and Discussion

As a typical example of the Diels-Alder reactions investigated, the cycloaddition of acetoxy ketone **1** with 2,3-dimethyl-1,3-butadiene will be discussed in detail. A mixture of 4-oxo-2-cyclopentenyl acetate (**1**), aluminum chloride and 2,3-dimethyl-1,3-butadiene was heated at 25°C for 2.5 h. Then catalyst and diene were added again and the reaction temperature raised to 40°C to afford, after 18.5 h, a 27:22:1 mixture of the tricyclic ketones **2a:3a:4a** respectively, in 62% overall yield[9] (see Experimental). The further addition of both diene and catalyst, as well as the raising up of the reaction temperature, are of crucial importance to obtain the best reaction yield. The overall configuration of the tricyclic ketones showed that **3a** and **4a** were epimers of the cycloadduct **2a** which was a 2:1 diene-enone adduct of a "Tandem Diels-Alder Reaction". The sequence of the reactions leading to the tricyclic compound **2a** was rigorously demonstrated as follows: g.l.c. monitoring of the reaction showed that acetates **5** underwent $AlCl_3$-induced ß-elimination of acetic acid[10] affording bicyclic ketone **6** which reacted with a second molecule of diene, leading to the tricyclic ketone **2a**. By quenching the reaction after 2.5 h at 25°C, a 85:15 mixture of acetates could be obtained: IR, NMR and GC-Mass measurements supported their structures[11,12]. The mixture of acetates was then converted quantitatively to enone **6**[5] by treatment with $AlCl_3$ under reaction conditions. Finally, the Diels-Alder reaction of bicyclic enone **6** with 2,3-dimethyl-1,3-butadiene under $AlCl_3$ catalysis led to the expected mixture of tricyclic ketones.

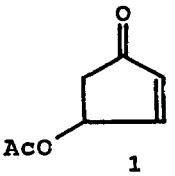
In conclusion these experiments showed that the sequence of reactions of acetoxy ketone **1** with 2,3-dimethyl-1,3-butadiene en route to ketone **2a** is a "Tandem Diels-Alder Reaction". The cycloadduct epimerized to stereoisomers **3a** and **4a** under acidic experimental conditions.

Whereas the reaction of ketone **1** with 1,3-butadiene led to a 2.4:1.2:1 mixture of products **3b:2b:4b** (63%)[14], the cycloaddition with (E)-piperylene afforded a 21:7:4:1 mixture of ketones **2c:7:4c:3c** (62%). Clearly, the cycloadducts, **2b** and **2c**, partially epimerize under the acidic experimental conditions. Furthermore, the Diels-Alder reactions of (E)-piperylene with both acetoxy ketone **1** and the bicyclic enone intermediate, are totally regioselective and endo-diastereoselective.

When acetoxy cyclopentenone **1** interacted with (E)-1-methoxy-1,3-butadiene under Yb $(fod)_3$ catalysis[3c] at 100°C, the tricyclic ketone **8** was obtained in 51% yield. The structure of this compound was shown to be a 2:1 diene-enone adduct of a "Tandem Diels-Alder Reaction", without hydrofluorenone skeleton. The most probable explanation according to previously investigated cycloadditions of (E)-1-methoxy-1,3-butadiene with cycloalkenones[3b,c] is that the monocycloadduct underwent ß-elimination of methanol and acetic acid to afford trienone **9** which then underwent a second cycloaddition at 7,7a-carbon-carbon double bond[2a,b].

Finally, the reaction of a cyclic diene, cyclopentadiene, was also examined. When acetoxy ketone **1** interacted with cyclopentadiene at 25°C for 24 h, a 2.7:1 mixture of two compounds **10** and **11**, was obtained in 50% yield[15].

Whereas previously described reactions of **1** with acyclic dienes required a second addition of diene and catalyst and increasing the reaction temperature, the reaction with cyclopentadiene occurred with the best yield at 25°C without no further addition of reactants. It probably depends on the high reactivity of cyclopentadiene in normal demand Diels-Alder reactions.



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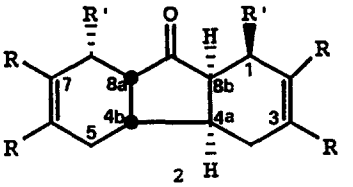

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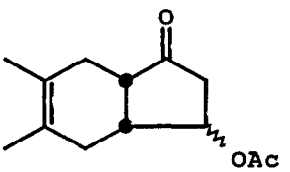

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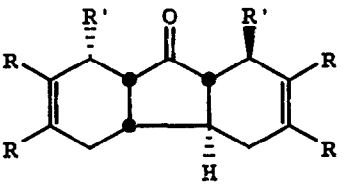

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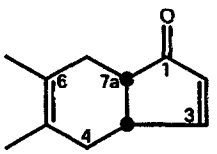

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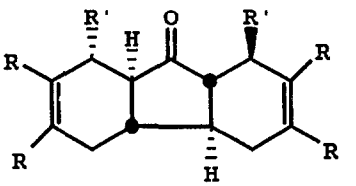

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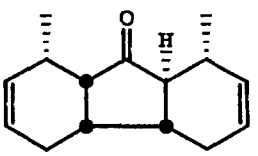
a: R=Me, R'=H; b: R=R'=H; c: R'=Me, R=H



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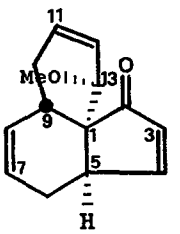

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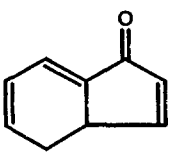

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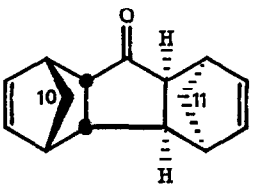

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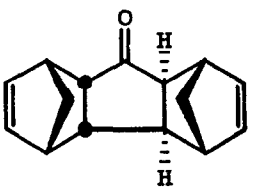

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In conclusion, this study has shown that 4-oxo-2-cyclopentenyl acetate (**1**) can behave, under the experimental conditions described, as a conjunctive reagent for "Normal Tandem Diels-Alder Reaction". This one-pot methodology represents a mild and convenient tool to rapidly synthesize hydrofluorenones. Our efforts are now directed at studying the "Cross Tandem Diels-Alder Reaction" by interaction of **1** with two different dienes, cyclic and acyclic, thus increasing the power and the synthetic utility of this methodology.

Structure Analysis

The structure and stereochemistry of the tricyclic products were inferred from the analysis of their high-field ^1H and ^{13}C NMR spectra. The pertinent data are collected in the Experimental Section. Inspection of ^1H-^1H and ^1H-^{13}C connectivities of compounds **2c-4c** and **7** reveals the regiochemistry. The stereochemistry at the ring junctions as well as the relationship of the methyl groups with the bridgehead hydrogens were based on $J_{H,H}$ coupling constant values and ^1H-^1H NOE experiments. Selective pre-irradiation of the resonance due to H(8a) resulted in signal enhancement of the resonances attributed to H(4b), H(8) and H(9a) for ketone **3c**; in the case of ketone **7** mutual enhancement occurred for resonances of H(4b), H(8) and H(4a), thus indicating the stereochemistry at ring junctions and the *trans*-relationship of 8-Me with H(8a), for both ketones. The 13.5 Hz coupling constant value between H(4a) and H(9a) for both ketones reveal their *trans*-relationship. Furthermore, mutual enhancements occurred for resonances of the methyl group at C(1) and H(9a) indicating their *cis*-relationship. The structure assignment of C_2-symmetric tricycles **2c** and **4c** was based on selective pre-irradiation of the pertinent resonances in NOE experiments. Mutual dipolar contacts between H(1), H(4a) and H(9a) were observed for ketone **2c** and between H(1) and H(4a), H(9a) and methyl group at C(1), for ketone **4c**, thus indicating the stereochemistry depicted in the formulas. Further support to this stereochemical assignment is given by the coupling values, i.e., $J_{1,9a}$=$J_{4a,9a}$=7.0 Hz for **2c**; $J_{1,9a}$=9.6 Hz and $J_{4a,9a}$=12.0 Hz for **4c**.

The assignment of the structures to the tricyclic ketones obtained by reaction of **1** with 1,3-butadiene and 2,3-dimethyl-1,3-butadiene was based, first of all, on the similarity of their proton spectra with those of the tricycles **2c-4c** above discussed. This observation suggested a fluorenone type skeleton for tricyclic ketones **2a-4a** and **2b-4b** and also gave information about the stereochemistry. Mutual carbon chemical shift correlations between related tricycles **2-4** using suitable hydrindanones[16] as models to calculate the substituent parameters for methyl group, allowed the stereochemistry at the ring junctions to be confirmed.

The analysis of IR spectrum, carbon chemical shifts and their multiplicity reveals the presence of a conjugated carbonyl function, six olefinic carbon atoms and one quaternary carbon atom, indicating compound **8** to be a trienic ketone possessing three non-linearly fused rings. The stereochemistry was inferred from a series of selective NOE experiments which proved the steric proximity of H(9) and H(13) as well as H(5) and the methoxy group and the values of the relevant proton-proton couplings, i.e. $J_{5,4}$ = 2.9 Hz, $J_{5,6}$ = 0.9,7.5 Hz, $J_{8,9}$ = 7.3 Hz, $J_{9,10}$ = 9.1,8.3 Hz and $J_{12,13}$ = 2.2 Hz.

It should be emphasized that the formation of tricyclic ketone **8** is reminiscent of (but not identical with) previously observed Yb(fod)$_3$-catalyzed cycloaddition of 2-cyclohexenone and (E)-1-methoxy-1,3-butadiene[3c]. Further support to the assignment of structure to tricyclic ketones was also given by the study of base-catalyzed equilibration of the reaction products.

Experimental

All operations for preparing the starting reaction mixtures were executed in a dry box. Melting points were determined on a Büchi 510 melting point apparatus and are uncorrected. Infrared spectra of $CHCl_3$ solutions were recorded on a Perkin-Elmer 257 spectrophotometer. GC analyses were performed on a Carlo Erba HRGC-5160 and Hewlett-Packard 5880A chromatographs. Absorption chromatography was carried out on a Merck Lichoprep Si 60 pre-packed column. All compounds gave a correct elemental analysis. All NMR spectra were run at room temperature (internal Me_4Si) on a Varian Associates VXR-400 multinuclear instrument. The reaction products were crystallized from n-hexane.

$AlCl_3$-catalyzed Diels-Alder reaction of 4-oxo-2-cyclopentenyl acetate (1) with 2,3-dimethyl-1,3-butadiene. The following discussion of the reaction of 4-oxo-2-cyclopentenyl acetate (1) with 2,3-dimethyl-1,3-butadiene is also the typical procedure used for the cycloaddition with 1,3-butadiene and (E)-piperylene. A solution of 2.7 mL of 1 M nitrobenzene solution of $AlCl_3$ (2.7 mmol) was added to a solution of 1.5 g (10.7 mmol) of 4-oxo-2-cyclopentenyl acetate (1) in 96 mL of dry toluene and the mixture stirred at 25°C for 40 min[17]. 2,3-Dimethyl-1,3-butadiene (1.75 g, 21.4 mmol) was then added and the mixture was kept at 25°C for 2.5h. Then 2.7 mL of 1 M nitrobenzene solution of $AlCl_3$ (2.7 mmol) were added again and after stirring for an additional 40 min. at 25°C, 13.2 g (160.5 mmol) of 2,3-dimethyl-1,3-butadiene were poured into the mixture. After heating for 18.5h at 40°C, the reaction mixture was worked-up as usual to afford a residue which was chromatographed (elution with 97:3 n-hexane-ethylacetate) to give pure compounds **2a**, **3a**, **4a** (62%).

2,3,6,7-Tetramethyl-1,4,4aα,4bβ,5,8,8aβ,9aα-octahydro-9H-fluoren-9-one (2a): mp 123-124°C; IR 1728 (s, C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.61 (br.s, 12H, Methyls), 1.78-2.23 (m, 10H), 2.39 (m, 2H, H-8a,H-9a); ^{13}C NMR ($CDCl_3$) δ 18.9 (2-Me, 7-Me), 19.4 (3-Me, 6-Me), 29.3 (C-1,C-8), 33.5 (C-4, C-5), 38.1 (C-4a, C-4b), 44.6 (C-9a, C-8a), 124.6 (C-3, C-6), 125.0 (C-2, C-7), 221.3 (C-9); mass spectrum, m/e (relative intensity), 244 (M^+, 13), 107 (47), 93 (72), 91 (base), 77 (66), 55 (46).

2,3,6,7-Tetramethyl-1,4,4aα,4bβ,5,8,8aβ,9aβ-octahydro-9H-fluoren-9-one (3a): m.p. 104-105°C; IR 1728 (s, C=0) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.40 (m, 1H, H-4a), 1.56 (s, 6H, 2-Me, 7-Me), 1.58 (s, 6H, 3-Me, 6-Me), 1.84-2.17 (m, 10H), 2.47 (ddd, 1H, H-8a); ^{13}C NMR ($CDCl_3$) δ 19.1 (2-Me), 19.2 (7-Me), 19.4 (3-Me), 19.7 (6-Me), 28.6 (C-8), 31.4 (C-1), 31.6 (C-5), 37.4 (C-4), 39.3 (C-4b), 41.6 (C-4a), 45.6 (C-8a), 51.5 (C-9a), 124.9 (C-6), 125.3 (C-2, C-3), 125.8 (C-7), 219.4 (C-9); mass spectrum, m/e (relative intensity) 244 (M^+, 28), 107 (70), 93 (80) 91 (base), 79 (43), 77 (61).

2,3,6,7-Tetramethyl-1,4,4aα,4bβ,5,8,8aα,9aβ-octahydro-9H-fluoren-9-one (4a): mp 156-158°C; IR 1728 (s, C=0) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.40 (m, 2H, H-4a, H-4b), 1.58 (s, 12H, Methyls), 1.78-2.20 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 19.3 (2-Me, 7-Me), 19.4 (3-Me, 6-Me), 31.7 (C-1, C-8), 36.5 (C-4, C-5), 43.9 (C-4a, C-4b), 53.2 (C-8a, C-9a), 125.5 (C-3, C-6), 125.9 (C-2, C-7); mass spectrum, m/e (relative intensity), 244 (M^+, 37), 107 (70), 93 (base), 77 (66), 55 (40).

$AlCl_3$-Catalyzed Diels-Alder reaction of 4-oxo-2-cyclopentenyl acetate (1) with 1,3-butadiene. According to the typical procedure described for the reaction of 1 with 2,3-dimethyl-1,3-butadiene, a 0.1 M solution of 1 (1.5 g, 10.7 mmol) in toluene with 1,3-butadiene (42.8 mmol) in presence of aluminum chloride (5.35 mmol) was kept at 25°C for 5 h. $AlCl_3$ (2.7 mmol) was then added, and after 40 min at 25°C, a toluene solution of 1,3 butadiene (107.0 mmol) was added. After 16 h at 55°C, the reaction mixture was worked-up as usual and the tricyclic ketones **2b**, **3b** and **4b** were purified by column chromatography eluting with 4.5:4.5:1 n-hexane-petroleum ether-ethylacetate (63%).

1,4,4aα,4bβ,5,8,8aβ,9aα-octahydro-9H-fluoren-9-one (2b): mp 55-56°C; IR 1727 (s, C=0) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.85 (m, 2H), 2.20-2.40 (m, 8H), 2.44 (m, 2H, H-8a, H-9a), 5.70 (br.s, 4H, olefinic Hs); ^{13}C NMR ($CDCl_3$) δ 22.4 (C-1, C-8), 26.0 (C-4, C-5), 36.9 (C-4a, C-4b), 43.4 (C-8a, C-9a), 220.4 (C-9); mass spectrum, m/e (relative intensity) 188 (M^+, 9), 91 (35), 80 (36), 79 (base), 77 (57).

1,4,4aα,4bβ,5,8,8aβ,9aβ-octahydro-9H-fluoren-9-one (3b): colorless liquid;. IR 1729 (s, C=0) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.58 (m, 1H, H-4a), 1.92-2.34 (m, 10H), 2.51 (q, 1H, H-8a), 5.68 (br.s, 2H, H-2, H-7), 5.72 (br.s, 2H, H-3, H-6); ^{13}C NMR ($CDCl_3$) δ 21.8 (C-8), 23.7 (C-1), 25.8 (C-5), 30.8 (C-4), 38.6 (C-4b), 40.9 (C-4a), 44.0 (C-8a), 50.7 (C-9a), 125.7 (C-6), 126.3 (C-3), 126.4 (C-2), 126.8 (C-7), 218.7 (C-9); mass spectrum, m/e (relative intensity) 188 (M^+, 48), 91 (39), 79 (base), 77 (51).

1,4,4aα,4bβ,5,8,8aα,9aβ-octahydro-9H-fluoren-9-one (4b): mp 81-82°C; IR 1726 (s, C=0) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.52 (m, 2H, $J_{4a,9a} = J_{4b,8b}$=12 Hz, H-4a, H-4b), 1.89 (m, 2H, $J_{9a,1} = J_{8a,8} = 5.4$, 10.0 Hz, H-8a, H-9a), 1.96-2.02 (m, 4H), 2.41-2.44 (m, 4H), 5.73 (br.d., 4H, olefinic Hs); ^{13}C NMR ($CDCl_3$) δ 25.9 (C-1, C-8), 30.1 (C-4, C-5), 43.3 (C-4a, C-4b), 52.0 (C-8a, C-9a), 126.7 (C-3, C-6), 126.9 (C-2, C-7); mass spectrum, m/e (relative intensity) 188 (M^+, 57), 91 (42), 79 (base), 77 (52).

$AlCl_3$-Catalyzed reaction of 4-oxo-2-cyclopentenyl acetate (1) with (E)-piperylene. A 0.1 M toluene solution of ketone **1** (0.92 g; 6.6 mmol), with (E)-piperylene (1.3 mL; 13 mmol) in presence of aluminum chloride (1.6 mmol) was kept at 25°C for 4.5 h according to the procedure described above. Then 1.6 mmol of 1 M nitrobenzene solution of aluminum chloride and 52.7 mmol of (E)-piperylene were added and the reaction mixture heated at 40°C for 15 h. After usual work up the residue was chromatographed on silica gel impregnated with 20% silver nitrate, and elution with 95:5 hexane-ethyl acetate furnished pure adducts **2c**, **3c** and **4c**. Fractions enriched in isomer **7** were combined and chromatographed again; elution with 98:2 hexane-ethyl acetate gave pure ketone **7** (overall yield 62%).

1β,8α-Dimethyl-1,4,4aα,4bβ,5,8,8aβ,9aα-octahydro-9H-fluoren-9-one (2c): mp 78-79°C; IR 1727 (s, C=0) cm^{-1}; ^1H NMR (C_6D_6) δ 1.38 (d, 6H, J = 7.3 Hz, 1-Me, 8-Me), 1.82 (m, 2H, H-4a, H-4b), 2.17 (m, 2H, H-1, H-8), 2.26 (dd, 2H, $J_{9a,1} = J_{8a,8} = 6.9$ Hz, $J_{9a,4a} = J_{8a,4b} = 7.0$ Hz, H-8a, H-9a), 5.59 (m, 4H, H-2, H-3, H-6, H-7); ^{13}C NMR ($CDCl_3$) δ 17.7 (1-Me, 8-Me), 28.1 (C-4, C-5), 30.1 (C-1, C-8), 40.1 (C-4a, C-4b), 50.6 (C-8a, C-9a), 125.9 (C-3, C-6), 133.0 (C-2, C-7), 219.3 (C-9); mass spectrum, m/e (relative intensity), 216 (M^+, 3), 93 (69), 91 (56), 79 (base), 77 (77).

1β,8α-Dimethyl-1,4,4aα,4bβ,8,8aβ,9aβ-octahydro-9H-fluoren-9-one (3c): colorless oil; I.R. 1725 (s, C=0) cm^{-1}; ^1H NMR (C_6D_6) δ 1.02 (d, 3H, J=7.4 Hz, 8-Me), 1.26 (dd, 1H, $J_{9a,4a}$ = 13.6, $J_{9a,1}$ = 10.0 Hz, H-9a), 1.31 (d, 3H, J=6.9 Hz, 1-Me), 1.38 (m, 1H, $J_{4a,4b}$ = 10.4 Hz, H-4a), 1.65 (m, 1H, H-4b), 2.28 (dd, 1H, H-8a), 2.54 (m, 1H, $J_{8,8a}$ = 7.2 Hz, H-8), 5.38 (m, 1H, H-2), 5.51 (m, 1H, H-3), 5.62 (m, 1H, H-6), 5.82 (m, 1H, H-7); ^{13}C NMR ($CDCl_3$) δ 17.4 (8-Me), 19.8 (1-Me), 25.0 (C-5), 28.9 (C-8), 31.3 (C-4), 31.8 (C-1), 38.8 (C-4b), 44.6 (C-4a), 49.3 (C-8a), 57.0 (C-9a), 125.1 (C-3), 125.8 (C-6), 133.8 (C-7), 134.4 (C-2), 219.2 (C-9); mass spectrum, m/e (relative intensity), 216 (M^+, 8), 93 (81), 91 (63), 79 (base), 77 (80).

1β,8α-Dimethyl-1,4,4aα,4bβ,5,8,8aα,9aβ-octahydro-9H-fluoren-9-one (4c): mp 120-121°C; IR 1727 (s, C=O) cm^{-1}; ^1H NMR (C_6D_6) δ 1.13 (m, 2H, H-4a, H-4b), 1.20 (dd, 2H, $J_{1,9a} = J_{8,8a} = 9.6$ Hz, $J_{4a,9a} = J_{4b,8a} = 12$ Hz, H-8a, H-9a), 1.35 (d, 6H, J=7.0 Hz, 1-Me, 8-Me), 2.28 (m, 2H, H-1, H-8), 5.39 (m, 2H, H-2, H-7), 5.52 (m, 2H, H-3, H-6); ^{13}C NMR ($CDCl_3$) δ 19.9 (1-Me, 8-Me), 29.8 (C-4, C-5), 33.4 (C-1, C-8), 42.9 (C-4a, C-4b), 58.0 (C-8a, C-9a), 125.4 (C-3, C-6), 134.6 (C-2, C-7), 218.5 (C-9); mass spectrum, m/e (relative intensity), 216 (M^+, 17), 93 (86), 91 (65), 79 (base), 77 (75).

1α,8α-Dimethyl-1,4,4aβ,4bβ,5,8,8aβ,9aα-octahydro-9H-fluoren-9-one (7): colorless oil; IR 1727 (s, C=0) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.13 (d, 3H, J=6.9 Hz, 1-Me), 1.27 (d, 3H, J=7.5 Hz, 8-Me), 1.53 (dd, 1H, $J_{9a,1}$ = 10.0 Hz, $J_{9a,4a}$ = 13.5 Hz, H-9a), 1.95-2.22 (m, 6H, H-1, H-4, H-4a, H-5), 2.38 (dd, 1H, $J_{8a,4b} = J_{8a,8}$ = 7.2 Hz, H-8a), 2.54 (m, 2H, H-4b, H-8), 5.37 (m, 1H, H-2), 5.65 (m, 3H, H-3, H-6, H-7); ^{13}C NMR ($CDCl_3$) δ 17.9 (8-Me), 19.9 (1-Me), 22.1 (C-5), 27.3 (C-4), 30.5 (C-8), 33.5 (C-1), 35.1 (C-4b), 40.8 (C-4a), 52.8 (C-8a), 53.9 (C-9a), 125.6 (C-3), 126.2 (C-6), 133.8 (C-7), 134.1 (C-2), 219.3 (C-9); mass spectrum, m/e (relative intensity), 216 (M^+, 3), 93 (91), 91 (62), 79 (base), 77 (78).

Diels-Alder reaction of 4-oxo-2-cyclopentenyl acetate (1) with (E)-1-methoxy-1,3-butadiene. A solution of 0.7 g (5 mmol) of ketone **1** in 12 mL of dry toluene was added to a solution of 1.33 g (1.25 mmol) of $Yb(fod)_3$ in 11 mL of dry toluene in an ampule and the mixture stirred at 25°C for 40 min.

Then 0.84 g (10 mmol) of (E)-1-methoxybutadiene was added to the reaction mixture, the ampule sealed under vacuum, and the mixture warmed at 100°C for 18h. It was then cooled and worked-up as usual, giving crude product **8**, which was chromatographed. Elution with 4:1 hexane-ethyl acetate led to pure ketone **8** (yield 51%).

Tricyclic ketone 8: mp 55-57°C, IR 1696 (s, C=0) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.76 (ddd, 1H, $J_{9,8}$ = 7.3 Hz, $J_{9,10}$ = 9.1, 8.3 Hz, H-9), 3.16 (s, 3H, OCH_3), 3.27 (m, 1H, $J_{5,4}$ = 2.9 Hz, H-5), 3.81 (br.s, 1H, H-13), 5.48 (m, 1H, H-7), 5.73 (m, 2H, H-11, H-12), 5.94 (m, 1H, H-8), 6.13 (d, 1H, $J_{3,4}$ = 5.8 Hz, H-3), 7.46 (dd, 1H, H-4); ^{13}C NMR ($CDCl_3$) δ 26.1 (C-6), 29.5 (C-10), 33.3 (C-9), 42.5 (C-5), 54.9 (C-1), 58.2 (OMe), 80.7 (C-13), 125.2 (C-7), 127.2 (C-11), 128.2 (C-12), 133.3 (C-3), 133.5 (C-8), 168.9 (C-4), 214.5 (C-2); mass spectrum, m/e (relative intensity), 216 (M^+, 3), 115 (9), 84 (base), 77 (9), 69 (24).

$AlCl_3$-catalyzed Diels-Alder reaction of 4-oxo-2-cyclopentenyl acetate (1) with cyclopentadiene. 2.7 mL (2.7 mmol) of 1 M nitrobenzene aluminum chloride solution were added to a solution of 1.5 g (10.7 mmol) of 4-oxo-2-cyclopentenyl-acetate (**1**) in 30 mL of dry toluene and the reaction mixture was stirred at room temperature for 40 min. A solution of cyclopentadiene (2.84 g, 42.8 mmol) in 70 mL of dry toluene was added and the mixture was kept at 25°C for 26h. Then the reaction mixture was worked-up as usual to afford 4 g of residue which was chromatographed eluting with 4:1 hexane-ethylacetate (57%).

1,4:5,8-Dimethano-1β,4β,4aα,4bβ,5α,8α,8aβ,9aα-octahydro-9H-fluoren-9-one (10): mp 123-124°C (lit[15] mp 121-122°C); IR 1716 (C=0) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.26, 1.44 (ddd, 4H, J=8.3 Hs-10, Hs-11), 2.41 (dd, 2, $J_{4a,9a}$ = 8.5, $J_{4a,4}$ = 3.3, H-4a, H-4b), 2.58 (dd, 2, $J_{9a,1}$ = 4.6, H-8a, H-9a), 3.05 (m, 4, H-1, H-4, H-5, H-8), 6.06 (dd, 2, J=5.4, 3.3, H-2, H-7), 6.19 (dd, 2, J=5.4, 2.9, H-3, H-6); ^{13}C NMR ($CDCl_3$) δ 45.8 (C-4a, C-4b), 46.6 (C-1, C-8), 47.6 (C-4, C-5), 51.4 (C-10, C-11), 59.7 (C-8a, C-9a), 136.0 (C-3, C-6), 137.1 (C-2, C-7), 224.0 (C-9); mass spectrum, m/e 212 (relative intensity), (M^+, 0.5), 147 (65), 117 (19), 91 (15), 66 (base).

1,4:5,8-Dimethano-1α,4α,4aα,4bβ,5α,8α,8aβ,9aα-octahydro-9H-fluoren-9-one (11): mp 78-80°C (lit[15] mp 76-78°C); IR 1715 (s, C=0) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.26, (ddd, 2H, J=8.9, 1.6, 1.5 Hz, Hs-10), 1.35 (ddd, 1H, J=8.1, 1.6,1.5 Hz, H-11), 1.48 (ddd, 1H, H-11), 1.76 (dt, 1H, $J_{4b,8a}$ = 7.7, $J_{4b,4a}$ = 2.1, H-4b), 1.92 (dd, 1H, H-8a), 2.50 (ddd, 1H, $J_{4a,9a}$ = 8.7, $J_{4a,4}$ = 4.15, H-4a), 2.95 (m, 1H, H-8), 3.07 (m, 1H, H-9a), 3.09 (m, 1H, H-4), 3.19 (br.s, 1H, H-1), 6.01-6.20 (m, 4, olefinic Hs); ^{13}C NMR ($CDCl_3$) δ 45.6 (C-10), 46.5 (C-4a), 46.9 (C-4b), 47.4 (C-1), 47.7 (C-4), 48.0 (C-8), 49.9 (C-5), 51.2 (C-11), 59.1 (C-8a), 60.5 (C-9a), 135.4 (C-3), 135.9 (C-2), 137.1 (C-7), 138.4 (C-6), 222.3 (C-9); mass spectrum, m/e (relative intensity) 212 (M^+, 1), 117 (20), 91 (15), 66 (base).

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References and Notes

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9. a) The overall reaction yields refer to the isolated compounds.
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   c) All compounds are named on the basis of the numbering system depicted in the formulas.
10. When 4-oxo-2-cyclopentenyl acetate (**1**) was treated with $AlCl_3$ in dry toluene for 26 h more than 90% of the starting material was recovered unchanged.
11. Since only the bicyclic ketone **6** was obtained by $AlCl_3$-induced ß-elimination of acetic acid from **5**, the acetates are expected to be a mixture of *syn*- and *anti*-adduct.
    Bicyclic ketone 6: colorless oil; I.R. 1696 (s, C=0) cm^{-1}; ^{1}HNMR ($CDCl_3$) δ 1.19 (br s, 6H, Methyls), 1.5-2.1 (m, 5H, H_s-4, H-3a, H_s-7), 2.82 (br.s, 1H, H-7a), 5.68 (m, 1H, H-2), 7.10 (m, 1H, H-3); ^{13}C NMR ($CDCl_3$) δ 18.3 (5-Me, 6-Me) 30.4 (C-7), 32.3 (C-4), 40.5 (C-3a), 43.5 (C-7a), 124.2 (C-5), 125.9 (C-6), 133.7 (C-3), 166.1 (C-3), 210.7 (C-1); mass spectrum, m/e (relative intensity) 162 (M^+, 68), 147 (base), 91(71), 55(61).
12. It should be noted that Danishefsky et al. reported that the Diels-Alder reaction of 4-OTBS-cyclopenten-1-one with 1,3-butadiene under $AlCl_3$ catalysis, afforded a 96:4 mixture of *syn:anti* adducts respectively[13].
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