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Photoaddition of methyl 2,4-dioxopentanoate to norbornadiene and quadricyclane

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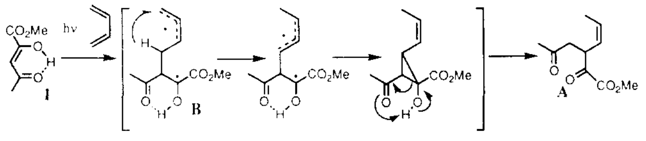
Abstract

The photocycloaddition of methyl 2,4-dioxopentanoate (**1**) to norbornadiene gave a diketo ester (**4**), derived from the expected $[2\pi+2\pi]$ cycloadducts, together with a $[2\pi+2\pi+2\pi]$ cycloadduct (**6**), rearranged tricyclic ester (**5**), 7-substituted norbornene (**7**) and norbornadiene (**8**). The similar reaction of **1** with quadricyclane gave **4**, **5** and an oxetane (**9**), but no **7**. The occurrence of **5** signifies the formation of zwitter ions via an electron transfer process.

Keywords: Photoaddition; Methyl 2,4-dioxopentanoate; Norbornadiene; Quadricyclane

1. Introduction

The photocycloaddition reaction of methyl 2,4-dioxopentanoate (**1**), an enolized β-dicarbonyl compound, with olefins, including conjugated dienes and trienes [1], has wide synthetic application in organic syntheses to construct both functionalized cyclohexenes and cyclopentenes [2,3] (Scheme 1).



Scheme 1.

Our recent finding of the formation of methyl 3-(1-*Z*-propenyl)-2,5-dioxohexanoate (**A**) from **1** with 1,3-butadiene [4] suggests the involvement of hydrogen migration followed by skeletal rearrangement in the biradical intermediate (**B**).

In this paper, we describe the photocycloaddition of **1** to norbornadiene (**2**) and quadricyclane (**3**) to furnish skeletal rearrangement photoproducts with independent photochemical pathways. Compound **2** is a homoconjugated diene and its valence isomer **3** is a strained cycloalkane with no genuine π electrons, although its cyclopropanes adjacent to each other have enhanced π character.

According to the literature, the benzophenone-sensitized photoreaction of **2** causes isomerization to **3** [5]. Also the photocycloaddition of **2** with various enones gives skeletal rearrangement products and ene reaction products [6].

2. Results and discussion

UV irradiation of a mixture of **1** and **2** using a high-pressure mercury lamp afforded five products (**4**–**8**), which were separated by chromatography; all the compounds, except **6**, possessed the norbornene skeleton, judging from the characteristic nuclear magnetic resonance (NMR) chemical shifts in the olefinic proton region. The structural elucidation of these products is described below.

The major product **4** (Scheme 2) was identified to be the expected retro-aldolized product; its ^{13}C NMR spectrum showed three carbonyl carbon signals at $\delta = 162.1$, 197.0 and 209.1, and the IR spectrum revealed strong peaks due to $\nu_{C=O}$ at around 1710 cm^{-1}. The ^{1}H NMR spectrum also showed a pair of methylene proton signals ascribable to the acetonyl group at 2.66 and 2.71 whose mutual coupling constant was 18.7 Hz, and two olefinic proton signals at 6.20 and 6.27, indicating the 5,6-disubstituted 2-norbornene derivative. The stereochemistry of the vic substituents was shown to be exo-cis since the coupling constants between the bridgehead protons and the methine protons were nearly zero.

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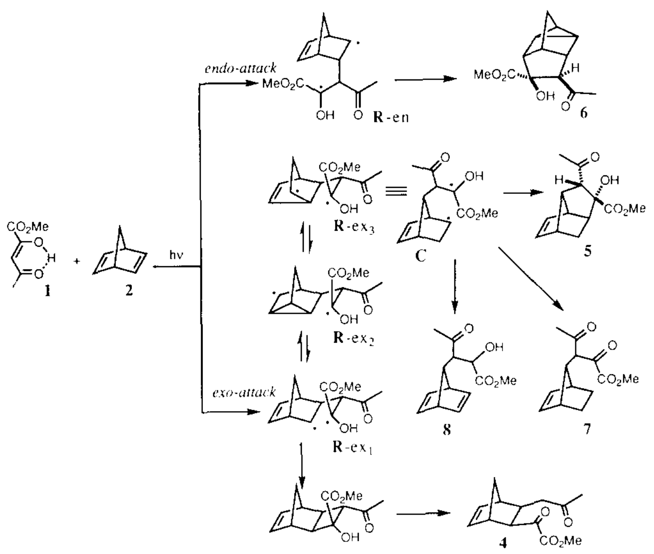


Scheme 2.

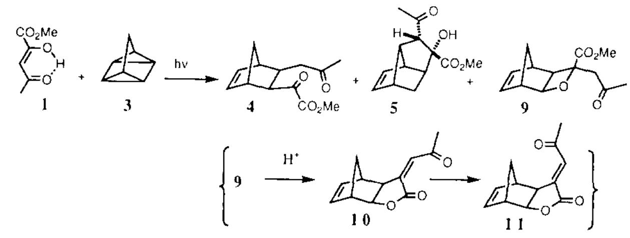
The ^{13}C NMR spectrum of product **5** showed only two carbonyl carbon signals at 173.6 and 208.7; the third oxygen function was a hydroxyl group, since the signal appeared at 88.1, together with a strong hydroxyl stretching band at 3430 cm^{-1} in the IR spectrum. These features are compatible with the proto-photocycloadducts of **1**, and a rearranged five-membered aldol system was assigned in terms of its stability under the work-up conditions. Further information was obtained from the ^{1}H NMR spectrum; the gem protons of the methylene carbon at 0.86 and 1.42 showed a large magnitude with J = 12.5 Hz, which eliminated the possibility that they were on the bridging carbon (i.e. C-7 position of the norbornyl system). Since only two olefinic proton signals are observed in the ^{1}H NMR spectrum, **5** should be a tricyclic derivative, and the tricyclo[3.3.1.0^{4,8}]non-2-ene skeleton is plausible.[1] Orientation of the acetyl group was deduced from the small coupling constant observed for the *vic*-methine protons on C-5 and C-6.

Compound **6** was tetracyclic, since its ^{1}H NMR spectrum revealed no olefinic proton signals, and its ^{13}C NMR spectrum showed three cyclopropane carbon signals at 11.9, 14.9 and 15.1, together with two carbonyl carbon signals at 175.1 and 207.6 and one carbon signal bearing a hydroxylic oxygen at 83.7. These findings led to the assignment of a formal proto-cycloadduct of **1** to quadricyclane (**3**).

Compound **7** was assigned as a seven-substituted norbornene derivative; its ^{13}C NMR spectrum showed three pairs of closely related carbon signals, 21.6 and 21.8, 42.9 and 43.2, and 136.1 and 136.6, together with three carbonyl carbon signals at 161.2, 188.7 and 201.9. This should be a hydrogen transfer product from the intermediate biradical (**C**).

The remaining compound **8** was obtained as a mixture with **7**, and ^{1}H NMR spectral analysis deduced it to be a 7-substituted norbornadiene derivative; it showed four olefin proton signals at 6.71 (2H) and 6.84 (2H). Consequently, **7** and **8** were derived from a common biradical intermediate (**C**), but the direction of hydrogen transfer was opposite. Hydrogen abstraction by the excited carbonyl is common, but the reverse, the mode of formation of **7**, has not been observed in the photocycloaddition of **1**.

The formation of a nortricyclane derivative **6** prompted us to extend the photoreaction to **1** and **3**. Thus the photoreaction of **1** with **3** afforded, together with **4** and **5** as common products, different types of products (**9** and **10**) (Scheme 3). Compound **10** was a secondary product derived from **9**. The major product **9** was an oxetane derivative; in the ^{1}H NMR spectrum, the olefinic proton signals indicated a norbornene derivative, and the proton signal on the ethereal carbon appeared at δ = 4.70 as a broad doublet, J = 5.1 Hz. The exo stereochemistry of the oxetane ring was assigned by NMR spectral comparisons with a related compound, an adduct of dimethyl oxomalonate to **1** [7].



Scheme 3.

Compound **9** changes to **10** on brief contact with the silica gel column during work-up. Furthermore, **10** gives **11** simply on standing in a chloroform solution. The structures of **10** and **11** were clarified by physicochemical data; the mass spectral determination of the molecular weight clarified a loss of the methanol unit, and the IR spectra showed the $\nu_{C=O}$ absorption peaks at 1752 and 1700 cm^{-1} (**10**) and 1770 and 1700 cm^{-1} (**11**), indicating the formation of the exo-methylene γ-lactone chromophore. Together with the carbonyl stretching frequencies, the ^{1}H NMR spectral comparison of the chemical shifts for the low-field-shifted protons, δ = 6.43

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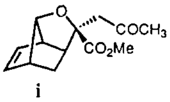
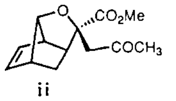
[1] In addition to these, trace amounts of **i** (^{1}H NMR δ = 0.99 (1H, dd, J = 12.5, 6.0 Hz), 1.96 (1H, dd, J = 12.5, 5.5 Hz), 2.17 (3H, s), 2.35 (1H, dd, J = 6.0, 1.0 Hz), 2.71 (1H, br s), 3.06 (1H, br s), 3.15 (1H, d, J = 15.5 Hz), 3.17 (1H, d, J = 15.5 Hz), 3.79 (3H, s), 4.22 (1H, br s), 5.70 (1H, ddd, J = 6.0, 3.3, 1.0 Hz) and 6.16 (1H, ddm, J = 6.0, 3.3 Hz)) and **ii** (^{1}H NMR δ = 0.96 (1H, ddd, J = 12.0, 6.0, 1.0 Hz), 1.61 (1H, dd, J = 12.0, 7.0 Hz), 2.16 (3H, s), 2.23 (1H, dd, J = 5.0, 1.5 Hz), 2.78 (1H, m), 2.94 (1H, d, J = 15.4 Hz), 3.28 (1H, br s), 3.82 (3H, s), 4.20 (1H, br s), 5.74 (1H, dd, J = 5.5, 3.3 Hz) and 6.22 (1H, ddd, J = 5.5, 3.3, 1.0 Hz)) were occasionally detected.



i

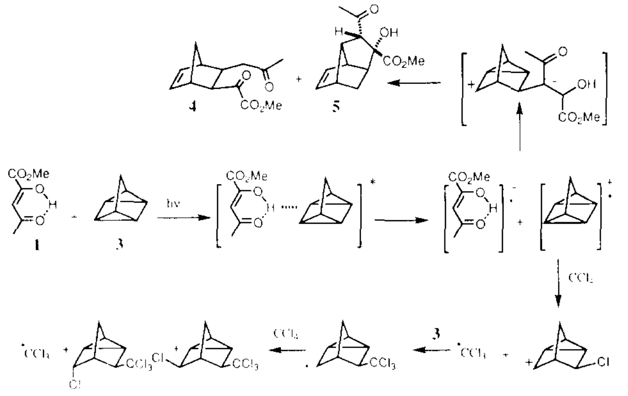


ii

for **10** and 7.70 for **11**, confirmed the geometrical isomerism, i.e. *Z* for **10** and *E* for **11**. At the same time, the changes in the chemical shifts of the norbornene olefinic protons were considerable, i.e. 5.87 and 6.21 (**9**) to 6.10 and 6.35 (**10**) to 6.10 and 6.48 (**11**).

According to Fehnel and Brokaw [8], the benzophenone-sensitized photoreaction of **2** gives **3**. The formation of the common products (**4** and **5**) from both **2** and **3** may therefore suggest that the irradiation of **2** in the presence of **1** also causes valence isomerization to **3**. However, gas–liquid chromatographic analysis confirms the absence of **3** in the reaction mixture of **2** and **1**. This eliminates the possibility of generating the photostationary mixture from **2** and **3** on exposure to UV light, and therefore the photoadditions of **2** and **3** with **1** proceed via independent pathways.

From a mechanistic point of view, the absence of **6** among the photoproducts of **3** is noteworthy, i.e. **1** attacks exclusively from the exo side of **3**, and the skeletally rearranged **5** is formed, but not **7** or **8**; if **R-ex$_2$** is formed by the reaction with **3** as a precursor of **5**, **7** and **8** should also be among the products as in the case of **2**. The formation of **5** from **3** can be explained by a different mechanism, i.e. via a zwitterionic intermediate (Scheme 4).[2] Taking the low oxidation potential of **3** into account, photoelectron transfer from **3** to the excited state of **1** is probable. To confirm this, the photoreaction was carried out in acetonitrile; a slight increase in the ratio of **4**/**5** favoured this prediction, but was not conclusive. However, a dramatic change occurred when the photoreaction was carried out in carbon tetrachloride [9]; the sole products were the cis and trans radical chain adducts (**12** and **13**) of **3**[4]. This could only be explained in terms of the generation of the radical species of **3**, i.e. the cation radical, to initiate the homolysis of the solvent. The abstraction of atomic chlorine from the solvent initiates the radical chain process to give the non-stereoselective formation of **12** and **13**.



Scheme 4.

3. Experimental details

Elemental analyses were performed by Mrs. R. Hatazoe of the Institute of Advanced Material Study, Kyushu University. The ^1H and ^{13}C NMR spectra were measured with a JEOL GSX-270H spectrometer in $CDCl_3$. The IR spectra were measured with a JASCO A102 spectrophotometer, and the mass spectra with a JEOL JMS-01SG-2 spectrometer.

3.1. *Photocycloaddition of 1 to 2*

A mixture of **1** (1.00 g) and **2** (6.4 g) dissolved in EtOAc solution (60 cm^3) was internally irradiated for 10 h by a 400 W high-pressure Hg lamp through a Pyrex glass filter under an N_2 atmosphere. The irradiation was stopped at the stage of 70% conversion. After evaporation of the volatile materials in vacuo, the residue obtained was washed with dilute $NaHCO_3$ and extracted with ether. The organic extract was dried over Na_2SO_4 and chromatographed on a silica gel column to furnish **4** (colourless oil, 342 mg, 28%; ^1H NMR $\delta = 1.35$ (1H, dq, $J = 9.2$, 1.6 Hz), 1.86 (1H, dm, $J = 9.2$ Hz), 2.07 (3H, s), 2.17 (1H, m with fine splitting, supposed to contain $J = 8.8$, 6.5 Hz), 2.56 (1H, br s), 2.66 (1H, dd, $J = 18.7$, 6.5 Hz), 2.71 (1H, dd, $J = 18.7$, 8.8 Hz), 2.89 (1H, br s), 3.47 (1H, dd, $J = 8.6$, 1.6 Hz), 3.87 (3H, s), 6.20 (1H, dd, $J = 5.5$, 3.1 Hz) and 6.27 (1H, dd, $J = 5.5$, 2.9 Hz); ^{13}C NMR $\delta = 30.1$, 38.9, 43.6, 46.1, 46.4, 47.0, 47.7, 53.1, 136.7, 139.0, 162.1, 197.0 and 209.1; IR ν: 2980, 1715, 1360, 1280, 1270, 1155, 1120, 1080, 1040, 760 and 715 cm^{-1}; mass spectrum (MS) *m/z* 236 (M^+, 7), 218 (29), 204 (12), 177 (100), 171 (15), 135 (10), 111 (34) and 66 (42); found: C, 65.84%; H 6.75%; calculated for $C_{13}H_{16}O_4$: C, 66.09%; H, 6.83%), **5** (colourless needles, melting point (m.p.) 99–100 °C, 32 mg, 3%; ^1H NMR $\delta = 0.86$ (1H, ddd, $J = 12.5$, 6.2, 1.1 Hz), 1.42 (1H, ddm, $J = 12.5$, 4.5 Hz), 1.94 (1H, dm, $J = 6.2$ Hz), 2.15 (3H, s), 2.50 (1H, m), 2.55 (1H, m), 3.25 (1H, s), 3.48 (1H, m), 3.85 (3H, s), 3.91 (1H, s, OH), 5.83 (1H, dd, $J = 5.3$, 3.1 Hz) and 6.24 (1H, dd, $J = 5.3$, 2.8 Hz); ^{13}C NMR $\delta = 28.3$, 30.6, 44.5, 44.7, 51.4, 52.9, 53.6, 60.0, 88.1, 129.2, 139.6, 173.6 and 208.7; IR ν: 3430, 2990, 2950, 1735, 1700, 1370, 1280, 1230, 1210, 1045 and 710 cm^{-1}; MS *m/z* 236 (M^+, 2), 128 (2), 193 (2), 177 (39), 176 (29), 122 (43), 121 (21), 117 (47) and 43 (100); found: C, 66.06%; H, 6.78%; calculated for $C_{13}H_{16}O_4$: C, 66.09%; H, 6.83%), **6** (colourless crystals, m.p. 113–114 °C, 96 mg, 8%; ^1H NMR $\delta = 0.90$ (1H, tm, $J = 5.5$ Hz), 1.05 (1H, br t, $J = 5.5$ Hz), 1.30 (1H, br t, $J = 5.5$ Hz), 1.53 (1H, br d,

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[2] The photocycloadditions of **1** with olefins in CCl_4 generally furnish normal [2 + 2] cycloadducts. Therefore the incorporation of the solvent residue in this case should be explained in terms of a different mechanism.

J = 11 Hz), 1.62 (1H, br d, J = 11 Hz), 2.06 (1H, quint, J = 2 Hz), 2.12 (3H, s), 2.37 (1H, tm, J = 2 Hz), 2.45 (1H, m), 3.45 (1H, s), 3.55 (1H, br s, OH) and 3.87 (3H, s); ^{13}C NMR δ = 11.9, 14.9, 15.1, 31.1 (2C), 40.9, 43.7, 53.0, 55.2, 60.4, 83.7, 175.1 and 207.6; IR ν: 3440, 2935, 1740, 1700, 1370, 1265, 1195, 1160, 1050 and 830 cm^{-1}; MS *m/z* 236 (M$^+$, 6), 193 (2), 177 (100), 135 (13), 117 (20), 91 (20) and 43 (67); found: C, 66.19%; H, 6.96%; calculated for $C_{13}H_{16}O_4$: C, 66.09%; H, 6.83%), **7** (colourless oil, 32 mg, 3%; ^{1}H NMR δ = 1.07 (2H, m), 1.59 (1H, m), 1.75 (1H, m), 2.17 (1H, dm, J = 11.7 Hz), 2.32 (3H, s), 2.63 (2H, br s), 3.88 (3H, s), 3.91 (1H, d, J = 11.7 Hz) and 6.10 (2H, m); ^{13}C NMR δ = 21.6, 21.8, 30.5, 42.9, 43.2, 53.4, 56.0, 62.6, 136.1, 136.6, 161.2, 188.7 and 201.9; IR ν: 2960, 1740, 1705, 1600, 1440, 1360, 1270, 1120, 1050 and 710 cm^{-1}; MS *m/z* 236 (M$^+$, 6), 177 (33), 166 (25), 106 (45), 93 (34), 83 (26) and 43 (100); found: *m/z* 236.1043 (M$^+$); calculated for $C_{13}H_{16}O_4$: M, 236.1048), and **8** (a trace amount; ^{1}H NMR δ = 2.13 (3H, s), 2.88 (1H, dm, J = 10.3 Hz), 3.20 (1H, dm, J = 10.3 Hz), 4.07 (1H, dm, J = 3.3 Hz), 6.71 (2H, m) and 6.84 (2H, m)).

3.2. Photocycloaddition of 1 to 3

(1) A mixture of **1** (1.00 g) and **3** (6.4 g) in EtOAc solution (30 cm^3) was internally irradiated for 8 h by a 400 W high-pressure Hg lamp through a Pyrex glass filter under an N_2 atmosphere. The irradiation was stopped at the stage of 29% conversion. After evaporation of the volatile materials in vacuo, the residue obtained was washed with dilute $NaHCO_3$ and extracted with ether. The organic extract was dried over Na_2SO_4 and chromatographed on a Florisil column to obtain **4** (69 mg, 15%), **5** (47 mg, 10%), **9** (a colourless oil, 8 mg, 2%; ^{1}H NMR δ = 1.53 (1H, dm, J = 9.1 Hz), 2.16 (3H, s), 2.17 (1H, d, J = 9.1 Hz), 2.45 (1H, dm, J = 5.1 Hz), 2.91 (1H, br s), 3.04 (1H, br s), 3.09 (1H, d, J = 17.6 Hz), 3.21 (1H, d, J = 17.6 Hz), 3.82 (3H, s), 4.70 (1H, dm, J = 5.1 Hz), 5.87 (1H, dd, J = 5.5, 3.1 Hz) and 6.21 (1H, dd, J = 5.5, 3.3 Hz); ^{13}C NMR δ = 30.5, 40.9, 42.3, 44.2, 44.7, 45.0, 52.7, 80.9, 82.2, 132.5, 139.8, 174.3 and 204.8. IR ν: 2960, 1715, 1435, 1360, 1260, 1230, 1080 and 940 cm^{-1}; MS *m/z* 236 (M$^+$, 5), 218 (10), 190 (44), 177 (28), 176 (22), 175 (4), 131 (20) and 66 (100); found: *m/z*, 236.1052 (M$^+$); calculated for $C_{13}H_{16}O_4$: M, 236.1048) and **10** (colourless needles, m.p. 108–109 °C, 56 mg, 100%; ^{1}H NMR δ = 1.53 (1H, dm, J = 10 Hz), 1.67 (1H, dm, J = 10 Hz), 2.46 (3H, s), 2.85 (1H, m), 2.92 (1H, dm, J = 6.2 Hz), 3.13 (1H, m), 4.52 (1H, dt, J = 6.2, 1 Hz), 6.10 (1H, dd, J = 6, 3 Hz), 6.35 (1H, d, J = 6, 3 Hz) and 6.43 (1H, d, J = 2.2 Hz); ^{13}C NMR δ = 30.7, 41.9, 44.1, 46.7, 48.8, 81.7, 133.3, 133.8, 137.6, 140.1, 169.9 and 202.1. IR ν: 2990, 2950, 1752, 1700, 1354, 1320, 1190, 1120, 1030, 1005 and 720 cm^{-1}; MS *m/z* 204 (M$^+$, 6), 175 (6), 161 (14), 139 (18), 66 (100) and 43 (25); found: C, 70.64%; H, 6.01%; calculated for $C_{12}H_{12}O_3$: C, 70.57%; H, 5.92%).

(2) A mixture of **1** (300 mg) and **3** (1.9 g) in MeCN (30 cm^3) and MeOH (10 cm^3) was internally irradiated for 8 h by a 400 W high-pressure Hg lamp through a Pyrex glass filter under an N_2 atmosphere. The irradiation was stopped at the stage of 47% conversion. After evaporation of the volatile materials in vacuo, the residue obtained was washed with dilute $NaHCO_3$ and extracted with ether. The organic extract was dried over Na_2SO_4 and chromatographed on a silica gel column to obtain **4** (160 mg, 21%), **5** (62 mg, 8%) and **10** (71 mg, 11%).

(3) A mixture of **1** (1.00 g) and **3** (3.3 g) in hexane (90 cm^3) was internally irradiated for 8 h by a 400 W high-pressure Hg lamp through a Pyrex glass filter under an N_2 atmosphere. The irradiation was stopped at the stage of 47% conversion. After evaporation of the volatile materials in vacuo, the residue obtained was washed with dilute $NaHCO_3$ and extracted with ether. The organic extract was dried over Na_2SO_4 and chromatographed on a silica gel column to obtain **4** (428 mg, 29%) and **5** (198 mg, 14%).

(4) A mixture of **1** (1.00 g) and **3** (3.0 g) in CCl_4 (60 cm^3) was internally irradiated for 8 h by a 400 W high-pressure Hg lamp through a Pyrex glass filter under an N_2 atmosphere. The irradiation was stopped at the stage of 83% conversion. After evaporation of the volatile materials in vacuo, the residue obtained was washed with dilute $NaHCO_3$ and extracted with ether. The organic extract was dried over Na_2SO_4 and chromatographed on a silica gel column to obtain **12** and **13** (colourless oil, 306 mg, 22%; ^{1}H NMR δ = 1.43 (1H, br d, J = 11.6 Hz), 1.6–1.8 (4H, m), 2.46 (1H, br s), 3.59 (1H, br s) and 3.99 (1H, br s); ^{13}C NMR δ = 15.5, 15.9, 20.1, 28.5, 42.5, 63.6, 65.5 and 100.7 for **12**; ^{1}H NMR δ = 1.6–1.8 (3H, m), 2.00 (1H, br d, J = 12.0 Hz), 2.35 (1H, br d, J = 12.0 Hz), 2.52 (1H, br s), 2.80 (1H, br s) and 3.89 (br s); ^{13}C NMR δ = 13.0, 18.8, 20.3, 26.3, 42.6, 63.9, 64.1 and 100.0 for **13**; found: *m/z*, 243.9374, 245.9342, 247.9318; calculated for $C_8H_8Cl_4$: M, 243.9374, 245.9342, 247.9318), but no **4**, **5**, **9** or **10**.

3.3. Conversion of 9 to 10

A hexane solution of **9** (4.0 mg) was kept on a silica gel column for 1 h, and then eluted with EtOAc to give **10** (3.9 mg, 89%).

*3.4. Conversion of **10** to **11***

A $CHCl_3$ solution of **10** (26 mg) was kept at room temperature for 16 h. Evaporation of the solvent left **11** (colourless needles, m.p. 76–77 °C, 26 mg, 100%; ^1H NMR $\delta = 1.33$ (1H, br d, $J = 9.9$ Hz), 1.59 (1H, br d, $J = 9.9$ Hz), 2.40 (3H, s), 3.05 (1H, br s), 3.16 (1H, br s), 3.37 (1H, br d, $J = 5.9$ Hz), 4.54 (1H, br d, $J = 5.9$ Hz), 6.10 (1H, dd, $J = 5.9$, 3.3 Hz), 6.48 (1H, dd, $J = 5.9$, 3.0 Hz) and 7.20 (1H, d, $J = 2.5$ Hz). δ (C_6D_6) = 1.13 (1H, br d, $J = 9.9$ Hz), 1.21 (1H, br d, $J = 9.9$ Hz), 1.67 (3H, s), 2.68 (1H, br s), 2.88 (1H, br s), 3.02 (1H, br d, $J = 6.2$ Hz), 3.93 (1H, br d, $J = 6.2$ Hz), 5.51 (1H, dd, $J = 5.5$, 3.3 Hz), 6.05 (1H, dd, $J = 5.5$, 3.0 Hz) and 6.77 (1H, d, $J = 2.6$ Hz); ^{13}C NMR $\delta = 32.1$, 42.4, 44.9, 47.0 (2C), 82.5, 128.9, 133.2, 141.4, 142.4, 172.4 and 197.8; IR ν: 2980, 1770, 1700, 1340, 1330, 1290, 1250, 1210, 1100, 1030 and 1010 cm^{-1}; MS m/z 204 (M^+, 11), 175 (1), 162 (9), 161 (60), 139 (30), 66 (100) and 43 (17); found: C, 70.80%; H, 5.95%; calculated for $C_{12}H_{12}O_3$: C, 70.57%; H, 5.92%).

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