Novel Acid-catalysed Rearrangement of 4-Substituted Pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decan-6-ones; X-Ray Molecular Structure of 1-Phenylpentacyclo[4.4.0.0^{2,10}.0^{3,8}.0^{5,7}]decan-4-one

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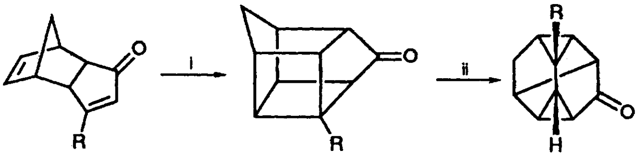
4-Substituted pentacyclo[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]decan-6-one derivatives **2a** and **b** undergo a novel acid- or Ag$^+$-catalysed rearrangement to the hitherto unknown pentacyclo[4.4.0.0^{2,10}.0^{3,8}.0^{5,7}]decane ring system **3a** and **b**. The structure of compound **3a** was established by X-ray crystallographic analysis.

Although it is well documented that certain metal-catalysed rearrangements of cubane, homocubane, and 1,8-bishomocubane derivatives give cuneanes or their congeners by skeletal reorganisation,[1] 1,3-bishomocubane derivatives have been known to undergo only cage-opening reaction by reaction with acid,[2] Rh^I,[3] or Ag^I ion[4] and no report has appeared on such skeletal rearrangements with 1,3-bishomocubane derivatives.

In connection with our previous papers concerning the ring-opening reactions of trishomocubanones with acid or Rh^I,[5] we report here the first acid- or Ag$^+$-catalysed skeletal rearrangement of 4-phenyl- and 4-methyl-1,3-bishomocubanones **2a** and **2b** to a new pentacyclo[4.4.0.0^{2,10}.0^{3,8}.0^{5,7}]decan-4-one system **3a** and **b**, and the X-ray structure determination of one of the products.



(1) **(2)** **(3)**

a; R = Ph
b; R = Me
c; R = H
d; R = OMe

a; R = Ph
b; R = Me

Reagents and conditions: i, *hv*; ii, $BF_3 \cdot Et_2O$.

The cage ketones **2a** and **2b** were obtained by irradiation of the dienones **1a** and **1b**, which were prepared by the reaction of compound **1d**[2] with PhLi and MeLi, respectively. While compound **2b** was obtained as the sole photochemical product, compound **2a** was obtained along with the head-to-head, *cis-anti-cis* photodimer of compound **1a**.†

Reaction of compound **2a** with BF_3 in benzene at room temperature for 30 min and chromatographic separation of the products, furnished compound **3a** in 41% yield. No dienone products were isolated.

The IR spectrum of compound **3a** showed an absorption band for a saturated carbonyl group (1720 cm^{-1}), and the ^1H NMR spectrum did not show any signals for olefinic protons, suggesting that the product is a saturated pentacyclic ketone.

Moreover, the ^{13}C NMR spectrum of compound **3a** (see Table 1) showed six signals upfield of δ_C 35, a region where no signals were observed in the spectrum of compound **2a**. This strongly suggests the presence of two cyclopropane rings in compound **3a**. From these spectral data and from mechanistic considerations analogous to those for the Ag$^+$-catalysed reactions of cubanes[1] the structure **3a** can be deduced for the product of acid-catalysed reaction of compound **2a**.

Table 1. ^{13}C NMR chemical shifts and multiplicities of compounds **3a** and **3b**.

3a	3b	
215.36 (s)	216.46 (s)	C-4
48.05 (d)	47.83 (d)	C-2, -3, -5, -6, -7, -8 and -10
40.68 (d)	38.51 (d)	
37.03 (d)	37.11 (d)	
32.17 (d)	32.38 (d)	
28.95 (d)	29.00 (d)	
26.07 (d)	26.00 (d)	
25.57 (d)	25.34 (d)	
30.24 (t)	30.10 (t)	C-9
24.24 (s)	15.63 (s)	C-1
143.48 (s) 128.52 (2 C, d) 127.31 (2 C, d) 126.31 (d)	22.39 (q)	Ph for **3a**; Me for **3b**

An X-ray crystallographic analysis was carried out to establish the structure of compound **3a**. Figure 1 shows a perspective view of one molecule of compound **3a**. Selected fractional atomic co-ordinates are listed in Table 2, and interatomic distances and bond angles are listed in Table 3.

Although compound **2b** was similarly transformed into compound **3b** in 33% yield (room temperature; 21 h), the unsubstituted cage ketone **2c**[6] was recovered unchanged after reaction with BF_3 for 55 h at room temperature. The structure of compound **3b** was deduced from its spectral data, especially the ^{13}C NMR spectrum (see Table 1), which closely resembled those for compound **3a**.

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† Our photochemical studies of compounds **1a** and **1b** and the structure elucidation of the photodimer of compound **1a** will appear elsewhere.

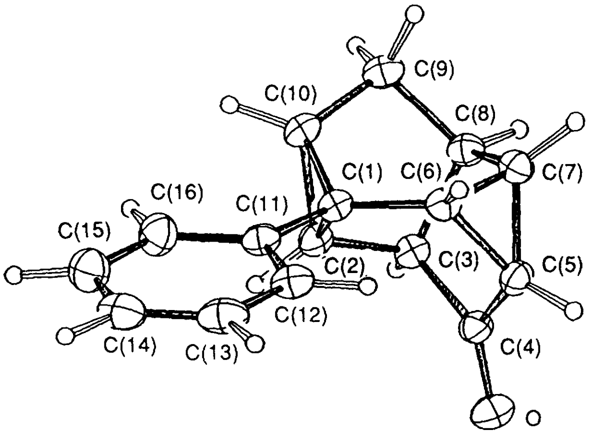
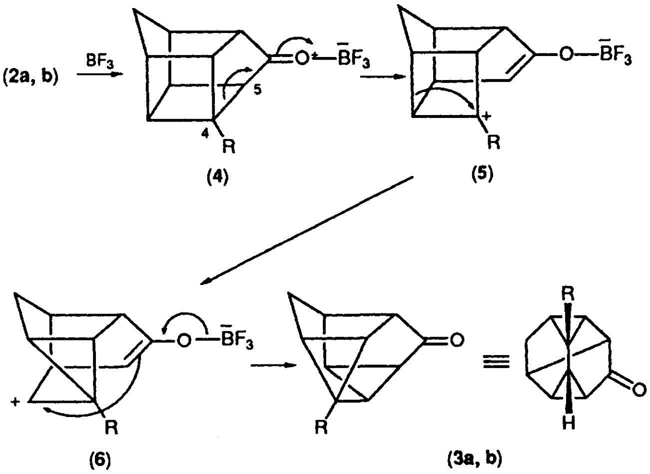


Fig. 1. ORTEP drawing of the compound **3a**.

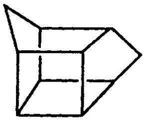
Table 2. Fractional co-ordinates ($\times 10^4$) for *compound* **3a** with esds in parentheses.

Atom	*x*	*y*	*z*
O	5633(1)	745(2)	3684(2)
C(1)	4920(2)	−3562(3)	1979(2)
C(2)	4482(2)	−3024(3)	2924(2)
C(3)	5434(2)	−2174(3)	4066(2)
C(4)	5841(2)	−698(3)	3577(2)
C(5)	6557(2)	−1332(3)	2991(2)
C(6)	6121(2)	−2973(3)	2281(2)
C(7)	7008(2)	−2993(3)	3624(2)
C(8)	6458(2)	−3415(3)	4483(2)
C(9)	5914(2)	−5124(3)	4112(2)
C(10)	4824(2)	−4796(3)	2906(2)
C(11)	4030(2)	−3600(3)	623(2)
C(12)	4250(2)	−2899(3)	−327(2)
C(13)	3411(2)	−2882(3)	−1569(2)
C(14)	2336(2)	−3537(3)	−1900(2)
C(15)	2094(2)	−4240(3)	−986(3)
C(16)	2931(2)	−4269(3)	254(2)

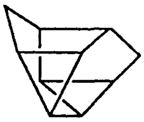
The formation of products **3a** and **3b** can be rationalised as depicted in Scheme 1. Taking into account the fact that the reaction is accelerated by the substituent at C-4 in the order Ph > Me > H, the formation of the cyclobutanium cation **5** *via* fission of the C-4–C-5 bond in the BF_3 complex of the substrate **4** may be regarded as the rate-determining step, and the remaining rearrangement $\mathbf{5} \longrightarrow \mathbf{6} \longrightarrow \mathbf{3a,b}$ proceeds rapidly. The strain energy obtained by MM2 calculation[7] for the skeletal hydrocarbon **7** is 27.5 kJ mol^{-1} lower than that for hydrocarbon **8** as shown below. The driving force of the reaction $\mathbf{2} \longrightarrow \mathbf{3}$ can thus be explained in terms of thermodynamic control.



Scheme 1.



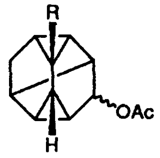
(7)



(8)

Strain energy (kJ mol^{-1})	320.6	293.1

Although the reaction $\mathbf{2} \longrightarrow \mathbf{3}$ is strikingly similar to the silver ion-catalysed rearrangements observed for cubane, homocubane, and 1,8-bishomocubane systems,[1] to the best of our knowledge this is the first example of this type of reaction observed as an acid-catalysed ketone–ketone rearrangement.[8] The reaction $\mathbf{2} \longrightarrow \mathbf{3}$ was also catalysed by $AgClO_4$ (benzene; room temp.; 5 h; 26%). However, the presence of the carbonyl group seems to be essential for this ring system to undergo the silver ion-catalysed rearrangement, because treatment of the corresponding acetate **9** [obtained as a single compound by reduction of compound **2a** with $NaBH_4$ followed by conventional acetylation; see Experimental section] with $AgClO_4$ only resulted in recovery of the starting material.



(9)

Experimental

M.p.s were determined on a Yanaco micro melting point apparatus and are uncorrected. IR spectra were recorded on a JASCO A-3 spectrophotometer. UV spectra were obtained on a JASCO UVIDEC-505 spectrophotometer. ^1H NMR spectra were determined on JEOL JNM-GX 270 (270 MHz) and Hitachi R-600 (60 MHz) spectrometers. ^{13}C NMR spectra (in $CDCl_3$) were obtained on a JEOL JNM-GX 270 (67.5 MHz) spectrometer. Mass measurements were obtained on a Hitachi M-60 mass spectrometer at an ionisation potential of 70 eV. Photochemical reactions were carried out on solutions under nitrogen in Pyrex tubes by using a 300 W high-pressure mercury lamp. Extracts were dried ($MgSO_4$).

5-Phenyltricyclo[5.2.1.0^{2,6}]*deca-4,8-dien-3-one* **1a**.—To a stirred solution of compound **1d**[2] (19.3 g, 0.11 mol) in dry Et_2O (300 cm^3 at 0 °C under nitrogen was added an ethereal solution of phenyl-lithium (1.09 mol dm^{-3}; 95 cm^3 during 1 h, and the mixture was refluxed for another 2 h. The solution was poured into ice-cold 25% sulphuric acid, and stirred vigorously for 2 h. Most of the organic solvent was evaporated off and the aq. solution was extracted with CH_2Cl_2. The extract was washed successively with aq. sodium hydrogen carbonate and brine, dried, and evaporated to dryness. Chromatography on silica gel and crystallisation from CH_2Cl_2–hexane yielded *compound* **1a** (15.2 g, 62%), m.p. 123–124 °C (Found: C, 86.4; H, 6.4. $C_{16}H_{14}O$ requires C, 86.45; H, 6.35%); $\nu_{max}(CHCl_3)$ 1675 cm^{-1} (α,β-unsaturated ketone); λ_{max}(cyclohexane) 222 and

Table 3. Selected bond distances/Å and angles (°) with esds in parentheses.

O–C(4)	1.215(3)	C(1)–C(2)	1.522(3)
C(1)–C(6)	1.497(3)	C(1)–C(10)	1.524(3)
C(1)–C(11)	1.489(3)	C(2)–C(3)	1.515(3)
C(2)–C(10)	1.501(3)	C(3)–C(4)	1.517(3)
C(3)–C(8)	1.549(3)	C(4)–C(5)	1.470(3)
C(5)–C(6)	1.533(3)	C(5)–C(7)	1.518(3)
C(6)–C(7)	1.478(3)	C(7)–C(8)	1.512(3)
C(8)–C(9)	1.520(4)	C(9)–C(10)	1.504(4)
C(2)–C(1)–C(6)	114.7(2)	C(2)–C(1)–C(10)	59.0(2)
C(2)–C(1)–C(11)	115.7(2)	C(6)–C(1)–C(10)	116.4(2)
C(6)–C(1)–C(11)	118.2(2)	C(10)–C(1)–C(11)	119.0(2)
C(1)–C(2)–C(3)	111.3(2)	C(1)–C(2)–C(10)	60.6(2)
C(3)–C(2)–C(10)	108.7(2)	C(2)–C(3)–C(4)	107.3(2)
C(2)–C(3)–C(8)	102.7(2)	C(4)–C(3)–C(8)	103.9(2)
O–C(4)–C(3)	125.8(2)	O–C(4)–C(5)	126.7(2)
C(3)–C(4)–C(5)	107.5(2)	C(4)–C(5)–C(6)	113.9(2)
C(4)–C(5)–Ç(7)	105.0(2)	C(6)–C(5)–C(7)	57.9(2)
C(1)–C(6)–C(5)	119.3(2)	C(1)–C(6)–C(7)	117.9(2)
C(5)–C(6)–C(7)	60.5(2)	C(5)–C(7)–C(6)	61.5(2)
C(5)–C(7)–C(8)	109.7(2)	C(6)–C(7)–C(8)	110.6(2)
C(3)–C(8)–C(7)	103.3(2)	C(3)–C(8)–C(9)	106.3(2)
C(7)–C(8)–C(9)	107.8(2)	C(8)–C(9)–C(10)	102.9(2)
C(1)–C(10)–C(2)	60.4(2)	C(1)–C(10)–C(9)	116.8(2)
C(2)–C(10)–C(9)	108.0(2)	C(1)–C(11)–C(12)	121.1(2)

277 nm (ε 10 000 and 19 900 dm^3 mol^{-1} cm^{-1}; δ_H(270 MHz; $CDCl_3$) 1.70 (1 H, d, *J* 8.2 Hz, 10-H), 1.79 (1 H, d, *J* 8.2 Hz, 10-H), 3.03 (1 H, t, *J* 5.2 Hz, 2- or 6-H), 3.18 (1 H, m, 1- or 7-H), 3.26 (1 H, m, 7- or 1-H), 3.83 (1 H, t, *J* 5.2 Hz, 6- or 2-H), 5.63 (1 H, dd, *J* 6 and 3 Hz, 8- or 9-H), 6.01 (1 H, dd, *J* 6 and 3 Hz, 9- or 8-H), 6.30 (1 H, s, C=CHC=O), and 7.25–7.67 (5 H, m, Ph); δ_C(67.5 MHz; $CDCl_3$) 209.23 (s, C=O), 173.80 (s), 133.89 (s), 133.55 (d), 132.02 (d), 131.00 (d), 129.85 (d), 128.93 (2 C, d), 127.08 (2 C, d), 52.15 (d), 52.06 (t), 47.53 (d), 44.85 (d) and 44.35 (d); *m*/*z* 222 (M^+), 157 ($M^+ - C_5H_5$) and 66 (C_5H_6, 100%).

5-*Methyltricyclo*[5.2.1.0^{2,6}]*deca*-4,8-*dien*-3-*one* **1b**.—To a stirred solution of compound **1d** (5.24 g, 0.0297 mol) in dry Et_2O (80 cm^3) at room temperature under nitrogen was added a solution of methyllithium in Et_2O (0.93 mol dm^{-3}; 50 cm^3) during 80 min. The reaction mixture was refluxed for 80 min, poured into ice-cold 25% sulphuric acid, and stirred vigorously for 2 h. Most of the organic solvent was evaporated off and the aq. solution was extracted with CH_2Cl_2. The extract was washed successively with aq. sodium hydrogen carbonate containing Na_2SO_3 and brine, dried, and evaporated to dryness. Chromatography on silica gel with CH_2Cl_2 as eluant and bulb-to-bulb distillation yielded *compound* **1b** (3.18 g, 67%), m.p. 48.0–48.5 °C (Found: C, 82.0; H, 7.5. $C_{11}H_{12}O$ requires C, 82.46; H, 7.55%); ν_{max}($CHCl_3$) 1680 and 1615 cm^{-1} (α,β-unsaturated ketone); λ_{max}(cyclohexane) 223 nm (ε 10 470 dm^3 mol^{-1} cm^{-1}); δ_H(270 MHz; $CDCl_3$) 1.59 (1 H, d, *J* 8.5 Hz, 10-H), 1.77 (1 H, d, *J* 8.5 Hz, 10-H), 1.98 (3 H, s, 5-Me), 2.85 (1 H, t, *J* 5.5 Hz, 2- or 6-H), 3.00 (1 H, m, 1- or 7-H), 3.19 (1 H, m, 7- or 1-H), 3.22 (1 H, t, *J* 5.5 Hz, 6- or 2-H), 5.69 (1 H, s, C=CHC=O), 5.79 (1 H, dd, *J* 5.5 and 2.75 Hz, 8- or 9-H), and 5.99 (1 H, dd, *J* 5.5 and 2.75 Hz, 9- or 8-H); δ_C(67.5 MHz; $CDCl_3$) 209.86 (s, C=O), 178.16 (s), 133.67 (d), 133.13 (d), 131.52 (d), 52.43 (t), 51.77 (d), 51.23 (d), 44.37 (d), 43.36 (d) and 18.13 (q, Me); *m*/*z* 160 (M^+), 95 ($M^+ - C_5H_5$) and 66 (C_5H_6, 100%).

4-*Phenylpentacyclo*[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]*decan*-6-*one* **2a**.—A solution of compound **1a** (1.10 g, 4.95 mmol) in benzene (800 cm^3) was irradiated at room temperature for 6.5 h, and evaporated to dryness. Chromatography on silica gel with benzene–Et_2O yielded *compound* **2a** (0.60 g, 54%) as an oil, together with the photodimer (0.24 g, 22%) of compound **1a** and unchanged substrate **1a** (0.11 g, 10% recovery). For compound **2a** (Found: C, 86.35; H, 6.4. $C_{16}H_{14}O$ requires C, 86.45; H, 6.35%); ν_{max}($CHCl_3$) 1755 cm^{-1} (cyclopentanone); δ_H(270 MHz; $CDCl_3$) 1.72 (1 H, d, *J* 11.6 Hz, 10-H), 1.81 (1 H, d, *J* 11.6 Hz, 10-H), 2.40 (1 H, m), 2.57 (1 H, d, *J* 5.5 Hz), 2.95 (1 H, q, *J* 6.0 Hz), 3.02 (1 H, m), 3.10 (1 H, q, *J* 5.0 Hz), 3.22 (1 H, m), 3.32 (1 H, dt, *J* 6.7 and 5.0 Hz), and 7.04–7.35 (5 H, m, Ph); δ_C(67.5 MHz; $CDCl_3$) 216.62 (s, C=O), 142.48 (s), 128.50 (2 C, d), 126.36 (d), 124.94 (2 C, d), 51.05 (d), 48.32 (d), 46.29 (d), 46.24 (d), 45.50 (s), 43.18 (d), 41.67 (t), 41.51 (d) and 35.54 (d); *m*/*z* 222 (M^+) and 194 ($M^+ - CO$, 100%).

4-*Methylpentacyclo*[5.3.0.0^{2,5}.0^{3,9}.0^{4,8}]*decan*-6-*one* **2b**.—A solution of compound **1b** (3.18 g, 19.9 mmol) in benzene (1000 cm^3) was irradiated at room temperature for 21 h, and evaporated to dryness. Chromatography on silica gel with CH_2Cl_2 as eluant yielded *compound* **2b** (2.07 g, 65%) as an oil (Found: C, 82.2; H, 7.6. $C_{11}H_{12}O$ requires C, 82.46; H, 7.55%); ν_{max}($CHCl_3$) 1750 cm^{-1} (cyclopentanone); δ_H(270 MHz; $CDCl_3$) 1.13 (3 H, s, Me), 1.59 (1 H, d, *J* 11.3 Hz, 10-H), 1.71 (1 H, d, *J* 11.3 Hz, 10-H), 2.13 (1 H, d, *J* 5 Hz), 2.25 (1 H, m), 2.67 (1 H, q, *J* 5 Hz), 2.81 (2 H, m), 2.92 (1 H, br s), and 3.04 (1 H, br s); δ_C(67.5 MHz; $CDCl_3$) 217.55 (s, C=O), 51.50 (d), 46.27 (d), 46.20 (d), 46.00 (d), 43.22 (d), 41.55 (t), 40.61 (d), 40.13 (s), 35.71 (d) and 19.68 (q, Me); *m*/*z* 160 (M^+), 145 ($M^+ - Me$), 132 ($M^+ - CO$) and 117 ($M^+ - CO - Me$, 100%).

BF_3-Catalysed Transformation of Compound **2a** *into Compound* **3a**.—To a solution of compound **2a** (774 mg, 3.49 mmol) in benzene (60 cm^3) was added BF_3–diethyl ether (0.8 cm^3), and the mixture was stirred for 30 min at room temperature, then washed with aq. sodium hydrogen carbonate, and the washings were extracted with benzene. The combined organic solution was washed with brine, dried over $MgSO_4$, and evaporated under reduced pressure. The residue was chromatographed on silica gel with benzene as eluant to yield *compound* **3a** (325 mg, 42%), m.p. 61–61.5 °C (Found: C, 86.4; H, 6.35. $C_{16}H_{14}O$ requires C, 86.45; H, 6.35%); ν_{max}($CHCl_3$) 1720 cm^{-1}; λ_{max}(cyclohexane) 218 nm (ε 9960 dm^3 mol^{-1} cm^{-1}); δ_H(270 MHz; $CDCl_3$) 1.63 (1 H, ddd, *J* 7.6, 5.0 and 1.6 Hz), 2.00–2.19 (6 H, m), 2.42 (1 H, t, *J* 5.3 Hz), 2.91 (1 H, q, *J* 5.3 Hz) and 7.18–7.35 (5 H, m, Ph); δ_C(67.5 MHz; $CDCl_3$) see Table 1; *m*/*z* 222 (M^+), 194 ($M^+ - CO$) and 91 ($C_7H_7^+$, 100%).

BF_3-Catalysed Transformation of Compound **2b** *into Compound* **3b**.—To a solution of compound **2b** (90 mg, 0.56 mmol) in benzene (6 cm^3) was added BF_3–diethyl ether (0.2 cm^3), and the mixture was stirred for 21 h at room temperature, then washed with aq. sodium hydrogen carbonate, and the washings were extracted with benzene. The combined organic solution was washed with brine, dried over $MgSO_4$, and evaporated under reduced pressure. The residue was chromatographed on silica gel with benzene as eluant to yield *compound* **3b** (30 mg, 33%) as pale yellow oil (Found: C, 82.1; H, 7.7. $C_{11}H_{12}O$ requires C, 82.46; H, 7.55%); ν_{max}($CHCl_3$) 1715 cm^{-1}; λ_{max}(EtOH) 216 nm (ε 2290 dm^3 mol^{-1} cm^{-1}); δ_H(270 MHz; $CDCl_3$) 1.16 (3 H, s, Me), 1.42 (1 H, m), 1.51 (1 H, ddd, *J* 8.0, 4.0 and 1.5 Hz), 1.67 (2 H, m), 1.88 (1 H, br s), 2.06 (1 H, dt, *J* 8.0 and 5.4 Hz), 2.29 (1 H, t, *J* 5.4 Hz), and 2.81 (2 H, q, *J* 5.4 Hz); δ_C(67.5 MHz; $CDCl_3$) see Table 1; *m*/*z* 160 (M^+), 132 ($M^+ - CO$) and 117 ($M^+ - CO - Me$, 100%).

Ag^+-Catalysed Transformation of Compound **2a** *into Compound* **3a**.—A solution of compound **2a** (200 mg, 0.90 mmol) and silver perchlorate (270 mg, 1.30 mmol) in benzene (6.5 cm^3) was stirred at room temperature in the dark for 5 h.

The mixture was washed with aq. sodium hydrogen carbonate, and the washings were extracted with benzene. The combined extract was washed with brine, dried over $MgSO_4$, and evaporated under reduced pressure. The residue was chromatographed on silica gel with benzene as the eluant to yield compound **3a** (52 mg, 26%) and compound **2a** (110 mg, 55% recovery).

Acetate **9**.—To a solution of $NaBH_4$ (36 mg, 0.95 mmol) in methanol (5 cm^3) at 0 °C was added a solution of compound **2a** (110 mg, 0.495 mmol) portionwise. The solution was stirred for 30 min and then concentrated under reduced pressure. The residue was dissolved in CH_2Cl_2 and the solution was washed with brine, dried over $MgSO_4$, and evaporated to give an alcohol (102 mg, 92%), m.p. 105.5–107 °C. The product was dissolved in acetic anhydride (5 ml) and refluxed for 1 h. The mixture was poured into water, and the mixture was stirred at room temperature for 1.5 h, and extracted with CH_2Cl_2. The extracts were washed successively with aq. $NaHCO_3$ and brine, dried over $MgSO_4$, and evaporated. The residue was chromatographed on silica gel with benzene as eluant to yield the *acetate* **9** (95 mg, 78%) as an oil (Found: C, 80.9; H, 6.9. $C_{18}H_{18}O_2$ requires C, 81.18; H, 6.81%); $\nu_{max}(CHCl_3)$ 1725 cm^{-1}; δ_H(60 MHz; $CDCl_3$) 1.36 (1 H, d, J 11.2 Hz, 10-H), 1.72 (1 H, d, J 11.2 Hz, 10-H), 1.90 (3 H, s, Ac), 2.04 (1 H, s), 2.5–3.2 (6 H, m), 5.7 (1 H, br s, C*H*OAc) and 7.1–7.4 (5 H, m, Ph).

X-Ray Structure Analysis of Compound **3a**.—*Crystal data:* $C_{16}H_{14}O$, $M = 222.27$. Monoclinic; space group $P2_1/a$, $a = 12.863(3)$, $b = 8.079(2)$, $c = 11.793(4)$ Å, $\beta = 101.76(2)°$, $V = 1094.3(5)$ Å^3, $Z = 4$ and $D_c = 1.35$ g cm^{-3}. A crystal of dimension *ca.* 0.3 × 0.3 × 0.5 mm was used. The lattice parameters were obtained from least-squares analysis of 25 reflections with $7.3 < \theta < 14.2°$ from graphite-monochromated Mo-Kα radiation ($\lambda = 0.710\,73$ Å) on a Syntex-R3 diffractiometer.

Intensity data of 2691 reflections were collected at room temperature by ω–2θ scan technique with $1 < \theta < 27.5°$ and $-17 \le h \le 17$, $0 \le k \le 11$, $0 \le l \le 16$. Intensity standards were measured every 200 reflections; no significant decomposition of the crystal was observed.

Of the 2691 total unique reflections, 2028 were considered observed at the level of $|F_o| > 3.0\sigma|F_o|$. Data were corrected for Lorentz and polarisation effects in the usual way but not for absorption as the linear absorption coefficient was small [$\lambda(MoK\alpha) = 0.9\ cm^{-1}$].

The structure was solved by direct methods (MULTAN78). All non-hydrogen atoms were located on the initial *E*-synthesis. All hydrogens were located by the difference Fourier map and included in the further calculations. Block-diagonal least-squares refinements with 17 anisotropic non-hydrogen atoms and 14 isotropic hydrogens were used. The weighting scheme $w = 1/[\sigma^2(F_o)]$, with $\sigma(F_o)$ from counting statistics, gave satisfactory agreement analysis. Final R- and R_w-values were 0.061 and 0.051.

All calculations were performed on a HITAC M-200H computer at the Hiroshima University using structure analysis program system UNICS3.[9,*]

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[*] *Supplementary data* (see section 5.6.3 of Instructions for Authors, January issue). Full lists of atomic co-ordinates and tables of thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.