Rearrangement of dithianylcyclobutachromanol derivatives to 1,2,2a,8,9,9a-hexahydrocyclobuta[*b*][1]benzoxepin-8,9-dione

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A novel rearrangement of dithianylcyclobutachromanol derivative 3a on treatment with mercuric oxide and fluoroboric acid in aqueous tetrahydrofuran leads to 1,2,2a,8,9,9a-hexahydro-2a,9a-dimethylcyclobuta[*b*]-[1]benzoxepin-8,9-dione whose structure is established by X-ray analysis.

A few years ago we reported a novel and efficient strategy for the stereocontrolled construction of a functionalised seven-membered ring system by simple acid-catalysed rearrangement of an α-hydroxycyclobutane derivative followed by retroaldol cleavage in one pot.[1] This methodology has become generally used in the synthesis of a variety of *cis*- and *trans*-fused angularly functionalised six- and seven-membered carbocycles.[2] To make it more useful for natural product synthesis we sought to construct the seven-membered heterocyclic system with oxygen as the heteroatom from the dithianylcyclobutachromanol **3a** following the same strategy.

For this purpose a solution of **1a**[3] and ethene in benzene was irradiated to produce the cyclobutachromanone **2a**[4] which was then treated with 2-lithio-1,3-dithiane[2] to furnish the desired dithiane alcohol **3a** in good yield (Scheme 1). When this alcohol was subjected to rearrangement with mercuric oxide and fluoroboric acid in aqueous THF in the usual way,[1] instead of the expected product, **6a**, a pale yellow solid α-diketone **4a** (mp 85 °C, 60% yield) and a small amount (15%) of an α-hydroxy aldehyde **5a**† were isolated. The structure of the diketone **4a** was in agreement with its spectral and analytical data‡ and was finally confirmed by single-crystal X-ray analysis.§ This α-diketone **4a** constitutes an interesting and unique system incorporating a 1,2,2a,8,9,9a-hexahydrocyclobuta[*b*][1]benzoxepin-8,9-dione unit (Fig. 1) which to the best of our knowledge has not been reported. This rearrangement is also observed when the dithiane alcohols **3b** and **3c** were treated in the same way, producing α-diketones **4b** and **4c** respectively associated with the regenerated aldehydes **5b** and **5c** (Scheme 1). Lower yield (6%) of α-diketone from the alcohol

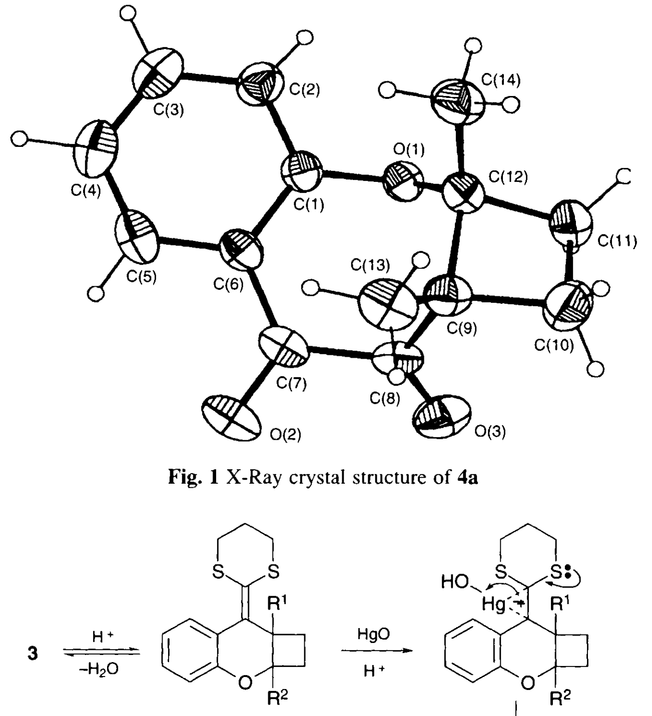
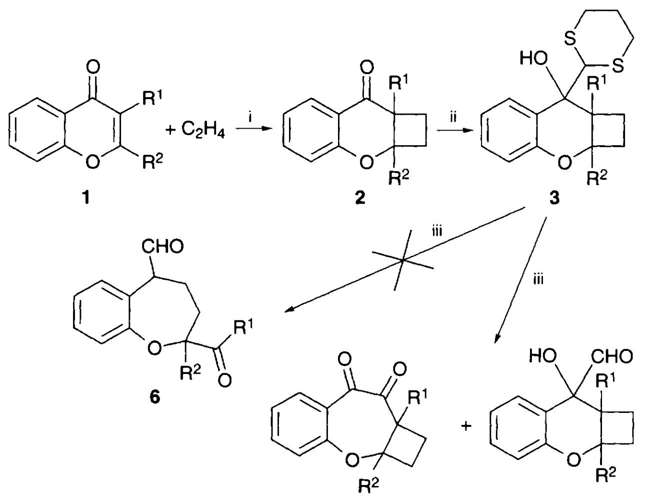
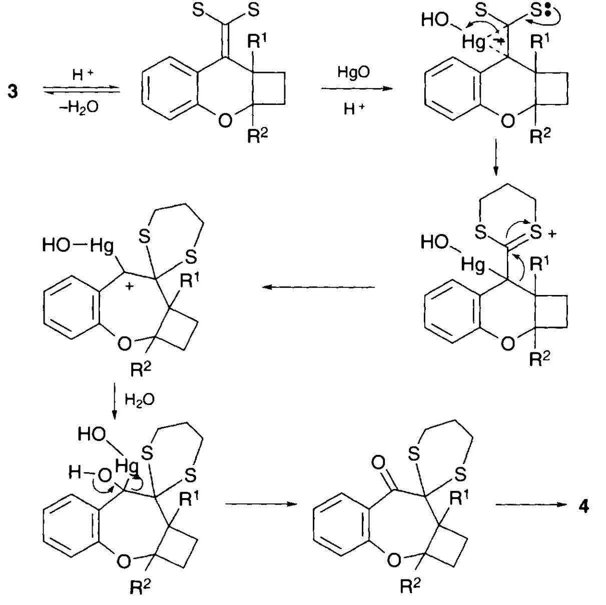


Fig. 1 X-Ray crystal structure of **4a**



	4	5
a $R^1 = R^2 = Me$	60%	15%
b $R^1 = Me, R^2 = H$	65%	20%
c $R^1 = R^2 = H$	6%	80%

Scheme 1 *Reagents and conditions*: i, *hν*, C_6H_6; ii, 1,3-dithiane, BuLi, THF, −20 °C; iii, HgO (red), HBF_4 in 85% aq. THF, room temp.



Scheme 2

3c indicates the necessity for the presence of a substituent at position 8a in the cyclobutane ring juncture. Obviously, the electron density on this carbon atom seems to have a key role in guiding this rearrangement. Although the mechanism has not yet been established a speculative pathway towards the formation of the α-diketone is shown in Scheme 2.

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Footnotes

† The aldehyde **5a** originates from the deprotection of dithiane alcohol **3a**.

‡ *Selected spectroscopic data*: IR ν_{max}/cm^{-1} 1600, 1680 and 1720; ^{1}H NMR (300 MHz) δ ($CDCl_3$) 1.14 (3 H, s, CH_3) 1.34 (3 H, s, CH_3), 1.47–1.56 (1 H, m, cyclobutane-H), 2.14 (1 H, dt, J 11.1, 3.4 Hz, cyclobutane-H), 2.40 (1 H, q, J 10.7 Hz; cyclobutane-H), 2.82 (1 H, dt, J 11.1, 3.4 Hz; cyclobutane-H), 7.06 (1 H, d, J 8 Hz; ArH), 7.29 (1 H, t, J 7.5 Hz; ArH), 7.59 (1 H, dt, J 7.5 Hz, 1.7 Hz; ArH) and 8.04 (1 H, dd, J 7.84, 1.6 Hz; Ar-*peri*-H *ortho* to Ar–C=O); ^{13}C NMR (75 MHz) δ ($CDCl_3$) 17.80 (CH_3), 19.59 (CH_3), 19.65 (CH_2), 31.35 (CH_2), 55.19 (C), 84.73 (C), 124.87 (CH), 125.11 (CH), 127.50 (C), 129.66 (CH), 136.45 (CH), 158.15 (C), 193.87 (Ar–C=O), 200.38 (C=O); mass: m/z: 230 (M^+, 31.68%), 215 (14.90%), 187 (36.64%), 174 (19.25%), 161 (55.28%), 148 (24,22%), 121 (100%), 120 (30.43%) and 118 (29.19%).

§ *Crystal data* for **4a**. $C_{14}H_{14}O_3$, M = 230.25. Monoclinic, space group $P2_1/c$, Z = 4, a = 10.596(2), b = 9.171(3), c = 13.090(4) Å, β = 112.21(2)°, V = 1177.7(6) Å^3, D_c = 1.299 g cm^{-3}, μ(Mo-Kα) = 0.91 cm^{-1}. Crystal size = 0.4 × 0.3 × 0.25 mm, T = 293 K. Enraf-nonius CAD4 diffractometer, λ = 0.71079 Å, in ω-2θ scan mode was used to record 1523 reflections (+h, +k, ±l). Range $2 \rightleftharpoons \theta \rightleftharpoons 23$. Unique reflections 1468 and 1231 observed reflections [$I > 2\sigma(I)$]. The structure was solved by direct methods (MULTAN88) and refined by full-matrix least-squares on F^2 with anisotropic thermal parameters to non-hydrogen atoms and isotropic thermal parameters for hydrogen atoms. Final R indices: $R1$ (F) = 0.0359, $wR2$ (F^2) = 0.1018, Largest difference peak and hole = 0.171 and −0.137 eÅ^{-3} respectively. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/149.

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