

Synthesis and Photolysis of Some Lanostanes Unsaturated in Rings B and C. Characterisation of the Stable Dithiet Tautomer of a Dithio-*o*-quinone

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The preparation of 3 β -acetoxy-7,7-ethylenedithio-5 α -lanosta-8,11-diene (1) and its novel conversion by phosphoryl chloride in pyridine into 3 β -acetoxy-5',6'-dihydro-19-norlanosta-5,7,9,11-tetraeno[6,7-*b*][1,4]dithin (4) are described. Photolysis of the latter affords quantitatively the stable, crystalline lanostatetraeno[6,7-*c*][1,2]-dithiet (6). The structure of this new class of product was confirmed by X-ray analysis. Irradiation of the diene (1) converts rings C and D into a tricyclo[4.3.0.0^{2,9}]nonene system (3: R = Ac).

IRRADIATION of a cyclohexa-1,3-diene system normally leads to isomerisation by one or more of a number of

well documented processes.¹ In connection with partial synthesis studies, we investigated the behaviour upon irradiation of such a diene, the lanosta-8,11-diene (1).

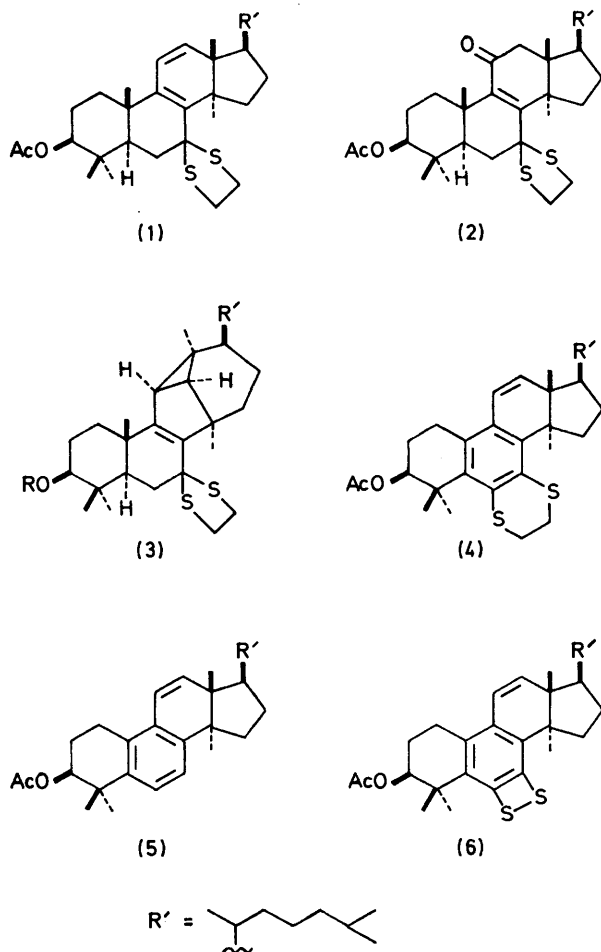
Reduction of the known 3 β -acetoxy-7,7-ethylenedithio-5 α -lanost-8-en-11-one (2)² with lithium aluminium

¹ R. B. Woodward and R. Hoffmann, 'The Conservation of Orbital Symmetry,' Verlag Chemie, Weinheim, 1970; H. Meier, 'Houben-Weyl, Methoden der Organischen Chemie, Photochemie I,' ed. E. Muller, Thieme Verlag, Stuttgart, 1975, Band IV/5a, pp. 255—271.

² M. V. Mijovic, W. Voser, H. Heusser, and O. Jeger, *Helv. Chim. Acta*, 1952, **35**, 964.

hydride and heating the product with acetic anhydride in pyridine afforded the required diene (1), λ_{\max} 292 nm (ϵ 6 300), in 33% yield. The presence of the ethylenedithio-group at C-7 was synthetically convenient since it prevented isomerisation of the 8,11-diene to the more stable 7,9(11)-system. Irradiation of the diene (1) in *n*-heptane with a medium-pressure mercury vapour lamp brought about a clean isomerisation to a photo-product, λ_{\max} 239 nm (ϵ 7 800). An X-ray structure analysis of the β -*p*-bromobenzoate of this photo-product carried out by Professor G. A. Sim (University of Glasgow) indicated the unexceptional 1,3 structure (3; R = *p*-BrC₆H₄·CO).

Treatment of the reacetylated hydride reduction product of the ketone (2) with phosphoryl chloride in



pyridine under reflux gave, with prolonged reaction times, increasing amounts of a colourless compound, C₃₃H₄₈O₂S₂, λ_{\max} 263 and 309 nm (ϵ 14 500 and 12 500). Identical material was obtained by treatment of the diene (1) with phosphoryl chloride in pyridine. The

³ D. H. R. Barton, R. Bernasconi, and J. Klein, *J. Chem. Soc.*, 1960, 511; W. G. Dauben, R. G. Williams, and R. D. McKelvey, *J. Amer. Chem. Soc.*, 1973, **95**, 3932.

⁴ D. H. R. Barton, P. J. L. Daniels, J. F. McGhie, and P. J. Palmer, *J. Chem. Soc.*, 1963, 3675; J. R. Dias, *J. Org. Chem.*, 1974, **39**, 1767, and references therein.

manner in which the necessary dehydrogenation occurs was not further investigated, but clearly phosphorus(v) is acting as an oxidant. The n.m.r. spectrum of the new product indicated the presence of only four quaternary methyl groups, two of which resonated at exceptionally low field (τ 8.34 and 8.37). The chemical shift changes observed in the n.m.r. spectra on varying the substituent at C-3 from acetoxy to hydroxy to *p*-bromobenzyloxy indicated that the C-30 and -31 methyl groups were intact, and suggested the structure (4). Confirmation of this structure was obtained following desulphurisation with Raney nickel. The n.m.r. spectrum of the product (5) clearly showed the presence of two aromatic *ortho*-protons [τ 2.86 and 3.17 (each 1 H, d, *J* 8 Hz)] and of two benzylic protons [τ 7.15 (2 H, m)]. Other miscellaneous reactions leading to ring B aromatic lanostanes have been described.⁴

The dihydro-1,4-benzodithiin (4) was sensitive to laboratory lighting. On irradiation with a medium-pressure mercury vapour lamp a rapid and quantitative conversion into a stable yellow crystalline compound, C₃₃H₄₄O₂S₂, λ_{\max} 249, 253, and 300 nm (ϵ 24 000, 24 000, and 12 100), was observed. Ethylene was also formed, as shown by g.l.c. analysis of the derived dibromide. (We thank Dr. S. C. Misra for this experiment.) Unequivocal identification of the photolysis product as the dithiet (6) was achieved by an X-ray analysis carried out under the supervision of Dr. M. F. C. Ladd (University of Surrey)⁵ (full details will be published separately).

There are few reports of the preparation of α -dithiones or their valence tautomers, 1,2-dithiets.⁶ Dithioquinones were previously unknown. The exceptional stability of the dithiet (6) must, at least in part, be attributed to the steric protection afforded by this particular molecular environment.

EXPERIMENTAL

N.m.r. data were recorded at 90 MHz and refer to solutions in deuteriochloroform with tetramethylsilane as internal standard. Rotations are of solutions in chloroform (*c* 0.5). I.r. spectra are of Nujol mulls, and u.v. spectra of solutions in ethanol. Alumina was Laporte type O, and light petroleum refers to the fraction of b.p. 40–60 °C. Unless otherwise stated compounds were recrystallised from chloroform–methanol.

β -Acetoxy-7,7-ethylenedithio-5 α -lanosta-8,11-diene (1).— β -Acetoxy-7,7-ethylenedithio-5 α -lanost-8-en-11-one² (8 g) in dry ether (600 ml) was stirred at room temperature with lithium aluminium hydride (3.4 g) for 1 h. The excess of hydride was destroyed by careful addition of water, the mixture was filtered, and the residue was washed thoroughly with ether. The combined filtrates were washed with water, dried, and evaporated, and treated with pyridine (150 ml) and acetic anhydride (30 ml) on a steam-bath for 3 h. The mixture was poured into water and extracted with ether; the extracts were evaporated, and the residue

⁵ Preliminary communication, R. B. Boar, D. W. Hawkins, J. F. McGhie, S. C. Misra, D. H. R. Barton, M. F. C. Ladd, and D. C. Povey, *J.C.S. Chem. Comm.*, 1975, 756.

⁶ W. Kusters and P. de Mayo, *J. Amer. Chem. Soc.*, 1974, **96**, 3502 and references therein; J. L. Hencher, Q. Shen, and D. G. Tuck, *J. Amer. Chem. Soc.*, 1976, **98**, 899.

was chromatographed on alumina. Elution with light petroleum-benzene (1:1 v/v) afforded the *diene* (2.6 g, 33%), m.p. 133–134°, $[\alpha]_D +55^\circ$, ν_{\max} 3 050 cm^{-1} , λ_{\max} 292 nm (ϵ 6 300), τ 3.85 and 4.16 (each 1 H, d, J 10 Hz, 11- and 12-H), 5.45 (1 H, t, 3 α -H), 9.09 and 9.16 (6 H, 26- and 27-H₃), and 8.84, 8.96, 9.04, 9.06, and 9.11 (each 3 H, s) (Found: C, 72.9; H, 9.5; S, 11.4. C₃₄H₅₄O₂S₂ requires C, 73.1; H, 9.7; S, 11.45%). The 3 β -*p*-bromobenzoate had m.p. 241–243°, $[\alpha]_D +86^\circ$ (Found: C, 67.1; H, 8.1; S, 9.1. C₃₉H₅₅-BrO₂S₂ requires C, 66.9; H, 7.9; S, 9.2%).

3 β -Acetoxy-5',6'-dihydro-19-norlanosta-5,7,9,11-tetraeno-[6,7-b][1,4]dithin (4).—The previous experiment was repeated and the total crude product was treated with phosphoryl chloride (60 ml) in pyridine (150 ml) under reflux for 43 h. The black mixture was filtered through Celite and the Celite washed thoroughly with ether. The combined filtrates were processed as above and the residue was chromatographed on alumina. Elution with light petroleum-benzene (3:2 v/v) gave the *tetraene* (24%), m.p. 161–163°, $[\alpha]_D +45^\circ$, ν_{\max} 3 040 cm^{-1} , λ_{\max} 263 and 309 nm (ϵ 14 500 and 12 500), τ 3.56 (2 H, s, 11- and 12-H), 5.18 (1 H, t, 3 α -H), 6.6–7.5 (6 H, m), 7.95 (3 H, s, OAc), 8.95 and 9.01 (3 H, 21-H₃), 9.09 and 9.16 (6 H, 26- and 27-H₃), and 8.34, 8.37, 8.80, and 9.22 (each 3 H, s), M^+ 540 (Found: C, 73.1; H, 9.35; S, 11.7. C₃₃H₄₈O₂S₂ requires C, 73.3; H, 8.95; S, 11.8%). Identical material was obtained when the pure diene (1) was similarly treated with phosphoryl chloride in pyridine. The corresponding 3 β -alcohol had τ 8.27, 8.37, 8.79, and 9.22 (each 3 H, s). The derived 3 β -*p*-bromobenzoate had m.p. 179–181°, τ 8.28 (6 H, s) and 8.77 and 9.18 (each 3 H, s).

3 β -Acetoxy-19-norlanosta-5,7,9,11-tetraene (5).—The tetraene (4) (180 mg) in acetone (60 ml) was stirred overnight at room temperature with W2 Raney nickel (2 g damp weight). The mixture was filtered through Celite and the Celite washed thoroughly with ether. Evaporation of the filtrate and crystallisation of the residue from ethanol afforded the *tetraene* (5) (120 mg, 80%), m.p. 118–120°, $[\alpha]_D +84^\circ$, λ_{\max} 219, 225, 232, and 275 nm (ϵ 22 800, 27 200, 23 700, and 9 300), τ 2.86 and 3.17 (each 1 H, d, J 8 Hz, 6- and 7-H), 3.53 and 3.65 (each 1 H, d, J 10 Hz, 11- and 12-H), 5.05 (1 H, q, 3 α -H), 7.15 (2 H, m, 1-H₂), 7.95 (3 H, s, OAc), 8.72 (6 H, s), 8.95 and 9.01 (3 H, 21-H₃), 9.09 and

9.16 (6 H, 26- and 27-H₃), and 8.89 and 9.22 (each 3 H, s), M^+ 450 (Found: C, 82.4; H, 10.2. C₃₁H₄₆O₂ requires C, 82.6; H, 10.3%).

Irradiation of 3 β -Acetoxy-7,7-ethylenedithio-5 α -lanosta-8,11-diene (1).—The diene (200 mg) in dry n-heptane (40 ml) at –20 °C was irradiated in dry nitrogen with a 125 W medium-pressure mercury vapour lamp (Pyrex filter). The reaction could be followed by t.l.c., u.v. spectroscopy, or $[\alpha]_D$ measurements. When no starting material remained (ca. 4 h) the solvent was removed at room temperature. The oily residue was solidified by addition of methanol and subsequently crystallised from ethyl acetate. The *tricyclo*-[4.3.0.0^{2,9}]nonene (3; R = Ac) had m.p. 148–150°, $[\alpha]_D -87^\circ$, λ_{\max} 239 nm (ϵ 7 800), M^+ 558 (Found: C, 73.05; H, 9.8. C₃₄H₅₄O₂S₂ requires C, 73.1; H, 9.7%). Hydrolysis of this material with 5% potassium hydroxide in benzene-methanol at room temperature for 6 h gave the 3 β -alcohol (3; R = H), which on acetylation gave back the acetate (3; R = Ac). Treatment of the 3 β -alcohol (3; R = H) with *p*-bromobenzoyl chloride in pyridine at room temperature for 12 h yielded the 3 β -*p*-bromobenzoate (3; R = *p*-BrC₆H₄CO), m.p. (from ethanol) 154–156°, $[\alpha]_D -36^\circ$ (Found: C, 67.2; H, 8.0; S, 9.2. C₃₉H₅₅BrO₂S₂ requires C, 66.9; H, 7.9; S, 9.2%).

3 β -Acetoxy-19-norlanosta-5,7,9,11-tetraeno[6,7-c][1,2]-dithiet (6).—The tetraene (4) (100 mg) in dry n-heptane (30 ml) at –20 °C was irradiated in dry nitrogen with a 125 W medium-pressure mercury vapour lamp (Pyrex filter). After 4 h the solvent was removed at room temperature. Crystallisation of the residue afforded the *dithiet* (6) as yellow needles (86 mg, 91%), m.p. 168–170°. $[\alpha]_D +60^\circ$, ν_{\max} 3 050 cm^{-1} , λ_{\max} 249, 253, and 300 nm (ϵ 24 000, 24 000, and 12 100), τ 3.56 and 3.68 (each 1 H, d, J 10 Hz, 11- and 12-H), 5.12 (1 H, q, 3 α -H), 7.20 (2 H, m, 1-H₂), 7.97 (3 H, s, OAc), 8.68 (6 H, s), 8.96 and 9.02 (3 H, 21-H₃), 9.09 and 9.16 (6 H, 26- and 27-H₃), and 8.89 and 9.16 (each 3 H, s), M^+ 512 (Found: C, 72.5; H, 8.8; S, 12.4. C₃₁-H₄₄O₂S₂ requires C, 72.6; H, 8.65; S, 12.5%).

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