Direct Oxidation of Allylic Methylene to Carbonyl[1]

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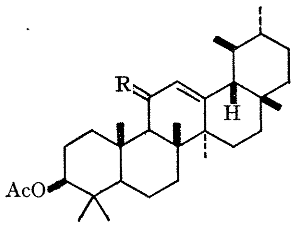
Summary Triterpene 12-enes with various substituents in ring A, taraxeryl acetate, and cholesteryl acetate are oxidised, essentially quantitatively, to the corresponding αβ-unsaturated ketones by irradiated solutions of *N*-bromosuccinimide in moist solvents.

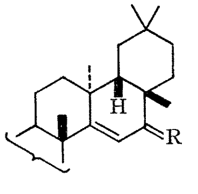
IT has been reported[2] that 11-oxo-urs-12-en-3β-yl acetate (II) is formed in *ca.* 80% crude yield by treatment of α-amyrin acetate (I) with *N*-bromosuccinimide in aqueous dioxan. In our hands, the reaction as described gave very variable yields (up to 60%) of the required ketone (II) together with a number of by-products which will be described elsewhere. However, we find that when the reaction mixture is irradiated with visible light, reproducible—essentially quantitative—yields of αβ-unsaturated ketones are obtained from a number of compounds containing an allylic methylene group.

Thus, a solution of the olefin (1 mole) in a water-miscible, inert solvent† containing water (1—10%) is stirred (1 hr.) at room temperature with freshly crystallised *N*-bromosuccinimide (2·5 moles) and finely divided calcium carbonate (*ca.* 2 moles) while being irradiated with visible light. The mixture is filtered, diluted with an excess of water, and the product extracted into ether or chloroform.

In this way, α-amyrin acetate (I) gives 98% α-amyrenonyl acetate (II), m.p. 289—290°, $[\alpha]_D$ +96°; β-amyrin acetate yields 100% β-amyrenonyl acetate, m.p. 268—269°, $[\alpha]_D$ +102°; and taraxeryl acetate (III) affords 96% 16-oxotaraxeryl acetate (IV), m.p. 251—252°, $[\alpha]_D$ +92°. Similar yields of αβ-unsaturated ketones are obtained from α- and β-amyrene, their 3-oxo- and 3β-benzoyloxy-derivatives, and, surprisingly, their 3β-ols (t.l.c. of the crude product shows only traces of 3,11-diketone). In the case of cholesteryl acetate the crude product (96%) shows traces of impurities on t.l.c. but is probably pure enough for most purposes. Crystallisation from chloroform–methanol gives 81% 7-oxocholesteryl acetate, m.p. 159—160°, $[\alpha]_D$ −98°.



(I)R=H_2 (II)R=O



(III)R=H_2 (IV)R=O

Satisfactory analytical data were obtained for (IV); other products were compared with authentic samples.

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† *e.g.* Dioxan, tetrahydrofuran, glyme, or diglyme. The volume of the solution is adjusted so that the reaction mixture is translucent.

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[2] S. Corsano and G. Piancatelli, *Ann. Chim.* (*Italy*), 1965, **55**, 742.