

Intramolecular Hydrogen Abstraction. (Diacetoxyiodo)benzene, a Useful Reagent for the Remote Functionalization of Non-activated Carbon Atoms

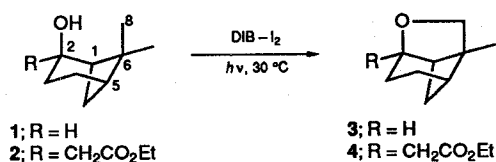
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In previous papers³ we have reported that the system (diacetoxyiodo)benzene and iodine is more efficient and convenient to generate alkoxy radicals from alcohols than those constituted from heavy metal derivatives (e.g. Pb^{IV}, Hg^{II}, and Ag^I) and iodine usually employed in such reactions.¹ We now report that *in situ* photolyses with visible light of several hydroxy compounds such as (-)-6,6-dimethylbicyclo[3.1.1]heptan-2 β -ol [(*-*)-*cis*-nopinol] (**1**), 2-ethoxycarbonylmethyl-6,6-dimethylbicyclo[3.1.1]heptan-2 β -ol (**2**), cedrol (**5**), isolongifolol (**8**), the hydrindane derivative **12**, labdane-8 α ,15-diol (**18**), methyl 8 α -hydroxylabdane-15-oate (**19**), labdanolic acid (**20**), methyl 3 β -hydroxyfriedelane-29-oate (**27**), and friedelane-3 β ,30-diol 30-acetate (**30**) in the presence of (diacetoxyiodo)benzene and iodine lead to alkoxy radicals which undergo intramolecular abstraction of suitably positioned hydrogen atoms to produce γ -functionalized derivatives.

Irradiation of (*-*)-*cis*-nopinol (**1**) with visible light (2 \times 100-W tungsten filament lamps) in cyclohexane containing DIB and iodine at 30 $^{\circ}$ C for 1 h gave the ether **3** in 72% yield (Scheme). The related tertiary alcohol **2** was irradiated under similar conditions to give the expected ether **4** in 96% yield.



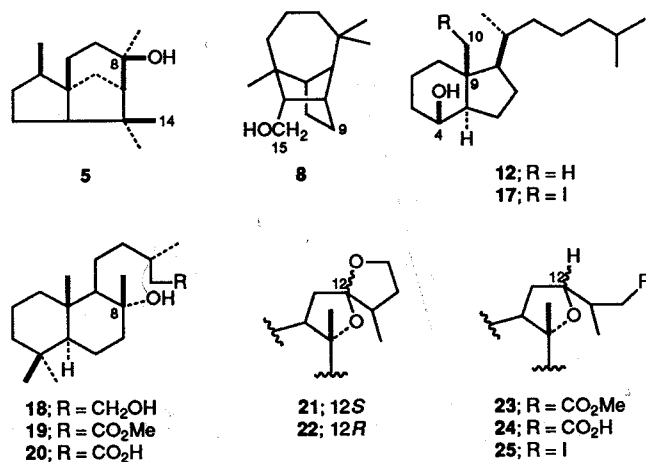
Scheme

Under the reaction conditions the sesquiterpene alcohols cedrol (**5**) and isolongifolol (**8**) gave the corresponding 8,14-cedranoxide and 9,15-epoxylongifolane respectively; minor side-products of these reactions are also studied in the full-text version of this paper.

The functionalization of the angular methyl group in compound **12** proceeded by double hydrogen abstraction to give a complex mixture of compounds similar to that previously described for 5 α -cholestan-4 β -ol.^{3b}

A reaction mechanism that can explain the observed double hydrogen abstraction can be rationalized on the basis of the hindered rotation of the C-9-C-10 bond in the iodohydrin **17** initially formed. Calculation of the rotational energy barrier of the C-9-C-10 bond in this compound using the rigid rotor approximation for acyclic dihedral angles made with the aid of PCMODEL program¹² reveals that the rotation is effectively hindered and that in the more stable conformation (dihedral angle C-5-C-9-C-10-I = 166 $^{\circ}$) the cyclization is not propitious but instead a second hydrogen abstraction can easily take place.

When the reaction was performed with the labdane derivatives **18**, **19**, and **20**, the isomeric epoxy-derivatives **21** and **22**, **23**, and **24** respectively were obtained in good yields.



The photolyses accomplished with the triterpene 3 β -hydroxy-friedelane derivative **27** gave two types of compounds: the expected 3 β ,24-ether derivative **33** and the 25-iodo-3 β ,24-ether **32**. Two consecutive hydrogen abstractions are needed to produce **32**. This 'billiard' reaction has previously been observed in triterpenoid and diterpenoid skeletons and is caused by a second intramolecular hydrogen abstraction promoted by a C-24 carbon radical generated from initially formed alkoxy,¹⁷ cyanamidyl,¹⁸ or nitroamidyl¹⁹ radicals.

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Techniques used: ¹H and ¹³C NMR, MS, IR

References: 21

Table 1: Reactions of alcohols with (diacetoxyiodo)benzene-iodine reagent

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