Photolysis of Carboxylic Esters: Conversion of Alcohols into Alkanes[1]

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Summary Alkanes are formed in good yields when diluted solutions of non-activated carboxylic esters in HMPA–H_2O (95:5) are irradiated at 254 nm.

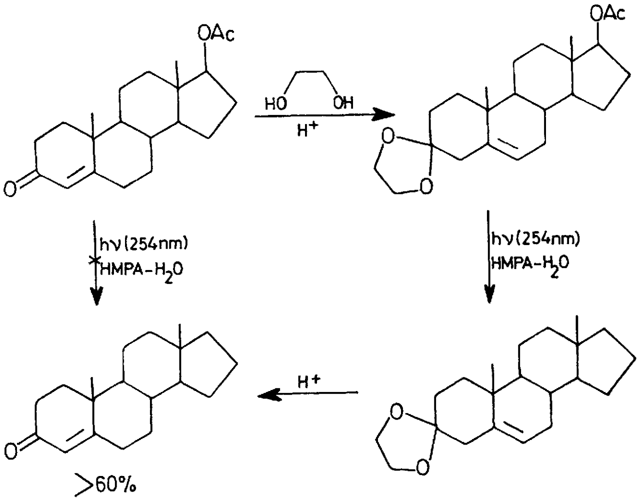
We have already reported that alcohols and amines are produced in good yields by irradiation at 254 nm of arenesulphonates and arenesulphonamides respectively.[2] Under the same conditions, carboxylic esters such as benzoates or acetates were recovered quantitatively. Beugelmans and his co-workers also reported little decomposition when these esters were photolysed in dry HMPA (hexamethylphosphoric triamide).[3,4] After irradiation for 30 h alkane (5% yield) resulting from reduction of the alkoxy-part of the ester was the only new product.

We report here that carboxylic esters are readily reduced in HMPA–H_2O (see Scheme 1 and Tables 1 and 2). In a typical experiment, 10 quartz tubes each containing a solution of 3β-acetoxy-5α-cholestane (100 mg) in HMPA–H_2O (95:5; 20 ml) were irradiated for 3 h in a 'merry go round' apparatus using 12 × 15 W low-pressure mercury lamps. Deoxygenation of the solution was not necessary. After evaporation under reduced pressure the crude product was dissolved in ether. The ethereal solution was washed with water and evaporated; chromatography of the residue on silica gel with pentane as eluant gave 5α-cholestane (80%).

$$R^1\text{–CO–O–}R^2 \xrightarrow[\text{HMPA–H}_2\text{O}]{h\nu\ (254\ \text{nm})} \underset{\text{major}}{R^2H} + \underset{\text{minor}}{R^1OH}$$

Scheme 1

Table 1 shows that the reduction is quite general for carboxylic esters since alkanes are obtained in good yield from formates, acetates, and benzoates. Under the same conditions sulphonates are converted into alcohols in high yields[2] (run 5) and carboxylic acids may be formed in good yield (run 4).



Scheme 2

Two main reasons explain the difference between the results of Beugelmans and his co-workers and ours. (i) They used a high-pressure mercury lamp and only a very small amount of the emitted light was absorbed by the solution. (ii) Water is needed to accelerate the reaction and they used dry HMPA.

Table 1

Runs	Ester	Irradiation time/h	Conversion /%	Alkane /%	Alcohol /%	Carboxylic acid/%
1	5α-Cholestan-3β-yl formate	5	100	79	19[a]	
2	5α-Cholestan-3β-yl acetate	3	100	80	—	
3	5α-Cholestan-3β-yl benzoate	5	100	52	36[a]	
4	Methyl 3α-chloro-5α-cholan-24-oate . .	3·5	100	—	—	70[b]
5	5α-Cholestan-3β-yl methanesulphonate	5	64	—	>95	

[a] The formation of the alcohol will be discussed elsewhere.[5] [b] The C–Cl bond was reduced and the isolated product is 5α-cholan-24-oic acid.

TABLE 2

Runs		Irradiation time/h	Conversion /%	Alkane (yield/%)
6	n-Nonyl acetate	4	90	n-Nonane (70)
7	*cis*-4-t-Butyl-1-acetoxycyclohexane	4	90	t-Butylcyclohexane (70)
8	*trans*-4-t-Butyl-1-acetoxycyclohexane	4	90	t-Butylcyclohexane (70)
9	Cholesteryl acetate	3	100	Cholest-5-ene (67)
10	3α-Methyl-5α-cholestan-3β-yl acetate	3	58	3β-Methyl-5α-cholestane (70)
11	3β-Methyl-5α-cholestan-3α-yl acetate	3	94	3β-Methyl-5α-cholestane (67)
12	3α-Acetoxy-cholan-24-oic acid	4	100	Cholan-24-oic acid (87)
13	4,4-Dimethyl-5α-cholestan-3β-yl acetate	3	62	4,4-Dimethyl-5α-cholestane (68)

Since alkanes are obtained from the alkoxy-part of the acetates, we have studied the scope of this photoreduction. The results in Table 2 show that primary, secondary, and tertiary as well as neopentyl acetates are efficiently reduced to the corresponding alkanes. To be useful in synthesis, this method would have to be applicable in the presence of other functions: alkene, alcohol, ether, acid, and acetal groups are inert under these conditions; ketones, however, are readily reduced to alcohols and the carbon–halogen bond is efficiently cleaved (run 4).

We have also irradiated testosterone acetate in HMPA, but a clean reaction was not observed. However, this compound could be reduced in 60% overall yield by the route in Scheme 2.

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[1] Part of this work was presented at the 5th I.U.P.A.C. Symposium on photochemistry at Enschede, July 21—27, 1974.

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[4] For reviews on this solvent see: H. Normant, *Bull. Soc. chim. France*, 1968, 791; *Angew. Chem. Internat. Edn.*, 1967, **6**, 1046.

[5] H. Deshayes, J. P. Pete, C. Portella, and D. Scholler, unpublished results.