Light-mediated Cyanomethylation of Cycloalkenes with Acetonitrile†

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Addition of cyanomethyl radicals generated from acetonitrile involving initiation by photoinduced decomposition of hydrogen peroxide, to cycloalkenes has been achieved; a method for the synthesis of two homologous nitriles is first reported.

The Kharasch addition[1–3] of aldehydes, alcohols and amines to alkenes by a free radical mechanism has been investigated some time ago. However, such an addition of nitriles to alkenes to yield homologous alkanonitriles has not been achieved; the only reports pertain to the addition of acetonitrile to norbornene, wherein its triplet excited-state chemistry[4] or direct excitation of its silver salt complex[5] was investigated. The low quantum efficiencies of the photoprocesses involved in the generation of cyanomethyl radicals proved to be the limiting factor in providing satisfactory reaction yields. We herein first report a convenient and improved procedure for the generation of cyanomethyl radicals and their addition to cycloalkenes.

While exploring further our earlier findings[6] on the light-mediated transformation of alkenes to alcohols involving the addition of hydroxyl radicals generated from hydrogen peroxide, we have discovered a highly substrate-dependent competitive cyanomethylation reaction of cycloalkenes *via* cyanomethyl radicals generated *in situ*. The method comprises the UV irradiation (vycor filter) of a solution of an alkene in acetonitrile in the presence of hydrogen peroxide (80%) for

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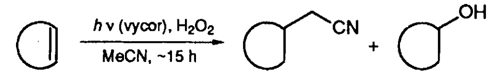
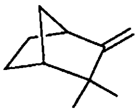
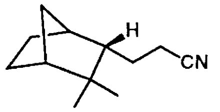
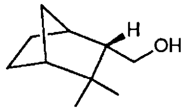
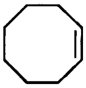
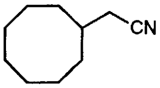
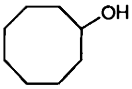
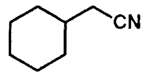
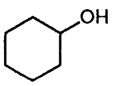
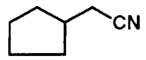
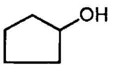
Table 1 Photo-mediated cyanomethylation/hydroxylation of cycloalkenes with H_2O_2/MeCN



I^a II^b III^b

Alkene	Isolated yield^{b,c} (%)	Product composition (GLC, %)	
		II	III
$CH_3(CH_2)_5CH{=}CH_2$	76	$CH_3(CH_2)_5CH_2CH_2CH_2CN$ 50	$CH_3(CH_2)_5CH_2CH_2OH$ 50
	44	 49	 51
	54	 44	 56
	45	 34	 66
	42	 57	 43
1	72	**1d** 80	**1b** 20

[a] A solution of alkene (0.05 moles) in 300 ml MeCN was irradiated with portion-wise addition of 0.02 moles of H_2O_2. [b] Isolable by column chromatography, almost quantitatively. [c] In each case, the weights of **II** and **III** are computed from the weight of the total product and its GLC. Based on the reaction stoichiometry, *viz.* $H_2O_2 \rightarrow R\text{-}OH + RCH_2CN$. The yields of alcohols and nitriles are calculated and summated to give the isolated yield.

about 15 h. The products were easily separated by column chromatography and were characterized by comparison of their spectral data with those of authentic samples.‡ Alkaline hydrolysis of the nitriles to the corresponding known acids provided further support to the structural assignments of the cyanomethylated products. The results are shown in Table 1.

It is noteworthy that the reference alkene, *viz.* oct-1-ene, gave equal amounts of cyanomethylated and hydroxylated products; camphene and cyclooctene showed comparable selectivities. However, cyclohexene and cyclopentene under similar conditions, show very different chemoselectivities. Various factors, such as the electrophilicity of $^{\bullet}CH_2CN$ and $^{\bullet}OH$ radicals and steric effects, may be responsible for the observed results.[7,8] The unique behaviour of norbornene **1** in showing a high proclivity for cyanomethylation (80%) leading to the formation of *exo*-cyanomethyl norbornane **1d** could be ascribed to stereoelectronic factors.[9] The trend observed in the cyanomethylation, *viz.* cyclohexene < cyclopentene < norbornene, has an interesting parallel in the reported reactivity of these alkenes towards various electrophilic reagents;[10] however, the reversal of this order towards hydroxylation is surprising.

A plausible chain transfer mechanism depicting the probable modes of product formation is shown in Scheme 1, eqns. (1)–(6). Although the addition of OH radicals to alkenes is known to be a fast reaction[11] (rate constants in the order of $5.0 \times 10^9\ dm^3\ mol^{-1}\ s^{-1}$), the initiation step, *viz.* the generation of $^{\bullet}CH_2CN$ radicals, may occur *via* the reaction of the β-hydroxy adduct radical **1a** with acetonitrile, eqn. (3); generation of $^{\bullet}CH_2CN$ radicals involving direct hydrogen abstraction from acetonitrile by hydroxyl radicals, eqn. (6), appears less favourable on energetic considerations.[12,13]

Lewis and coworkers have achieved the cyanomethylation of norbornene and other alkenes using metal ion/alkene

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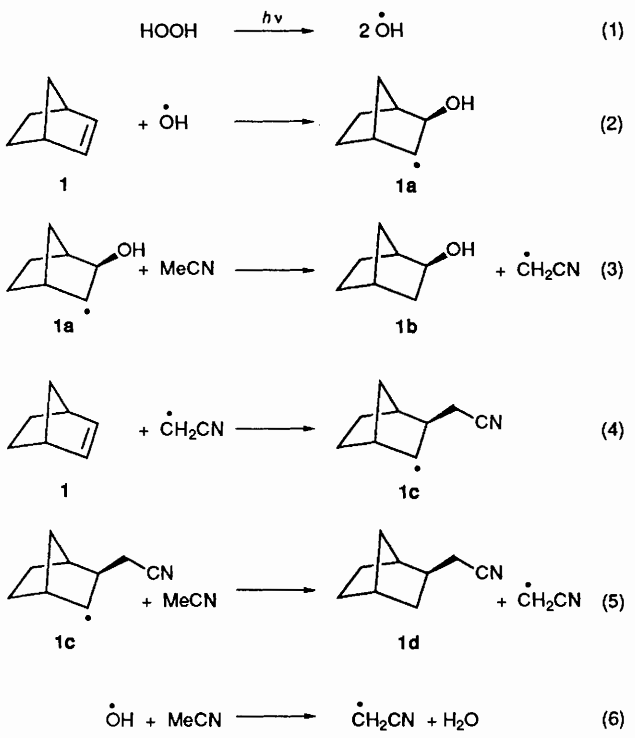
‡ *Selected spectroscopic data* for: 2,2-dimethyl-3-*endo*-(2-cyanoethyl)-bicyclo[2.2.1]heptane: IR 2220 cm^{-1}; δ_H 0.95 (s, 3H), 1.02 (s, 3H), 2.2 (m, 2H) and 2.44 (m, 1H). *endo*-Camphanol:[14] IR 3320 cm^{-1}; δ_H 0.82 (s, 3H), 0.98 (s, 3H), 1.56 (br. s, 1H), 2.02 (br. s, 1H), 3.12–3.62 (d, 2H). *exo*-2-(Cyanomethyl)bicyclo[2.2.1]heptane, **1d**: IR 2248 cm^{-1}; δ_H 1.0–1.68 (m, 9H), 2.16 (m, 2H) and 2.22 (m, 2H), lit.[5] *exo*-norborneol, **1b**, 3320 cm^{-1}, δ_H 1.0–1.6 (10H), 2.1 (s, 1H) and 3.73 (m, 1H).



Scheme 1

photochemistry.[5] Irradiation of **1** in acetonitrile in the presence of silver trifluoromethane sulphonate for several days, with periodic removal of silver which had deposited on the lamp, afforded **1d** (35% yield). It is noteworthy that the yields of cyanomethylation in the case of acyclic alkenes, cyclopentene and cyclohexene depended on the intrinsic coordinative preferences of the metal ion with the double bond and were extremely low relative to norbornene.

In this context, the cyanomethylation method reported here is favoured over the existing methods in terms of simplicity of operation and the good yields obtained. The substrate-dependent chemoselectivities of different cycloalkenes towards two electrophilic radicals of diverse nature observed here is unprecedented. Further work to investigate the underlying principles of chemoselectivity is in progress.

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