Conformational Effects in Photocyclization of Six and Seven-membered Ring Alkoxyketones

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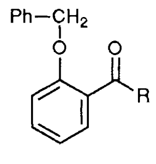
Irradiation of 8-alkoxytetrahydro-1-naphthalenones **5** gave rearranged naphthyl alcohols **11** as major products and in contrast, 4-alkoxytetrahydrobenzocyclohepten-5-ones **6** afforded tetrahydrocyclohepta[*cd*]benzofurans **14** in good yields; the difference in reactivities is attributed to the conformation of six- and seven-membered rings.

It is well known that irradiation of aromatic carbonyl compounds possessing δ-hydrogen atoms gives indanols[1,2] or benzofuranols.[3–5] For example, irradiation of 2-benzyloxybenzophenone **1a** (R = Ph) affords *cis*- and *trans*-isomers of 2,3-diphenyl-2,3-dihydro-3-benzofuranol.[4] The reactions proceed through intramolecular cyclization of 1,5-biradicals formed from δ-hydrogen abstraction by the carbonyl group. The p-orbital at the benzylic carbon in 1,5-biradicals is parallel to the π-orbitals of the benzene ring and fully conjugated. For effective cyclization to dihydrobenzofuranols fast rotation of the p-orbital is necessary around the bond between the benzene ring and benzylic carbon (Ar–C bond). Such a rotation reduces benzylic conjugation; however, the substituent R = Ph makes the rotation easier because benzylic conjugation is maintained by another phenyl group after rotation of about 90°.[4] In the case of 2′-benzyloxyacetophenone **1b** (R = Me), the rotation of the p-orbital is slow because it reduces benzylic conjugation, so that the spiroenol **2**



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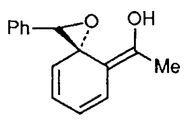
a; R = Ph
b; R = Me



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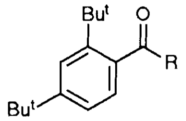

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a; R = Ph
b; R = Me

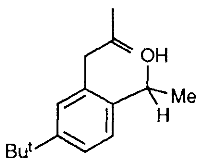

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Table 1 Photocyclization of 8-alkoxytetrahydro-1-naphthalenones **5**[a]

Compound	R	Irradiation time/min	Product (yield, %)	
			9	**11**
5a	H	60	34	36
5b	Me	20	5	62
5c	Et	15	8	48
5d	Pr^i	15	11	60
5e	Ph	30	9	71

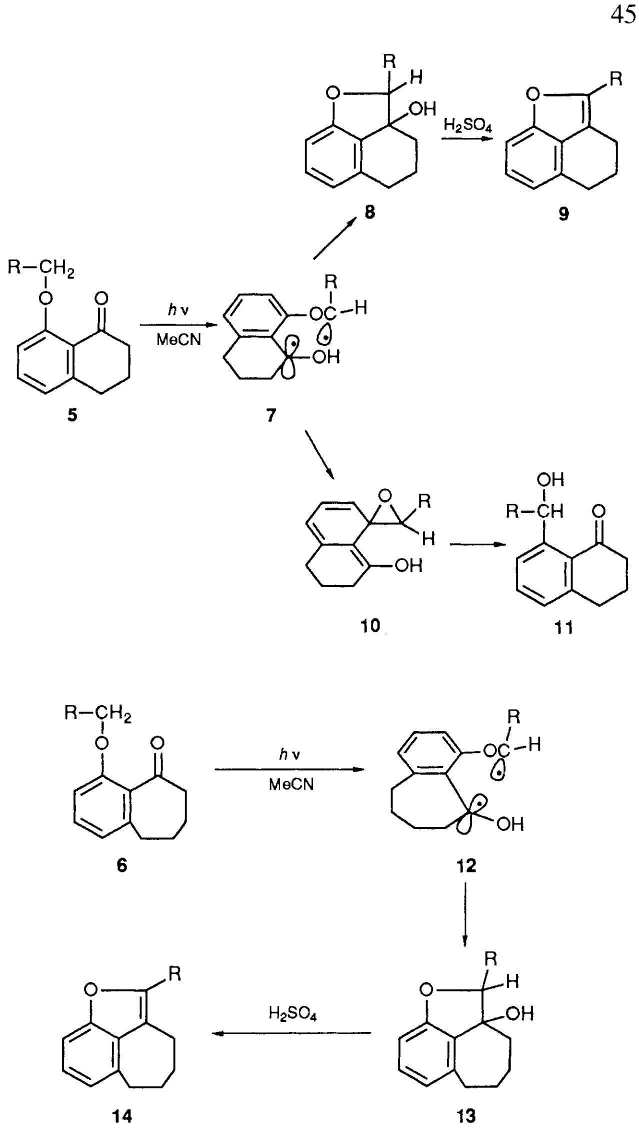
[a] An acetonitrile solution (500 ml) of **5** (4.00 mmol) was irradiated after deoxygenation and the reaction products were treated with dilute sulphuric acid.

Table 2 Photocyclization of 4-alkoxytetrahydrobenzocyclohepten-5-ones **6**[a]

Compound	R	Irradiation time/min	Product (yield, %) **14**
6a	H	30	80
6b	Me	20	78
6c	Et	25	73
6d	Pr^i	30	79
6e	Ph	15	87

[a] An acetonitrile solution (500 ml) of **6** (4.00 mmol) was irradiated after deoxygenation and the reaction products were treated with dilute sulphuric acid.

is produced, which is further oxidized with oxygen in the solvent to give 2′-benzoylacetophenone as the major product.[4] Similarly, when 2,4-di-t-butylbenzophenone **3a** (R = Ph) is used, 5-t-butyl-3,3-dimethyl-1-phenyl-1-indanol is the only product; however, using 2′,4′-di-t-butylacetophenone **3b** (R = Me) the major product is a rearranged alcohol **4** rather than 5-t-butyl-1,3,3-trimethyl-1-indanol.[2] The above results suggest that the fast rotation of the p-orbital around the Ar–C bond is an important factor for effective cyclization. We report photocyclization of 8-alkoxytetrahydro-1-naphthalenones **5** and 4-alkoxytetrahydrobenzocyclohepten-5-ones **6** in which the carbonyl group is not free to rotate. Six-membered ring ketones **5** are conformationally fixed and have a small dihedral angle between the carbonyl group and benzene ring.[6] In contrast, seven-membered ring ketones **6** are flexible and the p-orbital in the carbonyl group is not parallel to the π-orbitals of the benzene ring.[6] The difference in conformation would lead to large effects on product formation.



Scheme 1

Irradiation of six-membered ring ketones **5** with a 400 W high-pressure mercury lamp in acetonitrile gave naphthofuranols **8** and rearranged alcohols **11**. It was difficult to isolate **8** and **11** in a pure state. Therefore, the reaction mixture was treated with sulphuric acid to give naphthofurans **9** (5–34%) and rearranged alcohols **11** (36–71%) (Table 1). The structures of **9** and **11** were confirmed by the IR and NMR spectra. In contrast, irradiation of seven-membered ring ketones **6** afforded only cyclohepta[*cd*]benzofuranols **13** in high yields (80–90%) and no rearranged alcohols were obtained. In each experiment only one stereoisomer of **13** was produced and readily converted to cyclohepta[*cd*]benzofuran **14** with sulphuric acid (Table 2). The structures of **13** and **14** were confirmed by the IR and NMR spectra.

The large difference in reactivities between six- **5** and seven-membered ring ketones **6** could be explained by the conformation of the two ketones. In six-membered ring ketones **5**, the p-orbital in the 1,5-biradicals **7** formed by δ-hydrogen abstraction would be nearly parallel to the π-orbitals of the benzene ring.[5,6] Rotation by *ca.* 90° around the Ar–C bond is necessary for furan-ring formation. However, such a rotation reduces benzylic conjugation between the p-orbital and benzene ring and causes strain in the six-membered ring. Therefore, spirocyclization of **7** to **10** occurs predominantly. Spiroenols **10** afford rearranged alcohols **11** by cleavage of the ether linkage. In contrast, seven-membered ring ketones **6** are flexible and have a large dihedral angle between the carbonyl group and benzene ring in the ground state.[6] The stable conformation of 1,5-biradicals **12** formed by δ-hydrogen abstraction would be similar to that of seven-membered ketones **6**. Therefore, the p-orbital in 1,5-biradicals is not parallel to the π-orbitals of the benzene ring and not conjugated effectively. This conformation is desirable for cyclization to the furan ring. The results suggest that the dihedral angle between the carbonyl group and benzene ring of starting compounds play an important role in the cyclization step of 1,5-biradicals. The photocyclization method is useful for preparing a furan-ring from seven-membered ring carbonyl compounds.

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