308. Photochemistry of Tricyclo[3.3.1.$0^{2,7}$]nonan-6-ones

Preliminary communication

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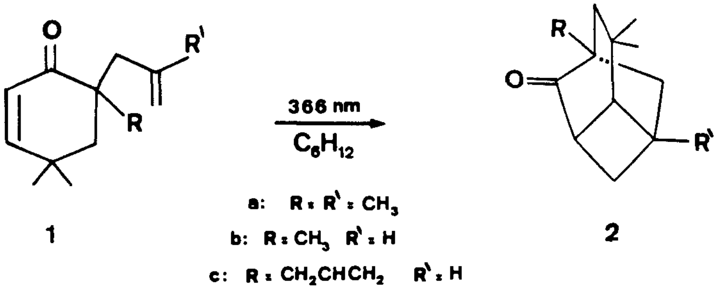
Summary. Sensitized irradiation (λ = 254 nm) of the title compounds **2a** and **2b** in benzene affords the tetracyclic oxetanes **3a** and **3b**. The irradiation of **2c** under similar conditions yields equal amounts of **3c** and the cyclopentadiene derivative **5**. The formation of the photoproducts is discussed.

The photochemical behaviour of bicyclic ketones has attracted the interest of several research groups [1–6]. We have recently reported [7] the intramolecular photocyclization of the 6-allyl-2-cyclohexenones **1a** and **1b** (*Scheme 1*). We now discuss results on the photochemistry of the tricyclo[3.3.1.$0^{2,7}$]nonan-6-ones **2**.

Scheme 1



The sensitized irradiation (λ = 254 nm) of **2a** and **2b** in benzene leads selectively[1]) to the formation of **3a** and **3b**. These were shown to be 2-oxatetracyclo[4.2.2.$0^{3,9}$.$0^{4,7}$] decanes on the basis of the spectroscopic data summarized in the Table. Their formation from **2** can readily be explained by preferential α-cleavage on the side of the carbonyl group remote from the four-membered ring [5] and abstraction of the more easily accessible hydrogen atom on C(4) to yield the intermediate aldehyde **4** which then photocyclizes to **3** (*Scheme 2*). Such oxetane formations have also been observed in direct irradiations of bicyclic ketones [1] [3].

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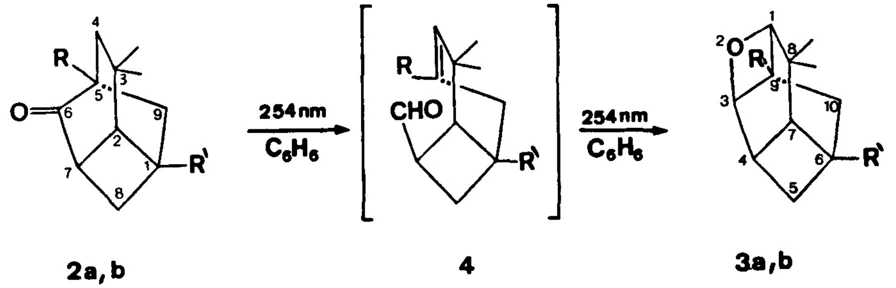
[1]) Minor amounts of aldehydic products were also detected and isolated by GLC. It remains unknown for the moment if these correspond to thermal cleavage products of **3** or to the unreacted precursors **4**.

Scheme 2



As for the assignment and determination of the structures **3a** and **3b** the IR.- and mass spectra present evidence for a ketone → oxetane transformation. The NMR.-spectra (decoupling-, shift- and simulation experiments) agree very well with the proposed structure. Besides, from the eight oxetanes which could have *a priori* been formed, three possible structures were eliminated as they do not contain one hydrogen atom on each of the carbon atoms vicinal to the oxetane heteroatom. The four other

Spectroscopic data for photoproducts **3** *and* **5**

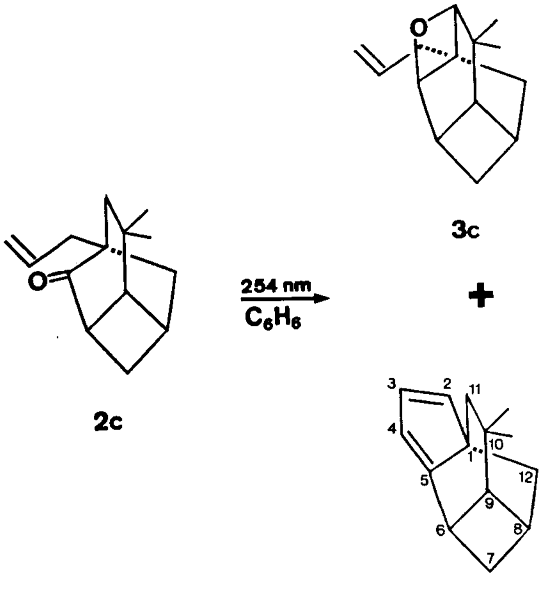
	3a	**3b**	**3c**	**5**	
MS.	192 (M^+) *135* (M^+-57)	178 (M^+) *121* (M^+-57)	204 (M^+) *147* (M^+-57) *105*	186 (M^+) *116* (M^+-70)	
IR. (in CCl_4)	950 cm^{-1}	952 cm^{-1}	950 cm^{-1} 1655 cm^{-1}		
UV. (in C_6H_{12})				$\lambda_{max} = 256$ nm $\varepsilon = 3240$	
NMR.	In $CDCl_3$	In C_6D_6	In C_6D_6	In C_6D_6	
H–C(1)	3.56(*t*)	3.51(*t*)	3.63(*t*)	H–C(2)	6.25(*d*)
H–C(3)	4.11(*t* × *d*)	4.09(*t* × *d*)	4.16(*t* × *d*)	H–C(3)	6.52(*d* × *d*)
H–C(4)	2.67(*d* × *d* × *d*)	2.65(*m*)	2.60(*m*)	H–C(4)	5.67(*d*)
H_a–C(5)	1.63(*d* × *d* × *d*)	≃ 1.75(*m*)	≃ 1.85(*m*)	H–C(6)	3.22(*q*)
H_b–C(5)	1.02(*d*)	0.72(*d*)	0.70(*d*)	H_a–C(7) ≃	2.20(*m*)
H–C(6)	–	2.18(*m*)	2.18(*m*)	H_b–C(7)	1.10(*d*)
H–C(7)	1.82(*d* × *d* × *d*)	2.04(*m*)	2.02(*m*)	H–C(8)	2.36(*m*)
H_a–C(10)	1.68(*d* × *d*)	1.70(*m*)	1.70(*m*)	H–C(9)	2.26(*m*)
H_b–C(10)	1.23(*d*)	1.06(*d*)	1.10(*d*)		
CH_3	1.53, 1.06, 0.98, 0.85	1.45, 1.08, 0.70	1.10, 0.70	+ 2*AB*-systems: (2H–C(11) and 2H–C(12))[a]	
$J_{\mathrm{H-C(1),H-C(3)}} = 2.5$, $J_{\mathrm{H-C(1),H-C(7)}} = 2.5$, $J_{\mathrm{H-C(3),H-C(4)}} = 2.5$, $J_{\mathrm{H-C(3),H-C(7)}} = 1.2$, $J_{\mathrm{H-C(4),H-C(5a)}} = 6.8$, $J_{\mathrm{H-C(4),H-C(6)}} = 5.5$, $J_{\mathrm{H-C(4),H-C(7)}} = 5.5$, $J_{\mathrm{H-C(5a),H-C(5b)}} = 10.0$, $J_{\mathrm{H-C(5a),H-C(10a)}} = 2.5$, $J_{\mathrm{H-C(5a),H-C(6)}} = 5.5$, $J_{\mathrm{H-C(10a),H-C(10b)}} = 14.0$				CH_3 0.94, 0.70 $J_{\mathrm{H-C(2),H-C(3)}} = 5.0$ $J_{\mathrm{H-C(3),H-C(4)}} = 1.9$ $J_{\mathrm{H-C(6),H-C(7a)}} = 5.5$ $J_{\mathrm{H-C(6),H-C(8)}} = 5.5$ $J_{\mathrm{H-C(6),H-C(9)}} = 5.5$	

[a] Not accurately resolved.

possible structures did not correlate with the observed coupling scheme. It is interesting to note that the majority of the derived coupling constants are associated with long-range couplings (H–C(1), H–C(3); H–C(1), H–C(7); H–C(3), H–C(7); H–C(4), H–C(6); H_a–C(5), H_a–C(10)).

6,6-Diallyl-4,4-dimethyl-2-cyclohexenone (**1c**) was synthesized in a similar way as other compounds **1** [7]. Irradiation of **1c** ($\lambda = 366$ nm) in cyclohexane gives 5-allyl-3,3-dimethyltricyclo[3.3.1.$0^{2,7}$]nonan-6-one (**2c**) specifically. **2c** was again irradiated ($\lambda = 254$ nm) in benzene in order to establish if the additional exocyclic C–C double bond would alter the reaction path observed (*Scheme 2*). Indeed, the formation of a second major product (**5**) with shorter GLC.-retention time than the anticipated oxetane **3c** was observed and the new compound was also isolated. Its spectral data (Table), especially NMR.- and UV.-spectra afford evidence for the presence of a cyclopentadiene moiety [8] and suggest **5** to be 10,10-dimethyltetracyclo[6.3.1.$0^{1,5}$.$0^{6,9}$]dodeca-2,4-diene (*Scheme 3*).

Scheme 3



The formation of **5** can be explained by abstraction of a hydrogen atom from the allylic side chain by the carbonyl group, followed by preferential ring closure on the terminal C-atom of the allyl radical (five-membered *vs.* three-membered ring formation) to give a tertiary cyclopentenyl alcohol which loses water to afford **5**. Only a few β-hydrogen abstractions, *i.e.*, hydrogen abstraction reactions proceeding through five-membered transition states have been observed [9] and studied in detail [10]. A comparison of our results with those discussed for the photolysis of the 1,3-

butadiene-*p*-quinone *Diels-Alder* adduct [10] suggests that in both cases the reaction is facilitated by the rigidity of the ring systems involved. On the other hand the transformation **3c** → **5** disproves the presumption that an additional C–C double bond in conjugation to the carbonyl group is necessary for such a reaction to proceed [10].

The quantum yields for the reactions discussed, results on direct irradiations of **2**, further structural evidence for **3** and **5** (using allyl bromide d_5 in the synthesis of **1b** and **1c**) and complete experimental details will be reported in the full paper.

Experimental Part

Materials. **2a** and **2b** were obtained according to literature [7]. **1c** was prepared by analogy to [10]. Thus from 0.1 mol 4,4-dimethyl-2-cyclohexenone, 100 ml 2M solution of sodium bis(trimethylsilyl) amide in toluene and 0.2 mol allyl bromide one obtains 75% **1c** of b.p. 77–80°/0.5 Torr. **2c** was obtained in 90% yield – again by analogy to [7] – by irradiating (λ = 366 nm) 6.10^{-3} mol **1c** in 100 ml cyclohexane for 45 h and subsequent bulb to bulb distillation (110°/0.5 Torr) of the residue. Benzene used in photolyses was of spectroscopic grade.

Photolyses. These were carried out with a *Minerallight* PCQXl low pressure mercury lamp. Before irradiation the solutions were flushed with argon. In a typical run 2.10^{-3} mol of **2** in 20 ml benzene were irradiated for 16–25 h. The isolation of the photoproducts **3** and **5** was achieved by preparative GLC. (15% QF_1 on chromosorb G-AW-DMCS at 190° and 5% QF_1 on chromosorb G-AW-DMCS at 160°).

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