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UNUSUAL COURSE OF A TYPE II PHOTOREACTION

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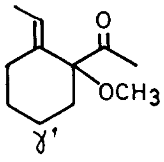
SUMMARY

The type II photoreaction of 1-acetyl-2-ethylidene-1-methoxycyclohexane (1) affords 2-ethylidene-1-methoxy-6-methylbicyclo[3.1.1]heptan-6-ol (2) as a result from ring closure of the least stable 1,4-biradical.

Although the γ -hydrogen abstraction (Norrish type II) rate in ketones can reasonably be predicted from bond strenghts[3], this does not necessarily mean that the major photoproduct is derived from the most stable 1,4-biradical[4]. One should therefore be cautious with the structural assignment of isomeric reaction products. This point has sometimes been overlooked in the literature[5].

In our work on the photochemistry of α-oxy-β,γ-enones[6] we encountered an illustrative case of unusual selectivity in the type II photorearrangement of 1-acetyl-2-ethylidene-1-methoxycyclohexane (1, fig. 1). The main product (40 % of volatiles) was unambiguously characterized as 2 by thorough ^{1}H NMR analysis at 360 MHz (Table 1). The alternative structure 3 (fig. 1) could be eliminated by the presence of 2 allylic long-range couplings on H-2'. The envelope conformation 2 (fig. 1) is substantiated by : nearly eclipsed disposition of H-3 and H-4 (see vicinal coupling constants), long-range couplings over a W-path between H-3B/H-5 and H-4A/H-7B, a small geminal coupling constant between H-7A/H-7B typical for a strained four-membered ring[7], a small and a large coupling constant between H-5 and the protons on C-4 as well as with those on C-7. The results are ascertained by extensive nmdr experiments.

The main type II photoproduct, 2-ethylidene-1-methoxy-6-methylbicyclo[3.1.1]-heptan-6-ol (2, fig. 1), is formed from 1 by abstraction of a secondary γ'-hydrogen instead of an allylic hydrogen atom by the n,π*-excited carbonyl group. The latter case would have led to 3 and 4 (a very minor product in the photolysis mixture), in which however a sp^2-hybridized carbon atom is incorporated in a four-membered ring. In an analogous system 5 (fig. 1) Dalton[5] concluded to the formation of type II product 6 (fig. 1) derived from the most stable 1,4-biradical. The assignment is based on the upfield shift of the methylcarbinol group by the shielding of the double bond. From molecular models it can be verified that the magnetic anisotropy effect is very comparable in structure 7 (fig. 1) arising from the less stable 1,4-biradical. Therefore, the alleged structure must be further confirmed.



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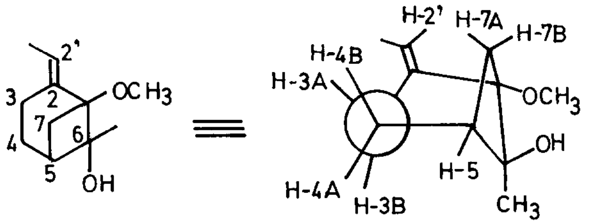

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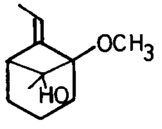

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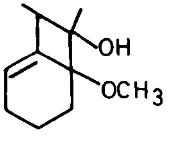

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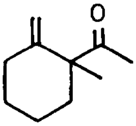

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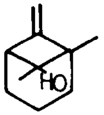

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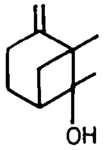

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Fig 1

TABLE 1 : ^{1}H NMR data of compound 2 in $CDCl_3$ (TMS-internal)

Chemical Shifts

H-2'	H-3A	H-3B	H-4A	H-4B	H-5	H-7A	H-7B	CH_3-2'	CH_3-6	OCH_3	OH
5.39	2.43	2.29	1.85	1.72	2.20	2.45	1.76	1.61	0.98	3.23	2.78

Coupling Constants

$^3J(CH_3\text{-}2',2')$	$^4J(2',3A)$	$^4J(2',3B)$
6.8	$\|1.5\|$	$\|2.9\|$

$^3J(3A,4A)$	$^3J(3A,4B)$	$^2J(3A,3B)$	$^3J(3B,4A)$	$^3J(3B,4B)$	$^2J(4A,4B)$
< 0.5	8.6	-18.6	9.8	1.8	-12.4

$^3J(4A,5)$	$^3J(4B,5)$	$^4J(3B,5)$	$^4J(4A,7B)$	$^3J(5,7A)$	$^3J(5,7B)$	$^2J(7A,7B)$
4.6	1.8	$\|0.5\|$	$\|1.4\|$	7.2	< 0.5	-8.8

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