

PHOTOLYSIS OF PINOCARVONE

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The photolysis of pinocarvone (1) was examined in this laboratory as part of a continuing programme to investigate the photochemistry of terpenes. This appears to be the first report concerning the photochemistry of an alicyclic α -methylene ketone, although a note concerning the photochemistry of a macrocyclic α -methylene ketone recently appeared¹.

Polymeric product was obtained when solutions of pinocarvone were irradiated in both protic and aprotic media with light from a medium pressure mercury arc. Irradiation with a 2W low pressure mercury arc gave predominantly monomeric material. Reaction mixtures were analysed by GLC on 5% DIDP with yields of the three products A, B and C (in order of R_f) being calculated

<u>Starting Material</u>	<u>Irrad. Time</u> (hr)	<u>Flushing Gas</u>	<u>Yield (%)</u>			
			A	B	C	(1)
200 mg/220 ml solvent						
1 in Hexane	6	N ₂	31	13	13	0.5
1 in Hexane	6	O ₂	24	13	15	16
1 in MeOH	11	N ₂	23	10	11	3

Table 1

relative to an internal standard (Table 1). In addition to the products shown for irradiation of pinocarvone in methanol solution, traces of two additional compounds were observed. A significantly slower reaction rate in hexane when the solution was charged with oxygen, is perhaps evidence that the reaction proceeds via a triplet intermediate.

therefore reasoned that a bridgehead and the point of attachment of the vinyl group were at one of the α positions to the carbonyl group in the five membered ring. The positions of the remaining groups followed. In corroboration an agreement factor of 0.031 was obtained between the calculated and observed paramagnetic shifts of protons in 2 (Table 2) with the optimised bonding site parameters O-Eu 3.5\AA , and C-O-Eu 140° . The calculated shift for each proton in 2 was determined by use of the McConnell Robertson expression³ where values were refined by a computer program similar to that described by Wilcott *et al*⁴.

Proton	C3exo	C3endo	C4	C6exo	C6endo	C7Me	C8Me	C9	C10(A)	C10(B)
δ (ppm)	2.23	2.23	2.42	2.63	1.43	0.90	1.20	5.80	5.03	5.27
Δ obs	1.06	1.06	0.44	0.50	0.76	0.62	0.38	1.13	0.62	0.33
Δ calc	1.06	1.04	0.43	0.49	0.78	0.65	0.33			

Table 2

The identification of B as 5,5-dimethyl-6-methylene-norbornan-2-one(3) also followed from NMR studies. This compound has previously been prepared by Gaitonde *et al*⁵ and an NMR spectrum obtained from these workers was identical to that of B. Lanthanide induced shift studies had favoured 3 over several other possible structures. An agreement factor of 0.093 was obtained between the calculated and observed paramagnetic shifts of protons in 3 (Table 3) with the optimised bonding site parameters O-Eu 3.7\AA , and C-O-Eu 145° .

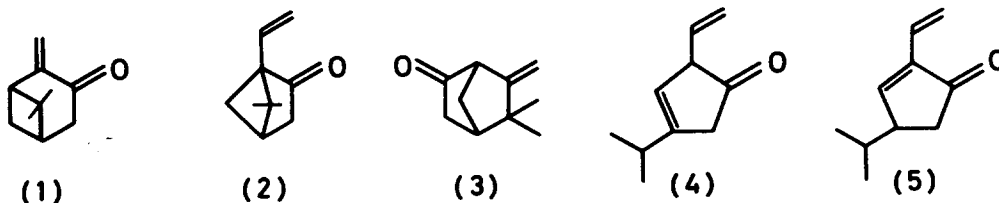
Proton	C4	C1	C3exo	C3endo	C7syn	C7anti	C8(A)	C8(B)	C9Me	C10Me
δ (ppm)	2.20	3.02	2.07	2.07	1.65	2.17	5.07	4.82	1.13	1.20
Δ obs	0.71	2.07	1.91	1.91	1.09	0.71	0.72	0.54	0.57	0.43
Δ calc	0.81	1.96	1.79	1.86	1.30	0.90	0.76	0.46	0.61	0.44

Table 3

The structure of the third photo-product has not yet been fully elucidated but the data available are not inconsistent with compound C being 5 which would have arisen from isomerisation of 4.

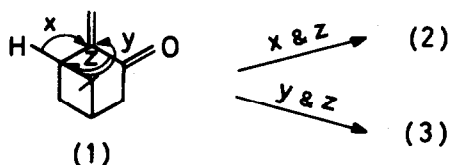
GC-MS of a crude reaction mixture showed A, B and C were isomeric with the starting material (MW 150), with only minor differences being observed in the ion breakdown pattern of the three compounds.

The three products were separated by preparative GLC after unsuccessful attempts to separate them by PLC. Compounds A and C were oils and compound B a solid m.p. 70°(sublm.). The UV spectra ($C=O \pi-\pi^* \approx 280 \text{ nm}$) and IR carbonyl absorption positions for A(1754 cm^{-1}) and B(1748 cm^{-1}) indicated in each case a five membered ring ketone while the UV spectrum of C($C=O \pi-\pi^* 245 \text{ nm}$) and its IR carbonyl absorption (1707 cm^{-1}) were consistent with a five membered ring α, β -unsaturated ketone. As the crude reaction product displayed no significant absorption at 245 nm it was concluded that thermal isomerisation of the initially formed third photoproduct had occurred, probably in the injection port of the GLC.

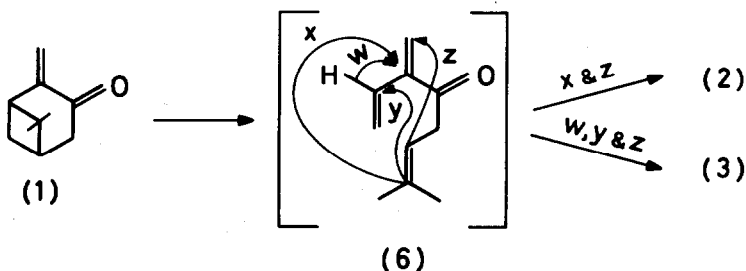


The identification of compound A as the new compound 5,5-dimethyl-1-vinylbicyclo(2,1,1)hexan-2-one(2) followed from NMR studies. The NMR spectrum showed presence of two methyl groups (0.90 and 1.20 δ) attached to a quaternary carbon atom and contained an ABM system (5.02-5.80 δ) indicating a vinyl group attached to a quaternary carbon atom. A doublet at 1.43 δ corresponding to one proton suggested an endo proton on a methano bridge which was deshielded by a carbonyl group². Lanthanide induced shift studies with $\text{Eu}(\text{Dpm})_3$ showed there were only two protons α to the carbonyl group, both attached to the same carbon atom. Double irradiation studies on the shifted peaks revealed that a single proton was coupled to both the methylene protons and to the proton which coupled with the suggested endo proton. The amount by which the methyl groups shifted relative to other peaks, on addition of successive portions of $\text{Eu}(\text{Dpm})_3$, indicated the methyl groups were remote from the carbonyl group and it was

The reaction mechanism operating has yet to be established, but products 2 and 3 could have arisen by either of two pathways, the first involving the unusual step of α - β bond rupture of an α, β -unsaturated ketone (Scheme 1), the second involving the intermediate 6 which undergoes the electrocyclic combinations indicated (Scheme 2). Compound 4 proposed for the third photoproduct could conceivably arise from either pathway.



Scheme 1.



Scheme 2.

Acknowledgments

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