

## MATRIX PHOTOCHEMISTRY OF CYCLIC KETONES: ESR STUDY

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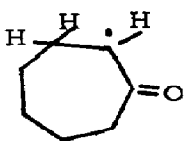
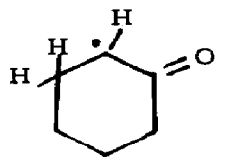
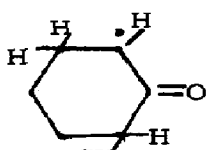
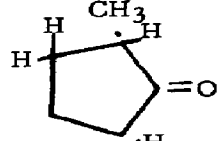
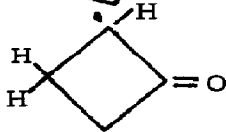
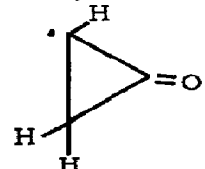
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A series of cyclic ketones has been photolyzed in an adamantane matrix at temperatures ranging from 123 to 296 K using an ESR spectrometer to identify radical intermediates. With cycloheptanone, cyclohexanone, cyclopentanone, cyclobutanone, and cyclopropanone as solutes, only 2-cycloalkanonyl radicals formed by loss of a hydrogen atom from the  $\alpha$ -carbon are observed. Table I shows the nuclear hyperfine splitting constants (due to H-atoms on adjacent  $\alpha$  and  $\beta$  carbon atoms) measured for the observed radicals.

Where no value is given in the table for  $a_{\beta}$ , both  $\beta$ -hydrogen atoms have effectively equivalent splitting constants. In the case of the cyclohexanonyl radical at the two higher temperatures this effect presumably results from rapid chair-boat-chair interconversion; in the cyclopentanonyl case the apparent equivalence of the  $\beta$  hydrogen atoms probably results from pseudorotation. The cycloheptanonyl radical shows a uniquely complex spectrum of 12 sharp lines which can be explained by three sets of inequivalent  $\beta$  hydrogen atoms, corresponding to three different ring geometries in the region of the unpaired electron.

The methyl cyclohexanonyl radical listed in Table I was formed by photolysis of 2,6-dimethyl cyclohexanone. Thus loss of a methyl radical was favored over loss of hydrogen atom from the  $\alpha$ -carbon in this case.

(1) Table 1. Hyperfine Splitting Constants (in Gauss)

Radical	T(K)	$a_{\alpha}$	$a_{\beta}$	$a_{\beta'}$
	263	17.8	21.7	44.4
	263	17.8	28.6	37.5
	263	17.8	32.6	33.5
	293	18.0	32.8	--
	223	18.0	32.6	--
	173	18.0	23.3	42.1
	123	18.0	23.7	42.6
	233	19.0	27.0	39.0
	173	19.0	25.0	41.0
	297	18.1	35.6	--
	255	18.7	36.1	--
	233	19.0	26.5	40.5
	173	19.0	24.5	42.5
	203	19.0	26.0	40.0
	173	19.0	24.0	42.0

(1)  $\nu \approx 9.25 \times 10^9$  Hz. Light source: Hg capillary arc,  
 $290 \leq \lambda \leq 340$  nm with filter, and unfiltered.

Photolysis of norcamphor led to a spectrum which could not be definitively analyzed but which indicated the presence of several radicals having different  $g$ -values. Probably cleavage of a bridgehead carbon-carbon bond and of the two different  $C_{\alpha}$  - H bonds are competing processes.

No spectra attributable to biradicals or triplet states were detected for any of the solutes at any of the temperatures employed.

Results obtained using deuterated compounds and other matrices will also be presented and possible reaction mechanisms for formation of the cyclo-alkanonyl radicals will be offered.