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THERMAL REORGANIZATION OF CIS-1,2-DIMETHYLCYCLOBUTANOL - THERMAL REVERSAL OF A PHOTOCHEMICAL PROCESS

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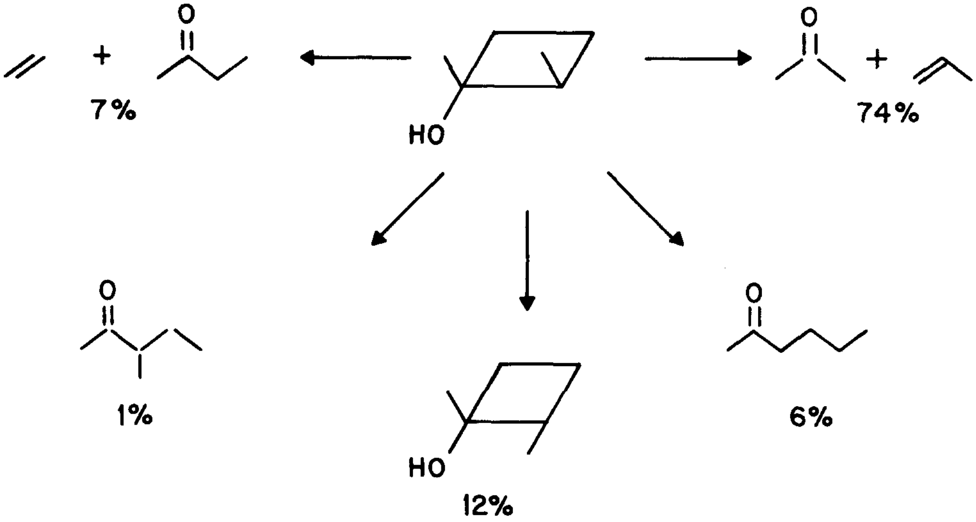
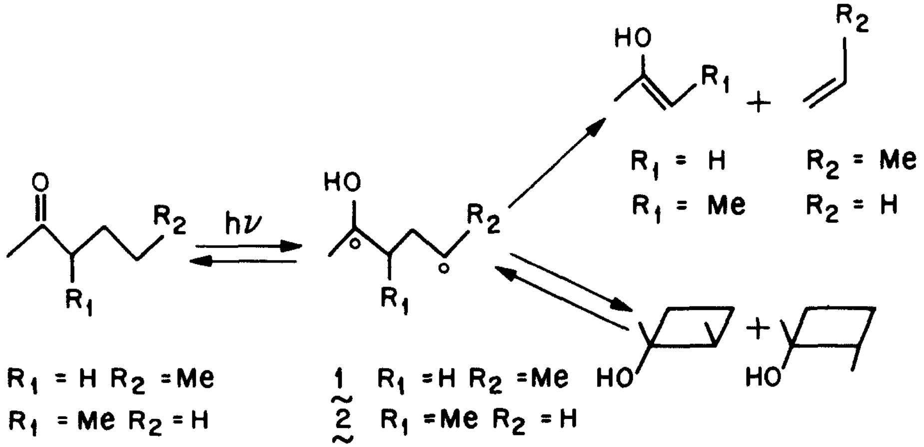
A 1-hydroxy-1,4-diradical is frequently considered as a photochemical intermediate and as a source of radiationless decay of the excited states of aliphatic carbonyl compounds (1). Optical (2) and geometrical (3) isomerization, isotope (4) and polar (5) effects and numerous structure-reactivity correlations (6) have focused on this diradical to substantiate its occurrence and to examine its chemistry. These studies have been limited, however, to the behavior in solution of the photochemically generated diradical. Fresh insight into the chemical transformations of this hydroxy diradical can now be reported from a study of the thermal reorganization of cis-1,2-dimethylcyclobutanol.

The thermal reorganization of cis-1,2-dimethylcyclobutanol at 381° leads to the formation of the products shown below.* The products can be



viewed as arising through the intermediate formation of a pair of 1,4-diradicals (**1** and **2**) by cleavage of the C_1-C_2 or the C_1-C_4 bond of the cyclobutane ring followed by further bond cleavage (fragmentation), hydrogen migration (isomerization to ketone) or ring closure (geometrical isomerization).

The hydrogen migration of 1,2-dimethylcyclobutanol thermally reverses the photochemical Yang reaction (7) and provides compelling evidence that reversible hydrogen transfer is a path for radiationless relaxation of excited carbonyl compounds (1). Indeed the thermal reorganization of 1,2-dimethylcyclobutanol represents the complete reversal of the solution photochemistry of two of the ketonic products (2-hexanone (4) and 3-methyl-2-pentanone) through the intermediacy of a common 1,4-diradical (**1** or **2**) as



depicted above. Padwa and Alexander reported a similar reversal in the thermal reorganization of strained 1-phenyl-bicyclo[1.1.1]pentanol (8).

The temperature dependence of the rate of ring opening of *cis*-1,2-dimethylcyclobutanol was examined in vapor phase and in a static system by the disappearance of the starting alcohol. The rate of ring opening in the range 372-394° follows an Arrhenius expression of the form

$$k = 0.96 + 0.11 \times 10^{15} \exp (58{,}000 + 1500/RT)$$

The activation energy for ring opening is 3 kcal mol^{-1} lower in the alcohol than in the parent hydrocarbon, *cis*-1,2-dimethylcyclobutane (9). This lowering is consistent with the sparse data on hydroxy assisted carbon-carbon (10) and carbon-hydrogen (11) bond cleavages.

The activation energy for cyclobutanol formation from **1** can be estimated from a few, simple calculations. The standard enthalpies of 2-hexanol (-79.9 kcal mol^{-1}) and of *cis*-1,2-dimethylcyclobutanol (-46.9 kcal mol^{-1}) are calculated from group additivities (12). The enthalpy of **1** is $\simeq$ +2 kcal mol^{-1} from the following reaction and bond dissociation energies:

$$CH_3CHOH(CH_2)_3CH_3 + 186 \text{ kcal} \rightarrow CH_3\overset{\circ}{C}OH(CH_2)_2\overset{\circ}{C}HCH_3 + 2H^{\circ}(104.2 \text{ kcal})$$

$$DH^{\circ}((CH_3)_2C(OH)\text{-}H = 91 \text{ kcal mol}^{-1} \ (13)$$

$$DH^{\circ}((CH_3)_2CH\text{-}H) = 95 \text{ kcal mol}^{-1} \ (13)$$

Making a small correction for temperature in the activation energy for ring opening ($-RT_{mean}$), the activation energy for ring closure of **1** is estimated as 58.0 kcal mol^{-1} $- RT_{mean} - \Delta H^{\circ}$ (**1**) + ΔH (*cis*-1,2-dimethylcyclobutanol) $\simeq$ 8 kcal mol^{-1}, a reasonable value in light of the estimated activation energy for ring closures in C_4 hydrocarbons (6 kcal mol^{-1} + *gauche* repulsions)(14).

In conclusion, *cis*-1,2-dimethylcyclobutanol undergoes thermal reactions analogous to the photochemistry of its isomeric ketones. Kinetic investigation provides insight into the chemistry of the common intermediate. Further studies on this and similar systems are in progress.

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*Product yields were determined by standard glc techniques and are based on unrecovered starting material. Products were separated and identified by comparing their ir spectra, mass spectra (accurate mass and fragmentation pattern), and glc retention times with the spectra and retention times of authentic samples.