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PHOTOCHEMISTRY OF 2,3-DIMETHYLCYCLOBUTANONE. TEMPERATURE AND WAVELENGTH EFFECTS.

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ABSTRACT: The ratio of products formed in the photochemistry of cis- and trans-2,3-dimethylcyclobutanone in alcohols is found to be wavelength and temperature dependent.

INTRODUCTION. The photochemistry of cyclobutanones in solution is dominated by a single primary photochemical process:[1] α-cleavage. In general, this process occurs from the S_1 (n,π*) state and leads to a singlet diradical that proceeds to products via (a) decarbonylation, which leads to cyclopropane products, (b) cycloelimination, which leads to an ethylene and a ketene and (c) ring expansion, which leads to an oxacarbene, that is usually trapped by alcohols as a tetrahydrofuranyl ether. In general, the stereospecificity of products produced by each reaction is very high (>95%).[2] We find that 2,3-dimethylcyclobutanone differs from the typical pattern in that the stereospecificity of cyclopropane formation is relatively low. We report here a study of the products formed from the photolysis of 2,3-dimethylcyclobutanone, as well as the variation in products as a function of temperature and wavelength.

RESULTS. Irradiation of cis or trans-2,3-dimethylcyclobutanone (c-1 and t-1) in isopropanol or t-butanol results in the products shown in Scheme I. Information relevant to the relative product yields and percentage stereospecificity are listed in Table 1 (wavelength effects at 25°C in t-butanol solvent) and Table 2 (temperature effects with 313 nm excitation in isopropanol).

DISCUSSION. Products. Like other cyclobutanones in alcohol solvents,[3(a)] 1 yields products expected from an initial primary process of α-cleavage that generates a diradical which partitions to products via decarbonylation (path a), cycloelimination (path b) or ring expansion by cyclization to an oxacarbene (which is trapped by alcohols, path c).[3(b)] A fourth pathway, cyclization to regenerate the starting ketone (path d) has been invoked to explain the observation that quantum yields for product formation are less than unity, although it appears that the primary photochemical process of α-cleavage occurs with unit efficiency.[1] At low conversions (≤5%) we were unable to detect significant interconversion of t-1 and c-1 during photolysis, so we conclude that either path d is insignificant under our conditions or, more likely, that path d occurs from a singlet diradical with essentially complete retention of stereochemistry. Although the types of products produced from photolysis of 1 are completely analogous to those observed from photolysis of many other alkyl cyclobutanones, the stereospecificity of products (values in parentheses in Table 1 and 2) and the regiospecificity of cycloelimination (ratio of path (b)-1 to path (b)-2 in Table 1) are in several cases much lower than expected from previous reports.

Table 1. Wavelength Effect on Product Yields and Stereospecificity.[a]

Process	cis-2,3-dimethylcyclobutanone		trans-2,3-dimethylcyclobutanone	
	254 nm	313 nm	254 nm	313 nm
Decarbonylation: Path (a)	13(66)	8(60)	18(88)	11(98)
Cycloelimination: Path (b)-1	50(88)	40(94)	55(94)	43(99)
Ring Expansion: Path (c)	37(92)	52(94)	27(95)	46(98)
Ratio of path (b)-1 to (b)-2	2.5	14	2.6	7.5

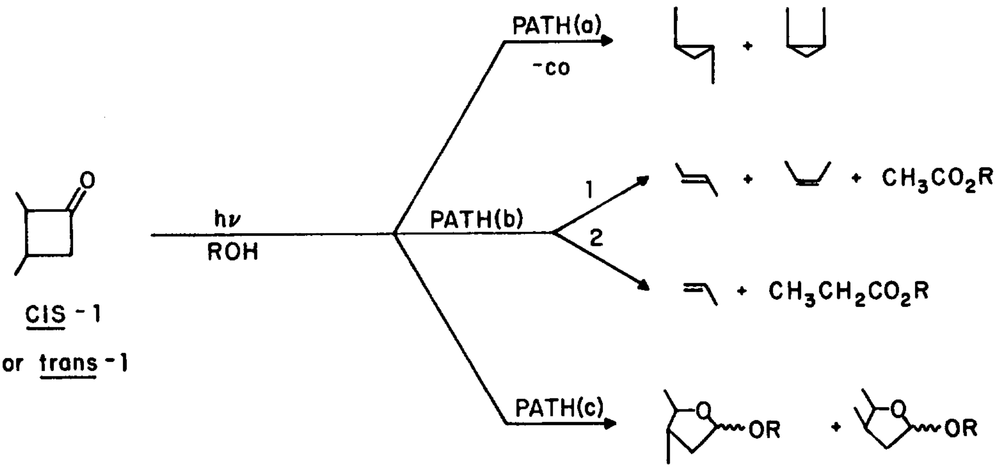
(a) The first number in the table is the relative yield of product based on cyclobutanone reacted. The overall product yield is nearly quantitative. Temperature 25°C, solvent t-butanol.

Table 2. Temperature Effects on Product Yields and Stereospecificity.[a]

Process	cis-2,3-dimethylcyclobutanone			trans-2,3-dimethylcyclobutanone		
	25°C	-78°C	-198°C	25°C	-78°C	-198°C
Decarbonylation: Path (a)	8(60)	3(44)	6(42)	12(95)	4(89)	7(95)
Cycloelimination: Path (b)-1	44(95)	16(97)	58(88)	45(98)	17(99)	38(98)
Ring Expansion: Path (c)	44(92)	81(95)	36(60)	43(98)	79(99)	55(45)

(a) The first number in the table is the relative yield of product based on cyclobutanone reacted. The overall product yield is nearly quantitative. Excitation wavelength 313 nm, solvent isopropanol.

Scheme I.



Stereospecificity as a function of excitation wavelength at 25°. At 25° and with 313 nm photoexcitation in t-butanol solvent, the stereospecificity of both cycloelimination and ring expansion (paths b and c) is high (≃94%), as is the stereospecificity of decarbonylation (path c) for t-1 (98%). On the other hand, for c-1, the products of decarbonylation, display only modest stereospecificity (60%). Decrease in the excitation wavelength (313 nm → 254 nm) generally causes a small decrease in stereospecificity of product formation, with the exception again of path (a) for c-1 which displays a modest increase in stereospecificity.

The generally high stereospecificity of product formation is consistent with α-cleavage from S_1 followed by formation of products faster than rotation about bonds in a singlet 1,4-diradical intermediate. The low stereospecificity toward path (a) observed from c-1 is consistent with leakage of S_1 to T_1 followed by selective decarbonylation of a triplet 1,4-diradical intermediate for which bond rotations compete with cyclization.[4]

Regiospecificity as a function of excitation wavelength. The ratio of 2-butenes to propene provides a measure of regiospecificity of overall cycloelimination, the latter alkene resulting from α-cleavage of the less substituted α carbon-CO bond. At 25° with 313 nm excitation, both c-1 and t-1 undergo predominate cleavage of the more substituted α-carbon-CO bond (path b-1). Decrease in the excitation wavelength (313 nm → 254 nm) causes a substantial decrease in regiospecificity. These results are consistent with an excess energy effect on the α-cleavage step. It is noted that the yield of cyclization also decreases with increase in excitation energy, a result which is interpretable as an excess energy effect on the partitioning of the intermediate diradical to products.

Product ratios and stereospecificity as a function of temperature. When the excitation wavelength is maintained at 313 nm, the effect of temperature on the reaction stereospecificity is minor. Isopropanol was employed as solvent for the temperature studies. From Table 2 it is noted that lowering of the temperature from 25°C to -78°C (solvent still liquid) increases the yield of cyclization product at the expense of cycloelimination and decarbonylation products. The stereospecificity of path (b)-1 and path (c) is not significantly influenced whereas the stereospecificity of path (a) displays a modest decrease by this temperature variation. At -196°C (solid isopropanol solvent) the relative yield of cyclization products is significantly lower than that found at -78°C. This result may be interpreted to result from the lower scavenging efficiency of carbene by isopropanol under these conditions. As a result, an equilibrium between the oxacarbene and 1,4-diradical may occur and cause a lower net yield of acetals. This interpretation is consistent with the rather substantial decrease in stereospecificity of ring expansion products upon going from -78°C to -198°C.

CONCLUSION. Both t-1 and c-1 undergo conventional photoreactions resulting from α-cleavage in t-butanol and isopropanol. The product ratios observed in fluid solution as a function of temperature and excitation wavelength are consistent with the occurrence of initiation of decarbonylation and cycloelimination from upper vibrational levels, whereas ring expansion is favored in lower vibrational levels (i.e., the yield of the latter is optimized at low temperature and long wavelengths). Some leakage from S_1 to T_1 evidentally occurs from lower vibrational levels. The regiospecificity of α-cleavage in fluid solution is shown to be wavelength dependent at 25°C. The stereospecificities of path (b) and (c) are high for both t-1 and c-1 under most conditions studied. However, for c-1, path (a) displays poor stereospecificity. In an isopropanol glass ring expansion is suppressed and displays low stereospecificity, a result consistent with reversibility of oxacarbene formation for a 1,4-diradical precursor.

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3. (a) Photolysis of 1 in methanol results in complicating formation of acetals presumably via an acid catalyzed process. Acetal formation was not observed in isopropanol or tert-butanol solvents.
   (b) Four acetals were formed from both t-1 and c-1. The stereochemistries were assigned from the results of equilibration methods and from oxidation to lactones. The isomers due to epimers at the OR bearing carbon are not distinguished in the discussion or in the Tables. Only the stereochemistry relevant to the cis or trans configuration of the starting cyclobutanone is considered.

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