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ORGANIC PHOTOCHEMISTRY WITH 6.7eV PHOTONS DECOMPOSITION OF 1,1-DISUBSTITUTED CYCLOPROPANES IN SOLUTION

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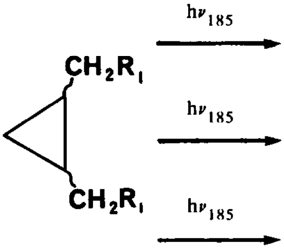
Abstract The course of the two-bond cleavage reactions of cyclopropanes in photolysis at 185nm in solution is strikingly influenced by disubstitution of one of the carbons in the ring

Photodecomposition of alkyl substituted cyclopropanes in solution with 185nm radiation has been shown to lead to both one- and two-bond cleavage [2-4] The former reaction (Eq. 1) which is



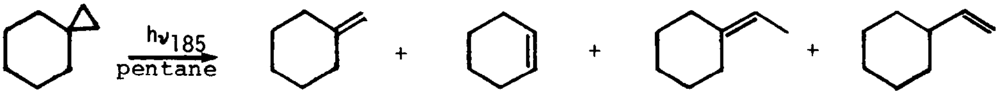
$R_1CH_2CH{=}CHCH_2CH_2R_1$ (1)

$R_1CH_2CH{=}CHCH_2R_1{+}CH_2$ (2a)

$R_1CH_2CH{=}CH_2{+}CH_2{=}CHR_1$ (2b)

common to the pyrolysis[5] as well as the long wavelength[6] and sensitized[6] photolysis of cyclopropanes has been shown to be strongly influenced by the pattern of substitution [2,3] In the two-bond cleavage process (Eq 2a and 2b) which is familiar only in far-UV photolysis[7], the effect of substituents has not been clearly established Our earlier work[2-4] which was exclusively on 1,2-disubstituted cyclopropanes showed that the loss of CH_2 (Eq 2a) competed poorly with the loss of a substituted carbene (Eq. 2b) In this Communication, we report results on the photolyses in solution with 185nm radiation of a 1-alkyl, a 1,1-dialkyl and two spiro cyclopropanes 1 and 2. This study demonstrates the striking effect of such a substitution pattern on the two-bond cleavage

Photolysis of spiro[5 2]octane (1)[8] gave the product

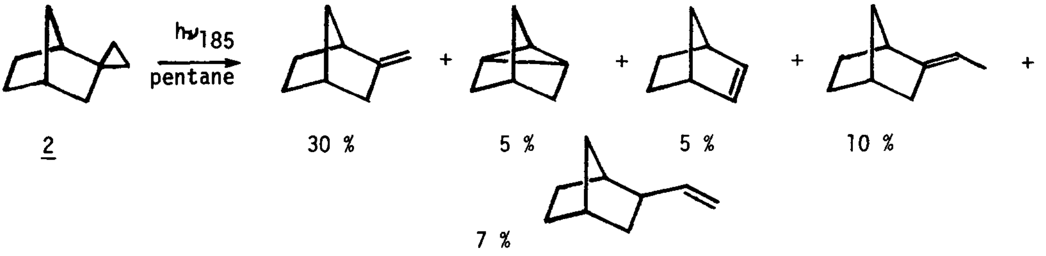


1 52 % 7 % 14 % 13 %

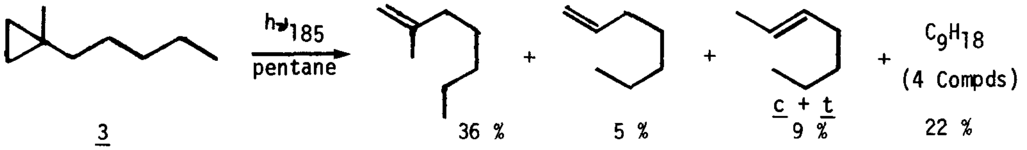
(3)

mixture shown in Eq 3 The percent yields were obtained from duplicate gas chromatographic traces at 20-30% conversion The material balance was 86% which should be considered satisfactory Although all of the products are olefins and therefore have more intense absorptions at 185nm than the starting material it was ascertained that secondary photolysis of the products (e g methylene cyclohexane, the major product) which could lead to a distortion in the composition of the product mixture or introduction of secondary photoproducts did not occur to any extent The major product from 1 is not only derived from a two-bond cleavage (as in nearly all cyclopropanes studied at 185nm[2-4]) but shows a surprising dominance of the process which eliminates methylene In passing, it may be noted that this is the opposite of the thermal process by which 1 is synthesized! (retro-carbene process)

In order to establish to what extent the loss of methylene is due to factors such as the strain, and the substitution pattern in 1, the cyclopropanes 2 and 3 were also investigated under similar conditions. Equations 4 and 5 summarize these results.



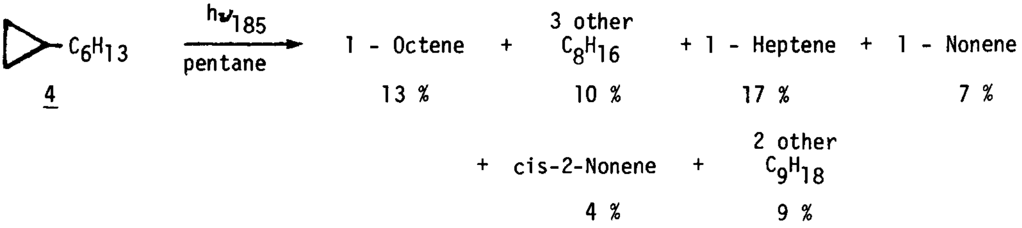
(4)



(5)

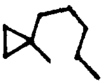
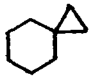
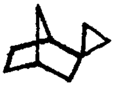
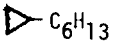
Certain surprising similarities among these three reactants were observed even though two of them were spirocyclopropanes and the strain energies must be considerably different among the three. Thus all three decomposed to give an olefin $+CH_2$ to a comparable extent (30-52%) but more importantly, with nearly the same quantum yield (1 0.19, 2 0.18; 3 · 0.15)[9] Since this suggested that 1,1-disubstitution was an important factor in determining the decomposition pattern, the monosubstituted cyclopropane 4 was also studied, Eq 6.

(6)



The relative rates of one bond cleavage, and two-bond cleavage to give either methylene and an olefin (Eq 2a) or a substituted carbene and an olefin (Eq 2b) in all four of the cyclopropanes considered so far and three of the 1,2-disubstituted cyclopropanes reported earlier[2,3] are given in Table I All of these data were obtained at low conversions under conditions in which the cyclopropanes absorbed essentially all of the radiation at 185nm

TABLE I Percent Yields of Products from Specific Reaction Modes in Solution Phase Photolysis of Cyclopropanes at 185nm

Compound					 a	 a	 b
1-Bond Cleavage	22	27	17	20	43	12	5
2-Bond Cleavage olefin+R_1R_2C:	15	7	10	17	57	88	85
olefin+CH_2:	37	52	30	23	?	0	11
TOTAL	52	59	40	40	57	88	96

a. Ref. 2 ; b. Ref. 3

1,1-disubstitution is seen to have a strongly directing effort towards loss of CH_2 and this effect is already significant even in a mono-substituted cyclopropane such as 4 This is in contrast with 1,2-diethyl cyclopropane or the bicyclic system It seems as if 1,2-disubstitution always causes the most substituted bond to break (both in 1-bond and 2-bond breaks) whereas with 1,1-disubstitution this rule is not rigidly observed

An interesting comparison can be made between the results in Table I and the published data[10] on the photochemistry of cyclopropanes at longer (λ>210nm) wavelengths At 185nm, the 2-bond cleavage is the major process and it is reasonable to attribute this to the singlet (valence) excited state of the cyclopropanes The long wavelength studies have all involved molecules in which the cyclopropane is in conjugation with a chromophore such as a phenyl group which funnels the energy into the former At these energies the singlet level of the cyclopropane would not be accessible It is possible that the observed photochemistry is from the excited states of the absorbing chromophore or the triplet levels of the cyclopropane

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7 Two examples are known of the loss of methylene in the long-wavelength photolysis of complex cyclopropanes See D. Richardson, L Durrett, J Martin, W. Putnam, S Slaymaker and I Dvoretzky, J. Am Chem Soc. **87**, 2763 (1965)

8 All photolyses were carried out in pentane solution ($\sim 10^{-2}$M) using a low-pressure mercury resonance lamp of 35 watts Solutions were outgassed before irradiation Analysis was by gas chromatography on two different columns.

9 For quantum yield measurements, a Hanovia spiral lamp with a Acton band-pass filter was used The cell with a Suprasil window contained the compound in pentane solution ($\sim 10^{-2}$M) The lamp was calibrated with a cyclooctene actinometer (Φ=0 35)

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