Table I. Proton Chemical Shifts of the $(CH_2)_4X$ Molecules[a]

	X							
	CH_2	O	S	Se	Se[b]	CO	SO_2	ref
$\gamma_{CS_2}{}^{\alpha}$		359.4	273.0		279.7			2
$\gamma_{CCl_4}{}^{\alpha}$	150.9	362.1	275.5	340.5	282.1	205.4	291.0	1
$\gamma_{CS_2}{}^{\beta}$		176.7	189.8		197.0			2
$\gamma_{CCl_4}{}^{\beta}$	150.9	179.6	191.8	204.0	198.8	192.2	218.7	1
Δ^{α}	5.3	4.4	21.3	66.4	23.7	35.0	63.8	1
Δ^{β}	5.3	37.5	45.3	63.8	43.6	62.0	99.7	1
$\mu_{C_6H_6}$	0.00	1.69	1.89	1.81	1.81	2.93	4.69	3

[a] All γ and Δ values are in hertz from Me_4Si at 100 MHz, and the dipole moments ($\mu_{C_6H_6}$) are in debye units. [b] This work.

The interpretation of the benzene shifts of the $(CH_2)_4X$ molecules is complicated because the rings are puckered, and their geometry is not fixed. Furthermore, the potential energy barrier to the rotation of the puckering around the ring (pseudorotation) depends on the nature of the functional group, X. Spectroscopic determinations of these barriers provided the values ~0, 50, 773, 1882, and 1687 cm^{-1} for X = CH_2, O, S, Se, and CO, respectively.[4] Correspondingly, the experimental electron diffraction data were found to be in good agreement with the theoretical results by assuming free pseudorotation for cyclopentane and THF and a fast inversion rate between the two half-chair conformations with C_2 symmetry for the other molecules.[5] The interpretation of the proton–proton coupling constants obtained in liquid phase for all these molecules can be satisfactorily carried out, assuming the same conformational behavior found in vapor-phase studies.[2,6] Therefore, the existence of free pseudorotation is perhaps the reason for the anomaly found for Δ^{α} of THF. This effect would be less important for cyclopentane whose small Δ^{α} value is due to its null dipole moment.

Our THS Δ values cannot be considered anomalous as do those of Strom et al., thus suggesting that we really used THS. Furthermore, the mass spectrum clearly indicated that the compound used was THS. Moreover, we have carried out the complete analysis of the proton spectrum of THS and properly interpreted the coupling constants obtained.[2c]

Experimental Section

Nuclear magnetic resonance spectra were recorded on a Varian XL-100 spectrometer. Me_4Si was used as an internal reference. The line frequencies were measured with an electronic counter (±0.1 Hz). Mass spectra were obtained with a Varian MAT 711 spectrometer operating at an ionization voltage of 75 eV and a source temperature of 180 °C.

THS was synthesized and purified by the procedure described by McCullough and Lefohn[7] using Merck products: mass spectrum, m/e (rel intensity) 138 (6), 137 (2), 136 (38), 135 (3), 134 (18), 133 (8),)132 (7), 110 (2), 109 (1), 108 (12), 107 (5), 106 (6), 105 (4), 104 (3), 96 (4), 95 (4), 94 (22), 93 (6), 92 (11), 91 (6), 90 (5), 82 (1.6), 81 (1.6), 80 (2.4), 79 (0.9), 78 (1.3), 77 (0.5), 76 (0.4), 55 (100).

Acknowledgment. This study was supported by the Comisión Asesora de Investigación Cientifica y Têcnica, Madrid.

Registry No. Cyclopentane, 287-92-3; tetrahydrofuran, 109-99-9; tetrahydrothiophene, 110-01-0; tetrahydroselenophene, 3465-98-3; cyclopentanone, 120-92-3; tetrahydrothiophene 1,1-dioxide, 126-33-0.

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(1) E. T. Strom, B. S. Snowden, Jr., H. C. Custard, D. E. Woessner, and J. R. Norton, *J. Org. Chem.*, **33**, 2555 (1968).

(2) (a) E. Diez, A. L. Esteban, and M. Rico, *J. Magn. Reson.*, **16**, 136 (1974); (b) A. L. Esteban, Ph.D. Thesis, Universidad Complutense, Madrid, Spain, 1976; (c) A. L. Esteban and E. Diez, *J. Magn. Reson.*, in press.

(3) A. L. McClellan, "Tables of Experimental Dipole Moments", W. H. Freeman, San Francisco, CA, 1963.

(4) (a) J. R. Durig and D. W. Wertz, *J. Chem. Phys.*, **49**, 2118 (1968); (b) J. A. Greenhouse and H. L. Strauss, *ibid.*, **50**, 124 (1969); (c) D. W. Wertz, *ibid.*, **51**, 2133 (1969); (d) W. H. Green, A. B. Harvey, and J. A. Greenhouse, *ibid.*, **54**, 850 (1971).

(5) (a) W. J. Adams, H. J. Geise, and L. S. Bartell, *J. Am. Chem. Soc.*, **92**, 5013 (1970); (b) H. J. Geise, W. J. Adams, and L. S. Bartell, *Tetrahedron*, **25**, 3045 (1969); (c) A. Almenningen, H. M. Seip, and T. Willadsen, *Acta Chem. Scand.*, **23**, 2748 (1969); (d) Z. Nahlovska, B. Nahlovsky, and H. M. Seip, *ibid.*, **23**, 3534 (1969); (e) *ibid.*, **24**, 1903 (1970); (f) H. J. Geise and F. C. Mijlhoff, *Recl. Trav. Chim. Pays-Bas*, **90**, 577 (1971).

(6) (a) R. L. Lipnick, *J. Mol. Struct.*, **21**, 411 (1974); (b) J. B. Lambert, J. J. Papay, S. A. Khan, K. A. Kappavf, and E. S. Magyar, *J. Am. Chem. Soc.*, **96**, 6112 (1974).

(7) J. D. McCullough and A. Lefohn, *Inorg. Chem.*, **5**, 150 (1966).

Organic Photochemistry with 6.7-eV Photons: Decomposition of *cis*- and *trans*-1,2-Diethylcyclopropanes, 1,1,2-Trimethylcyclopropane, and 1,1,2,2-Tetramethylcyclopropane

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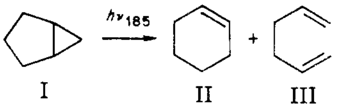
Received March 30, 1979

Recent work from this laboratory[1] has shown that bicyclic hydrocarbons such as I which incorporate a cyclopropane ring, on irradiation in pentane solution at 185 nm (≡6.7 eV), decompose according to eq 1 to give products



I II III (1)

which formally correspond to the cleavage of one or two bonds of the cyclopropane ring. These reactions are believed to occur from an electronically excited singlet state of the cyclopropane ring. Although the two-bond cleavage of cyclopropanes in gas-phase photolysis at wavelengths <185 nm is well-documented,[2] only a single example[3] of a disubstituted cyclopropane which is capable of giving stereochemical information on the photoprocess has hitherto been reported. This work will be referred to later.

The present work was intended to answer questions posed by our earlier report, which were: (i) is an alternative

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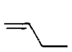
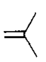
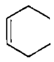
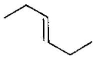
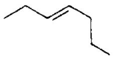
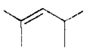
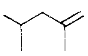
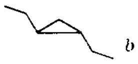
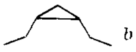
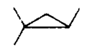
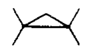
(1) R. Srinivasan and J. A. Ors. *J. Am. Chem. Soc.*, **100**, 7089 (1978).

(2) C. L. Currie, H. Okabe, and J. R. McNesby, *J. Phys. Chem.*, **67**, 1494 (1963); K. L. Hill and R. D. Doepker, *ibid.* **76**, 3153 (1972); E. Lopez and R. D. Doepker, *ibid.*, **82**, 753 (1978); A. A. Scala and P. Ausloos, *J. Chem. Phys.*, **49**, 2282 (1968); K. Shibuya, K. Obi and J. Tanaka, *Bull. Chem. Soc. Jpn.*, **48**, 1974 (1975).

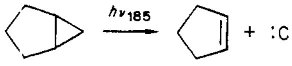
(3) J. H. Vorachek and R. D. Koob, *J. Phys. Chem.*, **76**, 9 (1972); K. Dees and R. D. Koob, *ibid.*, **77**, 759 (1973).

Table I. Photolysis of Alkylcyclopropanes in Solution at 185 nm

	products[a]										
reactants	C_2H_4	C_3H_6									
 [b]	NA[f]	1.56	1.59	NA	0.03	0.06		0.14[d]	0.20	NA	NA
 [b]	NA	1.78	1.93	NA	0.09	trace	0.40		*e*	NA	NA
 [c]	1.68	2.22	NA	1.80	NA	NA					
 [b]	NA	3.38	NA	3.11						3.03	3.60

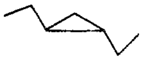
[a] Rates in μm mL^{-1} h^{-1}. [b] Results based on photolyses in pentane and 2,2,4-trimethylpentane. [c] Results in pentane only. [d] Includes a small contribution from *cis*-3-heptene. [e] Not separable from reactant under analytical conditions. [f] NA = not applicable.

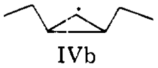
two-bond cleavage to give a cyclic olefin and a methylene (eq 2) of any importance? (ii) Is the two-bond cleavage

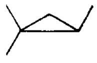


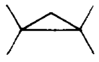
(2)

to be looked upon as being made up of two successive one-bond cleavages or as a concerted process? (iii) Is either the one-bond or the two-bond cleavages a reversible process? We have investigated the solution phase photolysis of the alkyl-substituted, monocyclic cyclopropanes IVa, IVb, V, and VI.


IVa


IVb


V


VI

In Table I, the rates of formation of the products are listed for all four reactants. The most extensive investigation was carried out on IVa and IVb because appropriate solvents were available which permitted analysis for low-boiling (C_2–C_4) as well as isomeric products. The absorbed intensities of light were the same in all four instances so that the rates of product formation are directly proportional to the quantum yields. The quantum yield for the disappearance of VI was ~1.0 based on the cis → trans isomerization of cyclooctene.[4]

The principal modes of decomposition of IVa are given in eq 3–6 (in the order of decreasing importance). The

$$\mathrm{IVa} + h\nu_{185} \rightarrow \mathrm{CH_3CH_2CH{=}CH_2} + \mathrm{CH_3CH{=}CH_2} \quad (3)$$

$$\rightarrow \mathrm{CH_3CH_2CH_2CH{=}CHCH_2CH_3} \quad (4)$$

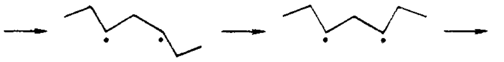
$$\rightarrow \mathrm{IVb} \quad (5)$$

$$\rightarrow \mathrm{CH_3CH_2CH{=}CHCH_2CH_3}(c + t) + [\mathrm{CH_2}] \quad (6)$$

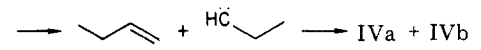
mass balance was satisfactory to ±10%.

Although process 3 is seen to be more than tenfold greater in importance than process 6, the occurrence of the latter answers the first of the questions. The fact that the 3-hexene was a cis,trans mixture suggests that the cleavage of two bonds proceeds with loss of stereochemistry and therefore cannot be held to be a concerted process. Recent calculations on the electronically excited states of alkylcyclopropanes by Rossi[5] suggest that the two-bond cleavage can be looked upon as being made up of two successive one-bond cleavage reactions. This would predict a loss of stereochemistry in reaction 6 if the second step is not faster than the time required for rotation of one of the alkyl groups. It is gratifying that this prediction is verified by the present results, but caution must be exercised in accepting it for two reasons: firstly, the ratios of *cis*- to *trans*-3-hexene are different for IVa and IVb. This suggests that the two systems may not go through a common intermediate and a simple stepwise scission mechanism would be inadequate. Secondly, it has been shown elsewhere[6] that the formation of not only vibrationally "hot" but electronically excited products which can subsequently rearrange is a possibility in photochemistry at 185 nm in solution. It should also be mentioned that the results of Dees and Koob[3] on the stereochemistry of the formation of 2-butene in the *gas-phase* photolysis of *cis*- and *trans*-1,2-dimethylcyclopropane at 165–123.6 nm seem incompatible with the present work in solution phase. Until some understanding of the excited states and mechanisms involved in these reactions is gained, it is difficult to unify results that were obtained under widely different conditions.

The stereoisomerization of IVa to IVb can occur in two ways (eq 5a and 5b). It is not possible to discard either

IVa

IVb

(5a)



IVa + IVb (5b)

of these possibilities with the present data.

The photolysis of V was undertaken to investigate the effect of alkyl substitution on the choice of the bond that undergoes cleavage. The two competing processes[7] are shown in eq 7 and 8. It can be seen that eq 7 is 50% more

$$\mathrm{V} + h\nu_{185} \rightarrow \mathrm{CH_3C(CH_3){=}CH_2} + \mathrm{C_2H_4} \quad (7)$$

$$\rightarrow 2\mathrm{CH_3CH{=}CH_2} \quad (8)$$

important that eq 8. From theoretical considerations, Rossi[5] has suggested that the most substituted C–C bond will be the first one to cleave. In V, this would be C_1–C_2. This is actually the bond that is cleaved in common in eq 7 and 8.

With tetrasubstitution of the cyclopropane ring (VI), the favored reaction is no longer a two-bond cleavage (eq 9) but an isomerization (eq 10 and 11). These isomerization

$$\mathrm{VI} + h\nu_{185} \rightarrow \mathrm{CH_3C(CH_3){=}CH_2} + \mathrm{CH_3CH{=}CH_2} \quad (9)$$

$$\rightarrow \mathrm{(CH_3)_2CHCH{=}C(CH_3)_2} \quad (10)$$

$$\rightarrow \mathrm{(CH_3)_2CHCH_2C(CH_3){=}CH_2} \quad (11)$$

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[4] R. Srinivasan and K. H. Brown, *J. Am. Chem. Soc.*, **100**, 2589 (1978).

[5] A. Rossi, *J. Phys. Chem.*, in press.

[6] R. Srinivasan and J. A. Ors, *J. Am. Chem. Soc.*, **101**, 3411 (1979).

[7] Isomerization products were found in only trace amounts in this system.

processes have been described before by Mazzocchi and Lustig[8] in the photolysis of phenylcyclopropane. Once again, the most substituted bond (C_1–C_2) is the one that cleaves preferentially.

Experimental Section

Apparatus. Photolyses were carried out in a cylindrical quartz cell 2 cm in diameter × 1 cm deep with Suprasil windows. The light source was a Hanovia 8-W mercury resonance lamp which was made of Suprasil glass. The lamp was operated from a constant voltage transformer.

Materials. 1,2-Diethylcyclopropane was synthesized by the addition of methylene to 3-hexene. The other alkylcyclopropanes were obtained from Chemical Samples Co. (Columbus, Ohio). The solvents used were spectroscopic grade pentane and isooctane from Baker (Photrex). All reactants were photolyzed separately in both solvents in order to be able to analyze for gaseous as well as isomeric products. No solvent effect was observed.

Analysis. Solutions were analyzed by gas chromatography on a Hewlett-Packard 5750 instrument fitted with a 10 ft oxydipropionitrile (20%) column and operated at ambient room temperature. The column was calibrated with authentic samples of the various products.

Procedure. Solutions (10^{-2} M) of the reactants were photolyzed at room temperature to conversions of 15% or less. Since the products were olefins which absorbed much more intensely than the starting materials, the rates of photolyses were strongly time dependent. The values given in Table I are initial rates of formation which were obtained by extrapolation of the experimental data to time zero.

Registry No. IVa, 71032-66-1; IVb, 71032-67-2; V, 4127-45-1; VI, 4127-47-3; C_2H_4, 74-85-1; C_3H_6, 115-07-1; 1-butene, 106-98-9; 2-methylpropene, 115-11-7; (*Z*)-3-hexene, 7642-09-3; (*E*)-3-hexene, 13269-52-8; (*E*)-3-heptene, 14686-14-7; 2,4-dimethyl-2-pentene, 625-65-0; 2,4-dimethyl-1-pentene, 2213-32-3; methylene, 2465-56-7.

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[8] P. H. Mazzocchi and R. S. Lustig, *J. Am. Chem. Soc.*, **92**, 2169 (1970); *J. Org. Chem.*, **38**, 4091 (1973); *J. Am. Chem. Soc.*, **95**, 7178 (1973); *ibid.*, **97**, 3707, 3714 (1975). See also: H. Kristinsson and G. W. Griffin, *J. Am. Chem. Soc.*, 88, 378 (1966); *Tetrahedron Lett.* 3259 (1966).

Ketene Dithioacetals. 2.[1] The Control of α vs. γ Allylation Using Cuprous Salts

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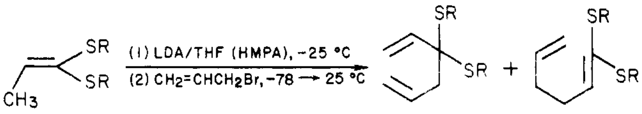
Ketene dithioacetals have recently received attention as viable synthetic intermediates.[3] It has been demonstrated[4] that their lithium anions undergo α alkylation to provide the dithianes of α,β-unsaturated ketones. We have sought to control the γ alkylation of these anions, thereby allowing them to serve as β-propionate anion equivalents.[5] Efforts to control α vs. γ alkylation in heteroatom-stabilized allylic anions[6] and resonance-stabilized enolates[7] have focused upon alteration of steric environment and variation of counterions and solvent.

Table I



1 α-2 γ-2

		with HMPA (3 equiv)			without HMPA		
entry	R	α	γ	yield[a]	α	γ	yield[a]
1a	$(CH_2)_3$	94	6	88	88	12	71[b]
1b	CH_3	73	27	66	74	26	82
1c	CH_2CH_3	70	30	80			
1d	$CH(CH_3)_2$	45	55	94	43	57	89

[a] Yields are of distilled material, unless otherwise noted. All new compounds provided satisfactory elemental analytical and spectral data. [b] VPC yield using an internal standard.

The effect of the variation of the alkyl group R on the α/γ ratio, in regard to both cyclic vs. acyclic structure and steric bulk, is outlined in Table I.

It is apparent that regioselectivity for α allylation is greater in the cyclic dithiane **1a** than in the acyclic analogues. Although the diisopropyl ketene dithioacetal has $\alpha/\gamma < 1$ (entry **1d**), it represents a limiting case in terms of steric bulk, since the *tert*-butyl analogues are not easily prepared. Moreover, the use of 3 equiv of hexamethylphosphoramide (HMPA) had no effect on the regioselectivity.[4b] Although Cope rearrangement of the 1,5-hexadienes α-**2** could be effected at 240 °C providing the ketene dithioacetals as the thermodynamic products, extensive decomposition occurred. It was confirmed by the collection–reinjection technique that rearrangement did not occur during VPC analysis.

Treatment of the red THF solution of lithium anion **1a** at −78 °C with cuprous iodide–trimethyl phosphite complex[8] provided a yellow solution containing a precipitated white solid. Warming of the reaction mixture to temperatures in excess of −25 °C caused the reaction mixture to turn black and become ineffective at alkylation. However, addition of an alkylating agent at −78 °C followed by warming to room temperature provided homogeneous yellow to yellow-green solutions. Often, solution was effected at −78 °C upon addition of the electrophile. By this procedure, exclusive γ allylation could be achieved as outlined in Table II. The γ-allylation products do not arise from copper-catalyzed isomerization of the α-allylation products. This was confirmed by reacting **4** with allyl bromide in the presence of α-**2** (R = $CH_2CH_2CH_2$). The product distribution indicated quantitative recovery of α-**2** and 70% yield of γ-**2** (R = $CH_2CH_2CH_2$).

Both allylic chlorides and bromides are suitable substrates. Since allylic alcohols are often conveniently

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[1] F. E. Ziegler and C. Chan, *J. Org. Chem.*, **43**, 3065 (1978).

[2] National Institutes of Health Career Development Awardee, 1973–1978.

[3] See ref 1, footnote 2, and N. H. Andersen, P. F. Duffy, A. D. Denniston, and D. B. Grotjahn, *Tetrahedron Lett.*, 4315 (1978); V. L. Mizyuk annd A. V. Semenovsky, *ibid.*, 3603 (1978); B. Cazes and S. Julia, *ibid.*, 4065 (1978).

[4] (a) D. Seebach, M. Kolb, and B.-T. Groebel, *Angew. Chem., Int. Ed. Engl.*, **12**, 69 (1973); (b) E. J. Corey and A. P. Kozikowski, *Tetrahedron Lett.*, 925 (1975); (c) D. Seebach and M. Kolb, *Justus Liebigs Ann. Chem.*, 811 (1977).

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