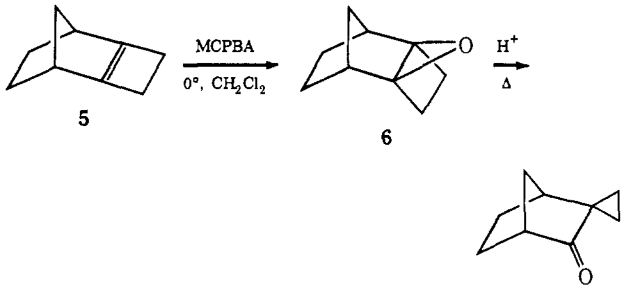
for ring closure of **7** is apparently responsible for the low efficiency of ring closure of **13**. Gajewski's conclusion that efficient photochemical isotopic scrambling in **13** results from opening to an intermediate bis allyl radical rather than closure to **2** is confirmed by these experiments.[10]

Epoxidation of **5** with *m*-chloroperbenzoic acid in methylene chloride at 0° under nitrogen and careful water work-up gave a mixture of two products (separated by preparative glc) identified as 2-spirocyclopropylbicyclo[2.2.1]heptanone (**12**)[4] and 10-oxatetracyclo[$4.2.1.1^{2,5}.0^{2,5}$]decane (**6**) [mass spectrum *m/e* 136.0894 (136.0888, calcd for $C_9H_{12}O$)]. A 100-MHz nmr spectrum in dichloromethane is consistent with the proposed structure **6** with multiplets centered at δ 1.95 (4 H) and 1.58 (4 H), the AB multiplet of an ABX_2 pattern centered at δ 0.97 (2 H) (J = 9.2 Hz), and the X_2 multiplet at δ 2.62 (2 H). The acid-catalyzed conversion of **6** to the known ketone **12**[4] is very rapid and quantitative and confirms the structure of **6**. In contrast to its instability to acid, **6** is relatively stable thermally. At 192° the half-life for conversion of **6** to **12** in diphenyl ether is 5 hr.



5 **6** **12**

Further studies on the synthesis of related strained cyclobutenes and electrophilic and cycloaddition reactions of these molecules are under active investigation.

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Internal Conversion in the Photolysis of 1,3-Cyclohexadiene in the Gas Phase. Relationships between the Thermal and Photochemical Reactions of 1,3-Cyclohexadiene

Sir:

The photolysis of 1,3-cyclohexadiene (Chd) in the gas phase has been studied previously by Srinivasan[1–4] who divided the products into two classes:[3,4] (class I) those observed only in the photolysis, *i.e.*, the isomers 1,2,4- and 1,3,5-hexatriene; and (class II) those presumably observed in both the photolysis and the thermal reactions of Chd, *i.e.*, H_2, benzene, C_2H_2, C_2H_4, dimer, and/or polymer. It was argued by Srinivasan[3,4] that in the photolysis the class II compounds might be formed from "thermal" reactions of vibrationally excited ground-state molecules which originate from the initially formed excited singlet state by internal conversion.

The relationship between the photolytic and thermal products of Chd does not seem to be as simple as postulated by Srinivasan.[3,4] Indeed more recent studies on the thermal reactions of Chd[5–7] indicate (1) that C_2H_2 and C_2H_4 are unimportant pyrolysis products over the temperature ranges used[5,7] (these products accounted for about 5% of the Chd reacted at 1233 °K),[8] (2) that hydrogen and benzene are not formed in equal yields and are formed in short chain reactions involving the cyclohexadienyl ($C_6H_7\cdot$) radical[5,7]

$$2\text{Chd} \longrightarrow C_6H_7\cdot + C_6H_9\cdot \tag{1}$$

$$C_6H_7\cdot \longrightarrow \text{benzene} + \text{H} \tag{2}$$

$$\text{H} + \text{Chd} \longrightarrow H_2 + C_6H_7\cdot \tag{3}$$

rather than in the unimolecular process 4 proposed for

$$\text{Chd}^{\dagger} \longrightarrow \text{benzene} + H_2 \tag{4}$$

the formation of these products in the photolysis (Chd†, in the internal conversion hypothesis, is a vibrationally excited molecule in its ground electronic state), and (3) that polymer is not formed in the thermal reactions, the pressure drop being entirely due to dimer (*exo*- and *endo*-dicyclohexadiene) formation.[6]

The present study was undertaken to determine the relative importance of dicyclohexadiene formation in the photolysis of Chd in the gas phase. *No evidence for the formation of the dimers has been found.* The Chd (K & K Labs) was purified as described previously.[9] The reaction cell consisted of a cylindrical quartz sleeve which was placed concentrically around a Philips Philora HPK 125 medium-pressure mercury lamp. Chd at 50.0 ± 0.05° and at pressures up to 120 Torr was irradiated by the unfiltered light from the lamp. The resulting pressure drop was followed by means of a Pyrex Bourdon gauge. The photolysis was stopped after the total pressure had decreased by 20–70%, and the reaction products were analyzed using the gas chromatographic technique and column used previously.[9] A small peak (corresponding to less than 1% of the Chd reacted) with a retention time similar to that of *trans,cis,trans*-tricyclo[$6.4.0.0^{2,7}$]dodeca-3,11-diene (the major product of photosensitization of Chd by triplet energy donors)[9–12] was observed. This product may have been formed by heterogeneous photosensitization of Chd[13] in spite of the precautions taken; the presence of this peak should therefore not be taken as evidence of the occurrence of the intersystem crossing $S_1 \rightarrow T_1$ in the photolysis. The only other gas chromatographic peaks observed have shorter retention times than those of the cyclohexadiene dimers formed in the thermal[6,10,11]

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[1] R. Srinivasan, *J. Amer. Chem. Soc.*, **82**, 5063 (1960).

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[7] G. R. De Maré, G. Huybrechts, and M. Toth, *J. Chem. Soc., Perkin Trans. 2*, 1256 (1972).

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[11] D. Valentine, N. J. Turro, Jr., and G. S. Hammond, *J. Amer. Chem. Soc.*, **86**, 5202 (1964).

[12] N. G. Minnaard, Doctoral Thesis, Rijksuniversiteit te Leiden, 1970, p 81.

[13] G. R. De Maré, M-C. Fontaine, and P. Goldfinger, *J. Org. Chem.*, **33**, 2528 (1968).

and photosensitized[9–12] reactions. *Thus the pressure decrease observed in the photolysis of Chd is the result of polymer formation by a reaction which has no parallel in the thermal reactions of Chd.*

The arguments in favor of internal conversion in the photolysis of Chd may be summarized as follows. (a) The decomposition reaction of Chd to acetylene and ethylene may be common to both the photolysis and the pyrolysis and might therefore proceed from the same vibrational levels of the ground electronic state in both cases.[14] (b) The calculated lifetime for Chd molecules in S_1 (4×10^{-9} sec)[2–4] is presumably too short to account for the observed pressure dependence of some product yields. (c) Chd fluorescence has not been observed even under extreme conditions.[15]

Taking into consideration the high quantum yield of the photoisomerization of Chd to 1,3,5-hexatriene in the liquid phase (0.40),[16] the different nature of the thermal and photochemical steps leading to H_2 + benzene, the absence of polymer formation in the gas-phase thermolysis, and the absence of dimer formation in the gas phase photolysis, it is concluded that internal conversion of electronically excited singlet-state molecules may not be as important in the photolysis of Chd as deduced from the earlier work.

One of the referees has asked us to speculate what might be happening in the photolysis of Chd. It is possible that the pressure dependence of the class II products is the result of one of the following.

(1) The products are formed after internal conversion as postulated by Srinivasan. In this case only very high vibrational levels are involved thus giving rise to products that differ from those observed in normal pyrolysis studies. Deactivation does not progress stepwise (otherwise the dimers should be formed) but in one or two collisions. It is possible that the reactions of these high vibrational levels might be observed in shock-tube studies.

(2) The class II products are formed from an upper triplet state of Chd which is reached by intersystem crossing. This triplet state has a configuration which does not permit it to phosphoresce nor can it be vibrationally deactivated to the lowest triplet state (otherwise the dimers typical of triplet photosensitization should be observed). Once again colllsional deactivation has to take place in only one or two collisions rather than in a stepwise fashion.

(14) P. Datta, T. D. Goldfarb, and R. S. Boikess (*J. Amer. Chem. Soc.*, **93**, 5189 (1971)) concluded that the absence of absorption bands due to benzene, ethylene, and acetylene in the photolysis of matrix isolated Chd (20°K) is consistent with the suggestion that these products arise *via* internal conversion to vibrationally excited ground states. As pointed out above, however, the thermal route to formation of benzene is not unimolecular decomposition of excited Chd to benzene + H_2 as proposed by Srinivasan for the photolysis.

(15) R. J. De Kock, Doctoral Thesis, Rijksuniversiteit te Leiden, 1959, p 66.

(16) Reference 12, p 72. The quantum yield of this isomerization, which is presumably a reaction of the electronically excited singlet state, is probably as high in the gas-phase photolysis. Srinivasan[8] reported 0.13 for the quantum yield of 1,3,5-hexatriene formation at 4.75 Torr Chd pressure. He pointed out that the quantum yield must be dependent on irradiation time as well as other factors.

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Kinetic Arguments for the Existence of Hydrogen Bonded Carbanion Intermediates during Dehydrohalogenation Reactions of $C_6H_5CHClCF_2Y$

Sir:

One experimental technique often used to look for carbanion intermediates during 1,2 elimination reactions is to see if the hydrogen atom, which is eventually lost, will exchange with bulk solvent prior to the formal elimination process.[1,2] Since there is current interest in whether or not base-initiated 1,2 eliminations are concerted,[3] we wish to report some kinetic results which strongly suggest that the dehydrochlorination of $C_6H_5CHClCF_2Cl$ proceeds through a carbanion intermediate even though exchange of the benzylic proton does not occur prior to the elimination process. The results of our kinetic studies and relevant previous work on β-phenylethyl halides[4] are summarized in Table I.

Table I. Relative Rates, Activation Parameters, and ρ Values of Dehydrohalogenation and Detritiation Reactions with Ethanolic Sodium Ethoxide

Compound	Process	Rel rate,[a] 25°	$\Delta H^{\ddagger}$,[a] kcal mol^{-1}	$\Delta S^{\ddagger}$,[a] eu	ρ[b]
$C_6H_5CHClCF_3$	-HF	17	28.4	8.6	3.73[c]
$C_6H_5CDClCF_3$	-DF[d]	39	28.0	9.1	
$C_6H_5CTClCF_3$	Detrit	222	27.0	9.1	3.94[c]
$C_6H_5CTClCF_3$	Detrit[d]	507	26.6	9.2	
$C_6H_5CHClCF_2Cl$	-HCl	5.5×10^6	19.7	4.7	3.94[c]
$C_6H_5CH_2CH_2F$[f]	-HF	1[e]	25.3	−5.4	3.12
$C_6H_5CH_2CH_2Cl$[f]	-HCl	80	23.2	−5.6	2.61

[a] Activation parameters calculated from at least four temperatures over a 30° range using the ACTENG program (D. F. DeTar, "Computer Programs for Chemistry," Vol. III, W. A. Benjamin, New York, N. Y., 1969, p 6). The program also calculated rates for all reactions at 25°. [b] Correlation coefficients for both literature and our plots are better than 0.994. [c] Substituents used were *p*-CH_3, *m*-CH_3, H, *p*-Cl, and *m*-Cl. [d] EtOD solvent. [e] Extrapolation of data from ref 4 gave a value of $k = 4.36 \times 10^{-8}\ M^{-1}\ \text{sec}^{-1}$ at 25°. [f] Data from ref 4.

The presence of an α chlorine and two β fluorines should substantially increase the acidity of the benzylic hydrogen, and the 68,000-fold faster rate for dehydrochlorination of $C_6H_5CHClCF_2Cl$ (I) than $C_6H_5CH_2CH_2Cl$ (II) was not unexpected in a process that requires base attack on the hydrogen. The surprising result was that the elimination of HF from $C_6H_5CHClCF_3$ (III) was only 17 times faster than from $C_6H_5CH_2CH_2F$ (IV). One explanation for the discrepancy could be that reactions of I, II, and IV proceed through standard E2 mechanisms while the elimination of HF from III proceeds through an intermediate carbanion. Our studies of ethoxide reactions with fluoroalkenes suggest that fluoride ion is a poorer leaving group when it comes from a trifluoromethyl group rather than a less highly fluorinated group.[5,6] This

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