Although the two resolutions are performed in the same solvent the medium is not exactly the same, since in one case there is an excess of A and in the other case an excess of B (the molar ratios are about four). The different medium has no effect on the result (even when an acid and a base was used, the solvent being pyridine).

Examples.—(1) Rotatory power of phenyl-n-propyl-carbinol, measured by means of successive use of α-phenylbutyric anhydride, is first dextrorotatory, then racemic; αD 29.6° (neat, $l = 1$ dm.), lit.[3,4] αD 29.3.°

(2) Rotatory power of amphetamine (neat) measured on an optically pure sample, is $[\alpha]^{15}$D 35.3° (neat), lit.[5] $[\alpha]^{15}$D 35.6° (neat, $l = 1$ dm.).

(3) Phenylisopropylcarbinol has αD 24.1° (neat, $l = 1$ dm.), lit.[5,6] αD 24.6°.

A more detailed account will be published elsewhere.[7]

(3) J. Kenyon and S. M. Partridge, J. Chem. Soc., 128 (1936).

(4) R. MacLeod, F. J. Welch, and H. S. Mosher, J. Am. Chem. Soc., 82, 876 (1960).

(5) W. Leithe, Ber., 65, 665 (1932).

(6) P. A. Levene and L. A. Mikeska, J. Biol. Chem., 70, 355 (1926).

(7) A. Horeau, Bull. soc. chim. France, in press.

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The Photolytic Decomposition of Some Sulfones by an Internally Sensitized Path

Sir:

Although the photolysis of ketones to carbon monoxide and other products is one of the most studied of photochemical reactions,[1] the analogous photochemical extrusion of sulfur dioxide from sulfones has never been observed.[2] We wish now to report the loss of sulfur dioxide from certain benzylic sulfones upon irradiation.[3]

Photolysis of 5,10-dihydroacepleiadene 5,10-sulfone (I),[4] 7,12 dihydropleiadene 7,12-sulfone (II),[4] and 1,3-diphenyl-1,3-dihydronaphtho[2,3-c]thiophene 1,1-dioxide (III)[5a] gave acepleiadene dimer, IV,[4] and *trans*-1,2-diphenylnaphtho[b]cyclobutene (VI),[5b] respectively, using light of 2800–3200 Å.; the yields of products IV, V, and VI were in the range of 50–75%. Neither 1,3-dihydronaphtho[2,3-c]thiophene 1,1-dioxide

(1) Advan. Photochem., 1, 83 (1963).

(2) It has been reported that the photochemical decomposition of diphenyl sulfone in the presence of chlorine gives chlorobenzene and sulfur dioxide: B. Miller and C. Walling, J. Am. Chem. Soc., 79, 4188 (1957). This reaction was demonstrated to be a free-radical process initiated by the photochemical dissociation of chlorine molecules into chlorine atoms; it is, therefore, mechanistically very different from the light-induced decomposition of the sulfones discussed in this communication.

(3) All irradiations were carried out in benzene under a nitrogen atmosphere at 15° for a period of 2 hr.; the light source was a 100 watt Hanau medium pressure mercury arc lamp. The light was varied by the use of (a) no filter (2200–4000 Å.); (b) a Pyrex filter (2800–4000 Å.); (c) a soft glass filter (3200–4000 Å.).

(4) M. P. Cava and R. H. Schlessinger, J. Am. Chem. Soc., 85, 835 (1963). This communication reports only one synthesis of sulfone II and the related pleiadene dimer, now known to have the head-to-tail structure V; the synthesis of the related acepleiadene dimer IV and the sulfone I will be described in a full paper which is in preparation for publication.

(5) (a) Sulfone III was obtained from 2,3-dibenzoylnaphthalene by the following consecutive operations: borohydride reduction, conversiou of the resulting diol to the cyclic sulfide, and oxidation of the sulfide to sulfone III (J. P. Van Meter, unpublished experiments). (b) M. P. Cava, B. Hwang, and J. P. Van Meter, J. Am. Chem. Soc., 85, 4031 (1963).

(VII)[6] nor 1,3-dihydrobenzo[c]thiophene 1,1-dioxide (VIII)[7] was affected by light over a wide energy range (2200–4000 Å.), but 1,3-diphenyl-1,3-dihydrobenzo[c]-thiophene 1,1-dioxide (IX)[8] gave *trans*-1,2-diphenyl-benzocyclobutene (X)[8] in 13% yield with light in the range of 2200–2800 Å.[9]; sulfone IX was changed by light of a wave length greater than 2800 Å.

None of the sulfones investigated (I, II, III, VII, VIII, and IX) was photolytically decomposed in the absence of a sensitizer using light of a wave length greater than 3200 Å. Sulfones III, VII, VIII, and IX were also unchanged by light of 3200–4000 Å. in the presence of a sensitizer (benzophenone or acetophenone), while the pleiadene sulfones I and II were decomposed under these conditions to the dimeric hydrocarbons IV and V. By studying the photolysis of sulfone II in the presence of a variety of sensitizers, it was found that the triplet state energy of II lies approximately in the range of 53.0–59.5 kcal. mole.[10]

As a consequence of the evidence outlined above, the sensitized photolytic decomposition of the pleiadene sulfones I and II clearly involves the intermediacy of a naphthalene-like triplet. The mechanism favored by us for the decomposition of this triplet state assumes intersystem crossing of it to a highly vibrationally excited singlet ground state.[11] The singlet thus formed may then decay to yield sulfur dioxide and an o-quino-noid pleiadene hydrocarbon, isolated as its stable dimer; the net result is analogous to the previously reported thermal decomposition of sulfone II at 210°.[4] The unsensitized photolysis of sulfones I and II may also involve naphthalene-like triplets; no definite conclusion regarding this point can be made, however, on the basis of presently available experimental data.

The failure of the diphenyl sulfones III and IX to undergo carbonyl-sensitized decomposition at wave lengths above 3200 Å., even in the presence of aceto-phenone,[10] suggests that the photochemical breakdown of III and IX by light of lower wave lengths involves excitation energies greater than 74 kcal./mole. The much higher activation energies for the decomposition of the diphenyl sulfones III and IX compared to the pleiadene sulfones I and II directly parallel the relative stabilities of the o-quinonoid hydrocarbons formed as the initial decomposition products of the sulfones in question. The failure of the simple sulfones VII and VIII to undergo decomposition by light of wave length as low as 2200 Å. is in accord with this trend. These sulfones, which are also thermally the most

(6) M. P. Cava and R. L. Shirley, ibid., 82, 654 (1960).

(7) M. P. Cava and A. A. Deana, ibid., 81, 4266 (1959).

(8) F. F. Jensen and W. E. Coleman, ibid., 80, 6149 (1958).

(9) Prolonged irradiation of sulfone IX results in the formation of a mixture of hydrocarbon X and 9,10-dihydro-9-phenylanthracene. The latter compound has been reported previously[8] to be formed by pyrolysis of sulfone IX.

(10) Using light of wave length greater than 3200 Å., it was found that sulfone II was stable in the presence of fluorenone, although it decomposed readily in the presence of β-naphthaldehyde. The triplet state energies of fluorenone and β-naphthaldehyde are 53.0 and 59.5 kcal./mole, respectively. We wish to thank Dr. G. S. Hammond and Dr. C. A. Stout for information concerning the triplet state energies of these and other carbonyl sensitizers, including that of acetophenone (73.6 kcal./mole).

(11) This type of mechanism for a photochemical reaction which proceeds to give products similar to those obtained by thermolysis has been proposed by J. Franck and H. Sponer, "Volume Commemoratif V. Henri," Maison Desoer, Liege, Belgium, 1948, p. 169. In order for such a photochemical reaction to occur in the liquid phase with sulfones I and II, it is obvious that the extrusion of sulfur dioxide from a highly vibrationally excited singlet ground state must take place within the time order of diffusion control.

stable of the group discussed here, correspond to the least stabilized o-quinodimethanes of the series.[12]

From the synthetic point of view, the sulfone photolysis reaction has practical utility. Thus, the conversion of the diphenyl sulfones III and IX to the corresponding condensed cyclobutenes VI and X can be accomplished only photochemically. The effective pyrolysis temperatures of sulfones III and IX are higher than the temperature at which the cyclobutenoid hydrocarbons VI and X rearrange to secondary pyrolysis products.[8,13]

I, R = CH₂—
II, R = H

IV, R = CH₂—
V, R = H

III, R = C₆H₅
VII, R = H

VI

IX, R = C₆H₅
VIII, R = H

X
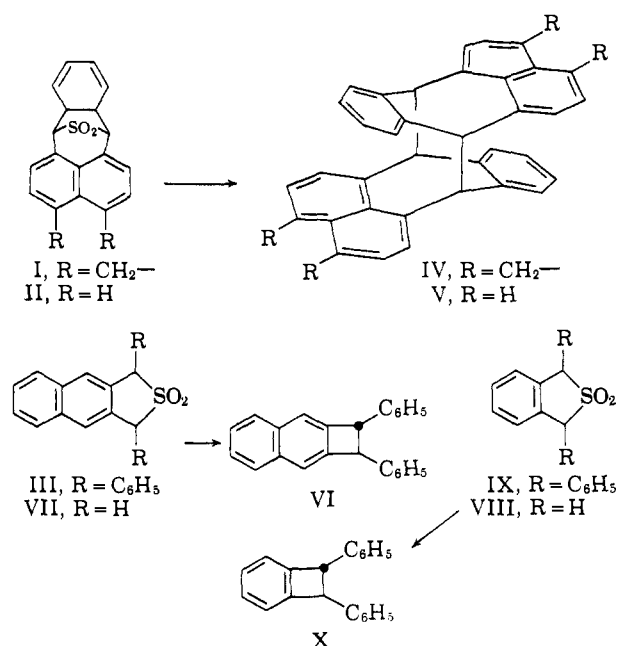
Acknowledgment.—We are grateful for support of this work by the U. S. Army Research Office (Durham) and the National Science Foundation.

(12) The possibility that sulfones I, II, III, and IX all decompose initially by homolytic fission to diradicals appears unlikely on the basis of the marked difference in the photolytic stabilities of II and III. Whereas the o-quinoid hydrocarbons generated from II and III (i and ii) by concerted loss of sulfur dioxide are structures of very different energy content, the diradicals (iii and iv) formed from II and III by rupture of a carbon–sulfur bond are structures which should have very similar energy.

i

ii

iii

iv
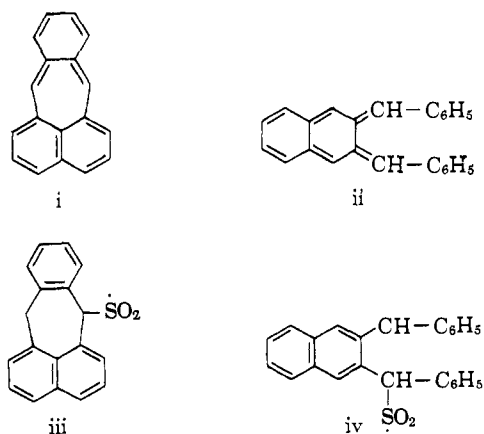
(13) Sulfone III is stable at 150°, at which temperature hydrocarbon VI rearranges to a phenyldihydronaphthacene.[5b]

EVANS CHEMICAL LABORATORY   M. P. CAVA
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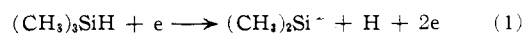## Bond Dissociation Energies and Ion Energetics in Organosilicon Compounds by Electron Impact

Sir:

Recent reports[1,2] of electron impact studies of silane, disilane, and alkyl-substituted silanes have indicated that silicon–silicon and silicon–hydrogen bonds are considerably stronger than thermochemical data would suggest, and that silicon–carbon bonds are of comparable strength to the analogous carbon–carbon bonds. In electron impact studies of the formation of the trimethylsiliconium ion from substituted trimethylsilanes we have obtained results of a similar nature. The compounds studied were synthesized in this laboratory by standard methods[3] from trimethylchlorosilane and hexachlorodisilane. Appearance potentials of the $(CH_3)_3Si^+$ ion were determined by the retarding-potential-difference method[4] on a modified Bendix Model 14-101 time-of-flight mass spectrometer. The energy spread of the electrons was approximately 0.1 e.v.; xenon was used to calibrate the electron energy scale. Results are shown in Table I, where the indicated errors are average deviations of replicate measurements.

TABLE I

$(CH_3)_3Si^+$ APPEARANCE POTENTIALS AND BOND DISSOCIATION ENERGIES IN SUBSTITUTED TRIMETHYLSILANES

Bond	$A[(CH_3)_3Si^+]$, e.v.	ΔH_f° [(CH₃)₃-Si⁺], kcal. mole⁻¹	ΔH_f° [(CH₃)₃-Si–X], kcal. mole⁻¹	D [(CH₃)₃-Si–X], kcal. mole⁻¹
$(CH_3)_3Si-H$	10.78 ± 0.07	137	− 60ᵃ	83
$(CH_3)_3Si-CH_3$	10.63 ± 0.13	143	− 69ᵃ	79
$(CH_3)_3Si-C_2H_5$	10.53 ± 0.09	...	− 77	77
$(CH_3)_3Si-CH(CH_3)_2$	10.56 ± 0.16	...	− 91	77
$(CH_3)_3Si-C(CH_3)_3$	10.53 ± 0.09	...	− 98	77
$(CH_3)_3Si-Cl$	12.42 ± 0.03	...	− 118	120
$(CH_3)_3Si-Si(CH_3)_3$	10.69 ± 0.04	...	− 129ᵇ	81

ᵃ Reference 7. ᵇ Estimated by group equivalent method of Franklin.[10]

Our appearance potential of $(CH_3)_3Si^+$ from trimethylsilane agrees well with that of Hobrock and Kiser.[5] On the other hand, the value of $A[(CH_3)_3Si^+]$ from tetramethylsilane is in serious disagreement with that determined by Hobrock and Kiser,[6] ours being lower by nearly 0.7 e.v. We believe our value is to be preferred, because taking simple dissociation processes, *viz.*

$$(CH_3)_3SiH + e \longrightarrow (CH_3)_2Si^- + H + 2e \qquad (1)$$

$$(CH_3)_3SiCH_3 + e \longrightarrow (CH_3)_3Si^+ + CH_3 + 2e \qquad (2)$$

assuming no excess energy involved, and combining with thermochemical data[7,8] leads to consistent values for $\Delta H_f^\circ[(CH_3)_3Si^+]$ (column 3, Table I). Assuming that $(CH_3)_3Si^+$ is formed from all compounds by simple

(1) W. C. Steele and F. G. A. Stone, *J. Am. Chem. Soc.*, **84**, 3599 (1962).
(2) W. C. Steele, L. D. Nichols, and F. G. A. Stone, *ibid.*, **84**, 4441 (1962).
(3) C. Eaborn, "Organosilicon Compounds," Academic Press, New York, N. Y., 1960.
(4) R. E. Fox, W. M. Hickam, and T. Kjeldaas, *Rev. Sci. Instr.*, **26**, 1101 (1955).
(5) B. G. Hobrock and R. W. Kiser, *J. Phys. Chem.*, **66**, 155 (1962).
(6) B. G. Hobrock and R. W. Kiser, *ibid.*, **65**, 2186 (1961).
(7) S. Tannenbaum, *J. Am. Chem. Soc.*, **76**, 1027 (1954).
(8) B. E. Knox and H. B. Palmer, *Chem. Rev.*, **61**, 247 (1961).