$$Z-Si(OMe)_3 + 2 \; \text{[o-C}_6\text{H}_4(\text{OH})\text{OH]} + R_3N \longrightarrow$$

$$[R_3NH]^+ \left[Si \begin{matrix} Z \\ \\ \end{matrix} \left(\begin{matrix} O \\ O \end{matrix} \right)_2 \right]^- + 3\,MeOH$$

These salts are prepared by merely warming the appropriate reactants in a suitable solvent (usually methanol). As an example, triethylammonium bis(o-phenylenedioxy)phenylsiliconate, i.e., $[Et_3NH]^+[PhSi(C_6H_4O_2)_2]^-$, deposited in 78% yield from a methanol solution of $PhSi(OMe)_3$, catechol, and Et_3N; m.p. 220–230° dec. Anal. Calcd. for $C_{24}H_{29}O_4NSi$: C, 68.1; H, 6.86; N, 3.31; Si, 6.64. Found: C, 68.6; H, 7.04; N, 3.29; Si, 6.57. In related fashion we have prepared analogous pentacoordinate organosilicon catecholates of many other bases ranging in strength from pyridine to quaternary ammonium hydroxides.[4] The infrared spectrum of each of these salts (obtained from mineral oil mulls) exhibited a strong band at 12.1–12.3 λ which is believed to be the silicon–oxygen stretching frequency. This is considerably displaced from the usual position of this band (10.2–10.9 λ)[5] and is a reasonable consequence of the somewhat longer Si–O bond lengths expected in such pentacoordinate species. To date we have been unable to isolate extracoordinate silicon catecholates bearing more than one carbon–silicon bond. An attempt to prepare such a derivative from diphenyldimethoxysilane resulted in an unusually facile Ph–Si bond cleavage.

$$Ph_2Si(OMe)_2 + 2C_6H_4(OH)_2 + Et_3N \xrightarrow[\Delta]{MeOH}$$

$$[Et_3NH]^+[PhSi(C_6H_4O_2)_2]^- + C_6H_6 + 2\,MeOH$$
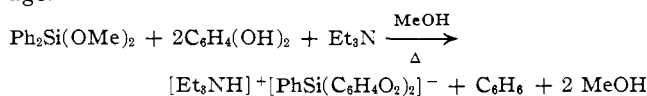
The observation that amines as weakly basic as pyridine may be used suggests that a species such as II would be a relatively strong acid, presumably due to the stability of the anion, I.

$$\text{II} \rightleftharpoons \text{I} + H^+$$
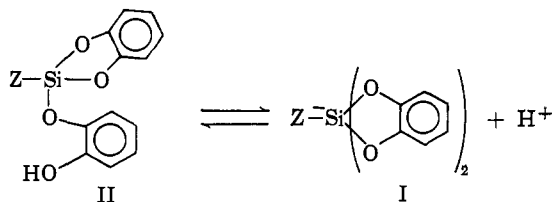
The stability of such extracoordinate species is further underscored by their formation in high yield even when alcohols are used as solvents, despite the ostensibly excellent opportunity for solvolytic reversal of reaction. This stability is perhaps not too surprising in view of the extensive charge delocalization presumably possible in the above anion; i.e., numerous canonical forms may be drawn in which the negative charge is distributed to the arylene rings.[6]

(4) When a strong base is used, the products form rapidly and often deposit quickly from solution without any heating at all being necessary. If, however, the base is weak, correspondingly longer reaction times and/or higher reaction temperatures are required.

(5) A. L. Smith, Spectrochim. Acta, 16, 87 (1960).

(6) That the stability of these pentacoordinate silanes is not entirely dependent upon the charge delocalizing arylene rings is demonstrated, however, by the existence of a related series of aliphatic 1,2-diol derivatives which we will describe in the near future.

Rosenheim's assignment of a monomeric hexacoordinate dinegative silicate ion has recently been criticized by Weiss, et al.,[7] who argued that such structures are precluded by the highly strained (sic) five-membered rings (III) containing compressed O–Si–O bond angles.

III
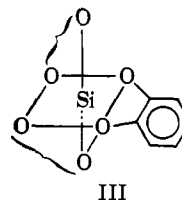
From an examination of Stuart–Brieglieb models we have concluded that the compressive strain admittedly present in tetrahedral formulations[8] is virtually absent in extracoordinate silicon species because of the availability of much smaller silicon valence bond angles (approximately 90°). The essentially complete release from such strain resulting upon rehybridization is presumably part of the driving force leading to stable extracoordinate silicon catecholates. The unnecessarily more complicated dimeric quadrinegatively charged species suggested by Weiss also fails to account for the ortho-diol structural requirement. Structural formulations depicting these materials as mere salts of tetrahedral silanes (IV) are likewise completely inconsistent with the observable facts; i.e., the strained ring in this sp[3] silicon species would certainly not resist alcoholysis, nor would we expect such strikingly stable ammonium salts. Their high melting points[2,7] are

IV
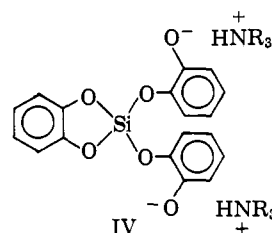
also more consistent with Rosenheim's highly symmetrical structure.

We cannot answer at this time the subtle question of whether the pentacoordinate catecholates involve trigonal bipyramidal or square tetragonal hybridization of the silicon valences.

(7) Ar. Weiss, G. Reiff , and Al. Weiss, Z. Anorg. Allgem. Chem., 311, 151 (1961).

(8) It is significant that even tetracoordinate silicon catecholates have been reported.[9]

(9) (a) M. Jacovic, Z. Anorg. Allgem. Chem., 288, 324 (1956); (b) J. J. Zuckerman, J. Chem. Soc., 873 (1962).

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Calculation of the Magnitude of the Rotation of the Components of a Racemic Modification, by way of Two Partial, Consecutive Resolutions in Homogeneous Medium

Sir:

When two racemic compounds A and B, each composed of two enantiomers (the enantiomers present in A are designated A_D and A_L, and the enantiomers
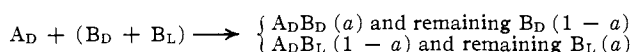
present in B are designated B_D and B_L), are allowed to react, four reactions, running simultaneously, are in evidence.

$$A_D + B_D \xrightarrow{K_1} A_D B_D \qquad (1)$$

$$A_D + B_L \xrightarrow{K_2} A_D B_L \qquad (2)$$

$$A_L + B_L \xrightarrow{K_3} A_L B_L \qquad (3)$$

$$A_L + B_D \xrightarrow{K_4} A_L B_D \qquad (4)$$

Each of these reactions leads to a distinct combination product, but the four isomers obtained are (two sets of two) mirror images, so that two racemic modifications are produced.
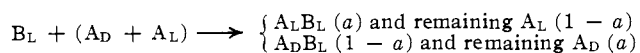
The principle of our proposed method is based on the following observations. (1) Because of the symmetry of the systems, the reactions which afford the two enantiomers of a given diastereoisomer have necessarily the same rates, and the rate constants of each pair are identical: $K_1 = K_3$; $K_2 = K_4$. (2) The reaction is usually stereospecific, but the racemic substances do not appear in the same proportion; i.e., K_1 differs from K_2. If a is the fraction of A_D which combines with B_D, it is also the fraction of A_L which combines with B_L.

Now, if A_D is allowed to react, in homogeneous medium,[1,2] with an excess of racemic product B (i.e., two moles, $B_D + B_L$) different amounts of $A_D B_D$ and $A_D B_L$ are obtained (i.e., a and $1 - a$), whereas the remaining quantities of B_D and B_L will be respectively equal to $1 - a$ and a, according to the following scheme

$$A_D + (B_D + B_L) \longrightarrow \begin{cases} A_D B_D \ (a) \text{ and remaining } B_D \ (1 - a) \\ A_D B_L \ (1 - a) \text{ and remaining } B_L \ (a) \end{cases}$$

A partial resolution of substance B is thus performed; since there is an excess of remaining B_L with respect to B_D ($a > 0.5$), the optical purity, equal to the difference divided by their sum, is equal to $2a - 1$.

If B_L is allowed to react, in homogeneous medium, with 2 moles of racemic substance A (i.e. $A_D + A_L$), as a result of the above considerations the process is exactly the same

$$B_L + (A_D + A_L) \longrightarrow \begin{cases} A_L B_L \ (a) \text{ and remaining } A_L \ (1 - a) \\ A_D B_L \ (1 - a) \text{ and remaining } A_D \ (a) \end{cases}$$

and the optical purity in this resolution is again $2a - 1$.

Let us consider a racemic modification A, composed of the two enantiomers A_D and A_L. It is possible to obtain the values of the rotatory power $+[X]$ or $-[X]$ of A_D or A_L using a substance B_D (or B_L)· optically pure or of known optical purity, then using it again but as a racemic modification ($B_D + B_L$). This substance B must be able to give, in homogeneous medium, a combination with substance A, the rotatory power of which we wish to measure; after a sufficient time the reaction must be complete or, at least, one must be able to determine its yield by titration. The method

(1) A. Horeau, *Tetrahedron Letters*, 506 (1961).

(2) A. Horeau. *ibid*., 965 (1962).

involves two easy physical separations and two polarimetric measurements. In a first operation, the auxiliary substance, B_D, for instance, is allowed to react, in homogeneous medium, with an excess of the racemic modification to be measured. After the reaction, a part of the compound A in its optically active form, A_L, for example, is isolated; its optical purity is $[\alpha]/[X]$, $[\alpha]$ being the rotatory power really measured. Since we know what quantities were allowed to react, we can calculate what this optical purity would have been had the reaction been completely stereospecific; moreover, we can express the unknown "optical yield" as a simple ratio in which $[X]$ appears in the denominator. (The optical yield obtained when a substance of optical purity "p" is used must, of course, be multiplied by $1/p$.)

In a second operation (a second partial resolution) in the same solvent and at the same temperature, a known quantity of the optically impure substance of rotatory power $[\alpha']$ and of optical purity $[\alpha']/[X]$ is allowed to react with an excess of substance B, which is employed this time as its racemic modification $B_D + B_L$. The scope of the reaction is analogous to the one described above, and the optical yield can be expressed by a simple mathematical formula, in which $[X]$ appears this time in the numerator. (Again the optical yield obtained when a substance of optical purity "p" is used must be multiplied by $1/p$.)

As can be demonstrated in the general case, the optical yields are equal in both experiments. If we express this identity, we obtain a simple equation in which the rotatory power $[X]$ appears as its square, so that its magnitude can be calculated very easily.

The general formula which gives the value of $[X]$ is

$$[X] = \pm \sqrt{[\alpha][\alpha'] \times \frac{[\alpha_2]}{[\alpha_1]} \times \frac{1}{p} \times \frac{\dfrac{2N}{nr} - 1}{\dfrac{2N'}{n'r'} - 1}} \qquad (5)$$

in which $[X]$ is the unknown rotatory power. The other symbols represent experimental data: $[\alpha]$, rotatory power of the substance to be determined, as isolated in the first resolution; $[\alpha']$, rotatory power of the substance to be determined, used in the second resolution; $[\alpha_1]$ rotatory power of substance B isolated in the second resolution; $[\alpha_2]$, rotatory power of optically pure B_D; p, optical purity of the product used in the first resolution; and $2N/nr$ and $2N'/n'r'$, for the two resolutions, the ratio between the number of molecules of racemic compound employed ($2N$ and $2N'$) and the number of molecules of optically active products which have actually reacted (nr and $n'r'$, r and r' being the yields measured in each reaction).

If in the second resolution we use, for the substance to be determined, the substance itself obtained from the first value resolution in a partially resolved form of rotatory power $[\alpha]$, we get

$$[X] = \pm [\alpha] \sqrt{\frac{[\alpha_1]}{[\alpha_2]} \times \frac{1}{p} \times \frac{\dfrac{2N}{nr} - 1}{\dfrac{2N'}{n'r'} - 1}} \qquad (6)$$

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, conversion 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-diphenylbenzocyclobutene (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-quinonoid 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 acetophenone,[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.