duced dihydrocorynantheane, and this possibility is ruled out since the base V differs from an authentic sample of dihydrocorynantheane.[6] Of the three remaining possibilities, rupture of bonds c or d would produce a new C-methyl group while cleavage of bond a is the only pathway that does not result in a new C-methyl group. A clear decision was made from the n.m.r. spectrum of the base V. The spectrum (deuteriochloroform) shows a triplet at τ 9.05 corresponding to three protons using the aromatic proton absorption (four protons) as an internal standard. The presence of two methyl groups in dihydrocorynantheane was readily apparent from its n.m.r. spectrum.

The cyclization reactions and the lithium aluminum hydride reductions of the acetoxylactam IIb, and the quaternary ammonium salt VI, may be examples of elimination–addition reactions involving intermediates of the type shown by structure VII.

VII
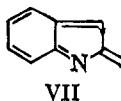
It should be pointed out that the conversion of benzylic tertiary amines to the corresponding benzyl esters on treatment with acid anhydrides is a well known reaction[7] and the quinuclidine ring of cinchonamine is cleaved by acetic anhydride to yield an acetylated 2-vinylindole.[8] Intermediates of the type shown by VII are currently under investigation along with the synthetic applications of the ring cleavage reaction.[9]

(6) Prepared by the procedure of M. M. Janot and R. Goutarel, Bull. soc. chim. France, 588 (1951).

(7) M. Tiffeneau, ibid., [4] 9, 825 (1911).

(8) R. Goutarel, M. M. Janot, V. Prelog, and W. I. Taylor, Helv. Chim. Acta, 33, 150 (1950).

(9) Satisfactory analytical data were obtained for all new compounds described in this communication.

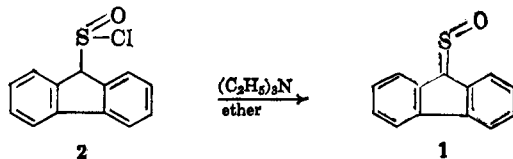DEPARTMENT OF CHEMISTRY LLOYD J. DOLBY
UNIVERSITY OF OREGON SHIN-ICHIRO SAKAI
EUGENE, OREGON

Sulfines

Sir:

We now report the first examples of a new class of compounds, S-oxides of thioketones, which we designate as "sulfines" (for example fluorenylidene sulfine, 1).

Sulfines, like the S-oxides of thioamides[1] and thioacid chlorides[2] (O=S=C(R)—X, X = NR₂ or Cl) are stable enough to be isolated. In contrast, sulfenes (R₂C=SO₂) are only proposed as unstable intermediates when nitrogen bases react with alkyl sulfonyl chlorides.[3]

As the route to 1, sulfur dioxide and 9-lithiofluorene gave the lithium salt of 9-fluorenesulfinic acid, 3. The

(1) W. Walter and K. D. Bode, Ann., 660, 74 (1962), and earlier papers of the series cited in this reference.

(2) J. F. King and T. Durst, Tetrahedron Letters, 585 (1963).

(3) (a) G. Stork and K. J. Borowitz, J. Am. Chem. Soc., 84, 313 (1962); (b) G. Opitz and H. Adolph, Angew. Chem., 74, 77 (1962); (c) W. E. Truce and J. R. Norell, J. Am. Chem. Soc., 85, 3231 (1963); (d) J. F. King and T. Durst, ibid., 86, 287 (1964); (e) W. E. Truce, R. W. Campbell, and J. R. Norell, ibid., 86, 288 (1964).

unstable sulfinyl chloride 2, extracted with methylene chloride from the reaction mixture of 3 and thionyl chloride, reacted with triethylamine in ether at room temperature. Triethylamine hydrochloride precipitated immediately and was separated by filtration. The filtrate was concentrated to give fluorenylidene sulfine (1, crude yield 75%) as orange crystals, m.p. 103–108°, recrystallized from benzene–hexane, m.p. 111.0–111.8°. Anal. Calcd. for C₁₃H₈OS: C, 73.6; H, 3.80; S, 15.1, mol. wt., 212. Found: C, 73.6; H, 4.14; S, 15.1, mol. wt., 264 (freezing point in benzene).

The absence of the 9-hydrogen resonance (in region τ 4.4) in the proton n.m.r. spectrum and the appearance of additional fine structure in the aromatic region[4] confirmed the sulfine structure. The infrared spectrum was extremely simple; in addition to the normal C–H and aromatic absorption bands, strong bands at 1120 and 1019 cm.$^{-1}$ were tentatively assigned to the C=S=O function. A strong absorption at 1087 cm.$^{-1}$ was attributed to the fluorenyl residue since a similar absorption band was found in fluorenone. The ultraviolet spectrum in dioxane was similar to fluorenone but with a hypsochromic shift, λ_{max} in mμ (ϵ): 362 (15,250), 273 (30,000), 265 (26,300), 238 (28,400), 232 (28,400). The orange color was the result of a tail in the visible region.

Compound 1 decomposed slowly on standing at room temperature for several days and rapidly at its melting point, evolving sulfur dioxide. Difluorenylidene, in 48% yield, was extracted from the brown residue; a few per cent of fluorenone was also isolated. Compound 1 was stable at reflux temperature in cyclohexene, benzene, or tetrahydrofuran solutions for several days, but added to a stoichiometric amount of 1-morpholino-1-cyclohexene in tetrahydrofuran to give a white crystalline solid, m.p. 142°. Anal. Calcd. for C₂₃H₂₅NO₂S: C, 72.8; H, 6.64; N, 3.69; S, 8.45. Found: C, 72.6; H, 6.74; N, 3.62; S, 8.77.

Two structures, 4a and 4b, are proposed for this
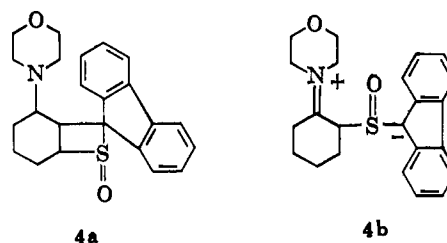
adduct although several other structures are possible; the polar structure, 4b, is preferred because of a strong absorption band at 1710 cm.$^{-1}$ in the infrared spectrum.

Aliphatic analogs were also prepared, but were too unstable for isolation or handling at room temperature.[5] For example, isopropyl sulfinyl chloride[6] reacted vigorously with triethylamine in methylene chloride at −20°,

(4) The CSO group is expected to be bent at an angle of almost 120° like sulfur dioxide. Since the CSO group probably lies in the plane of the fluorene rings, the protons in the two rings experience a different field. cis–trans isomers were proposed for the closely related S-oxides of thioacid chlorides.[2]

(5) Reference to an unsuccessful attempt to prepare and trap CH₂=S=O has been made.[3c] We have similarly found that methanesulfinyl chloride forms a salt with triethylamine and does not lose hydrogen chloride.

(6) I. B. Douglass and D. R. Poole, J. Org. Chem., 22, 536 (1957); I. B. Douglass and B. S. Farah, ibid., 23, 330 (1958) [prepared by procedures given in Org. Syn., 40, 62 (1960)].

and a stoichiometric yield of triethylamine hydrochloride was separated by filtration. Concentration of the cold filtrate gave a straw-colored liquid characterized as isopropylidene sulfine (5, thioacetone S-oxide) by spectral analysis (chemically nonequivalent
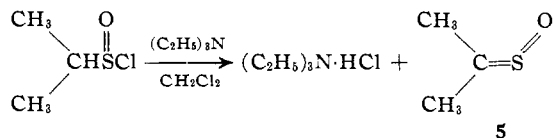
methyl groups were noted in the n.m.r. spectrum). On warming to room temperature, this product underwent a mildly exothermic rearrangement or self-condensation. Compound 5 was trapped with chlorine to give 2-chloroisopropyl sulfinyl chloride, but efforts to isolate 5 or any rearrangement product by distillation and crystallization or by trapping with reactive olefins or dienes have not been successful.

A full account of the preparation and properties of the sulfines will be published in the near future.

CONTRIBUTION No. 952   WILLIAM A. SHEPPARD
CENTRAL RESEARCH DEPARTMENT   JURGEN DIEKMANN
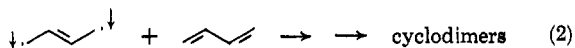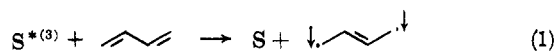EXPERIMENTAL STATION
E. I. DU PONT DE NEMOURS AND COMPANY
WILMINGTON, DELAWARE
RECEIVED MARCH 2, 1964

Photosensitized Cyclization of Myrcene:
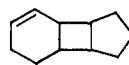## The Problem of Addition of Dienes to Alkenes[1]

Sir:

We believe that photosensitized cycloaddition reactions of conjugated dienes involve transfer of triplet excitation from the sensitizer to the diene, followed by addition of diene triplets to a molecule of diene in its ground state.[3]

$$S^{*(3)} + \diagup\!\!\!\!\diagdown\diagup \longrightarrow S + {\cdot}\diagup\!\!\!\!\diagdown\diagup^{\cdot} \qquad (1)$$

$${\cdot}\diagup\!\!\!\!\diagdown\diagup^{\cdot} + \diagup\!\!\!\!\diagdown\diagup \longrightarrow \longrightarrow \text{cyclodimers} \qquad (2)$$

Unconjugated olefinic compounds might reasonably be expected to play the role of the ground-state diene molecule in eq. 2 albeit with reduced reactivity. We have attempted to carry out a number of crossed addition reactions with very limited success. No cross adducts were obtained when solutions containing cyclopentadiene or 1,3-cyclohexadiene and 2-acetonaphthone in olefins such as cyclohexene, norbornene, and 1,5-hexadiene were irradiated with light absorbed by the sensitizer. However, irradiation of a solution of a 15:1 cyclopentene–1,3-cyclohexadiene mixture containing 0.02 M acetonaphthone led to formation of three new compounds in addition to the photodimers of cyclohexadiene.[4] The new compounds were formed in the ratio 4:2:1. The major component was isolated by vapor chromatography in sufficient amount to permit measurement of its n.m.r. and infrared spectra. A mixture of the major product and the second most abun-

(1) Mechanisms of Photochemical Reactions in Solution. XXVII.[2]
(2) Part XXVI: G. S. Hammond, C. A. Stout, and A. A. Lamola, J. Am. Chem. Soc., in press.
(3) G. S. Hammond, N. J. Turro, and R. S. H. Liu, J. Org. Chem., 28, 3297 (1963).
(4) D. Valentine, N. J. Turro, and G. S. Hammond, J. Am. Chem. Soc., submitted.

dant material was also isolated. The spectra of the mixture were essentially identical with that of the pure material and hydrogenation of the mixture gave a single product having a v.p.c. retention time identical with that of the product from hydrogenation of the major product. The n.m.r. spectra showed poorly resolved, broad absorption between τ 7.5 and 8.7 and an unresolved signal in the vinyl proton region centered at τ 4.22. There is no significant absorption between 7.0 and 7.5, the region in which we would expect to find the allylic proton attached to the cyclobutane ring of a structure such as 1. Consequently we believe that the compounds are the two stereoisomers of structure 2.


Although the crossed addition reaction is of some theoretical interest, it does not seem to offer great synthetic promise because of competition from dimerization of the diene even when the concentration of the latter is rather low. A much more promising situation was encountered when we attempted to effect intramolecular cycloaddition of a diene unit to an unconjugated double bond. Myrcene (3) seemed an appropriate material with which to attempt such experiments.
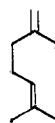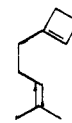

Crowley[5] has reported that direct irradiation of myrcene gives a complex mixture in which 4 is a major product. β-Pinene (5) is a minor product. In contrast, irradiation of 5% solutions of myrcene in n-hexane or benzene containing benzophenone, β-acetonaphthone, or fluorenone leads to formation of a single new product with a quantum yield of 0.05 in the case of benzophenone. For reasons outlined below, the reaction is formulated as follows.
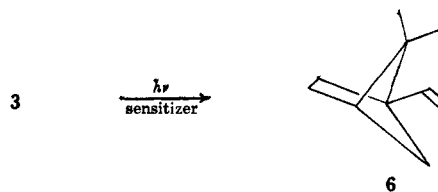
The photoproduct is easily isolated by preparative vapor chromatography. The structure is clearly indicated by the n.m.r. spectrum. The low-field signals have a relative area of 3.0 and fall into the ABC pattern characteristic of vinyl groups. Two strong, unsplit signals at τ 8.86 and 9.25 have relative areas of 3.1 and 2.9 (tetramethylsilane as an internal standard). The signals obviously belong to two isolated methyl groups and have chemical shifts virtually identical with those of the corresponding methyl groups in 7[6] (τ 8.89 and 9.30). A doublet with total relative area 1.1 is centered at 9.03 with a coupling constant of 8.0 c.p.s. This signal is

(5) K. J. Crowley, Proc. Chem. Soc., 245, 334 (1962).
(6) R. Srinivasan, J. Am. Chem. Soc., 83, 4923 (1961).