presence of 1.3 M DCPH, and 86% of octane was formed; our figures are 10% and 85%. San Filippo and Silberman[14b] found 14% of **1** and 85% of octane in the presence of 1.2 M DCPH. Thus excellent reproducibility is attainable.

With Me_3SnK the yields of **1** in the control experiments are the same, 83%, in both THF and TG. However, the presence of DCPH causes a decrease, to 23% in THF but only to 57% in TG; the yields diverted to octane are thus 60% and 26%, respectively. It should be noted that the yields of **1** with the two counterions are markedly different in THF in both control and trapping experiments but that these differences almost vanish in TG, in which yields are very similar.

The last four columns in the table show degrees of excess *inversion* in **1** presented as percent enantiomeric excess (ee) observed by using (+)-2-bromooctane. The stereochemistry with Me_3SnNa in THF (58% ee) is the same for the 60% of **1** formed in the control experiment as that of the 10% formed in the presence of DCPH. In TG a 74% ee is observed in the control experiment and is increased to 98% in the 56% of **1** formed in the presence of DCPH, indicative of an S_N2 mechanism. The data in column 2 show diversion of 34% of **1** diverted to octane in the presence of DCPH. Its ee would have been 35%, as can be estimated from the yield and ee data of entries 1 and 2. This is somewhat smaller than the value of 57% estimated from the data obtained in THF.

With Me_3SnK the values of percent enantiomeric excess in the control experiments are higher than those with Me_3SnNa in each solvent, and that **1** which is formed in the presence of DCPH shows complete inversion. That which was diverted to octane shows a higher percent enantiomeric excess in THF than in TG, as is the case for Me_3SnNa. However, the values for the two counterions may lie within the experimental error in TG.

Are results obtained in experiments with DCPH in the reaction mixture valid as indications of mechanisms occurring in its absence, or does it perturb the mechanisms as has been clamed?[14] Any substance added to a reaction mixture is a potential source of perturbation, and the question is one of degree. In the reactions with Me_3SnNa in THF, the presence of DCPH does not alter the stereochemistry, which should be a highly sensitive probe for distinguishing between electron-transfer (free radical) and S_N2 mechanisms. The results with DCPH show that no significant contribution from S_N2 is involved; the reaction proceeds in at least two steps; it involves a trappable intermediate, but it leads to excess inversion. The results of the other three sets of experiments are consistent with the occurrence of both mechanisms in competition with each other.

Further support for the validity of our conclusion concerning the reality of the electron-transfer process in the reactions of acyclic secondary bromides with trimethylstannyl alkalis in THF has been obtained by Kitching[18] and Ashby.[20] They showed independently that substantial cyclization occurs in the reaction of 6-bromo-1-heptene with Me_3SnLi[18] and Me_3SnNa[20] in THF to form isomeric [(2-methylcyclopentyl)methyl]trimethylstannanes as major products in addition to the normal acyclic product. Such cyclizations are generally taken to constitute diagnostic evidence for free radicals as reaction intermediates.[22]

The observation of excess inversion in the reaction of a trappable free radical is the most striking observation reported here. It clearly demonstrates that the radical is not the simple 2-octyl radical, for all available evidence indicates that it would yield racemic products due to its planarity.[23] Its structure must be such that it loses stereochemical identity with a rate constant comparable to that for the cyclization of 6-heptenyl radicals, ca. 10^5 s^{-1}.[24]

The electron-transfer mechanism appears to occur more readily via associated ion pairs because it competes more effectively with the S_N2 mechanism in the less effective cation-solvating reagent THF than in TG with both counterions. Potassium yields more S_N2 than does sodium. This pattern of solvent and counterion effects is the same as that which we observed in the reactions of trimethylstannyl alkalis with *syn*-7-bromonorbornene.[4] Preliminary results with lithium in the reaction with 2-bromooctane fall into this pattern. Continuing studies should provide more information concerning the driving forces for the competing mechanisms and the nature of the free-radical intermediates.[26]

Registry No. 1, 82918-07-8; 2-BrC_8H_{17}, 1191-24-8; Me_3SnNa, 16643-09-7; Me_3SnK, 38423-82-4.

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(26) We are grateful for support of this research by the National Science Foundation (Grant CHE 810502101) and to Carstab Corp. for gifts of chemicals. This work was reported at the Twelfth Northeast Regional Meeting of the American Chemical Society, Burlington, VT, June 1982.

Photochemistry in Multichromophoric Systems: Remote Energy Transfer from Naphthyl to a C–S Bond in 2,2-Bis(naphthylmethyl)-1,3-dithianes

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1,3-Dithiane derivatives play an important role in synthetic organic chemistry.[1-5] In contrast to the vast amount of literature concerning the chemical and physical properties of cyclic mercaptans, very little has been revealed about their photochemical behavior.[6] No information concerning the photochemistry of aryl-substituted 1,3-dithio derivatives is found in the literature.

As part of our interest in the photochemistry of bichromophoric systems, we have prepared a series of cyclic dithioketals of 1,3-diaryl-2-propanones and studied their photochemical properties. These chemically stable molecules were found to be photochemically labile and to exhibit unusual, conformation-dependent radiative and nonradiative decay paths. This communication describes the photochemical reactions of 2,2-bis(naphthylmethyl)-1,3-dithianes as representative models.

We have found that irradiation of 2,2-bis(naphthylmethyl)-1,3-dithianes, **1**, in degassed hexane or benzene (ca. 0.001 M) with Pyrex-filtered ultraviolet light absorbed only by the naphthyl chromophores results in clean cleavage of a remote C–S bond. Primary products are 1,3-dinaphthyl-2-(3′-mercaptopropylthio)-1-propenes, **2**, and 1,3-dinaphthylthioacetones, **3**. Scheme I shows the general pathway observed. Thioketones **3** are not isolated but are implicated as delineated below.

All three 2,2-bis(naphthylmethyl)-1,3-dithianes were prepared by a method similar to that of Seebach and co-workers[7] and were characterized by spectroscopic and elemental analyses. Irradiation of **1a** with Pyrex-filtered light[8] for 2 h resulted in loss of starting material and the formation of three new compounds as revealed by NMR and HPLC analyses. Chromatography provided, in

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(8) The irradiation was carried out by using an Hanovia 450-W medium-pressure mercury lamp and an immersion well.

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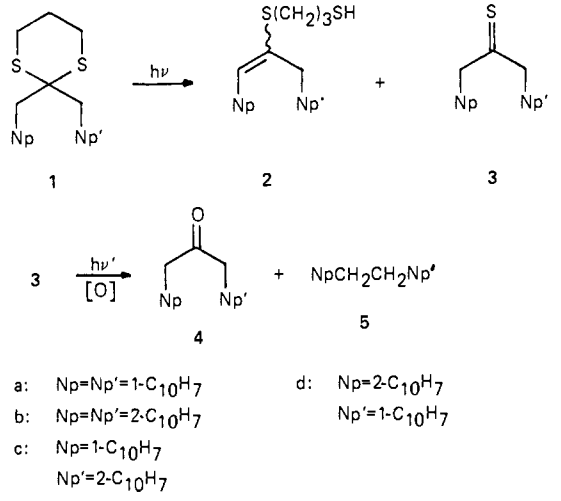
Scheme I



a: Np=Np'=1-$C_{10}H_7$
b: Np=Np'=2-$C_{10}H_7$
c: Np=1-$C_{10}H_7$, Np'=2-$C_{10}H_7$
d: Np=2-$C_{10}H_7$, Np'=1-$C_{10}H_7$

Table I. Product Distribution from Irradiation[a] of Dithianes 1

compd	products (yields)[b] path A	path B[f]
1a[c]	2a (60%)	4a + 5a (10%)
1b[d]	2b (63%)	4b + 5b (15%)
1c[e]	2c (28%) + 2d (15%)	4c + 5c (0%)[g]

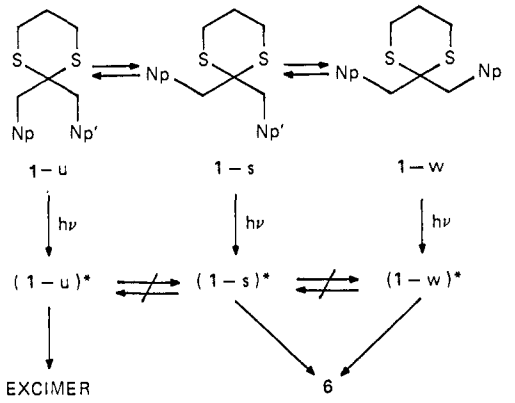
[a] 450-W Hanovia medium-pressure mercury lamp, Pyrex filter; 2 mmol of starting material in 250 mL of benzene with N_2 purging. [b] See Scheme I, absolute yields reported. [c] 2-h irradiation; 30% 1a recovered. [d] 12-h irradiation; 22% 1b recovered. [e] 2-h irradiation; 56% 1c recovered. [f] The ratioes of 4:5 varied with irradiation time, and only the sum is reported. [g] In another run to higher conversion (80%), products 2c and 2d were obtained as 80% of the product mixture and 5c as 20%.

addition to recovered **1a** (30%), a major component identified as a $Z + E$ mixture (1.2:1) of isomeric 1,3-di-α-naphthyl-2-(3'-mercaptopropylthio)-1-propenes (**2a**, 60%) on the basis of NMR (interalia, singlets at δ 4.27 and 4.12 and two triplets at δ 1.32 and 1.07 which disappear on D_2O exchange) and mass (m/e 400.1318) spectral evidence. Two minor products (10% total) were identified as 1,2-di-α-naphthylethane (**5a**)[9] and 1,3-di-α-naphthyl-2-propanone (**4a**)[10] by comparison of properties to literature values. Similar photoreactivity was found for the bis(β-naphthylmethyl)dithiane **1b** and the mixed α,β-isomer **1c**.[11] These observations are summarized in Table I.

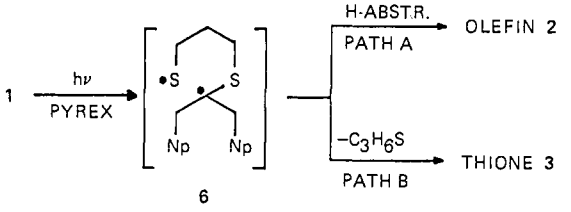
Before we propose a mechanism to account for the observed photochemistry, we present some spectroscopic details of compounds **1**, exemplified here by reference to the absorption spectrum of **1a**. In hexane the UV spectrum of **1a** exhibits a peak at 220 nm (ϵ 30 000) and a band extending from 250 to 320 nm with a maximum at 281 nm (ϵ 15 000). The position of band maxima are within normal error identical with those of 1-methylnaphthalene and 2-(1'-naphthylmethyl)-1,3-dithiane, model compounds lacking proximal sulfur atoms and/or a second naphthyl chromophore. 1,3-Dithiane itself absorbs only in the region below 250 nm.[6] Extinction coefficients of **1a** are nearly double those of the models, reflecting the presence of a second chromophore. We therefore feel confident that no strong Np–Np or Np–S interactions are present in the ground state of compounds **1**.[12]

The initial excitation energy (90 kcal/mol) is apparently naphthyl localized but is transferred, by a mechanism not yet

Scheme II



elucidated, to the weakest bond in the molecule, the ca. 70 kcal/mol[13] C–S bond, to effect cleavage. We propose that a biradical, e.g., **6**, is the first-formed intermediate in this photochemical reaction (eq 1). Biradical **6** may abstract an α hydrogen



(1)

from an adjacent methylene unit, to produce mercaptoolefin (path A), or fragment to give thione and a C_3H_6S unit (path B). Though the existence of thioketones **3** was not proved by isolation, the identification of the products **4** and **5** is an indication of their intermediacy.[13-15]

The photochemical transformations of **1** were found to be singlet reactions.[16] Though the chemical yields of product formation are high, quantum yields are low (ca. 0.01) and are both concentration and solvent dependent. These observations, together with information about the emission properties of these compounds, indicate that both intra- and intermolecular excimer formation pathways compete with the photochemical decay of compounds **1**. The radiative singlet lifetime of 1-methylnaphthalene is 67 ns[17] and the monomer lifetime of 1,3-di-α-naphthylpropane is 8 ns[18] in cyclohexane. Compound **1a** exhibits two-component emission decay, including a long excimer component (68.5 ns) and a short, monomer component (2.7 ns). The short monomer component indicates substantial perturbation of the naphthyl-localized excited state, beyond that to be anticipated by the introduction of a second naphthyl chromophore, occurs as a result of the presence of the remote sulfur atom. This interaction, which is apparently dependent on the molecular conformation, is presumably responsible for the initiation of the observed C–S bond cleavage leading to **6**. Though the detailed nature of this interaction is not known, we speculate that a charge-transfer component may be important.

A key finding of our emission studies is that conformations of **1** that lead to excimers effectively prohibit the photochemical energy translocation process leading to biradical **6**. In addition our data demand that excited-state decay processes are faster than

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conformational interconversions. This is seen clearly from the observations that the ratio of naphthalene-localized emission (I_m) to excimer emission (I_e) varies with solvent polarity and that decreases in I_m/I_e are paralleled by decreased reaction yield (ϕ_{dis}).

The data presented here illustrate the delicate interplay between excited-state potential surface minima, populated by excitation of multiple ground-state molecular conformations, and the nature of the decay processes observed in complex multichromophoric systems. Changes in the relative orientation of interacting chromophores can dramatically alter the course of excitation decay. Scheme II summarizes our conclusions concerning the effect of conformation on the photochemistry of compounds **1**.

Structure Elucidation of a Potent Mutagen from Human Feces

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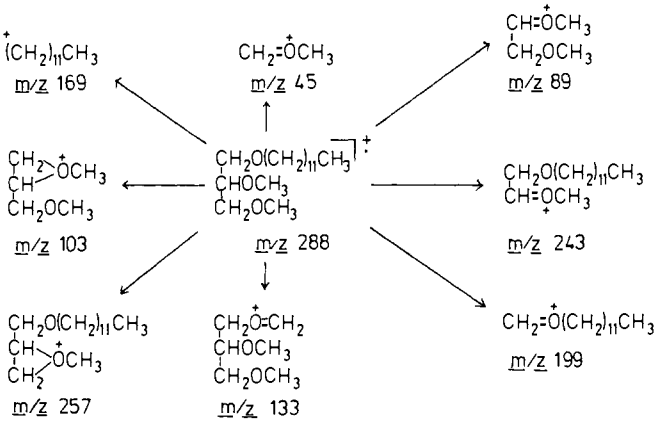
The occurrence of an ether-extractable strongly mutagenic agent in human feces was first reported by Bruce and his co-workers,[1,2] and their results have been confirmed and extended by ourselves[3-5] and others.[6] About 3% of the people in North America excrete feces that have a high level of mutagenic activity in their ether extracts as measured by the Ames test, and this activity has been shown to be due almost entirely to a single compound which has an intense UV absorption spectrum;[1,4,5,7] the purified compound is mutagenic at a level comparable to benzo[*a*]pyrene.[7] We now present evidence for the structure of this mutagen.[8]

The purified mutagen, prepared in microgram quantities as previously described,[7] is very unstable, decomposing rapidly on exposure to air or to traces of acid. It is a lipophilic compound, soluble in chloroform, benzene, and ether, and insoluble in water. Both acetylation and trimethylsilylation yield less polar substances, as determined by thin-layer chromatography, and *n*-butylboronation also yielded a less polar derivative, suggesting the presence of a diol function.[9]

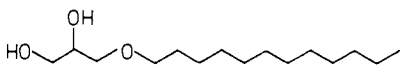
The UV absorption spectrum of the mutagen, with peaks at 325, 345, and 365 nm, is characteristic of a polyene. Simple pentaenes have their longest wavelength absorption at about 342 nm, while that for hexaenes is at about 380 nm,[10] so the mutagen must be a pentaene with some additional conjugation. The polyene nature is also indicated by the fact that purification by HPLC gave two closely related substances that could be collected separately but that interconverted on standing in solution at room temperature in daylight. We assumed that these substances were simple *E*–*Z* isomers of one or more of the double bonds, and all subsequent work was carried out with a mixture of these isomers.

Scheme I



Chemical ionization mass spectrometry (CIMS) of the mutagen gave a quasi-molecular ion at m/z 251. Hydrogenation (H_2/Pt) yielded a single major compound, which could be subjected to gas chromatography after derivatization with one of several reagents. CIMS of the hydrogenated compound itself showed a quasi-molecular ion (MH^+) at m/z 261, and corresponding ions were shown by the acetate, trimethylsilyl, and methyl derivatives at m/z 345, 405, and 289, respectively. Deuteration (D_2/Pt) of the mutagen followed by acetylation yielded a compound showing a molecular ion at m/z 354 on electron impact mass spectrometry.[11] These data indicate conclusively that the mutagen has two derivatizable hydroxyl groups and five double bonds.

Analysis of the mass spectrum of the dimethyl ether of the hydrogenated mutagen indicated it to be the dimethyl ether of 3-dodecyloxy-1,2-propanediol (**1**), with major fragment ions of



1

m/z 257, 243, 199, 169, 133, 103, 89, and 45 (Scheme I). Although the 2-dodecyloxy isomer would show most of these same fragmentations, the occurrence of an intense peak at m/z 89 was only consistent with the 3-dodecyloxy formulation. Confirmation of this structural assignment was achieved by comparison with a sample of **1** prepared by standard methods.[12] The synthetic compound[13] and its dimethyl, diacetyl, and bis(trimethylsilyl) derivatives showed chromatographic behavior identical with the hydrogenated mutagen[14] and its corresponding derivatives.[15] Although a synthetic sample of 2-dodecyloxy-1,3-propanediol[12,13] had chromatographic properties very similar to **1**, its dimethyl ether had a retention time on gas chromatography different from the dimethyl ether of **1** and from that of the hydrogenated mutagen. The mass spectrum of the dimethyl ether of synthetic **1** was identical with that of the methylated hydrogenated mutagen while the mass spectrum of the dimethyl ether of 2-dodecyloxy-1,3-propanediol differed from both of these spectra in lacking an intense ion at m/z 89 and in other respects.

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(15) Gas chromatography under the conditions specified earlier.[8]

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