

(1) there is an intrinsic rigidity of the neutral polymer backbone and/or (2) the rigidity is induced by the clustering of charges.<sup>7,8</sup> Recent reports dealing with 2% cross-linked polystyryl-diphenylphosphine ligands suggest that the neutral polystyrene framework has sufficient mobility to bring nonadjacent sites together;<sup>9,10</sup> this would seem to imply that ionic clustering may contribute significantly to polymer rigidity.

We are presently carrying out experiments which will measure the influence of charge clustering on the rigidity of polystyrene ion exchange resins.

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(7) The clustering of charges in polyelectrolytes can be considered as physical cross-linking.

(8) We treated non-cross-linked chloromethylated polystyrene (6% ring substitution) with 1 equiv of **2b** and found that  $50 \pm 5\%$  of the chlorine was displaced from the polymer after 70 hr and remained unchanged after an additional 170 hr. Although the molar ratio of bound nitrogen to chloride ion displaced for this reaction was approximately 2.0, a small amount of cross-linking must have taken place since the polymer rapidly precipitated from solution in the form of a gel. Reaction of the original linear chloromethylated polymer with 1 equiv of *N,N*-dimethyl-*n*-butylamine led to quantitative displacement of the chlorine after 20 hr, without the formation of a gel. Conclusions about the effect of ionic clustering on the rigidity of the ion exchange resin cannot be drawn from this set of experiments due to the onset of gel formation.

(9) J. P. Collman, L. S. Hegedus, M. P. Cooke, J. R. Norton, G. Dolcetti, and D. N. Marquardt, *J. Amer. Chem. Soc.*, **94**, 1789 (1972); J. P. Collman and C. A. Reed, *ibid.*, **95**, 2048 (1973).

(10) R. H. Grubbs, C. Gibbons, L. C. Kroll, W. D. Bonds, Jr., and C. H. Brubaker, Jr., *J. Amer. Chem. Soc.*, **95**, 2373 (1973).

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### Thiocarbonyl Ylides. Photogeneration, Rearrangement, and Cycloaddition Reactions

Sir:

We wish to report that under nonoxidative conditions,<sup>1</sup> naphthyl vinyl sulfides **1-4** undergo regiospecific photocyclization to thiocarbonyl ylides, e.g., **12**. These potentially useful reactive intermediates experience stereospecific hydrogen migration leading to naphtho[2,1-*b*]dihydrothiophenes (**5-8**). Photogeneration of thiocarbonyl ylides **12** in the presence of a dipolarophile results in cycloaddition to give multicyclic adducts **13-15**. This unique ring annelation method which involves the formation of three carbon-carbon bonds and the generation of six centers of chirality in one experimental operation should prove generally useful in the construction of complex ring systems.

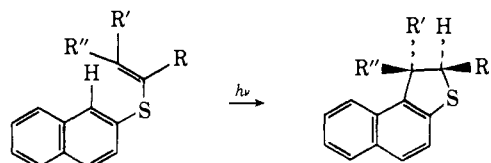
Vinyl sulfides **1-4** were prepared<sup>2</sup> by the *p*-toluenesulfonic acid catalyzed addition-dehydration of 1 equiv of  $\beta$ -naphthalenethiol to propiophenone (80%

(1) Photocyclization of phenyl vinyl sulfides in the presence of iodine or oxygen to give benzothiophenes in low yield has been reported. However, the mechanistic details as well as the synthetic application of this stilbene-like photocyclization have not been investigated: S. H. Groen, R. M. Kellogg, J. Buter, and H. Wynberg, *J. Org. Chem.*, **33**, 2218 (1968).

(2) E. Campaigne and J. R. Leal, *J. Amer. Chem. Soc.*, **76**, 1272 (1954); R. E. Ireland and J. A. Marshall, *J. Org. Chem.*, **27**, 1615 (1962).

yield), 1-indanone (85%), 3-methyl-2-butanone (90%), and phenylacetone (77%), respectively.<sup>3</sup>

Brief Pyrex-filtered irradiation of  $10^{-2}$  M degassed<sup>4</sup> benzene solutions of either geometric isomer **1a** or **1b** leads to photoisomerization about the double bond. Extended irradiation results in consumption of vinyl sulfides and formation of two photoproducts, **5** (15% yield) and **6** (70%). Dihydrothiophenes **5** and **6**



**1a**, R = C<sub>6</sub>H<sub>5</sub>; R' = CH<sub>3</sub>; R'' = H

**1b**, R = C<sub>6</sub>H<sub>5</sub>; R' = H; R'' = CH<sub>3</sub>

**2**, R = *o*-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub> = R'; R'' = H

**3**, R = R' = R'' = CH<sub>3</sub>

**4a**, R = CH<sub>3</sub>; R' = C<sub>6</sub>H<sub>5</sub>; R'' = H

**4b**, R = CH<sub>3</sub>; R' = H; R'' = C<sub>6</sub>H<sub>5</sub>

**5**, R = CH<sub>3</sub>; R' = H; R'' = C<sub>6</sub>H<sub>5</sub>

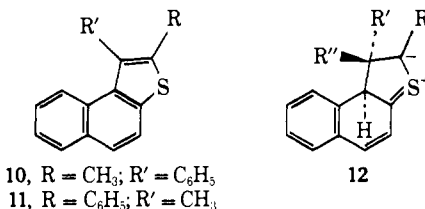
**6**, R = C<sub>6</sub>H<sub>5</sub>; R' = CH<sub>3</sub>; R'' = H

**7**, R = R' = R'' = CH<sub>3</sub>

**8**, R = CH<sub>3</sub>; R' = C<sub>6</sub>H<sub>5</sub>; R'' = H

**9**, R = *o*-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub> = R'; R'' = H

undergo dehydrogenation when treated with dichlorodicyanoquinone (DDQ) in refluxing benzene solution to give naphtho[2,1-*b*]thiophenes **10**, bp 166–168° at 0.25 Torr, and **11**, mp 131°, respectively. Thiophenes **10** and **11** have been unambiguously prepared by polyphosphoric acid cyclodehydration<sup>5</sup> of the corresponding naphthyl  $\beta$ -keto sulfides.



**10**, R = CH<sub>3</sub>; R' = C<sub>6</sub>H<sub>5</sub>

**11**, R = C<sub>6</sub>H<sub>5</sub>; R' = CH<sub>3</sub>

**12**

The assignment of stereochemistry in dihydrothiophenes **5** and **6** is based on their well-defined and predictable<sup>6</sup> nmr spectra. Thus, **5** exhibits nonaromatic resonance centered at  $\delta$  0.98 (methyl, doublet,  $J = 7.0$  Hz), 4.01 (methine adjacent to sulfur, five line multiplet,  $J = 7.0$  Hz), and 5.58 (methine, doublet,  $J = 7.0$  Hz), while **6** gives resonance at  $\delta$  1.53 (methyl, doublet,  $J = 7.0$  Hz), 4.15 (methine, eight-line multiplet,  $J = 7.0$  Hz and  $J = 1.5$  Hz), and 4.45 (methine adjacent to sulfur, doublet,  $J = 1.5$  Hz).

Orbital symmetry arguments suggest that cyclization of aryl vinyl sulfides to thiocarbonyl ylides in the photoexcited state will be conrotatory, whereas cyclization from a vibrationally excited ground state will be disrotatory.<sup>7</sup> Furthermore, stereochemistry of the final product will be fixed if intramolecular hydrogen migration occurs in the intermediate thiocarbonyl ylide. The mode of cyclization in **1** remains uncertain because photoisomerization of **1a** and **1b**

(3) Satisfactory elemental analyses and spectra compatible with the structural assignments were obtained for all new compounds. All melting points are uncorrected.

(4) Reaction solutions were irradiated in sealed Pyrex tubes degassed by four freeze-pump-thaw cycles with an oil-diffusion-pump vacuum.

(5) O. Dann and M. Kokorudz, *Chem. Ber.*, **91**, 172 (1958).

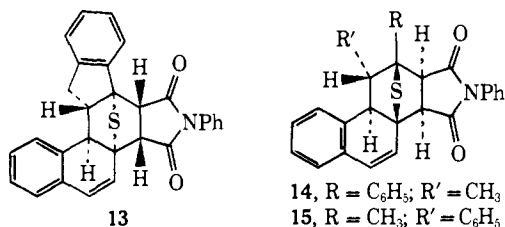
(6) M. Karplus, *J. Amer. Chem. Soc.*, **85**, 2870 (1963).

(7) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970. Cuppen and Laarhoven have shown that photocyclization of  $\alpha,\alpha'$ -diethyl-4,4'-stilbenediol occurs via the excited state to give a *trans*-dihydrophenanthrene: Th. J. H. M. Cuppen and W. H. Laarhoven, *J. Amer. Chem. Soc.*, **94**, 5914 (1972), and references cited therein.

occurs prior to ring formation. Photoisomerization of this kind is not possible for vinyl sulfide 2.

Pyrex-filtered irradiation of  $10^{-2}$  M degassed benzene solutions of 2 at room temperature resulted only in polymer formation and not the expected *trans*-dihydrothiophene 9. Cycloaddition of dipolarophiles to chemically generated thiocarbonyl ylides is known<sup>8,9</sup> and in the present case would provide evidence for the intermediacy of 12 in the photolysis of 2. When a  $10^{-2}$  M degassed benzene solution of 2 was irradiated in the presence of 2 equiv of *N*-phenylmaleimide, polymer formation was eliminated and a 90% yield of a single cycloadduct 13 (mp 264°, *m/e* 447.1321) was isolated.<sup>10,11</sup>

This trapping experiment is generally significant because, for the first time in stilbene-like photocyclizations,<sup>7</sup> the stereochemistry of the dihydro intermediate



(e.g., 12) can be clearly investigated.<sup>12</sup> From our observations, we conclude that conrotatory cyclization of 2 occurs in the photoexcited state to give the *trans*-thiocarbonyl ylide 12 (R = *o*-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub> = R', R'' = H), which then undergoes addition to *N*-phenylmaleimide to give adduct 13. The fate of intermediate 12 in the absence of dipolarophile is being studied.

The *N*-phenylmaleimide trapping experiment has provided information regarding the mechanism of dihydrothiophene formation in the photolysis of 1. Pyrex-filtered irradiation of  $10^{-2}$  M degassed benzene solutions of 1a or 1b in the presence of 2 equiv of *N*-phenylmaleimide resulted in the usual formation of *cis*-dihydrothiophene 5 (15%) but no 6. Instead, a single cycloadduct 14 was isolated (mp 266–267°, *m/e* 449.1457) in 60% yield. Irradiation of benzene solutions of *trans*-dihydrothiophene 6 and *N*-phenylmaleimide did not produce any 14. These data indicate that thiocarbonyl ylide 12 (R = C<sub>6</sub>H<sub>5</sub>, R' = CH<sub>3</sub>, R'' = H), presumably formed by conrotatory photocyclization of 1a, is the precursor to both 6 and 14.

That thiocarbonyl ylide 12 and dihydrothiophene 6 both possess *trans* stereochemistry is consistent with a suprafacial hydrogen migration occurring in 12 to give 6. Both a [1,4] hydrogen shift and two consecutive

[1,2] shifts in ground-state 12 are allowed and have been considered.<sup>12,13</sup> Irradiation of monodeuterio-1a (R'' = 90% D, 10% H) gave monodeuterio-6 (R'' = 90% D, 10% H)<sup>14</sup> which indicates that only a 1,4-hydrogen shift is important in the transformation 12 → 6.

Formation of 5 from 1 is unaffected by added dipolarophile suggesting that thiocarbonyl ylide 12 (R = C<sub>6</sub>H<sub>5</sub>, R' = CH<sub>3</sub>, R'' = H) is not involved in the formation of 5. As an alternative, we have considered vinyl sulfide 4 as a possible intermediate in the formation of 5.<sup>1</sup> Irradiation of 4 did not give any *cis*-dihydrothiophene, 5, but rather resulted in a complex mixture of products, the major component of which was the isomeric *trans*-dihydrothiophene 8 (50% isolated yield). The *cis*-dihydrothiophene 5 was stable to these reaction conditions. Furthermore, irradiation of 4 in the presence of *N*-phenylmaleimide resulted in the formation of adduct 15 (mp 170–172°, *m/e* 449.1433), but no 14. These results rule out the intermediacy of 4 in the formation of *cis*-dihydrothiophene 5 from 1.

The mechanism of hydrogen migration in various thiocarbonyl ylides is currently being investigated; however, it is clear that only a 1,4-hydrogen migration is occurring in the transformations 1 → 12 → 6 (*vide supra*) and 3 → 12 → 7. The structure of 7 (87% isolated yield, bp 126° at 0.08 Torr) was established by spectral data and the nickel boride desulfurization<sup>15</sup> to 2-( $\alpha$ -naphthyl)-2-methylbutane. This photoclosure-desulfurization sequence could be synthetically useful for the regiospecific substitution of aromatic rings.

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(13) A theoretical treatment of [1,4] *vs.* two consecutive [1,2] shifts has been presented: M. T. Rzewicz, *Tetrahedron*, **29**, 2189 (1973).

(14) Determined by nmr and mass spectral analysis.

(15) W. E. Truce and F. M. Perry, *J. Org. Chem.*, **30**, 1316 (1965); we thank Professor C. A. Brown for suggesting this method of desulfurization.

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## Nuclear Magnetic Resonance Relaxation in Lysozyme Crystals

Sir:

There has been a great deal of recent interest in the nature of specific interactions between water and protein molecules in a variety of environments including aqueous solutions,<sup>1</sup> frozen aqueous solutions,<sup>2</sup> and whole tissues.<sup>3</sup> Measurements of nmr line width, intensity, self-diffusion coefficients, and transverse and longitudinal relaxation times have been applied to this general study. A major feature of the results obtained

(1) S. H. Koenig, R. D. Brown, and C. F. Brewer, *Proc. Nat. Acad. Sci. U. S. A.*, **70**, 475 (1973).

(2) I. D. Kuntz, *et al.*, *Science*, **163**, 1329 (1969).

(3) J. A. Walter and A. B. Hope, *Progr. Biophys.*, **23**, 3 (1971).

(8) J. D. Bower and R. H. Schlessinger, *J. Amer. Chem. Soc.*, **91**, 6891 (1969), and references cited therein.

(9) H. Buter, S. Wassenaar, and R. M. Kellogg, *J. Org. Chem.*, **37**, 4045 (1972).

(10) The nmr spectral data for cycloadducts 13–15 are consistent with the assigned stereochemistry. X-Ray analysis of 13 and 14 is in progress and will serve to provide a totally unambiguous stereochemical proof. Stereochemical consequences of photogenerated thiocarbonyl cycloaddition to dipolarophiles will be discussed in a forthcoming paper.

(11) This cycloadduct forming process is truly synthetically useful and must proceed with high efficiency. Irradiation of a benzene solution of 2 (5.0 g), and *N*-phenylmaleimide in a conventional preparative photo-reactor under an Argon atmosphere gave 6.9 g (85% yield) of analytically pure 13 in 3.25 hr. We are attempting to utilize this highly efficient method for the construction of steroid and steroid-like ring systems.

(12) Chapman and coworkers attempted without success to trap an intermediate with furan and maleic anhydride in the photocyclization of *N*-phenylamines: O. L. Chapman, G. L. Eian, A. Bloom, and J. Clardy, *J. Amer. Chem. Soc.*, **93**, 2918 (1971).