

Figure 2. Surface pressure–area diagrams for films on water containing equal amounts of: (a) *cis*-1:TP, 1:2 (dashed line) and (b) *trans*-1:TP, 1:2 (solid line). In each case the films were prepared from 50 μ l of a CHCl_3 solution with $[1] = 0.18 \times 10^{-3} \text{ M}$ and $[\text{TP}] = 0.36 \times 10^{-3} \text{ M}$.

The difference between isomers is revealed more clearly in the surface pressure–area diagrams shown in Figure 2; at any surface pressure, the area for films containing *cis*-1 is greater than that for an equal number of molecules of *trans*-1. The differences can be strikingly illustrated by preparing films of *cis*-1 in the dark and monitoring the change in pressure (at constant area) upon illumination. In a typical experiment, the pressure of a stable film prepared from *cis*-1 was found to drop from 7.5 dyn/cm to less than 1 dyn/cm in less than 8 sec following the relatively weak illumination with a 15-W (Osram type L) desk lamp. Possible applications of this phenomenon as well as the influence of monolayer environment on other photoreactions are currently under investigation.

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(20) Alfred P. Sloan Foundation Fellow; correspondence should be addressed to the author at the University of North Carolina.

David G. Whitten²⁰

Max Planck Institute for Biophysical Chemistry
D3400 Göttingen-Nikolausberg, Federal Republic of Germany
Department of Chemistry, University of North Carolina
Chapel Hill, North Carolina 27514

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Competing [1,3]- and [3,3]-Sigmatropic Rearrangements of Electron-Rich Olefins

Sir:

Recently we described the first example of a [2,3]-sigmatropic rearrangement of an allylic carbene, **1** to **2**, where $\text{X} = \text{Y} = \text{sulfur}$.¹ In an attempt to find more

(1) J. E. Baldwin and J. A. Walker, *J. Chem. Soc., Chem. Commun.*, 354 (1972).

examples of this potentially useful process, we examined the reactions of *N*-allylbenzothiazolium salts (**3**, $\text{R} = \text{CH}_2\text{CH}=\text{CH}_2$) with base, since the well-established acidity of such salts is ascribed to the existence of a conjugate base (**4**), electronically similar to species **1**.² However, the transformation of *N*-allylbenzothiazolium bromide (**3**, $\text{R} = \text{CH}_2\text{CH}=\text{CH}_2$) with base has already been described in the literature, the product of this reaction being assigned structure **5** ($\text{R} = \text{CH}=\text{CH}_2$), arising from dimerization of the tautomeric species **6** ($\text{R} = \text{CH}=\text{CH}_2$).^{2g, 2j}

The unusual nature of this claim caused us to re-investigate this work. We discovered that compound **5** is incorrectly formulated, and we have elucidated its mode of formation. Thus upon treatment of salt **3** ($\text{R} = \text{CH}_2\text{CH}=\text{CH}_2$, $\text{X} = \text{Br}$) with triethylamine in DMF at 25°, we obtained a high yield (85%) of dimer, mp 98–99°, whose properties were identical with those previously reported.^{2j} Similarly the *N*-benzyl salt **3** ($\text{R} = \text{CH}_2\text{C}_6\text{H}_5$, $\text{X} = \text{Br}$) gave a corresponding dimer (84%), mp 144–147°, and our initial structural work was concentrated on this substance.³ We assigned structure **7** ($\text{R} = \text{CH}_2\text{C}_6\text{H}_5$) to this substance on the basis of the nmr spectrum (CDCl_3) δ 4.13 (2 H, AB q, $J = 12.0$ Hz) and 4.72 (2 H, AB q, $J = 15.3$ Hz), typical of two nonequivalent methylene groups, and its ultraviolet spectrum, λ_{max} (Et_2O) 257 (17,000) and 311 (5000), equivalent to that of an equimolar mixture of a 2-alkylbenzothiazole, λ_{max} 253 (10,000), and a 2,2-dialkylbenzothiazoline, λ_{max} 255 (7000) and 304 (3500), thus supporting the presence of these two units in **7**. Degradation of **7** ($\text{R} = \text{CH}_2\text{C}_6\text{H}_5$) in trifluoroacetic acid at 25° followed by treatment with sodium bicarbonate solution gave, quantitatively, benzothiazole and 2-benzylidene-*N*-benzylbenzothiazoline, identical with authentic samples. This retro-Aldol-type cleavage derives from the well-established acidity of benzothiazolium salts; cf. **8** arrows. Finally the ¹³C nmr spectrum of **7** ($\text{R} = \text{CH}_2\text{C}_6\text{H}_5$) shows a highly deshielded resonance at 96.5 ppm (relative to CHCl_3) characteristic of the 2-carbon atom of a 2-alkylbenzothiazole (2-benzylbenzothiazole, 93.0 ppm).⁴ Similar degradative and spectral data established the structure of the original dimer from *N*-allylbenzothiazolium bromide^{2j} as **7** ($\text{R} = \text{CH}_2\text{CH}=\text{CH}_2$).

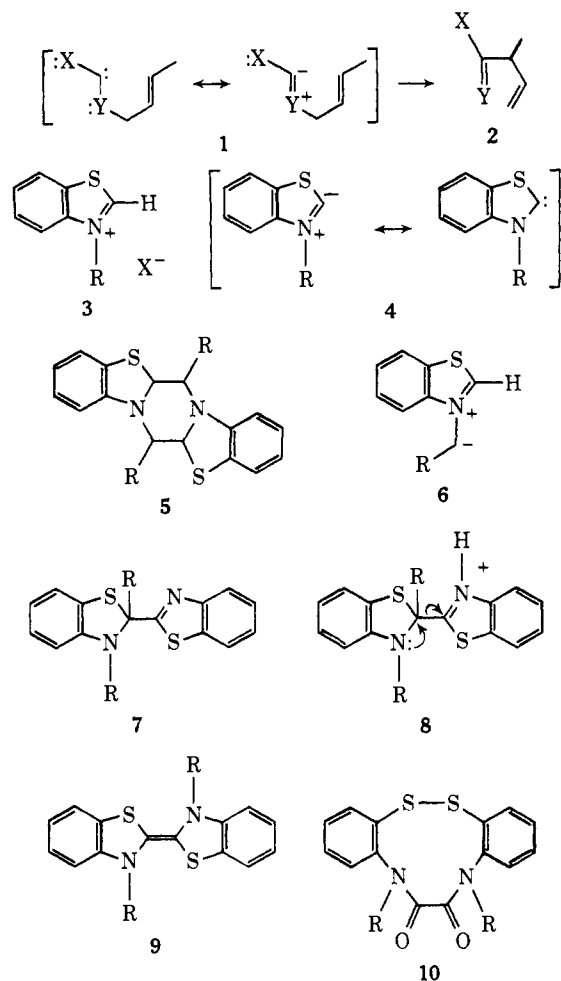
The formation of these dimers (**7**) was established to involve the unstable intermediate **9** ($\text{R} = \text{CH}_2\text{C}_6\text{H}_5$ or $\text{CH}_2\text{CH}=\text{CH}_2$) which could be isolated by treatment of the respective benzothiazolium salts (**3**) with triethylamine in dimethylformamide at 0°.⁵ These yellow ethylene dimers were extremely sensitive to oxygen, e.g., exposure of a CH_2Cl_2 solution of **9** ($\text{R} = \text{CH}_3$) to oxygen at 0° gave the amide (**10**, $\text{R} = \text{CH}_3$) in high

(2) (a) J. J. Vorsanger, *Bull. Soc. Chim. Fr.*, 119 (1964); (b) J. J. Vorsanger, *ibid.*, 1772 (1966); (c) H. Wahl and J. J. Vorsanger, *ibid.*, 3359 (1965); (d) J. Metzger, H. Larivé, R. Dennilauler, R. Baralle, and C. Gurat, *ibid.*, 2857 (1964); (e) W. Friedrich, H. Kehr, F. Kröhnke, and P. Schiller, *Chem. Ber.*, **98**, 3808 (1965); (f) F. Kröhnke and W. Friedrich, *ibid.*, **96**, 1195 (1963); (g) H. W. Wanzlich and H. J. Kleiner, *Angew. Chem., Int. Ed. Engl.*, **3**, 65 (1964); (h) H. W. Wanzlich, H. J. Kleiner, I. Lasch, and H. U. Földner, *ibid.*, **5**, 126 (1966); (i) H. Wuast and S. Hünig, *Chem. Ber.*, **99**, 2017 (1966); (j) H. W. Wanzlich, H. J. Kleiner, I. Lasch, H. U. Földner, and H. Steinmaus, *Justus Liebig's Ann. Chem.*, **708**, 155 (1967).

(3) All new compounds have given correct analytical and spectral data.

(4) Noise decoupled FT spectroscopy, for which we thank Dr. Traficante of this department.

(5) We do not know the geometry of these olefins.



yield, mp 205–206°,⁶ desulfurized with Raney Nickel to *N*-phenyl-*N*-methyloxamide. Warming solutions of these dimers (9, R = CH₂C₆H₅ or CH₂CH=CH₂) in chloroform or other nonpolar solvents, in the absence of oxygen, resulted in their smooth conversion to the stable dimers (7), thus proving their intermediacy in the transformation of the benzothiazolium salts (3). When the allyl substituents in 3 were marked by alkyl groups, as crotyl and dimethylallyl, less than 100% inversion of the migrating allylic group was observed in the product dimer 7, indicative of the presence of a competing [1,3]-sigmatropic migration of the allylic function. The contribution of this pathway was favored by higher temperatures, as is shown in Table I. The products of these reactions were stable to the reaction conditions.⁷

The above results show that ethylenes (9, R = CH₂-CH=CR₂) rearrange by two competing pathways, a thermally allowed [3,3]-sigmatropic process and a formally forbidden [1,3]-sigmatropic pathway,⁸ as shown

(6) The substance 10 (R = CH₃) was originally formulated as the isomeric cyclic thiocarbamate. This oxidative rearrangement has precedent in the autoxidation of tetrathioethylenes: cf. W. Adam and J. C. Liu, *J. Amer. Chem. Soc.*, **94**, 1206 (1972); W. Ando, J. Suzuki, T. Arai, and T. Migita, *Tetrahedron*, **29**, 1507 (1973).

(7) Since the dissociation of electron-rich ethylenes, such as 9, to nucleophilic carbenes has been shown not to be occur, this pathway, via 4, cannot be involved in the rearrangement of 9: cf. R. W. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **7**, 754 (1968). Furthermore the remote possibility of acid-catalyzed formation of 4 from 8, with subsequent rearrangement at the level of 4 and recombination to 7, was excluded by noting that 2-alkylbenzothiazoles are unable to intercept any intermediate in the conversion of 3 (R = CH₂CH=CH₂, X = Br) to 7 (R = CH₂CH=CH₂).

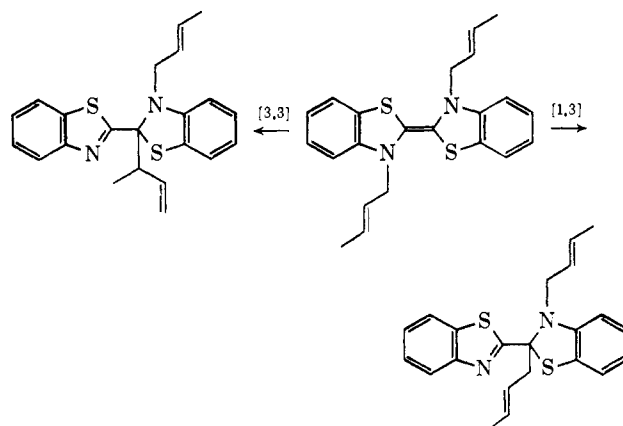
Table I

Salt 3 (X = Br) R	% [3,3]-sigmatropic pathway to compound 7 at °C ^a			<i>t</i> _{1/2} , 34° CHCl ₃ (min)
	25°	75°	100°	
CH ₂ C ₆ H ₅ ^b				100
CH ₂ C ₆ H ₄ (<i>p</i> -NO ₂) ^b				<10
CH ₂ CH=CD ₂	100			15
CH ₂ CH=CHCH ₃ (t)	90	85	75	10
CH ₂ CH=C(CH ₃) ₂	60		30	10

^a Determined *via* acidic degradation by pathway shown in 8.

^b These benzyl derivatives provide only [1,3] products.

Scheme I



in Scheme I. Although we cannot exclude the possibility that the latter process is an example of a forbidden yet concerted reaction^{9,10} the effect of *p*-nitro substitution, Table I, is typical of that found in the Stevens [1,2]-rearrangement, a process clearly radical in character,^{11b} and suggests to us that the same duality of concerted *vs.* radical pathways found in the [2,3]-sigmatropic reaction also operates in certain circumstances in the [3,3]-sigmatropic reaction.

Acknowledgments. We wish to thank the National Science Foundation, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and Eli Lilly and Co. for support.

(8) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970.

(9) J. A. Berson, *Accounts Chem. Res.*, **5**, 406 (1972).

(10) Attempts to observe CIDNP effects in these rearrangements have been unsuccessful.

(11) (a) J. E. Baldwin, W. F. Erickson, R. E. Hackler, and R. M. Scott, *Chem. Commun.*, 576 (1970); (b) U. Schöllkopf, *Angew. Chem., Int. Ed. Engl.*, **9**, 763 (1970).

Jack E. Baldwin,* Jerry A. Walker

Department of Chemistry, Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

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Thermal and Mercuric Ion Catalyzed [3,3]-Sigmatropic Rearrangement of Allylic Trichloroacetimidates. The 1,3 Transposition of Alcohol and Amine Functions

Sir:

The [3,3]-sigmatropic rearrangement of 3-heteroatomic-1,5-diene species (eq 1) is an important method for the stereospecific construction of unsaturated sys-