

tion is reflected by the excess oxygen-18 content of the carbon dioxide from this derivative. The results definitely show that scrambling does compete with the overall destruction of the starting material. Qualitatively the situation is the same as for the pivalate in that the reaction appears to be concerted by the isotope effect criterion yet oxygen-18 randomization is observed. The 1,3-sigmatropic shift could be the explanation. However, a second possibility is that the scrambling reflects the fraction of the overall reaction which proceeds by the nonconcerted path as a competition. The suggestion of an increased k_s ($1 \times 10^{-6} \text{ sec}^{-1}$) in Nujol compared to isooctane ($0.6 \times 10^{-6} \text{ sec}^{-1}$) is consistent with this possibility. Equation 1

$$\frac{k_0}{k_s} = \frac{k_{\text{con}}}{k_1} + \left[\frac{k_{\text{con}}}{k_1} + 1 \right] \left[\frac{k_2}{k_{-1}} + \frac{k_d}{k_{-1}} \right] \quad (1)$$

allows the quantitative treatment of such a competition.

The value of k_1 at 103° is estimated at $2 \times 10^{-6} \text{ sec}^{-1}$ using the reported⁹ activation parameters for *tert*-butyl peracetate. The value of k_{con} can be taken as the observed rate constant for the reaction of the isobutyrate ($2 \times 10^{-4} \text{ sec}^{-1}$). The value of $((k_2 + k_d)/k_{-1})$ is of the order of one for the peracetate at 130° . If the isobutyroxy-*tert*-butoxy pair behave similarly, the k_0/k_s ratio should be *ca.* 2×10^2 which is just what is observed. Thus, in this case, the quantitative analysis of the degree of scrambling is entirely consistent with the radical pair hypothesis.

The rate of scrambling for the isobutyrate at 50.6° is estimated at less than $1 \times 10^{-9} \text{ sec}^{-1}$ or 2 orders of magnitude smaller than that for the pivalate.⁵ The 1,3-sigmatropic shift could explain this discrepancy if it is accelerated by a factor of more than 100 by substitution of a remote methyl group. Such a substituent effect suggests that the 1,3 shift would be too slow for the peracetate or perpropionate to have any bearing on the observed randomization.

The present results are totally consistent with the radical pair hypothesis for scrambling of oxygen-18 in peresters and attest to the sensitivity of this method at detecting the small amount of nonconcerted reaction which competes with the major concerted pathway. The activation parameters,⁹ isotope effects (Table I), insensitivity of rate to fluidity (Table I), quantitative yields of carbon dioxide in the presence of olefins,⁶ negligible amount of oxygen-18 randomization (Table II), and absence of perester formation from the corresponding hyponitrite¹⁰ all lead to the conclusion of concerted conversion of the isobutyrate to the isopropyl-*tert*-butoxy radical pair through a reaction coordinate involving a single transition state which accounts for 99% of the overall reaction.

Acknowledgment. We are grateful to the National Science Foundation and the E. I. du Pont Co. for financial support of this work.

(9) J. P. Lorand, Ph.D. Thesis, Harvard University, Cambridge, Mass.

(10) T. Koenig and W. R. Mabey, *J. Amer. Chem. Soc.*, **92**, 3894 (1970).

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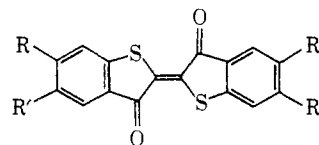
Received September 4, 1973

Photochemical Reactions in Organized Monolayer Assemblies. I. Cis-Trans Isomerization of Thioindigo Dyes

Sir:

Although olefin photoisomerization has been extensively studied in solution,¹ relatively little is known regarding the factors controlling the reaction in other environments.²⁻⁵ Of particular interest is the influence of environment on the cis-trans isomerizations and related reactions which occur in membranes or other semisolid environments in photobiological processes such as vision. In the present communication we report an investigation of olefin photoisomerization in organized monolayer assemblies. Results of this study demonstrate that the membrane-like monolayer environment can exert such a striking influence on reactivity that factors which are relatively unimportant in solution can dominate reactivity in the monolayer.

The olefins employed in this study are the alkyl-substituted thioindigo dyes **1-3**. These olefins undergo



trans-1, R = *n*-C₆H₁₃O; R' = H

trans-2, R = H; R' = *n*-C₄H₉

trans-3, R = H; R' = *tert*-amyl

direct and sensitized cis-trans photoisomerization processes more-or-less analogous to those observed with the stilbenes and other acyclic olefins.⁵⁻⁸ The isomerizations in solution are readily followed by the pronounced changes in spectra accompanying cis-trans isomerization; the rather large differences in spectra between isomers permit the isolation of isomerically enriched isomers by irradiation with selected monochromatic light. It was anticipated that in compounds **1-3** the combination of a polar chromophore with hydrophobic alkyl side chains would result in a surfactant capable of forming spread monomolecular films and monolayer assemblies.⁹ Mixtures of olefin dyes **1-3** and tripalmitine (TP) were found to form monomolecular films that were stable over a pressure range 5-30 dyn/cm; these monolayers were readily transferred to glass supports, and it was found possible to deposit several layers containing the olefins in the usual manner.¹⁰ In addition, **1** forms stable films from the pure

(1) For a comprehensive review see J. Saltiel, J. D'Agostino, E. D. Megarity, L. Metts, K. R. Neuberger, M. Wrighton, and O. C. Zafriou, *Org. Photochem.*, **3**, 7 (1973).

(2) Reports to date include studies of olefin isomerization on silica gel support,³ in glassy media,⁴ and in resins.⁵

(3) L. D. Weis, T. R. Evans, and P. A. Leermakers, *J. Amer. Chem. Soc.*, **90**, 6109 (1968).

(4) D. Gegiou, K. A. Muszkat, and E. Fischer, *J. Amer. Chem. Soc.*, **90**, 12 (1968).

(5) D. L. Ross, *Appl. Opt.*, **10**, 571 (1971).

(6) G. M. Wyman and B. M. Zarnegar, *J. Phys. Chem.*, **77**, 831 (1973).

(7) G. M. Wyman and B. M. Zarnegar, *J. Phys. Chem.*, **77**, 1204 (1973).

(8) G. M. Wyman, B. M. Zarnegar, and D. G. Whitten, *J. Phys. Chem.*, **77**, 2584 (1973).

(9) H. Kuhn and D. Möbius, *Angew. Chem., Int. Ed. Engl.*, **10**, 620 (1971).

(10) The techniques developed by Kuhn and coworkers^{8,11} were employed in these experiments.

(11) H. Kuhn, *Pure Appl. Chem.*, **27**, 421 (1971).

compound which can be deposited in any number of layers onto a glass support. For spectral and photochemical investigation it was found convenient to use an olefin:TP ratio of 1:2 and a surface pressure of 15 dyn/cm. In typical experiments¹² chloroform solutions of predominantly *trans*-1 and TP were prepared by irradiation at 453 nm; the preparation of spread monolayer films on water and transfer of these to glass supports could be accomplished in the dark without detectable *cis*-*trans* isomerization.¹⁸ Similarly solutions containing almost exclusively *cis*-1 were obtained by irradiation at 539 nm; from these solutions it was possible to obtain spread films and monolayers containing isomerically nearly pure *cis*-1 in the absence of light. Spectra of monolayer assemblies of *cis*- and *trans*-1 are compared in Figure 1. The monolayer assemblies containing olefins 1-3 were found to be stable indefinitely in the dark; no thermal isomerization of either isomer could be detected at room temperature. The spectra of *cis*- and *trans*-1 in the monolayer assemblies resemble those of the same compounds in solutions; however, for both isomers major transitions are somewhat red shifted in the assemblies.¹⁴ Studies of the spectra of assemblies of *trans*-1 (pure or in mixtures with TP) with polarized light¹⁵ show that transition moments of the main absorption bands lie in the layer plane; since these transitions should be in the plane of the chromophore, the chromophore must lie planar in the layer plane. Little variation of absorption strength is noted when the spectra of assemblies containing *cis*-1 are measured with polarized light at oblique angles; this is consistent with a random orientation of the chromophore planes or with a relatively nonplanar *cis* chromophore.¹⁵

Although assemblies containing only *cis*-1 show no detectable fluorescence, those containing either pure *trans*-1 or *cis*-*trans* mixtures show relatively strong fluorescence with λ_{max} 573 nm, approximately the same wavelength as for chloroform solutions of *trans*-1. The fluorescence is approximately 3.5 times as intense as that for chloroform solutions of *trans*-1 of the same optical density; since fluorescence quantum yields for *trans*-6,6'-dialkoxythioindigos are reported to be *ca.* 0.03,⁶ ϕ_f for the assemblies of *trans*-1 is *ca.* 0.1.

Irradiation of assemblies of isomerically pure *trans*-1 with light of $\lambda > 300$ nm produces no detectable change, even on prolonged irradiation. In contrast, irradiation of assemblies containing *cis*-1 leads to rapid¹⁶ and irreversible formation of *trans*-1 (Figure 1). The conversion of *cis*-1 to *trans* is quantitative; that no other reaction occurs is indicated by isosbestic points at 502 and 455 nm. The spectra and molecular orientation

(12) Details are described here for 1; analogous results were obtained for 2 and 3 although overlap of the absorption spectra of *cis* and *trans* isomers for the latter compounds and an unfavorable (~ 0.1)⁶ $\phi_t \rightarrow c / \phi_c \rightarrow t$ ratio render it difficult to isolate pure *cis* isomers.

(13) Depal interference filters were used to give nearly monochromatic light. Isomer composition was checked by measuring spectra both of the monolayer assemblies (*vide infra*) on the glass and of chloroform extracts of the olefin dissolved from the assemblies.

(14) The spectra are independent of the number of layers and the 1:TP mixing ratio; however, the possibility of aggregates cannot be excluded.

(15) H. Kuhn, D. Möbius, and H. Bücher in "Physical Methods of Chemistry," Vol. I, Part 3b, A. Weissburger and B. Rossiter, Ed., Wiley, New York, N. Y., 1972, p 588.

(16) Estimated quantum efficiency *ca.* 0.01-0.02; irradiation of a sample containing 12 monolayers of *cis*-1:TP, 1:2 at 453 nm with intensity 2.6 mW/cm² leads to essentially complete conversion in 8 min.

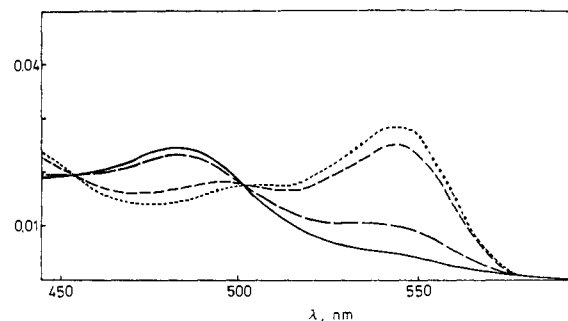


Figure 1. Spectra of monolayer assemblies (20 layers) of 6,6'-di-*n*-hexyloxythioindigo (1) with tripalmitine, mixing ratio 1:TP, 1:2: Solid line, *cis*-1; dotted line *trans*-1; dashed lines indicate intermediate points in the photoisomerization from *cis*-1 to *trans*.

of assemblies of *trans*-1 from irradiation of *cis*-1 in the assemblies are identical with those prepared directly from pure *trans*-1. Rapid photoisomerization of *cis*-1 to *trans*, but not the reverse, also occurs on irradiation of spread monolayers of pure *cis*-1 or *cis*-1:TP mixtures on a water surface. Although films containing *cis*-1 are stable for a long period in the dark, irradiation with visible light for only a few seconds is sufficient to produce quantitative conversion to *trans*. Thus in both spread films and monolayer assemblies, efficient photoisomerization of olefins 1-3 is observed but, in contrast to the solution photoisomerization, exclusively from *cis* to *trans*.

The observed phenomena can be attributed to a cooperative effect caused by two factors, the molecular environmental restraints imposed by the membrane-like monolayer assembly and the differing sizes of *trans* and *cis* isomers. Although limited diffusion of moderately large molecules and rapid diffusion of smaller molecules through similar monolayer assemblies are known to occur,⁹ molecular motion is somewhat restricted in these assemblies, and large volume expansions should be difficult if not prohibited during the lifetime of the excited state. For several olefins, especially stilbene derivatives, it has been shown that the planar *trans* isomer is smaller than the nonplanar *cis* isomer.¹⁷ For stilbene, the occurrence of *cis*-*trans* isomerization in semirigid glasses under conditions where the *trans*-*cis* conversion does not occur has been taken as evidence that the order of size is *trans* < twisted isomerization precursor < *cis*.^{4,18,19} Thus in the membrane-like monolayer assembly, the *cis*-*trans* process could result in a relaxation, or at least it should encounter little resistance,¹⁹ while the *trans*-*cis* process should be an expansion, sterically restricted in the semirigid environment. Evidence supporting this comes from an investigation of the surface pressure and area for spread films of the two isomers. At a constant pressure of 15 dyn/cm, the photochemical conversion of *cis*-1 to *trans* (in a 1:2 mixture with TP) is accompanied by $3.0 \pm 0.4\%$ reduction in volume.

(17) K. V. Auwers, *Ber.*, **68**, 1346 (1935).

(18) Although *cis*-stilbene is surely larger than *trans*, it appears less certain that the twisted intermediate is smaller than the moderately twisted *cis*. A study of viscosity effects on the *trans*-*cis* process for stilbene¹⁹ had led to a somewhat different interpretation that in semirigid media the solvent imposes a viscosity-dependent restriction to the initial distortion from a planar to twisted form.

(19) J. Saltiel and J. T. D'Agostino, *J. Amer. Chem. Soc.*, **94**, 6445 (1972).

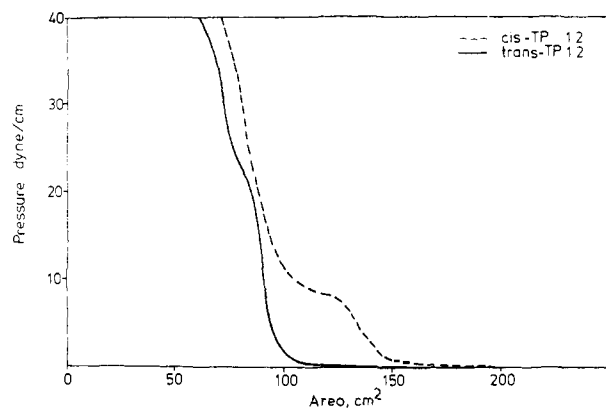


Figure 2. Surface pressure–area diagrams for films on water containing equal amounts of: (a) *cis*-1:TP, 1:2 (dashed line) and (b) *trans*-1:TP, 1:2 (solid line). In each case the films were prepared from 50 μ l of a CHCl_3 solution with $[1] = 0.18 \times 10^{-3} M$ and $[\text{TP}] = 0.36 \times 10^{-3}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

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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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 $X = Y = \text{sulfur}$.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**, $R = \text{CH}_2\text{CH}=\text{CH}_2$) 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**, $R = \text{CH}_2\text{CH}=\text{CH}_2$) with base has already been described in the literature, the product of this reaction being assigned structure **5** ($R = \text{CH}=\text{CH}_2$), arising from dimerization of the tautomeric species **6** ($R = \text{CH}=\text{CH}_2$).^{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** ($R = \text{CH}_2\text{CH}=\text{CH}_2$, $X = \text{Br}$) 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** ($R = \text{CH}_2\text{C}_6\text{H}_5$, $X = \text{Br}$) gave a corresponding dimer (84%), mp 144–147°, and our initial structural work was concentrated on this substance.³ We assigned structure **7** ($R = \text{CH}_2\text{C}_6\text{H}_5$) 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** ($R = \text{CH}_2\text{C}_6\text{H}_5$) 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** ($R = \text{CH}_2\text{C}_6\text{H}_5$) 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** ($R = \text{CH}_2\text{CH}=\text{CH}_2$).

The formation of these dimers (**7**) was established to involve the unstable intermediate **9** ($R = \text{CH}_2\text{C}_6\text{H}_5$ 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** ($R = \text{CH}_3$) to oxygen at 0° gave the amide (**10**, $R = \text{CH}_3$) 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. Fuldner, *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. Fuldner, 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.