It has been demonstrated that the two possible products (*erythro*- and *threo*-2-butanol-*3-d*) can be readily differentiated *via* nmr spectroscopy.[8] The differentiation is based on the fact that the methylene protons in 2-butanol are magnetically nonequivalent.

We have deuterioborated *cis*-2-butene and find that the oxidized product exhibits an nmr spectrum identical with the published spectrum of *erythro*-2-butanol-*3-d*.[8] There is no evidence for the presence of the threo isomer within the accuracy of our nmr analysis (approximately 1%). In addition we have deuterioborated *trans*-2-butene and find that the oxidized product exhibits an nmr spectrum identical with the published spectrum of *threo*-2-butanol-*3-d*[8] with no evidence for the presence of the erythro isomer.

Consequently, we conclude that the hydroboration–oxidation sequence achieves, exclusively, the stereospecific cis-hydration of simple, acyclic alkenes.

Experimental Section

Spectra.—The spectra were run on a Varian HA-100 spectrometer.

Materials.—Lithium deuteride (Merck Sharpe and Dohme), *cis*-2-butene (Matheson), and *trans*-2-butene (Matheson) were used as received. Diglyme (Ansul) and tetrahydrofuran (Fisher) were distilled from lithium aluminum hydride prior to use. Boron trifluoride etherate (Fisher) was distilled from calcium hydride prior to use.

Borane-d_3 in tetrahydrofuran was prepared according to standard procedures.[9,10]

Preparation of *erythro*-**2-Butanol-***3-d*.—*cis*-2-Butene (4.1 ml, 50 mmol) was condensed at −78° and then introduced (as a gas) to a stirred solution of borane-d_3 (8.3 mmol) in THF which was maintained at 0°. The introduction of the *cis*-2-butene is readily accomplished by attaching the flask containing the condensed alkene to the reaction flask *via* a section of Tygon tubing and then allowing the alkene to warm to room temperature. This affords a slow addition of the 2-butene to the borane-d_3 solution.

The reaction mixture was stirred at 0° for 30 min and then allowed to warm to room temperature. The resultant tri-*sec*-butylborane was oxidized at 50° (water bath) by the addition of 3 ml of 3 *N* sodium hydroxide followed by 3 ml of 30% hydrogen peroxide. The reaction mixture was stirred at 50° for 1 hr and then was saturated with potassium carbonate. The THF layer was separated and the water layer was extracted with 2 × 30 ml of ethyl ether. The ether layers were combined and dried ($MgSO_4$), and the solvent was removed under reduced pressure. Gc analysis of the product at this point (utilizing decane as an internal standard) indicated a 96% yield of pure 2-butanol-*3-d*. The product was isolated by preparative gc (10% Carbowax on Chromosorb W, 20 ft).

Preparation of *threo*-**2-Butanol-***3-d*.—The synthesis was carried out exactly as described above for the *erythro-3-d* except that *trans*-2-butene (4.1 ml, 50 mmol) was utilized rather than *cis*-2-butene.

Gc analysis of the resultant 2-butanol-*3-d* (decane as internal standard) indicated a 92% yield of pure alcohol. The product was isolated by preparative gc (10% Carbowax on Chromosorb W, 20 ft).

Registry No.—I, 10277-59-5; II, 10277-60-8; *cis*-2-butene, 590-18-1; *trans*-2-butene, 624-64-6.

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(9) H. C. Brown and G. Zweifel, *Org. React.*, **13**, 32 (1961).

(10) H. C. Brown, K. J. Murray, L. J. Murray, J. A. Snover, and G. Zweifel, *J. Amer. Chem. Soc.*, **82**, 4233 (1960).

The Configuration of the Thioindigo Anion Radical

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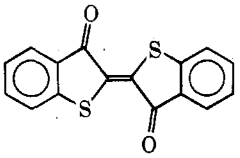
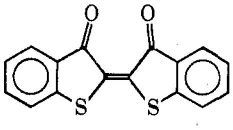
Although thioindigo was first reported in 1906,[2] the question of cis–trans isomerism does not appear to have been treated explicitly until 45 years later. Wyman and Brode established that the relative amounts of cis and trans isomers in solution were a function of temperature and irradiation.[3] Subsequently, Wyman studied the photochemical aspects of this system in greater detail.[4,5] We have recently elucidated the structure of the stilbene anion radical by ultraviolet and electron spin resonance spectroscopic techniques.[6] As part of a study to define the utility of this combined uv–esr procedure, we directed our attention to the thioindigo system (**1**).


trans-**1**


cis-**1**

From the visible spectrum of **1** in 1,2-dimethoxyethane (DME) it was determined that the cis:trans ratio was 15:85. These relative concentrations were estimated by computer simulation, based on the line shapes reported by Blanc and Ross.[7] When a small amount of thioindigo anion radical (1^-) was generated by reduction with potassium, the visible spectrum of the solution was altered. The result was a complete shift to the trans isomer. The fact that no change in the spectrum was observed when the solution was quenched by exposure to air demonstrated that the anion radical concentration was very low. From these data it can be concluded that the anion radical does not affect the absorption curves but only serves to shift the relative concentrations toward the trans isomer; this behavior is the same as that observed in the stilbene system.[6] The isomerization can be considered to proceed *via* those species shown in Scheme I.[8] Simple molecular orbital calculations suggest that the conversion of **1** to 1^- is accompanied by a decrease in the bond order of the central ethylenic linkage. Since the cis isomer is presumably less stable owing to repulsion between the carbonyl groups, the

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(1) Based in part on the Honors Thesis of D. G. K., Williams College, 1972.

(2) P. Friedländer, *Ber.*, **39**, 1060 (1906).

(3) G. M. Wyman and W. R. Brode, *J. Amer. Chem. Soc.*, **73**, 1487 (1951).

(4) D. A. Rogers, J. D. Margerum, and G. M. Wyman, *ibid.*, **79**, 2464 (1957).

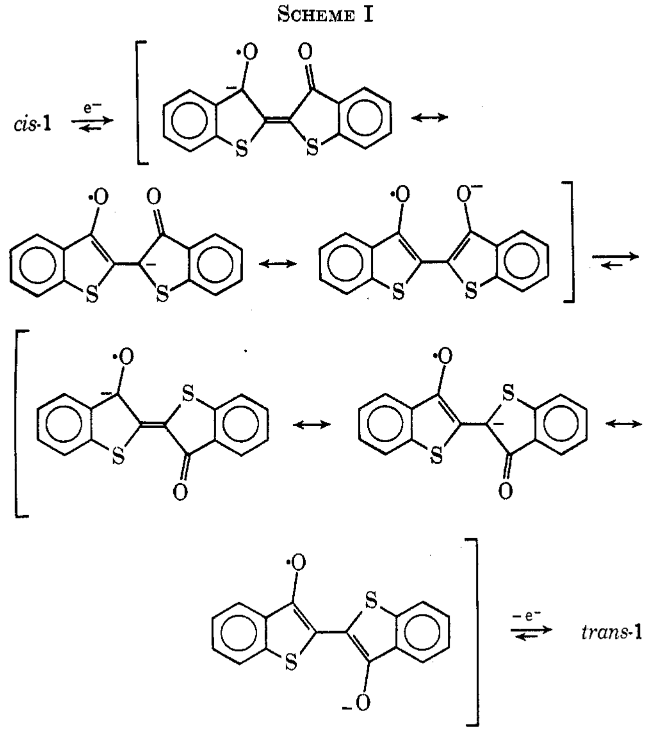
(5) G. M. Wyman, *Chem. Commun.*, 1332 (1971).

(6) R. Chang and J. H. Markgraf, *Chem. Phys. Lett.*, **13**, 575 (1972).

(7) J. Blanc and D. L. Ross, *J. Phys. Chem.*, **72**, 2817 (1968).

(8) Only those contributing structures of the anion radical which seem pertinent to the isomerization are represented, although it is known from the esr spectrum that the unpaired electron is delocalized throughout both benzene rings.

SCHEME I



observed isomerization of *cis*-**1** to *trans*-**1** is in accord with these considerations.

The complementary portion of the investigation involved esr spectra. Although such a spectrum has been reported for $\mathbf{1}^-$, no configurational assignments were discussed.[9] Ideally it is desirable to observe $\mathbf{1}^-$ in the presence of **1**, while irradiating at the appropriate wavelengths. Wyman and Brode[3] showed that when a neutral solution of **1** was irradiated with blue light the conversion to the trans isomer was almost quantitative, whereas the cis isomer was the major product when yellow light was employed. Thus irradiation with blue light of a solution of **1** in the presence of $\mathbf{1}^-$ should increase the esr line width as a result of faster electron transfer between the neutral molecule and the anion, if the latter also has the trans configuration. Conversely, a decrease in line width should be observed upon irradiation with yellow light.[10]

Since a saturated solution of **1** in DME was not greater than 10^{-3} *M*,[12] only an upper limit of the transfer rate could be estimated. No line width alterations were observed over a temperature range of −60 to 35°. Based on the analogy to the stilbene system, it was inferred that the species present was the trans isomer. Irradiation with blue light, therefore, would not bring a change in the line width; this was indeed observed. Although it was anticipated that irradiation with yellow light would sharpen the esr lines, such a procedure caused no detectable change.[13] Two factors may contribute to this absence of line sharpening. One is the low initial concentration of **1**; the other comprises the following relative rate considerations. The equilibria in the present example involve the neutral cis and trans molecules (c and t) and the corresponding anion radicals (c^- and t^-). Unlike the stilbene case,

$$t \overset{k_1}{\rightleftarrows} c \tag{1}$$

$$t^- + t \overset{k_2}{\rightleftarrows} t + t^- \tag{2}$$

$$t^- + c \overset{k_3}{\rightleftarrows} t + c^- \tag{3}$$

$$c^- \overset{k_4}{\rightleftarrows} t^- \tag{4}$$

the rate constant for eq 3 was comparable in magnitude to that of eq 2. In fact, k_3 was so fast that immediately after irradiation with yellow light there was no detectable change in the visible spectrum. The fact that k_3 was comparable to k_2 ($>10^7\ M^{-1}\ \text{sec}^{-1}$) was not totally unexpected in view of the overall similarity in shape of the two geometric isomers. Therefore, the absence of line sharpening is a consequence of the inability to increase the steady-state concentration of the neutral cis species.

From the results with stilbene and thioindigo we conclude that configurations of radicals can be deduced most effectively by the combined uv–esr method only when the geometries differ significantly. Although it is difficult to specify the precise spatial requirements necessary for electron transfer reactions, our studies of these two systems constitute a preliminary understanding of the dependence of such rates on structure.

Experimental Section

Thioindigo (**1**) was kindly supplied by Dr. George M. Wyman (Durham, N. C.); high-resolution mass spectral analysis established the absence of impurities.[14] Tetrahydrofuran and 1,2-dimethoxyethane were refluxed over calcium hydride for 24 hr, distilled, and stored over sodium–potassium alloy prior to use.

The usual high-vacuum methods for the preparation of the anion radicals were employed.[15] A deoxygenated solution of **1** in a completely sealed system was brought into brief contact with a potassium mirror, which was isolated from the rest of the system by a breakseal. The resulting solution was then poured into the appropriate sidearm to obtain either esr or visible spectra. The former were recorded on a Varian E-3 spectrometer with a variable temperature controller; the latter were recorded on a Cary Model 14 spectrophotometer. For combined esr–optical studies the sample was irradiated in the cavity with a PEK 100-W high-pressure mercury lamp. A 5-cm quartz cell containing water was used to filter infrared radiation; blue or yellow filters were used for isomerization studies.

Registry No.—*cis*-**1**, 3583-39-9; *trans*-**1**, 3844-31-3; *cis*-$\mathbf{1}^-$, 38425-40-0; trans-$\mathbf{1}^-$, 38425-41-1.

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[9] M. Bruin, F. Bruin, and F. W. Heineken, *J. Chem. Phys.*, **37**, 135 (1962). The coupling constants obtained in our study are essentially the same as those reported by these authors.

[10] The dependence of electron transfer rate on structure is based on the Franck–Condon principle, which was first employed in this manner by Libby[11] to explain certain inorganic electron transfer reactions. In essence, this application states that electron transfer from one species to another in a collision complex may be treated as if it were an electronic transition and that to lower the free energy of activation both species must have similar configurations.

[11] W. F. Libby, *J. Phys. Chem.*, **56**, 863 (1952).

[12] Other solvents proved no more suitable. The solubility of **1** in tetrahydrofuran was comparable to that in DME. In benzene and toluene, in which **1** was more soluble, $\mathbf{1}^-$ was very unstable.

[13] At low temperature a reversible dimerization of the thioindigo anion radical was observed with concomitant formation of a diamagnetic species. Under more drastic conditions of irradiation at least two different types of neutral radicals were produced from either **1** or $\mathbf{1}^-$.

[14] C. W. Koch and J. H. Markgraf, *J. Heterocycl. Chem.*, **8**, 225 (1971).

[15] D. E. Paul, D. Lipkin, and S. I. Weissman, *J. Amer. Chem. Soc.*, **78**, 116 (1956).