

RESEARCH NOTE

CIS-TRANS ISOMERISM OF 2, 2'-DIMETHOXYAZOBENZENE

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Abstract—Upon exposure to daylight, *trans*-2,2'-dimethoxyazobenzene isomerized to give an equilibrium mixture of 70% *cis* and 30% *trans* isomer. The high photo-steady concentration of *cis* isomer is discussed compared with that of azobenzene.

INTRODUCTION

Cis-trans isomerism has been studied continuously¹⁻⁴ since the discovery and isolation of *cis*-azobenzene by Hartley.⁵ The general method for preparing a *cis*-isomer has been via the photochemical equilibration with the *trans*-isomer and chromatographic separation of the *cis*-isomer,^{6,7} although Hyatt reported the stereospecific synthesis of *cis*-azo compounds by treating hydrazobenzenes or substituted anilines with active manganese dioxide at room temperature.⁸

Herein, *cis-trans* isomerism of 2, 2'-dimethoxyazobenzene (**1**) by daylight is reported. Both the velocity of *trans* → *cis* and the steady concentration of *cis*-**1** in the equilibrium mixture was much higher compared with those of azobenzene.

MATERIALS AND METHODS

Trans-2, 2'-dimethoxyazobenzene (*trans*-**1**) was prepared by refluxing *o*-anisidine with manganese dioxide in benzene for 6 h. The crude azobenzene was purified by column chromatography. Recrystallization from aqueous ethanol gave orange-red *trans* product (mp 153–155°C, lit⁹ mp 153°C and 155°C). ¹H and IR spectra of 2, 2'-dimethoxyazobenzene were as follows. ¹H NMR (acetone-*d*₆) 4.05 (s, 6H) and 7.0–7.8 (m, 8H); IR (KBr) 2980–2800 (w, br), 1580 (s), 1485 (s), 1470 (s), 1280 (s), and 1245 cm⁻¹ (s).

RESULTS AND DISCUSSION

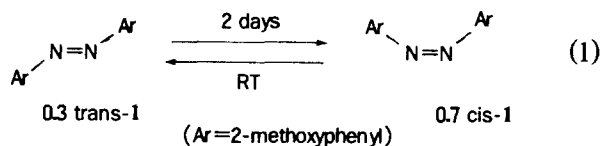
A solution of *trans*-**1** having R_f = 0.28 (on Analtech silicagel 254 plate activated by heating at 125°C for 10 min), began to give another spot of R_f = 0.08 (using benzene as an eluting solvent), after staying on the bench for 20 minutes. Obviously, this slower moving compound was the *cis*-**1**, since a solu-

tion of *trans*-**1**, placed in the dark drawer for several days, remained unchanged.

Obviously the rate of *trans* → *cis* isomerization of *trans*-**1** was much faster than that of unsubstituted azobenzene (**2**). For example, a solution of *trans*-**1** in acetone gave high concentration of *cis*-**1** after placing the solution on the bench (where the direct sunshine was not available) for 5 h, during which time only a minute amount of *trans*-**2** changed into *cis*-**2**.

In order to study the isomerism of *trans*-**1** in a more quantitatively, a solution of *trans*-**1** in acetone was placed on the bench. After 2 days, the acetone solution was subjected to preparative TLC (E. Merck, 20 × 20 cm, 2 mm, silica gel F 254) in order to purify each isomer by eluting with benzene. Each band was extracted with ether, and the ether solution was evaporated using a rotary evaporator at 25–30°C.

Although all this work was carried out in a dim light at room temperature, a concentrated solution of *cis*-**1** again showed a small amount of *trans*-**1**. The amount of each isomer obtained by preparative TLC was 52 mg of *trans*-**1** and 138 mg of *cis*-**1** containing a small amount of newly formed *trans*-**1**. This results showed that 30% of *trans*-**1** was in equilibrium with 70% of *cis*-**1**.

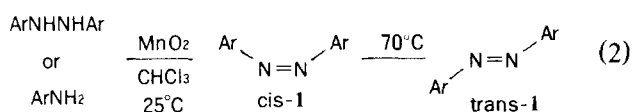


The content of 70% of *cis*-**1** in the equilibrium mixture was unusually large one compared with that of unsubstituted azobenzene (**2**) which is known, when exposed to daylight, to make the equilibrium mixture containing 15–40% of *cis*-**2**, depending on the

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solvent.

In the literature, a detailed description of *cis-trans* behavior of **1** at room temperature was not available. However, *cis-1* (mp 96-98°C) is reported to be obtained by mild oxidation of corresponding hydrazobenzene with MnO₂ at room temperature in 96% yield as shown in Eq 2.

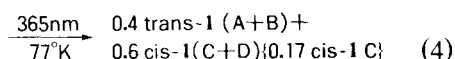
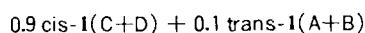
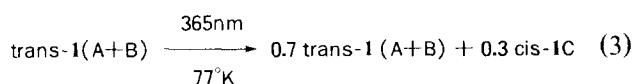


On the other hand, Gabor and Bar-Eli¹⁰ studied the photoisomerism of **1** at low temperature. They found that the photochemistry of **1** was similar to that of **2** down to -120°C; That is, on irradiation, geometrical isomers were obtained and the *cis/trans* ratio at photoequilibria was independent of the contribution of these species in the initial mixture. However, at 77 K, Gabor and Bar-Eli found that the composition of the photochemical steady state depended on the content of one (D) of the two conformational *cis* isomers (C and D) in the initial mixture since only C was converted into the *trans* isomer while D remained unchanged at 77 K by 365 nm monochromatic light. (Gabor and Bar-Eli reported evidence of the conformational isomers for *cis-* and *trans-1* from a study of the absorption spectra and designated the two conformational *trans* isomers as A and B, while the two conformational *cis* isomers as C and D).

Therefore, starting with pure *trans-1*, the contribution of *trans-1* at the photochemical steady state, attained by irradiation by 365nm monochromatic light, was 70% (Eq 3), while when the initial mixture had only 10% *trans*, the contribution of the *trans-1* was 40% (Eq 4).

The last mixture contains 0.17 *cis-C* assuming that at photoequilibrium the (A+B)/C ratio is the same as in Eq 3, while *cis-D* is inert to irradiation.

It is interesting to compare our result (Eq 1) with that of Gabor and Bar-Eli (Eq 3), since they are exactly the opposite of each other.



Although our attempts failed to isolate the pure *cis-1*, a mixture of *cis-1* and a small amount of *trans-1* was obtained.

This mixture was used to examine the melting point behavior. A hot stage microscope melting point apparatus showed that the mixture melted at 87-92°C, resolidified at 131°C, and melted again at 155°C (lit mp 155°C).

Our observation of melting point behavior can well be explained by comparing the melting point of *cis-1* (mp 96-98°C) reported by Hyatt.

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