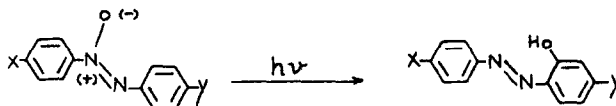


cis-AZOXYBENZENES. II. PHOTOEQUILIBRIUM STUDIES
OF AZOXYBENZENES

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(Received 23 May 1964)

A well-known method for the preparation of cis-azobenzenes is by irradiation of a solution of the corresponding trans isomer, followed by chromatographic separation of the isomers, usually on alumina.¹ Workers have studiously avoided using a similar technique for the preparation of cis-azoxybenzenes, presumably because of the possibility of a light-induced Wallach Rearrangement to o-hydroxyazobenzenes:



Badger and Buttery² report this reaction and postulate an intramolecular reaction pathway which has received corroboration from the work of Shemyakin *et al.*³, who used O¹⁸ and N¹⁵ labeled compounds to study the nature of the reaction.

However, the reaction of Badger and Buttery required one month in sunlight (yields = 5-15%), and Shemyakin used ultraviolet light at temperatures of 150-200^o. Under these conditions the thermally unstable cis isomer would certainly be destroyed, if indeed, in the latter case, it is formed at all.

We wish now to report the formation of cis-azoxybenzenes by irradiation of the trans isomer with unfiltered light from a mercury arc lamp at temperatures low enough to effectively suppress the cis → trans thermal rearrangement.

In a previous paper⁴ on the cis-azoxybenzenes, we reported the use of NMR data to demonstrate the existence of methyl substituted cis-azoxybenzenes. Using the data so obtained, we found that the irradiation with ultraviolet light of trans-p,p'-dimethylazoxybenzene in benzene solution at $5^{\circ} \pm 1^{\circ}$ produced, in ten hours, a mixture of isomers from which a 6% yield of the cis compound was isolated by adsorption chromatography on silicic acid.

Previously, we were unable to obtain any cis-p,p'-dimethoxyazoxybenzene by low temperature peracid oxidation of a cis/trans mixture of the corresponding azo compound. However, irradiation of the trans azoxy compound gave, in ca eighteen hours, a photoequilibrium mixture of 11% cis and 89% trans compound, inferred from integration of NMR peaks (see Table I). The same phenomenon has been found in m,m'-dimethylazoxybenzene and in an equimolar mixture of α - and β -p-methylazoxybenzene. It is interesting to note that in the latter case, where we have reported⁴ a difference in the thermal stability of the cis α and β isomers, the rate of photochemical formation of the two compounds differed considerably. Since the ultraviolet spectra of trans α and β isomers of a monosubstituted azoxybenzene differ only slightly in ϵ_{\max} for the absorption band at ca 350 μ , and since the peracid oxidation of cis-p-methylazoxybenzene gives approximately an equimolar ratio of α and β cis isomers at 0° , we can infer that there is further an appreciable difference in the light

stability of these compounds, that is, the photochemical cis → trans rearrangement of the β isomer is more facile than that of the α isomer, assuming that the thermal rearrangement is negligible at 5°C.

In an experiment with an approximate equimolar mixture of trans α - and β -p-dimethylaminoazoxybenzene, there was no evidence for a photochemical trans → cis rearrangement after fifteen hours. The NMR data previously unreported are given in Table I.

TABLE I
Methyl Group Chemical Shifts of Some
Azoxybenzenes in Benzene
 [in cps downfield from internal TMS]

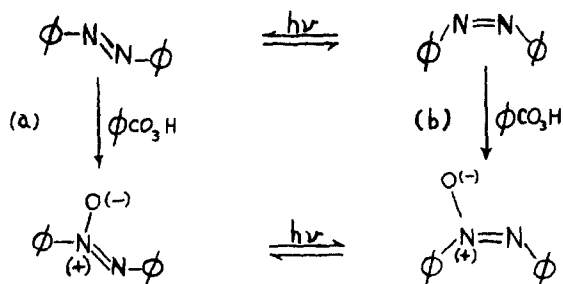
<u>Substituents</u>	<u>Configuration</u>	δ^a
<u>p,p'</u> -CH ₃ O	trans	190.6, 195.6
" " "	cis	181.8, 188.4
<u>m,m'</u> -CH ₃	trans	120.7, 128.4
" " "	cis	98.0, 105.6
<u>p</u> -(CH ₃) ₂ N-(α)	trans	148.5
" " " (β)	trans	144.0

^a measured by audio oscillating side-band technique.

There is some indication of the formation of o-hydroxyazo products from a discoloration of the reaction solutions, which usually acquire a slight orange cast during irradiation. However, only traces of a darker material were visible in those experiments when chromatographic separation was used. These were held up more strongly than either of the azoxy

isomers, but were present in such small quantity that no suitable spectra could be obtained.

The cis-azoxybenzene reported by Badger *et al.*¹ from the oxidation of trans-azoxybenzene in the presence of sunlight may thus be derived from either of two reaction pathways, (a) or (b), shown below.



We suggest that the (b) sequence is likely since the long wavelength $n \rightarrow \pi^*$ transition found in azo compounds has undergone a hypsochromic shift and is buried under the $\pi \rightarrow \pi^*$ transition at about 350 m μ , and since we have shown⁴ that the oxidation of a photoequilibrium mixture of cis- and trans-azobenzenes gives both cis- and trans-azoxybenzenes.

References

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2. G. M. Badger and R. G. Buttery, J. Chem. Soc., 2243 (1954).
3. (a) M. M. Shemyakin, Ts. E. Agadzhanyan, V. I. Maïmind, R. V. Kudryavtsev, and D. N. Kursanov, Doklady Akad. Nauk S.S.S.R., 135, 346 (1960); [Chem. Abst. 52, 11337d (1960)].
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