245. Photoisomerization of Phenylazoalkenes¹)²)

Preliminary Communication

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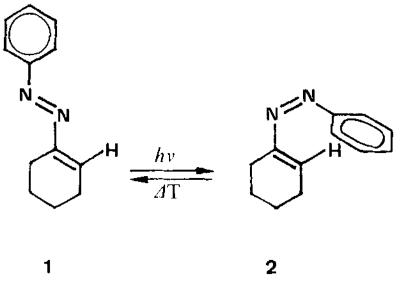
Summary

(*E*)-Phenylazocyclohexene (**1**) undergoes photoisomerization to *s-cis*-(*Z*)-phenylazocyclohexene (**2**). Compound **2** reisomerizes to **1** at room temperature.

While the photochemical behaviour of azoalkanes [1] and arylazo compounds [2] is now rather well understood, no results on light induced reactions of phenylazoalkenes are found in the literature. We now report preliminary results on the photoisomerization of *s-trans*-(*E*)-phenylazocyclohexene (**1**) [3].

Scheme



Irradiation of **1** in cyclohexane at room temperature with light of $\lambda = 313$ nm leads to a photoequilibrium mixture of **1** and a new isomer **2**. As **2** reverts to **1** thermally, attempts to isolate pure **2** were unsuccessful.

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¹) Reported at the VIIIth IUPAC-Symposium on Organic Photochemistry at Seefeld (Austria), July 1980.

²) The experimental part of this work was performed in the Département de Chimie Organique, Université de Genève. *J.G.S.* thanks the *European Photochemical Association* for a travel grant.

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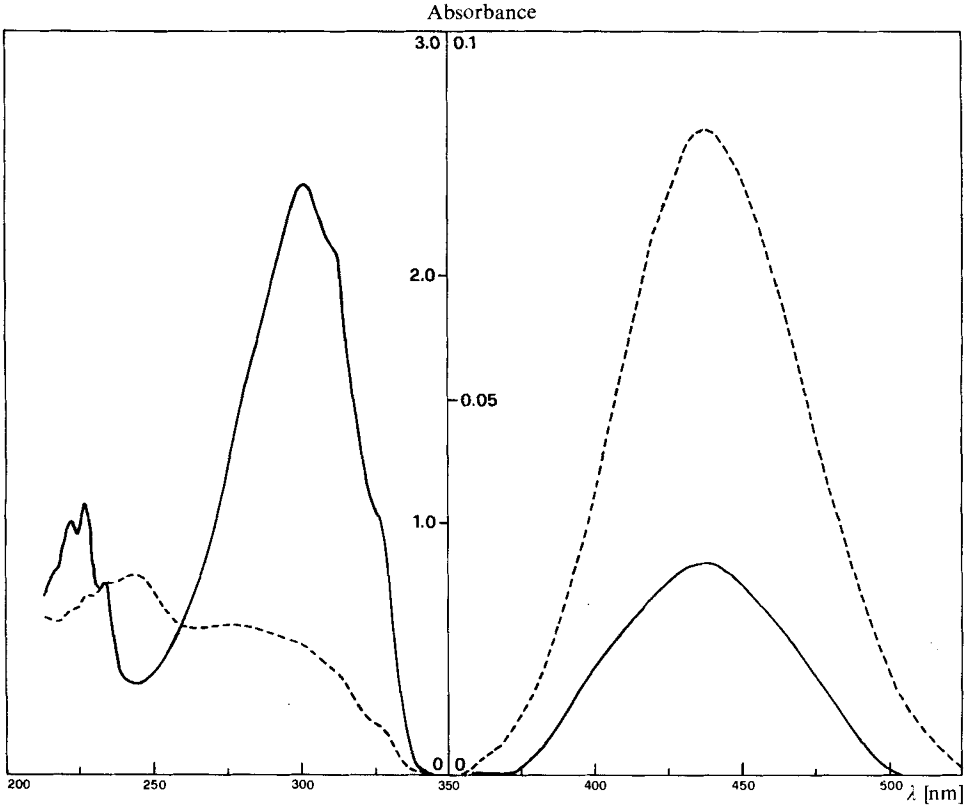

Figure. *UV.-spectrum of* s-trans-(E)-*phenylazocyclohexene* (**1**) (1.15 mM in C_6H_{12}); a: *before* (——) *and* b: *1 h after irradiation at 313 nm* (---)

The structure of **2** was elucidated by monitoring the photoreaction by UV. and ^{1}H-NMR. spectroscopy. From the UV. spectrum *(Fig. 1)* the formation of a (*Z*)-azo compound is evident, as the (n, π^*)-band is strongly enhanced whereas the (π, π^*)-band is shifted to shorter wavelengths and lowered in intensity [4]. Supporting evidence for existence of **2** preferentially in the s-*cis* conformation is obtained by comparing the chemical shifts [5] of the olefinic proton in the ^{1}H-NMR.-spectra of **1** ($\delta = 6.95$ ppm) and of **2** ($\delta = 5.44$ ppm) in cyclohexane; this indicates a strong shielding effect of the olefinic proton of **2** by the phenyl ring. As the deviation from planarity of the π-system of the (*Z*)-azoalkene is smaller in the s-*cis* than in the s-*trans* form (there should be less interaction between the phenyl ring and the olefinic proton than with one of two allylic H-atoms on C(6) of the cyclohexene ring), one can safely assume from these data that compound **2** exists predominantly as s-*cis*-(*Z*)-phenylazocyclohexene.

It is interesting to note that the cycloaddition of **1** (and of other phenylazo-alkenes) to α,β-unsaturated ketones [6] is accelerated by light, suggesting that **2** undergoes *Diels-Alder* reaction faster than **1**. Detailed results will be published in the full paper.

Experimental Part

Compound **1** was prepared according to [3] and had UV. (C_6H_{12}): λ_{max} = 439 nm (logε = 2.42) and 302 nm (logε = 4.35).

Irradiations of the argon-degassed solutions were performed in a *merry-go-round* apparatus with a mercury 125 W lamp using a liquid filter system ($NiSO_4$ + $CoSO_4$ in H_2O) [7] with a transmission gap between 300-325 nm.

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