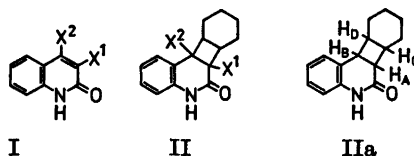


## The Photocycloaddition of Cyclohexene to Carbostyrils

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Photocycloaddition of cyclohexene to carbostyryl, and to carbostyrils with methyl groups in the 3- and 4-position, has been investigated. The reaction was shown to proceed from the lowest triplet state of the carbostyrils. In the case of 4-methyl- and 3,4-dimethylcarbostyryl the addition was stereospecific, and the unsubstituted carbostyryl gave predominantly *cis*-product, whereas 3-methylcarbostyryl gave a mixture of products. The predominant products in the two former cases were shown to be *cis* by NMR spectroscopy.



- a.  $X^1 = X^2 = H$   
 b.  $X^1 = CH_3, X^2 = H$   
 c.  $X^1 = H, X^2 = CH_3$   
 d.  $X^1 = X^2 = CH_3$

We have previously demonstrated that unsubstituted carbostyrils readily dimerize to give cyclobutane dimers.<sup>1-3</sup> The unsubstituted carbostyryl dimer was shown to be *trans*-head-head by chemical means, and the same type of stereochemistry was found for a series of carbostyryl dimers by NMR spectroscopy.<sup>3</sup> From these and other studies<sup>4</sup> it appeared that substituents in the 3- and/or 4-position of carbostyrils hindered the dimerization reaction.

The carbostyryl dimerization was later shown to proceed from a triplet excited state, presumably *via* a triplet excimer,<sup>5</sup> and it was found that unsubstituted carbostyryl underwent photoaddition to a series of alkenes.<sup>6</sup>

In this paper we present results which demonstrate that the triplet state of the carbostyrils is responsible for the addition to cyclohexene, and that cycloaddition, as opposed to photodimerization, also proceeds with carbostyrils substituted in the 3- or the 4-position.

Irradiation of compounds Ia-d in methanol containing ca. 10 % of cyclohexene gives products IIa-d in good yields. The structures of the products were assigned on the basis of UV, IR, and NMR spectroscopy, as well as

elemental analysis. The stereochemistry of the cyclobutane ring was elucidated by means of NMR spectroscopy.<sup>3</sup>

The 220 MHz NMR spectrum of IIa shows two triplets  $\delta$  3.89 (A) and 3.41 (B). The protons H<sub>C</sub> and H<sub>D</sub> give rise to two multiplets, which are assigned on the basis of a decoupling experiment;  $\delta$  2.80 (C) and 3.02 (D). The coupling constants were all equal, *i.e.*  $J_{AC} = J_{BD} = J_{AB} = 9.2$  Hz. On the basis of the values of the coupling constants we conclude that the compound has the *cis* configuration.<sup>3</sup> It was not possible to obtain a sharp melting point for the compound due to the presence of a small amount of impurity, presumably *trans* isomer (< 5 % estimated by NMR spectroscopy). It should be noted that Evanega and Fabiny<sup>6</sup> obtained a 1:3 mixture of the *cis* and *trans* isomers from the photocycloaddition of cyclopentene to carbostyryl.

No 220 MHz NMR spectrum was obtained for the product from the carbostyryl Ib. The reaction mixture resisted all attempts at crystallization. Thin layer chromatography revealed that the reaction mixture was not homogeneous. It consisted of at least six products, the major one being isolated by

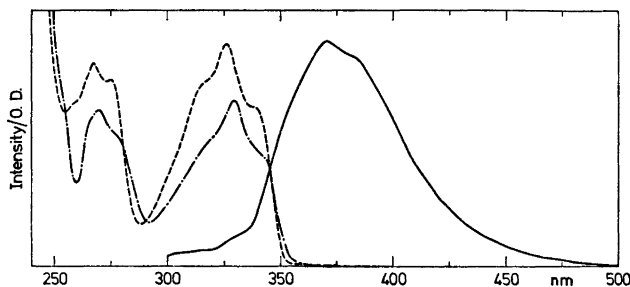


Fig. 1. UV absorption (dashed line), corrected fluorescence (full line), and corrected fluorescence excitation of 4-methylcarbostyryl in absolute ethanol at room temperature. Intensity is in arbitrary units.

means of preparative layer chromatography. It is believed to be *cis* IIb.

In the 220 MHz NMR spectrum of IIc, the  $H_A$  proton gives rise to a doublet,  $\delta$  2.98 (A), with a coupling constant,  $J_{AC}=9.0$  Hz, indicating, that this compound also has the *cis* configuration. No *trans* isomer was present.

For compound IIId it was not possible to elucidate the stereochemistry by means of proton NMR spectroscopy.

From these results we conclude, that whereas substituents in the 3- and 4-position hinder photodimerization, presumably by steric hindrance, they do not hinder photocycloaddition.

The mechanistic studies were performed on 4-methylcarbostyryl in order to avoid photodimerization.

The first excited singlet state of 4-methylcarbostyryl was characterized by means of spectroscopic methods. The UV spectrum of 4-methylcarbostyryl was recorded at room temperature in various solvents. No noticeable solvchromism was observed. Neither did we observe any change in vibrational fine structure by increasing the solvent polarity. In Fig. 1 the UV spectrum of 4-methylcarbostyryl in absolute ethanol at room temperature is shown. For the maximum at 325 nm,  $\log \epsilon = 2.80$ . Fig. 1 also shows the corrected fluorescence spectrum and the corrected fluorescence excitation spectrum of 4-methylcarbostyryl in absolute ethanol at room temperature. This is in good agreement with the absorption spectrum. The excitation spectrum was corrected according to Parker<sup>7</sup> with Rhodamin B as quantum counter.

The total corrected emission spectrum of 4-methylcarbostyryl was recorded in EPA† at 77 K (Fig. 2). From the 0-0 transition the energy of the first excited singlet state  $S_1$  (82.7 kcal mol<sup>-1</sup>) and of the lowest triplet state  $T_1$  (66.4 kcal mol<sup>-1</sup>) were determined. The energy gap between the singlet and the triplet state is 16.3 kcal mol<sup>-1</sup> = 5700 cm<sup>-1</sup>.

The phosphorescence lifetime of 4-methylcarbostyryl at 77 K was determined to be 1.04 s in EPA and 1.20 s in absolute ethanol.

On the basis of these results we conclude that the first excited singlet of 4-methylcarbostyryl is ( $\pi, \pi^*$ ) in character.<sup>8</sup>

In order to determine the multiplicity of the excited state, from which the photocycloaddition proceeds, the influence of piperylene (triplet energy 57 kcal mol<sup>-1</sup>) on the quantum yield of 4-methylcarbostyryl disappearance

† Diethyl ether-isopentane-ethanol, 5:5:2.

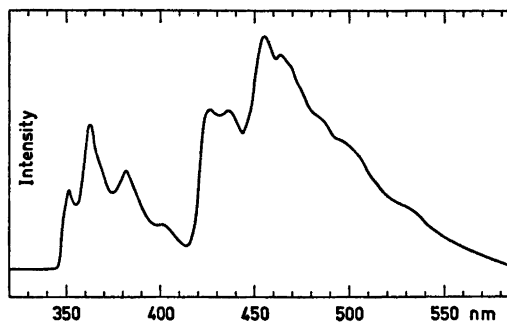


Fig. 2. Corrected total emission of 4-methylcarbostyryl in EPA at 77 K. Intensity is in arbitrary units.

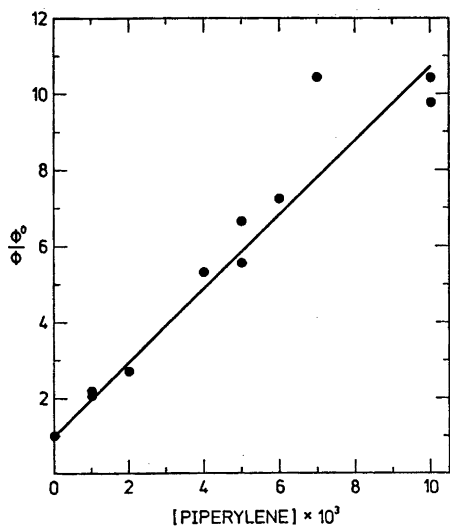


Fig. 3. Stern-Volmer plot of 4-methylcarbostryril disappearance with piperylene as triplet quencher; degassed methanol at room temperature. Starting concentrations of 4-methylcarbostryril and cyclohexene were  $5.2 \times 10^{-4}$  mol/l and  $2 \times 10^{-3}$  mol/l, respectively.

was investigated. Fig. 3 shows the plot of the relative quantum yield of 4-methylcarbostryril disappearance ( $\Phi^0/\Phi$ ) against piperylene concentration.  $\Phi^0$  and  $\Phi$  are the quantum yields of 4-methylcarbostryril disappearance in the absence and presence of piperylene. The plot follows the Stern-Volmer relation

$$\Phi^0/\Phi = 1 + k[Q]$$

We have also investigated the influence of cyclohexene on the fluorescence quantum yield of 4-methylcarbostryril. The corrected fluorescence spectrum of 4-methylcarbostryril in absolute ethanol with various concentrations of cyclohexene at room temperature was recorded (0 to  $5 \times 10^{-3}$  mol/l). No variation in the fluorescence quantum yield was observed.

Thus it is concluded that the photocycloaddition proceeds from the lowest triplet state of 4-methylcarbostryril.

## EXPERIMENTAL

The carbostryrils used were prepared by UV irradiation of the quinoline *N*-oxides in ethanol<sup>4</sup> and purified by several recrystallizations

from ethanol. Reagent grade cyclohexene (BDH) was purified by passage through a column packed with neutral active aluminium oxide. In the preparative experiments reagent grade methanol was used. In the mechanistic experiments methanol (*pro analysi*, Merck) was used. Absolute ethanol was purified by means of activated carbon.

Microanalysis were carried out in the microanalysis department of this laboratory by Mr. Preben Hansen and his staff.

Melting points (uncorrected) were determined on a Reichert melting point microscope.

Infrared spectra were recorded on a Perkin Elmer 337 Grating Infrared Spectrophotometer.

Ultraviolet spectra were recorded on a Unicam SP 800 A spectrophotometer.

Nuclear magnetic resonance spectra were recorded on a Varian A-60 A NMR Spectrometer, a Bruker 90 MHz NMR spectrometer, or a Varian 220 MHz NMR spectrometer.

Emission spectra were recorded on a Hitachi-Perkin Elmer Fluorescence Spectrophotometer, MPF-3, with the phosphorescence accessory.

Thin layer chromatograms (TLC) were undertaken on  $8 \times 10$  cm plates with a 0.25 mm layer of aluminium oxide (PF<sub>254+366</sub> Merck) using a 9:1 mixture of benzene and 2-propanol and visualized with UV light.

The preparative irradiations were performed through a Pyrex filter. The light source was either an "Original Hanau" Q-700 lamp or the 300 nm lamps of a Rayonet reactor (Type RS). The irradiations were monitored by TLC or by UV spectroscopy, and continued until no more starting material could be detected.

**Photocycloaddition of cyclohexene to carbostryril (Ia).** Carbostryril (1.00 g) was dissolved in 500 ml ethanol containing 50 ml cyclohexene and irradiated in a Rayonet reactor. Evaporation of the solvent gave a yellow oil, which after treatment with petroleum ether gave colorless crystals (1.47 g; 94%), m.p. 173–188 °C. Recrystallization from benzene-petroleum ether several times raised the m.p. to 180–194 °C. (Found: C 79.25; H 7.55; N 6.16. Calc. for C<sub>15</sub>H<sub>17</sub>NO: C 79.15; H 7.32; N 6.13). IR 1670 cm<sup>-1</sup>. UV (EtOH): 258 nm, log  $\epsilon$  = 2.92. NMR (220 MHz):  $\delta$  0.91–2.04 (m, 8 H); 2.80 (m, 1 H); 3.02 (m, 1 H); 3.41 (t, 1 H); 3.89 (t, 1 H); 6.77–7.27 (m, 4 H).

**Photocycloaddition of cyclohexene to 3-methylcarbostryril (Ib).** 3-Methylcarbostryril (0.50 g) was dissolved in 225 ml methanol containing 25 ml cyclohexene and irradiated in a Rayonet reactor. Evaporation of the solvent gave a yellow oil (3.59 g), which could not be brought to crystallization. A portion of this oil (1.04 g) was purified by preparative layer chromatography on silica gel using benzene–2-propanol (9:1 by volume) as the eluent, with two developments. The major fraction was isolated and extracted with methanol using

a Soxhlet apparatus. Evaporation gave a semi-crystalline mass (280 mg). IR:  $1670\text{ cm}^{-1}$ . UV (EtOH): 258 nm. NMR (60 MHz):  $\delta$  0.7–2.9 (m, 10 H); 1.52 (s, 3 H); 3.1–3.6 (m, 1 H); 6.7–7.2 (m, 4 H); 9.7 (s, 1 H). Obviously the cyclohexene had undergone some degree of polymerization as well, but no attempt was made to examine this.

*Photocycloaddition of cyclohexene to 4-methylcarbo-styryl (Ic).* 4-Methylcarbo-styryl (3.00 g) was dissolved in 1000 ml methanol containing 100 ml cyclohexene and irradiated with an "Original Hanau" Q-700 lamp contained in a Pyrex immersion well. After 9 h irradiation no more starting material could be detected by TLC. Evaporation gave colorless crystals (4.70 g ~ 100%), m.p. 212–226 °C. Recrystallization from methanol several times gave needles, m.p. 238–239 °C. (Found: C 79.71; H 7.46; N 5.88. Calc. for  $C_{15}H_{19}NO$ : C 79.62; H 7.93; N 5.81). IR:  $1670\text{ cm}^{-1}$ . UV (EtOH): 256 nm,  $\log \epsilon = 2.91$ . NMR (220 MHz):  $\delta$  1.18–1.86 (m, 8 H); 1.63 (s, 3 H); 1.86–2.12 (m, 1 H); 2.32–2.54 (m, 1 H); 2.98 (d, 1 H); 6.80–7.27 (m, 4 H).

*Photocycloaddition of cyclohexene to 3,4-dimethylcarbo-styryl (Id).* 3,4-Dimethylcarbo-styryl (3.00 g) was dissolved in 1000 ml methanol containing 100 ml cyclohexene and irradiated as above. After 10 h irradiation no more starting material could be detected by TLC. Evaporation gave a yellow oil, which after treatment with ether crystallized (2.79 g ~ 63%), m.p. 162–198 °C. Recrystallization several times from methanol–water gave colorless crystals, m.p. 206–207 °C. (Found: C 79.75; H 8.09; N 5.32. Calc. for  $C_{17}H_{21}NO$ : C 79.84; H 8.31; N 5.32). IR:  $1670\text{ cm}^{-1}$ . UV (EtOH): 256 nm,  $\log \epsilon = 3.03$ . NMR (220 MHz):  $\delta$  1.14–1.59 (m, 8 H); 1.30 (s, 3 H); 1.48 (s, 3 H); 1.64–2.22 (m, 2 H); 6.80–7.27 (m, 4 H).

*The Stern-Volmer plot.* Samples (10 ml) containing  $5.20 \times 10^{-4}$  mol/l 4-methylcarbo-styryl and  $2.0 \times 10^{-3}$  mol/l cyclohexene in methanol, and various concentrations of piperylene ranging from 0 to  $1 \times 10^{-3}$  mol/l were prepared. The piperylene used was the 90% technical product from Aldrich, which is a mixture of the isomers with cyclopentene as an impurity. The cyclopentene was assumed to have no significant influence on the results.

The samples were placed in Pyrex test tubes fitted with glass stoppers and provided with magnet stirrers. Degassing was performed by purging the solutions with argon before closing the tubes. The tubes were placed on a carousel and irradiated (magnet stirring) at room temperature with the Q-700 lamp. The irradiation was continued until about 40% conversion in the absence of piperylene. The disappearance of 4-methylcarbo-styryl was measured spectrophotometrically at 325 nm after dilution by a factor of 10.

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