The Photocycloaddition of Cyclohexene to Carboxystyrils

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Photocycloaddition of cyclohexene to carboxystyril, and to carboxystyrils 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 carboxystyrils. In the case of 4-methyl- and 3,4-dimethylcarboxystyril the addition was stereospecific, and the unsubstituted carboxystyril gave predominantly cis-product, whereas 3-methylcarboxystyril gave a mixture of products. The predominant products in the two former cases were shown to be cis by NMR spectroscopy.

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

The carboxystyril dimerization was later shown to proceed from a triplet excited state, presumably via a triplet excimer, and it was found that unsubstituted carboxystyril underwent photoaddition to a series of alkenes.

In this paper we present results which demonstrate that the triplet state of the carboxystyrils is responsible for the addition to cyclohexene, and that cycloaddition, as opposed to photodimerization, also proceeds with carboxystyrils 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. The 220 MHz NMR spectrum of IIa shows two triplets at 3.89 (A) and 3.41 (B). The protons HC and HD give rise to two multiplets, which are assigned on the basis of a decoupling experiment; δ 2.80 (C) and 3.02 (D). The coupling constants were all equal, i.e. JAC = JBD = JAB = 9.2 Hz. On the basis of the values of the coupling constants we conclude that the compound has the cis configuration. 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 obtained a 1:1 mixture of the cis and trans isomers from the photocycloaddition of cyclopentene to carboxystyril.

No 220 MHz NMR spectrum was obtained for the product from the carboxystyril 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
means of preparative layer chromatography. It is believed to be cis IIb.

In the 220 MHz NMR spectrum of IIc, the Hₐ proton gives rise to a doublet, δ 2.98 (A), with a coupling constant, Jₐc = 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-methylcarbostyril in order to avoid photodimerization.

The first excited singlet state of 4-methylcarbostyril was characterized by means of spectroscopic methods. The UV spectrum of 4-methylcarbostyril was recorded at room temperature in various solvents. No noticeable solvochromism 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-methylcarbostyril in absolute ethanol at room temperature is shown. For the maximum at 325 nm, log ε = 2.80. Fig. 1 also shows the corrected fluorescence spectrum and the corrected fluorescence excitation spectrum of 4-methylcarbostyril in absolute ethanol at room temperature. This is in good agreement with the absorption spectrum. The excitation spectrum was corrected according to Parker† with Rhodamin B as quantum counter.

The total corrected emission spectrum of 4-methylcarbostyril was recorded in EPA† at 77 K (Fig. 2). From the 0−0 transition the energy of the first excited singlet state S₁ (82.7 kcal mol⁻¹) and of the lowest triplet state T₁ (66.4 kcal mol⁻¹) were determined. The energy gap between the singlet and the triplet state is 16.3 kcal mol⁻¹ = 5700 cm⁻¹.

The phosphorescence lifetime of 4-methylcarbostyril 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-methylcarbostyril is (π, π*) in character.

In order to determine the multiplicity of the excited state, from which the photocycloaddition proceeds, the influence of piperylene (triplet energy 57 kcal mol⁻¹) on the quantum yield of 4-methylcarbostyril disappearance...
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 analyti, 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, MFF-3, with the phosphorescence accessory.

Thin layer chromatograms (TLC) were undertaken on 8 x 10 cm plates with a 0.25 mm layer of aluminium oxide (PF$_{254}$+PF$_{274}$, 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 carbostyryl (1a).* Carbostyryl (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 C₈H₈N=O: C 79.15; H 7.32; N 6.13.) IR 1670 cm⁻¹. UV (EtOH): 286 nm, log ε = 2.92. NMR (220 MHz): δ 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-methylcarbostyryl (1b).* 3-Methylcarbostyryl (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

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The carbostyryls used were prepared by UV irradiation of the quinoline N-oxides in ethanol and purified by several recrystallizations

a Soxhlet apparatus. Evaporation gave a semi-crystalline mass (280 mg). IR: 1670 cm⁻¹. UV (EtOH): 258 nm. NMR (60 MHz): δ 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.

**Photocyclodaddition of cyclohexene to 4-methylcarboxystyril (1c).** 4-Methylcarboxystyril (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 C₈H₇NO: C 79.62; H 7.31; N 5.81. IR: 1670 cm⁻¹. UV (EtOH): 256 nm, log ε = 2.91. NMR (220 MHz): δ 1.18 – 1.88 (m, 8 H); 1.93 (s, 3 H); 2.52 – 2.83 (m, 1 H); 2.92 – 3.04 (m, 1 H); 2.98 (d, 1 H); 6.30 – 7.27 (m, 4 H).

**Photocyclodaddition of cyclohexene to 3,4-dimethylcarboxystyril (1d).** 3,4-Dimethylcarboxystyril (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 8.08; N 5.32. Calc. for C₈H₁₈NO: C 79.84; H 8.31; N 5.32). IR: 1670 cm⁻¹. UV (EtOH): 256 nm, log ε = 3.03. NMR (220 MHz): δ 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 × 10⁻⁴ mol/l 4-methylcarboxystyril and 2.0 × 10⁻⁴ mol/l cyclohexene in methanol, and various concentrations of piperylene ranging from 0 to 1 × 10⁻⁴ 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 with 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-methylcarboxystyril was measured spectrophotometrically at 325 nm after dilution by a factor of 10.

**Acknowledgement.** We wish to thank Dr. Herman Ziffer for the 220 MHz NMR spectra and for a very helpful discussion.

**REFERENCES**


Received July 8, 1975.