

PHOTOCHROMISM OF 4-ISOPROPENYL-3-PHENYLSYDNONE AND ITS DIMER

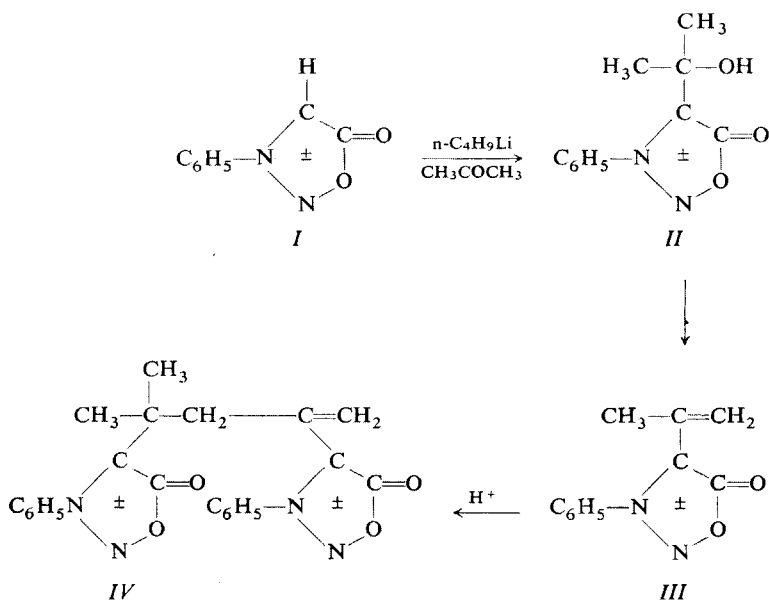
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Preparation, photochromism and electrical and magnetic properties of 4-isopropenyl-3-phenylsydnone and its dimer have been described.

Photochromic properties of mesoionic compounds were first observed by Tien and Hunsberger¹ for 3-(3-pyridyl)sydnone in the solid state². Other sydrones exhibited only insignificant changes in their absorption spectra if exposed to ultraviolet light^{3,4}. Greco and O'Reilly⁵ described the preparation of several 4-alkenyl-3-phenylsydrones, three of which were photochromic. Our interest in mesoionic compounds which



SCHEME 1

could be used for the preparation of polymeric compounds preserving their mesoionic system has led us independently of the above authors to the synthesis of 4-isopropenyl-3-phenylsydnone (*III*), its dimerization and a study of photochromism of the products.

4-Isopropenyl-3-phenylsydnone (*III*) was prepared by dehydration of 4-(1-hydroxy-1-methylethyl)-3-phenylsydnone (*II*) using a small excess of phosphorus pentoxide in benzene at elevated temperature (Scheme 1). Its dimerization to yield sydnone *IV* was carried out by treating it with a two-molar excess of 96% sulphuric acid at -70°C in an argon atmosphere. The dimerization also took place if other catalysts were used, such as *e.g.* phosphoric acid, $\text{TiCl}_4 \cdot \text{H}_2\text{O}$ *etc.*, in nonpolar organic solvents at room temperature or higher, but the yield was considerably lower. The NMR spectrum was in complete agreement with the structure suggested for dimer *IV* and at the same time ruled out other alternative structures.

The sydnones *III* and *IV* are pale yellow compounds, stable in the air at room temperature if stored in the dark. Immediately on exposure to radiation of wavelengths shorter than $\lambda \sim 470$ nm, *III* turned blue ($\lambda_{\text{max}} = 635$ nm), while *IV* turned blue-green ($\lambda_{\text{max}} = 750$ nm), even at low temperatures. This photochromic change was reversible; the bleaching took place owing to a thermal monomolecular process. The bleaching half-time in the dark of *III* after exposure to the "colour-producing" light with wavelengths of $300 \text{ nm} < \lambda < 400 \text{ nm}$ was $t_{1/2} \sim 750$ s at 20°C . At higher temperatures the bleaching process was faster. The activation energy of the bleaching rate constant is $E = 12$ kcal/mol. The bleaching process of sydnone *IV* was faster compared to sydnone *III* (bleaching half-time was $t_{1/2} \sim 100$ s at 10°C). Fast bleaching of *III* and *IV* also took place after exposure to light having wavelengths longer than $\lambda \sim 470$ nm. The colour forms were also produced with the simultaneous formation of free radicals if the crystals were bombarded with 0.8 MeV electrons. The photochromic change was restricted to the crystalline solid state at room temperature; no such change was observed in solution. The pale yellow colour of *III* stable in the dark was a result of the thermochromic process: at -190°C the compound lost its colour almost completely.

The fatigue of the material depended on the wavelength of the "colouring" light. In the case of exposure to a mercury discharge tube HBO 200 with a band filter $\lambda = (310 \div 400)$ nm photochromic changes were still observed after several tens of cycles. The number of cycles decreased rapidly with decreasing light wavelength and increasing time of exposure. The quantum yield of the colouring process gradually decreased with the number of cycles while brown-yellow degradation products were formed at the same time. No changes were detected in the frequency of the absorption maxima of the infrared spectra of sydnone *III* after exposure to the "colour-producing" light. On the other hand, however, with increasing length of exposure the intensity of some bands decreased irreversibly, especially that of the carbonyl band, while new bands appeared at 1630 and 1360 cm^{-1} .

Neither the pale yellow nor the blue form of *III* exhibited any EPR signal in a vacuum of 10^{-5} Torr (the sample was heated to 50°C for two hours before measurement). If irradiated with the "colour-producing" light, a weak EPR signal appeared already in a vacuum of 10^{-2} Torr without any preceding heating of the compound. Neither thermal nor optical bleaching reduced the intensity of the EPR signal significantly. A fast decrease in the intensity of the EPR absorption occurred at elevated temperatures. The presence of free charge carriers was followed by means of photoconductivity. The photocurrent was detected both on exposure to "colour-producing" light and on exposure to "bleaching" light; the photocurrent kinetics was faster in the latter case.

At room temperature the behaviour of photochromic sydnones *III* and *IV* was similar to that of 3-(3-pyridyl)sydnones⁶. However, basic differences in behaviour were observed at lower temperatures. While photochromic changes of *III* and *IV* could be seen even at the liquid nitrogen temperature, 3-(3-pyridyl)sydnone required supplementary thermal energy to yield coloured products.

EXPERIMENTAL

The melting points were determined with a Kofler block and were not corrected. The infrared spectra of the products were recorded with a Perkin-Elmer 457 spectrometer in KBr pellets. The ultraviolet spectra were obtained with a Carry 14 spectrophotometer. The NMR spectra were measured with a JEOL PS 100 spectrometer, frequency 100 mc/s, hexamethyldisiloxane as the internal standard. An AEI-MS 902 spectrometer was used for measuring the mass spectra.

Chemicals. The stock solution of butyllithium in benzene was prepared by a reaction of butyl bromide with lithium powder; its concentration (0.855 mol/l) was determined by double titration. All reactions with butyllithium were carried out in an argon atmosphere. 4(1-Hydroxy-1-methylethyl)-3-phenylsydnone (*II*) was obtained by a reaction of 4-lithio-3-phenylsydnone^{7,8} with acetone in an ether-benzene mixture at -20°C .

4-Isopropenyl-3-phenylsydnone (*III*)

2 g of phosphorus pentoxide was added to a solution of 3 g of sydnone *II* in 60 ml of benzene. The mixture was heated 1 h under a reflux in the dark and filtered while hot. The insoluble inorganic residue was washed with benzene and the joined benzene filtrates were evaporated. The crystallization of the dry residue in the dark yielded sydnone *III* (74%). The melting point, elemental analysis and spectral data on sydnone *III* are in good agreement with those given elsewhere⁵.

4-Methyl-2,4-bis(3-phenyl-4-sydnonyl)-1-pentene (*IV*)

0.5 g (5.2 mmol) of conc. sulphuric acid was added dropwise with stirring at -70°C to a solution of 0.5 g (2.475 mmol) of sydnone *III* in 10 ml of dichloromethane. After 3 h of stirring at this temperature in an argon atmosphere the solvent was evaporated *in vacuo*. The liquid residue was decomposed with methanol; the precipitate thus obtained was washed with water and methanol. Dimer *IV* was obtained by crystallization of the raw product from acetone in a yield 80%, m.p. $231-233^{\circ}\text{C}$. Spectra: IR (KBr) 1738 (CO-sydnone) cm^{-1} ; UV (ethanol) λ_{max} 314 ($\epsilon =$

$\tau = 1.6 \cdot 10^4$), 236 ($1.4 \cdot 10^4$), 208 ($2.6 \cdot 10^4$) nm; NMR (hexadeuteriodimethylsulphoxide) τ 2.40 (10 H, m, aromatics), 4.64 (1 H, s, $\text{CH}_2=\text{C}$), 4.72 (1 H, s, $\text{CH}_2=\text{C}$), 7.62 (2 H, s, CH_2), 9, 10 (6 H, s, CH_3); mass m/e 360 (a fragment obtained by the splitting-off of CO_2 from a molecular ion which was not observed in the spectrum). For $\text{C}_{22}\text{H}_{20}\text{N}_4\text{O}_4$ (404.4) calculated: 65.40% C, 4.95% H, 13.86% N; found: 65.18% C, 5.13% H, 13.94% N.

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