PHOTOCOLOURATION OF HYPERVALENT HETEROCYCLES

Photochromism of Dihydropyridines, Pyrans and Thiopyrans

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1. Introduction

The notion of hypervalent molecule is usually used to describe a chemical entity which can be characterized by two or more mesoionic valence structures and/or by a structure in which valence states of some atoms do not follow the classical rules concerning the chemical bonding [1]. Typical examples represent some isomers of heterocyclic molecules, e.g. dihydropyridines (cf. Scheme 1). While 1,2-dihydroisomer (1) and 1,4-dihydroisomer (2) do not show any hypervalence, it is possible in the case of 1,3-dihydroisomer (cf. structures (3a) - (3d)) The chemical formulas (3a) - (3d) represent formal structures; usually, information concerning a real molecular structure, i.e., the conclusion whether an N-hypervalent structure (3a) or a hybrid of mesoionic resonant structures (3b) - (3d) is more probable, must be obtained by quantum chemical methods. It could be mentioned that "hypervalent" molecules often show properties different from non-hypervalent ones [2, 3] and they are very often unstable and coloured [4]. These materials, in agreement with theory, have relatively high internal energies and it is probable that also molecules of some photoproducts can be considered as hypervalent ones. In connexion with this fact, the phototropic behaviour of 2,4,4,6-tetraphenyl 4H-pyran (4, X = 0), its thio- (X = S), and aza- (X = NR, with R specified in Table 1) analogues seems to be of interest. Some of these compounds, which become reversibly coloured under UV or solar irradiation, can be utilized in some optical devices. In this paper, the photocolouration of compounds of the type (4) is described and the mechanism of the photochromism briefly discussed. A more extensive discussion of the photochromic behaviour, including also results of model quantum chemical calculations, is given in the accompanying paper [5].

2. Materials

We will discuss the behaviour of three groups of materials whose general chemical formula is represented by the structure (4) in Scheme 1:
(I) 2,4,4,6-tetraphenyl-4H-dihydropyridines (X = NR);
(II) 2,4,4,6-tetraphenyl-4H-thiopyrans (X = S);
(III) 2,4,4,6-tetraphenyl-4H-pyrans (X = O).

2.1. CHEMICAL SYNTHESIS

2.1.1. 2,4,4,6-Tetraphenyl-4H-Dihydropyridines

Compound Ia (see Table 1) was obtained by treatment of 1,3,3,5-tetraphenylpentane-1,5-dione (5) in glacial acetic acid with ammonium acetate [6]. N-substituted 1,4-dihydropyridines (Ib, Ic, Id) were prepared by cyclocondensation of diketone (6) with acetates of the respective primary amines in acetic acid. The yield of the benzyl and phenyl derivatives was lower than that of the methyl one, i.e. it followed the