Photocatalytic cleavage of hydroxytriazenes: a solidstate synthesis of azo-dyes under sunlight irradiation

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Abstract Sunlight-induced decomposition of hydroxytriazenes, and green photochemical synthesis of azo-dyes is described. Three substituted hydroxytriazenes, viz: 3-hydroxy-3-(2-methylphenyl)-1-(3-chloro-4-fluorophenyl)triazene (*o*-CFHT), 3-hydroxy-3-(3-methylphenyl)-1-(3-chloro-4-fluorophenyl)triazene (*m*-CFHT), and 3-hydroxy-3-(4-methylphenyl)-1-(3-chloro-4-fluorophenyl)triazene (*p*-CFHT) were co-crystallized with β -naphthol in equimolar ratio and exposed to sunlight for 9–10 h. The reaction resulted in formation of azo-dyes which were identified by comparison with the products obtained by the conventional method (standard azodye), by use of HPLC. A probable mechanism has been suggested. This is first ecofriendly synthesis of azo-dyes using hydroxytriazenes.

Keywords Hydroxytriazene · Solid-state photolysis · Azo-dye

Introduction

During the last few years, application of solar energy to chemical synthesis has acquired great importance [1–4]. Solid state photoreaction [3, 4] has also been reported. It has also been reported that organic compounds participate in photoaddition [5, 6] and photodegradation [7, 8] reactions. In this work, therefore, we investigated the use of three hydroxytriazenes, viz: 3-hydroxy-3-(2-methylphenyl)-1-(3-chloro-4-fluorophenyl)triazene (*o*-CFHT), 3-hydroxy-3-(3-methylphenyl)-1-(3-chloro-4-fluorophenyl)triazene (*m*-CFHT), and 3-hydroxy-3-(4-methylphenyl)-1-(3-chloro-4-fluorophenyl)triazene (*p*-CFHT) as photo-labile reagents for solid-state synthesis of azo-dyes.

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The hydroxytriazenes -N=N-N(OH)- were synthesized via a standard route reported in the literature [9]. The compounds were duly characterized by IR and the characteristic peaks were obtained, confirming the pure state of the compounds. In this work PTLC did not give the desired quantities suitable for characterization, as reported elsewhere [4], so high-performance liquid chromatography (HPLC) was used for identification of the azo-dyes. HPLC is an excellent technique for identification and quantification of azo-dyes [10, 11]. Separation was performed with methanol-water 90:10 as mobile phase. Details are given in the "Experimental" section.

Experimental

Synthesis of hydroxytriazenes

All three hydroxytriazenes were synthesized by the standard method. In this method o, m, and p nitrotoluenes (2 mmol) were reduced with Zn dust (4 g) in the presence of NH_4Cl (1.6 g) at 50–60 °C to obtain the respective phenyl hydroxylamines. The diazotized product was obtained by adding sodium nitrite (2 mmol) in small portions to 3-chloro-4-fluoroaniline (2 mmol) dissolved in a mixture of HCl (5 ml) and water (10 ml) at 0-5 °C and with constant magnetic stirring. The diazonium salts were coupled with the phenyl hydroxylamine at 0-5 °C under constant stirring with occasional addition of sodium acetate solution to maintain the pH close to 5. After coupling, the resulting product was purified by recrystallization from absolute alcohol. The compounds were identified by recording their M.P. and IR spectra. Each of the hydroxytriazenes gave all four characteristic bands reported elsewhere [12, 13]. The compounds gave bands for v_{O-H} (3,480 cm⁻¹), v_{N-H} (3,190 cm⁻¹), δ_{N-H} (1,520 cm⁻¹), and δ_{N-OH} (1,070 cm⁻¹) confirming the presence of the hydroxytriazene group. The M.P. of o-CFHT, m-CFHT, and p-CFHT were 118, 166, and 168 °C, respectively. The compounds synthesized were thus in pure state and suitable for further photolytic synthesis.

Synthesis of standard dye

The standard dyes were synthesized by the conventional chemical route for comparison purposes and for identification of the photochemical product. 3-Chloro-4-fluoroaniline (2.9 g) was dissolved in mixture of 6 ml HCl and 10 ml distilled water. To this, a solution of 1.4 g sodium nitrite in 10 ml water was added dropwise at 0–5 °C and the mixture was stirred for 1 h at 0–5 °C. Separately, β -naphthol (2.8 g) was dissolved in 10 ml 10 % NaOH solution and cooled to 0–5 °C. To this solution, the solution of the diazotized compound, prepared as described above, was added dropwise with vigorous stirring. The mixture was stirred for an additional 30 min in an ice-bath. The precipitate obtained was isolated by filtration, initially purified by washing with water, and further purified by recrystallization from absolute alcohol. A dark brown red solid was obtained in a yield of approximately 80 %. Its structure was verified on the basis of IR absorption bands occurring at

 v_{O-H} (3,350 cm⁻¹), $v_{N=N}$ (1,490 cm⁻¹), and v_{C-O} (1,200 cm⁻¹), confirming formation of the dye.

Photolysis of a mixture of hydroxytriazene and β -naphthol

Mixed co-crystals were obtained by mixing of 1 mmol of each CFHT with 1 mmolnaphthol in acetone followed by dissolution and evaporation. The mixed crystals were simple polycrystalline mixtures of the two components. They were finely ground in a mortar, spread over Petri dishes, and directly exposed to sunlight. After 9–10 h, the reaction mixtures gradually changed to a deep brown-red colour. The photoreactions were monitored by thin-layer chromatography using a 1:10 mixture of ethyl acetate and toluene as mobile phase. For this purpose three mixtures were photolysed; details are given in Table 1.

HPLC measurements

Apparatus, reagents, and solutions

HPLC was conducted with Merck–Hitachi equipment consisting of a pump (model L2130), autosampler (L2200), and a UV detector (L2400). Separation was accomplished on a 250 mm \times 4 mm (5 μ m) reversed-phase C₁₈ column (LiChro-CART) protected by a guard column of same material. Stock solutions of the standard synthetic dyes and photolytic samples were prepared at a concentration of 4 mg ml⁻¹. All solutions were prepared in HPLC-grade methanol. Filtration was required before injection into the HPLC.

Method

The objective was to develop flexible HPLC method for separation of the azo-dyes from the three photolysed samples. A 20-min isocratic method was chosen for sufficient separation of azo-dyes from the mixtures. The mobile phase was 90:10 (ν/ν) methanol–water containing trifluoroacetic acid. The flow rate of the mobile phase was 1 ml min⁻¹ and the column temperature was kept at 25 °C by use of an AC chamber. The volume of each sample injected was 20 µL; detection of each dye was by absorption at 350 nm.

No. 1	Coupling reagent		Initial colour	Final colour	Mixture code
	β -Naphthol	o-CFHT	Milky white	Coffee colour	CCM-o
2	β -Naphthol	m-CFHT	Yellow	Dark brown	CCM-m
3	β -Naphthol	p-CFHT	Light brown	Coffee colour	CCM-p

 Table 1
 Details of the photolysed mixtures



Fig. 1 HPLC chromatograms obtained from standard and photolysed mixtures

Results and discussion

In this work, the sunlight-induced photolytic addition reaction of three CFHT and β naphthol in the mixed crystalline state was studied. HPLC results as described in
Fig. 1 revealed the RT of CCM-o, CCM-m, and CCM-p samples corresponded to
the RT of the standard azo-dyes. Thus HPLC confirmed formation of the azo-dyes
via the photolytic route.

In the crystalline state the photoreactions proceeded at the interface of the two crystallites. Absorption of sunlight led to the observation of two primary photoprocesses:

- 1 N–N bond cleavage, with production of aryldiazenyl and *N*-phenylhydroxylaminyl radicals; and
- 2 free radical diazocoupling of the aryldiazenyl radical with β -naphthol yielding the azodye.

It is proposed that the aryldiazenyl radical attacks the more active site of the naphthol ring at the position ortho to the phenolic group giving adducts which, in turn, lose a hydrogen radical to afford the corresponding azo-dyes. The proposed mechanism of overall conversion is depicted in Fig. 2.

Conclusion

In this investigation, preparation of azo-dyes from hydroxytriazenes by use of solar radiation was attempted. This is first report of the use of hydroxytriazenes for photolysis. The photo labile triazene moiety can further be used for organic



Fig. 2 Proposed mechanism of conversion

synthesis via the aryldiazenyl free radical. The reaction involves trapping of sunlight for chemical synthesis and is thus a green route for chemical synthesis.

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