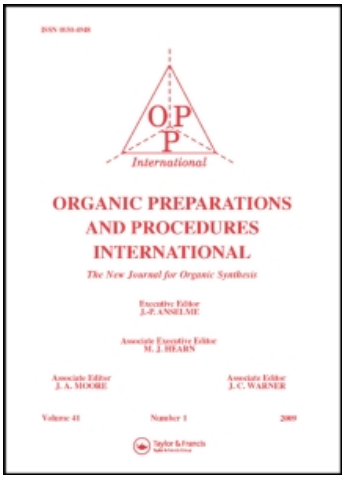

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A SIMPLE AND MILD PROCEDURE FOR THE REDUCTION OF 3-HYDROPEROXYINDOLENINES TO 3-HYDROXYINDOLENINES

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A SIMPLE AND MILD PROCEDURE FOR THE REDUCTION OF 3-HYDROPEROXYINDOLENINES TO 3-HYDROXYINDOLENINES

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I II

a: R_1, R_2= $-(CH_2)_4-$; R_3= H b: R_1= Ph; R_2= Me; R_3= H

c: R_1= Ph; R_2= R_3= Me d: R_1= Ph; R_2= Me; R_3= Cl

Catalytic hydrogenation,[2,3] sodium hydrosulfite[4,5] and sodium borohydride[2] have been employed for the reduction of 3-hydroperoxyindolenines to 3-hydroxyindolenines, but in some instances difficulties were reported to occur.

In connection with our studies on the photooxidation of indole derivatives, we have observed that 3-hydroperoxyindolenines, dissolved in dimethyl sulfoxide, were smoothly transformed into the 3-hydroxy derivatives in almost quantitative yield. This mild reaction could be a convenient reduction method because the hydroperoxides and some hydroxyindolenines are compounds of

little stability.[6]

The reactions were performed at room temperature and were easily monitored by changes in the nmr spectra in which the signal at about δ 12 (OOH) disappears whereas a new signal at around δ 6 (OH) appears.

EXPERIMENTAL

Preparation of hydroperoxides. To a solution of the indole (100 mg) in light petroleum (20 ml) a catalytic amount of benzoyl peroxide was added, and oxygen was bubbled through the cooled solution for about 5 hr. The reaction progress was followed by tlc (silica gel; benzene). The precipitate formed during the reaction was filtered and recrystallized from ethyl acetate-light petroleum; the hydroperoxides were obtained in 80-90 % yield. The spectral properties of compounds Ib and Ic have been reported previously.[7]

11-Hydroperoxy-1,2,3,4-tetrahydrocarbazolenine (Ia). Colorless prisms, mp. 122-25°, lit.[8] mp. 124-29°.
nmr (DMSO), CH_2 δ 0.90-2.85 (8 H); arom. prot. 7.11-7.56 (4 H); OOH 11.65.

2-Phenyl-3-methyl-5-chloro-3-hydroperoxyindolenine (Id). Colorless prisms, mp. 124-25°.
Anal. Calcd. for $C_{15}H_{12}ClNO_2$: C, 65.82; H, 4.41; N, 5.13; Cl, 12.95. Found: C, 65.46; H, 4.31; N, 5.43; Cl, 13.15.
nmr (DMSO), CH_3 δ 1.56; arom. prot. 7.41-7.73 (6 H); H_2, and H_6, 8.15-8.43; OOH 12.01.

Reduction of hydroperoxides. In a typical example, the hydroperoxide (100 mg) was dissolved in dimethyl sulfoxide (2 ml) and the solution was left at room temperature, in the dark, for 24-48 hr. To determine the reaction time a sample of the hydroperoxide was dissolved in deuterated DMSO and the reaction progress was monitored by nmr spectroscopy. When all the hydro-

peroxide disappeared the solution was diluted with water and extracted with benzene. The extract was evaporated and the crystalline residue was purified by recrystallization. The hydroxy derivatives were obtained in about 95 % yield.

The physical data of compound IId were previously reported.[7]

11-Hydroxy-1,2,3,4-tetrahydrocarbazolenine (IIa).
Colorless prisms from ethyl acetate, mp. 153-55°, lit.[8,9] mp. 153-54°, 159°.

nmr (DMSO), CH_2 δ 0.70-2.85 (8 H); OH 5.66 (d, J 1 cps); arom. prot. 7.11-7.56 (4 H).

uv (EtOH), λ max 257 nm (log ε 3.58).

2-Phenyl-3-methyl-3-hydroxyindolenine (IIb).
Colorless needles from light petroleum, mp. 145-47°, lit.[10] mp. 145°.

nmr (DMSO), CH_3 δ 1.58; OH 6.30; arom. prot. 7.33-7.83 (7 H); $H_{2'}$ and $H_{6'}$ 8.33-8.61.

uv (EtOH), λ max 313 nm (log ε 4.16); 245 (4.22); 238 (4.25); 232 sh (4.20).

2-Phenyl-3,5-dimethyl-3-hydroxyindolenine (IIc).
Colorless needles from ethanol-water, mp. 174-76°.

Anal. Calcd. for $C_{16}H_{15}NO$: C, 80.98; H, 6.37; N, 5.90.
Found: C, 80.70; H, 6.38; N, 6.16.

nmr (DMSO), 3-CH_3 δ 1.55; 5-CH_3 2.41; OH 6.26; arom. prot. 7.20-7.83 (6 H); $H_{2'}$ and $H_{6'}$ 8.40-8.61.

uv (EtOH), λ max 324 nm (log ε 4.09); 249 (4.16); 242 (4.19); 235 sh (4.12).

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