



Photo-oxidation of 2-Methyl-1-phenylcyclohexene

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ABSTRACT: Singlet oxygen (1O_2) reacted with 2-methyl-1-phenylcyclohexene (1) in the 'ene' mode only. The products of the reaction were isolated and identified as 2-methylene-1-phenylcyclohexyl hydroperoxide (2)(20.7%) and 1-methyl-2-phenylcyclohex-2-enyl hydroperoxide (3)(22.6%). A mixture of the two hydroperoxides (39.8%) was also isolated. @ JASEM

It has been established that no significant amount of degradation of petroleum fractions can occur without the preliminary photo-oxidative reactions to pre-dispose the hydrocarbon constituents to microbial attacks (Simiullah, 1985). This necessitates the need to understand the modes of photo-oxidation reactions of hydrocarbons structurally related to constituents of crude oils and their processed fractions. (Anderson, 1992). The photo-oxidation reaction of 6-methyl-1-phenylcyclohexene showed that the tri-substituted cycloalkene reacted in the 'ene' and [2 + 4] cycloaddition modes to give hydroperoxide and bis(endoperoxide) products respectively (Fekarurhobo, 1997). In the present work, the photo-oxidation reaction of the tetra-substituted 2-methyl-1-phenylcyclohexene (1) is reported.

MATERIALS AND METHODS

1H n.m.r. spectra were measured in $CDCl_3$ on a Jeol MH-100 spectrometer using TMS as an internal standard. Infra-red spectra were recorded on a Perkin-Elmer Infra-red spectrophotometer model 597. The oils were smeared on sodium chloride discs.

Preparation of 2-Methyl-1-phenylcyclohexene (1):

The cycloalkene (1) was prepared by the dehydration of 2-methyl-1-phenylcyclohexanol following a method already published (Fekarurhobo, 1997); δ_H : 7.1 (5H, m, aromatic), 2.3 - 1.8 (4H, m, H-3 and H-6), 1.7 (4H, m, H-4 and H-5) and 1.50 (3H, s, CH_3) ppm.

Photo-Oxidation of 2-Methyl-1-phenylcyclohexene (1):

The cycloalkene (1) (0.5g) was photo-oxidized following the usual procedure (Fekarurhobo, 1997).

The tlc. of the crude reaction mixture after 2.5h showed that it had been completely converted to two closely separated products. Concentration (rotary) and column chromatography (silica, gradient elution with ethyl acetate/petroleum spirit) gave the products, which were identified as 2-methylene-1-phenylcyclohexyl hydroperoxide (2) (0.123g, 20.7%) and 1-methyl-2-phenylcyclohex-2-enyl hydroperoxide (3) (0.134g, 22.6%), both as colourless oils. A 1:1 mixture (by 1H n.m.r.) of the two hydroperoxides (0.236g, 39.8%) was also isolated; (2) δ_H : 7.7 - 7.1 (6H, m, OOH and aromatic), 5.0 (1H, s, $\frac{1}{2} x =CH_2$), 4.6 (1H, s, $\frac{1}{2} x =CH_2$) and 2.7 - 1.0 (8H, m, 4 x CH_2) ppm; ν_{max} : 3350 (OOH), 1435 (aromatic) and 890 ($0-0$) cm^{-1} ; (3) δ_H : 8.1 (1H, s, OOH), 7.3 (5H, m, aromatic), 6.0 (1H, t, $J = 4Hz$, H-3), 2.7 - 1.3 (6H, m, 3 x CH_2 and 1.2 (3H, s, CH_3) ppm.

RESULTS AND DISCUSSION

Photo-oxidation of (1) gave two products (by t.l.c.), which were isolated unrearranged by column chromatography and identified (by 1H n.m.r.) as hydroperoxides. The higher R_f product showed no methyl signal in its 1H n.m.r. spectrum but the signals at 5.0 (1H, s) and 4.6 (1H, s) ppm were assignable to vinyl methylene protons. The product was consequently assigned the structure of 2-methylene-1-phenylcyclohexyl hydroperoxide (2) (Scheme 1). The other product displayed signals due to a vinylic proton at 6.0 (1H, t, $J = 4Hz$) and a methyl singlet at 1.2 ppm [cf. 1.5 for vinylic methyl in (1)], which enabled its identification as 1-methyl-2-phenylcyclohex-2-enyl hydroperoxide (3) rather than (4) (Scheme 1).

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