

Photo-oxidation of 2-Methyl-1-phenylcyclohexene

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ABSTRACT: Singlet oxygen $(^{1}O_{2})$ 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 predispose 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-1phenylcyclohexene showed that the tri-substituted cycloalkene reacted in the 'ene' and [2 + 4] cycloaddition modes to give hydroperoxide and respectively products bis(endoperoxide) (Fekarurhobo, 1997).. In the present work, the photooxidation reaction of the tetra-substituted 2-methyl-1phenylcyclohexene (1) is reported.

MATERIALS AND METHODS

¹H n.m.r. spectra were measured in CDCl₃ 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); $\delta_{\rm H}$: 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, CH₃) 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, identified 2-methylene-1which were as 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 = CH₂), 4.6 (1H, s, $\frac{1}{2}$ x = CH₂) and 2.7 – 1.0 (8H, m, 4 x CH₂) ppm; v_{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 CH₂ and 1.2 (3H, s, CH₃)ppm.

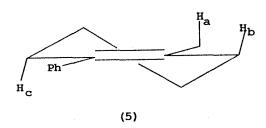
RESULTS AND DISCUSSION

Photo-oxidation of (1) gave two products (by t.l.c.), which were isolated unrearranged by column chromatography and identified (by 'H 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 The product was vinyl methylene protons. 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 1.2ppm [cf. 1.5 for vinylic methyl in (1)], which identification 1-methyl-2enabled its as phenylcyclohex-2-enyl hydroperoxide (3) rather than (4) (Scheme 1).

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Scheme 1

The formation of the hydroperoxides (2) and (3) in the 'ene' reaction of (1) is explainable on the basis of abstractions of the axial H_a and H_c respectively in the half-chair conformation (5). Thus the attack of ${}^{1}O_2$ at C-2 leads to the abstraction of H_c to form (3). Although the attack of ${}^{1}O_2$ at C-1 could, a priori, cause the



abstraction of H_a and H_b to form the hydroperoxides (2) and (4) respectively, the results obtained indicate that only the former was formed. The relative ease of abstraction of H_a , compared to H_b , probably reflects the ease with which the methyl protons can adopt the axial-orientation pre-requisite of the 'ene' reaction (Fekarurhobo, 2000). Thus while Ha can become axial by rotation, H_b can only be axial by the more energy-demanding flip of conformation. factor that could contribute to the exclusive abstraction of H_a is its statistical advantage over H_h , the protons being in the ratio 3:1 respectively. However, this would also have resulted in a product excess of (2) over (3), instead of the 1:1 ratio observed for the products. Thus the nonregeoselectivity observed in the 'ene' reaction is indicative of restricted rotation of the methyl group, possibly by the adjacent phenyl ring. In substituted acyclic alkenes, such restricted rotations caused by cis substituents have been used to explain the 'cis' effect-the phenomenon where abstractions of protons occur predominantly on the more sterically crowded side of an alkene (Houk, 1981).

The photo-oxidation reaction of (1) differs remarkably from that of 6-methyl-1-phenylcyclohexene (Fekarurhobo, 1997) in that no bis(endoperoxide) was formed in the present reaction. Bis(endoperoxides) are formed from cisoid 1,3-dienes in a concerted mechanism, which requires the coplanarity of the reacting olefinic bonds (Wasserman, 1979). Thus the non-formation of an endoperoxide in the present reaction suggests that the substrate (1) cannot adopt a conformation in which

the phenyl ring is coplanar with the cyclohexenyl double bond. Molecular models reveal that such a conformation represents an energy maximum for the alkene, corresponding to maximum steric interaction between the phenyl ring and the methyl protons.

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