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A FACILE CONVERSION OF AN ALDEHYDE INTO A HYDROPEROXIDE. ISOLATION OF A SALT OF A p-NITROBENZYL ANION

G.Bellucci, B.Macchia and F.Macchia
Institutes of Organic and Pharmaceutical Chemistry
University of Pisa, 56100 Pisa, Italy

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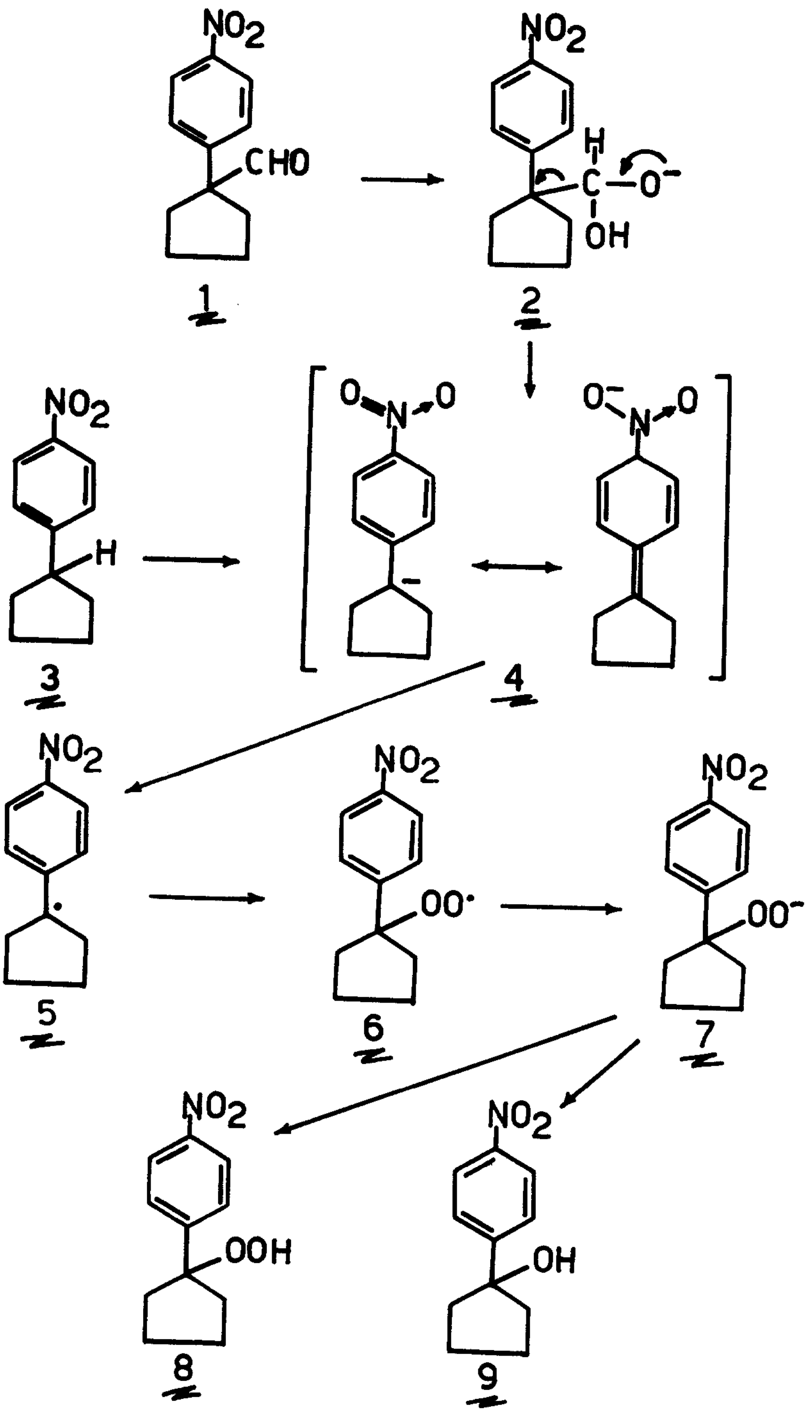
When a solution of 0.45 mmol of 1-(*p*-nitrophenyl)cyclopentane carboxaldehyde (1)(obtained from 1-*p*-nitrophenylcyclohexene oxide with boron trifluoride etherate in methylene chloride[1]) in tetrahydrofuran or ethanol was treated with an ethanolic solution of potassium hydroxide (1.5 mmol), a deep purple color appeared and a yellow crystalline precipitate formed immediately. If the suspension was left in contact with air the color slowly changed to red, then to yellow, while the precipitate dissolved; the same transformations took place very rapidly when oxygen was bubbled through the solution. Dilution with water gave a quantitative yield of a compound, m.p. 65-67°, which was identified as the hydroperoxide 8, through elemental analysis, spectroscopic data and chemical behaviour.

When the aldehyde 1 (0.45 mmol) was added to a solution of potassium *t*-butoxide (1.0 mmol) in dimethyl sulfoxide a yellow-brown color developed, which changed to green, then to yellow on emission of oxygen; after dilution with water the alcohol 9, m.p. 66-68°, was isolated in quantitative yield. The hydroperoxide 8, which was recovered unchanged from its solution in DMSO, was converted rapidly into 9 with potassium *t*-butoxide in DMSO, in accordance with a known method of reduction for hydroperoxides.[2]

Compounds 8 and 9 were also obtained when 1-cyclopentyl-4-nitrobenzene (3) was treated with potassium *t*-butoxide (not with potassium hydroxide) and oxygen in THF and in DMSO, respectively. The yield of 8 was, however, much lower than when 1 was used as the starting material, while the conversion of 3 into 9 with potassium *t*-butoxide in DMSO was practically quantitative. The latter


NO2
CHO
1
NO2
H
C
O−
OH
2
NO2
H
3
O
N
O
O−
N
O
4
NO2
5
NO2
OO·
6
NO2
OO−
7
NO2
OOH
8
NO2
OH
9

reaction closely resembles the oxidation of *p*-nitrocumene to *p*-nitrocumylic alcohol with potassium *t*-butoxide in *t*-butyl alcohol-DMSO, which however was reported to give only a very low yield in the alcohol.[3]

The analogy between the reactions of 1 and 3 with oxygen in the presence of base suggests that they probably have similar intermediates, and proceed through a mechanism of the type proposed by Russell *et al.*[3,4] involving formation of a carbanion 4, which is converted to the radicals 5 (possibly formed by reaction of 4 with oxygen, to give 5 and $O_2^{\cdot -}$), and 6, and to the anion 7, which can be protonated to the hydroperoxide 8, or reduced by DMSO in the presence of base to the alcohol 9. The anion 4 is formed in a particularly efficient way from the aldehyde 1, probably through the intermediate 2, its formation being favored by the facile elimination of formic acid and by the steric decompression connected with this elimination. Cases of displacement of the formyl group by base from a particularly activated benzyl carbon (such as in 9-aryl-9-formylfluorenes) are known.[5]

In accordance with the hypothesis formulated above, the yellow precipitate which was formed in the treatment of 1 with ethanolic potassium hydroxide in the absence of oxygen, could be collected and analyzed correctly for the potassium salt of 4. Furthermore, some 1-cyclopentyl-4-nitrobenzene (3), accompanied by other unidentified products with higher GLC retention times, was formed when the salt was treated with 1 N acetic acid.

The results reported above, beside providing what could be a useful new synthetic appoach to hydroperoxides and alcohols, are interesting as this appears to be, to our knowledge, the first case of isolation of a salt of a benzyl-type anion; evidence for species of this type has so far been only of an indirect type.[6,7,8]

It is particularly surprising that our salt has been isolated from an ethanolic solution. Russell and Janzen[4] have observed the formation of a paramagnetic solid in the treatment of *p*-nitrotoluene with t-butoxide in *t*-butyl alcohol, but have not commented on its structure. In preliminary EPR measurements our salt has given a rather strong signal; however no severe precautions had been taken to prevent contact with air, so that the observed signal was probably due to radicals formed by reaction with molecular oxygen. We are planning to investigate this point more extensively in future.

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