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A NOVEL CONVERSION OF TROPYLIUM ION TO BENZENOID COMPOUNDS IN THE REACTION WITH PEROXIDE ION

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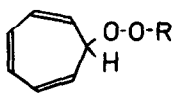
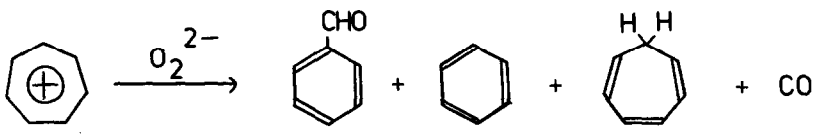
It has been shown that tropylium ion (1) reacts with hydrogen peroxide to give tropyl hydroperoxide (2) which is rapidly converted to benzene and carbon monoxide.[1] The related oxidation reaction with m-CPBA has recently been reported.[2] The tropyl hydroperoxides are also assumed as intermediates of the photo-oxidation of cycloheptatriene derivatives with singlet oxygen.[3] In spite of importance of the tropyl peroxide as an intermediate of oxidation reactions, none is known about tropyl peroxide such as 3. We have found that ditropyl peroxide is a possible intermediate in the reaction of tropylium ion with peroxide ion, O_2^{2-}, or superoxide ion, $O_2^{\cdot-}$. The results obtained by this study are remarkably different from those reported for the reaction of 1 with hydrogen peroxide.



2 R=H

3 R=tropyl

In a typical experiment, a dry DMSO solution (0.6 ml) containing tropylium bromide (30 mg) and sodium peroxide (7 mg) was stirred for 30 min at room temperature. The products were analyzed by nmr and GC mass spectra, by which benzaldehyde (4), benzene (5), cycloheptatriene (6) and carbon monoxide (7) were identified. In addition to these, a small amount of an unknown product possessing chemical shifts 6.84-7.23 (m) was detected by the nmr spectra.[4] Yield of these compounds except for 7 was determined by the nmr spectra with using dioxane as an internal standard. The results are presented in the table.



1 4 5 6 7

It is to be noted that the product ratio of 4, 5 and 6 is always 1:1:1 in any reaction run. The solvents did not influence the reaction. Interestingly, $O_2^{\cdot-}$ also reacted with 1 to give the same products in the same yields as in the case of O_2^{2-} (see the table).[5]

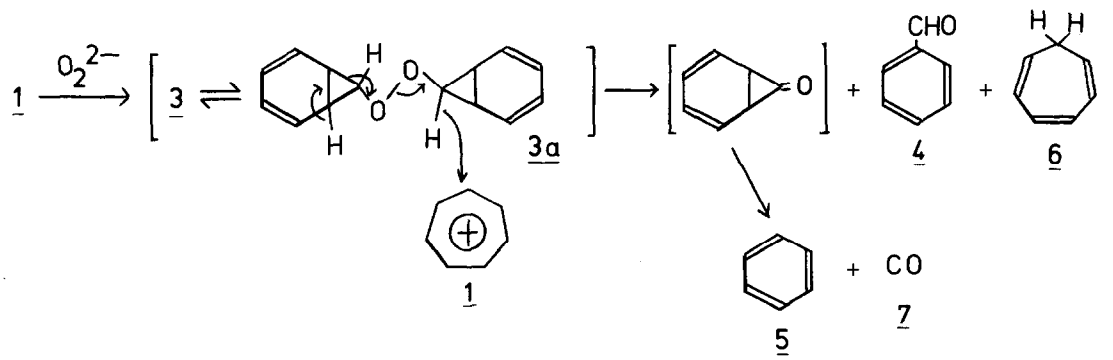
Table Reaction of 1 with O_2^{2-} and $O_2^{\cdot-}$ a)

Reagent	Mole ratio (Na_2O_2 or KO_2/ 1)	Yield % 4	5	6	7
Na_2O_2	0.5	26	22	27	11 b)
"	0.5 c)	25	23	20	(e)
"	0.5 d)	24	23	26	(e)
"	1	25	23	23	(e)
"	2	23	26	25	(e)
KO_2	1	25	26	22	(e)
"	1 d)	26	22	25	(e)

a) The reactions were carried out in DMSO-d_6 and the yield was calculated based on 1.
b) The CO gas was identified by glc analysis and its yield was estimated by measuring volumes of it evolved. c) Under a nitrogen stream. d) DMF-d_7 was used as a solvent.
e) The yield was not determined.

A plausible mechanistic path for the oxidation reaction of tropylium ion with O_2^{2-} is shown in the scheme. Ditropyl peroxide 3 or its norcaradiene isomer 3a, though they could not be detected by the nmr spectra under the reaction conditions used in this study, is most likely an intermediate of the reaction, since O_2^{2-} possess two reactive sites and the product ratio of 4 and 5 is always 1:1. The abstraction of hydride by 1[6] from an intermediate such as 3a may be involved, since an equivalent amount of 6 to 4 or 5 is always formed in this reaction. As to the stoichiometry of the reaction, 20-25% of the products are missing and amounts of 7 are less than those calculated on the basis of the proposed mechanism. Further studies to elucidate these points as well as details of the mechanism are in progress.

Scheme



References and Notes

1) M.E.Vol'pin, D.N.Kursanov and V.G.Dulova, Tetrahedron, 8, 33 (1960). 2) K.Nakasuji, T.Nakamura and I.Murata, Tetrahedron Lett., 1978, 1539. 3) A.S.Kende and J.Y.-C.Chu, Tetrahedron Lett. 1970, 4837; A.Mori and H.Takeshita, 37th Annual Meeting of the Chemical Society of Japan (Kanagawa April, 1978), Abstr. II, p 1026. 4) The chemical shift suggested that this was not benzoic acid, tropone and salicylaldehyde. 5) The reaction of troponoid compounds with superoxide ion will be reported elsewhere. 6) T.Ikemi, T.Nozoe and H.Sugiyama, Chem. & Ind., 1960, 932; A.P.Ter Borg, R.von Helden, A.F.Bickel, W.Renold and A.S.Dreiding, Helv. Chem. Acta, 43, 457 (1960).

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