CHEMISTRY LETTERS, pp. 1159-1162, 1978. Published by the Chemical Society of Japan

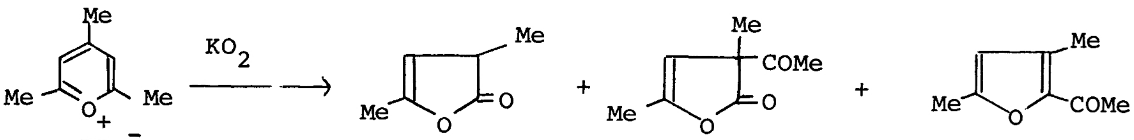
SUPEROXIDE ION CHEMISTRY. REACTION OF SUPEROXIDE ION WITH 2,4,6-TRISUBSTITUTED PYRYLIUM TETRAFLUOROBORATES

Shohei KOBAYASHI and Wataru ANDO*
Department of Chemistry, The University of Tsukuba
Niiharigun, Ibaraki 300-31

The reactions between 2,4,6-trisubstituted pyrylium tetrafluoroborates with superoxide ion were studied. Three main products, 3,5-disubstituted-2(3H)-furanone(2), 3-acyl-3,5-disubstituted-2(3H)-furanone(3), and 2-acyl-3,5-disubstituted furan (4), were obtained.

In recent years, special attention has been directed to superoxide ion, $O_2^{-\cdot}$, as an active species for biological oxidations.$^{1)}$ Most of the recent studies for $O_2^{-\cdot}$ were carried out in aqueous media in which it was likely that not only $O_2^{-\cdot}$ but also H_2O_2, $HO_2\cdot$, and $\cdot OH$ were the reactive species.$^{2)}$ The chemistry of $O_2^{-\cdot}$ in aprotic solvents can be now extended to general organic substances.$^{3)}$ From the reactions between those and $O_2^{-\cdot}$, it was found out that $O_2^{-\cdot}$ can act as a one-electron reducing agent$^{4)}$ or a strong nucleophile.$^{5)}$ Investigation of the reactions of $O_2^{-\cdot}$ with simple organic substrates could aid in understanding the mechanisms of biological reactions. We now report in this paper the reaction of $O_2^{-\cdot}$ with 2,4,6-trisubstituted pyrylium salts, which have a tendency to react with nucleophile at position 2.$^{6)}$

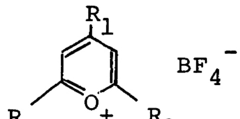
The following is a procedure of a typical experiment. Ten mmoles of potassium superoxide, KO_2, in 10ml of dry acetonitrile was added at once to 5mmol of 2,4,6-trimethylpyrylium tetrafluoroborate(1a) in 30ml of dry acetonitrile at -30°C and stirred for half an hour. The reaction was terminated by quenching with water. The mixture was extracted with ether several times and analyzed by glc. Three main products, 3,5-dimethyl-2(3H)-furanone(2a), 3-acetyl-3,5-dimethyl-2(3H)-



1a 2a 3a 4a

furanone(3a), and 2-acetyl-3,5-dimethylfuran(4a), were obtained. The reaction of 1b was also carried out under the same conditions. The structures of 2a, 4a, and 4b were determined by comparison of spectral data with authentic samples prepared by the methods of Hirsch7) and Balaban,8) and 3a, 2b, and 3b were characterized by nmr, ir, and mass spectra.9) The results are summarized in Table 1.

Table 1 Reaction of pyrylium salts with $O_2^{-\cdot}$. ***

	Reaction time	Yield %		
	min	2	3	4
R_1= R_2= Me 1a	30*	20	7	42
	30**	9	trace	31
	90*	trace	—	38
R_1= Me, R_2= Et 1b	30*	9	trace	25

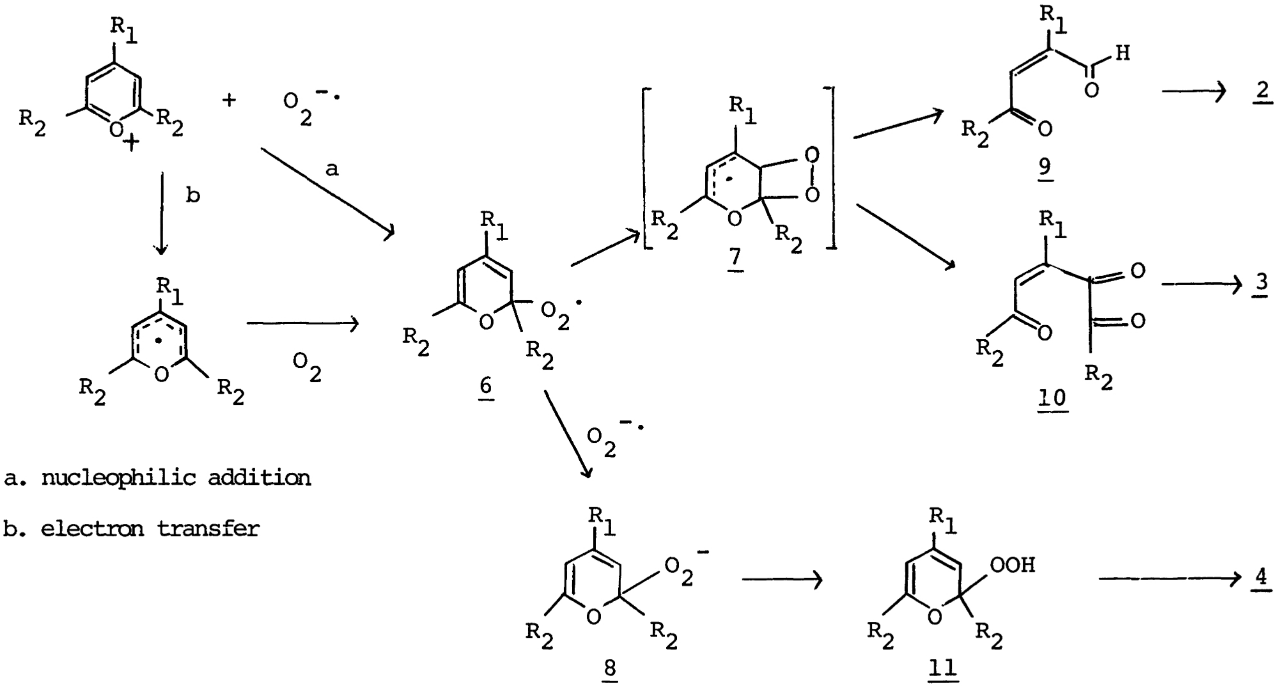
Temp. -30°C. *) Under air. **) Under nitrogen. ***) The substrates could not be recovered because of high solubility of those in water.

Small amounts of the products, 2a, 3a, and 4a, were obtained when the reaction of 1a was carried out at room temperature. 2-Acetyl-3,5-dimethylfuran(4a) was stable to $O_2^{-\cdot}$ under the reaction conditions used in this work, but 2-furanone derivatives(2a, 3a) were not stable.10) The products, 2a, 3a, and 4a, were not obtained by treatment of 1a with KOH and 18-crown-6-ether in 40ml of dry acetonitrile under air. The yield of the products from 1a became somewhat lower in the reaction under a nitrogen stream than under air.

In initial stage of this reaction, two possible passages can be considered, that is, a direct nucelophilic addition to α-position of pyrylium ring and one-electron transfer from $O_2^{-\cdot}$ to electron deficient pyrylium ring.

The following mechanism shown in scheme 1 presumably rationalizes the formation of the products. A 2H-pyran-2-peroxy radical(6) probably converts to three intermediates, 9, 10, and 11. The first two may be formed from 7 which is a possible transition state. The last one may be produced from 8 resulting from one-electron transfer from $O_2^{-\cdot}$. The transformation of 9 , which might be formed from 7 via fission of O-O bond and an elimination of an R_2CO group, to 2 has a precedent in a recent paper by Hirsch.[7] The elimination of a hydrogen atom and the fission of O-O bond in 7 may produce triketone intermediate(10) followed by cyclization to give 3.[11] The precursors of 2 and 3 may be cis-β-acylacrolein(9) and triketone intermediate(10) respectively. Product 4 may be obtained from 2H-pyran-2-hydroperoxide(11).[8]

Scheme 1 Possible mechanism



a. nucleophilic addition

b. electron transfer

2-Furanone derivatives were not obtained in the reaction of 2,4,6-trisubstituted pyrylium salts with H_2O_2 and OH^-, and in its base catalyzed autooxidation. We concluded that the products, 2 and 3, were formed from the reaction of 2,4,6-trisubstituted pyrylium salts with $O_2^{-\cdot}$.

References

1) I.Fridovich, Accounts Chem.Res.,5,321(1972); Ann.Rev.Biochem.,44,147(1975).

2) I.Fridovich, Free Radicals in Biology, W.A.Pryor ed.,p 321(1976) Academic Press.

3) E.Lee-Ruff, Chem.Soc.Rev.,1977,195.

4) R.Poupko and I.Rosenthal, J.Phys.Chem.,77,1722(1973); A.Frimer and I.Rosenthal, Tetrahedron Lett.,1976,2805;2809; A.Frimer, I.Rosenthal and S.Hoz, ibid,1977,4631.

5) W.C.Dane and R.J.Warner, ibid,1977,989.

6) A.T.Balaban, V.E.Sahini and E.Keplinger, Tetrahedron,9,163(1960).

7) J.A.Hirsch and A.J.Sezer, J.Heterocycl.Chem.,9,523(1972).

8) A.T.Balaban and C.D.Neuitzescu, Chem.Ber.,93,599(1960).

9) Spectral data are summarized.

3a nmr(CCl_4)δ 1.27(s,3H),1.93(s,3H),2.00(s,3H),4.93(br. s,1H);ir ν_{CO} 1800(βγ-unsaturated-γ-lactone),1725(acetyl group)cm^{-1};mass spectrum m/e 154(parent peak), 126(loss of CO),111(loss of CH_3CO).

2b nmr(CCl_4)δ 0.85-1.28(m,6H),2.09-2.53(m,3H),5.00(br. s,1H);ir ν_{CO} 1800(-unsaturated- -lactone)cm^{-1};mass spectrum m/e 126(parent peak),111(loss of Me),82 (loss of CO_2).

3b nmr(CCl_4)δ 0.87-1.28(m,6H),1.30(s,3H),2.32-2.64(m,4H),5.00(br. s,1H); ir ν_{CO} 1798(βγ-unsaturated-γ-lactone),1725(propionyl group)cm^{-1}; mass spectrum m/e 182(parent peak),125(loss of EtCO),110(loss of Me and EtCO).

10) J.S.Filippo,Jr.,L.J.Romano, C.I.Chern and J.S.Valentaine, J.Org.Chem.,41,586, (1976).

11) D.Yates and G.H.Stout, J.Amer.Chem.Soc.,76,5110(1954); H.H.Wasserman and D.L.Paiva, Tetrahedron Lett.,1970,1459.

(Received June 24, 1978)