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Oxidative Decarboxylation of Arylacetic Acids Mediated by Peroxysulfur Intermediate Generated from 2-Nitrobenzenesulfonyl Chloride and Superoxide

Yong Il Kim and Yong Hae Kim*

Department of Chemistry, Korea Advanced Institute of Science and Technology, 373-1, Taejon, 305-701, Korea

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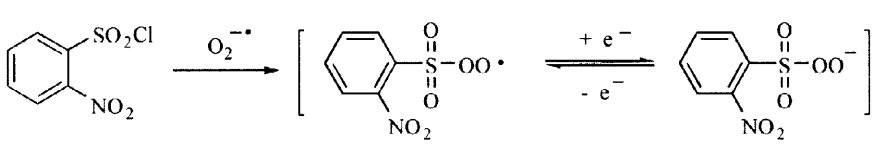
Abstract : The oxidative decarboxylation of aryl, α,α-diaryl, or arylalkylacetic acids has been achieved by a 2-nitrobenzenesulfonyl peroxy radical intermediate (I) generated by the reaction of 2-nitrobenzenesulfonyl chloride with potassium superoxide at -20℃ in dry acetonitrile.

The decarboxylation of carboxylic acids has been extensively investigated for the structural elucidation of natural compounds[1] and the transformation of carboxylic acids to the nor-ketone or aldehyde by such the oxidative decarboxylation *via* dianion oxygenations,[2] sulfenylation-chlorination,[3] tetrabuthylammonium peroxidate,[4] sodium hypochloride,[5] and Cu^{I}-O_2.[6] A series of works on the oxidative decarboxylation of arylcarboxylic acids mediated by sulfate anion radical have been well documented.[7-12] The mechanism is also well studied by an electron transfer from arene ring to sulfate anion radical. Intensive investigations of the biochemistry and chemistry of superoxide anion radical has been reported since the discovery of superoxide dismutase.[13] It has been amply demonstrated that $O_2^{-\cdot}$ displays four basic modes of action including deprotonation as a base, H-atom abstraction as a radical, nucleophilic attack as an anion, and electron transfer reagent.[14] However, the oxidizing ability of $O_2^{-\cdot}$ is limited, probably due to its relatively weak reactivity and poor solubility in aprotic organic solvent. In the course of our study on activation of superoxide, a 2-nitrobenzene peroxysulfur intermediate (2-NB-PSI), generated from 2-nitrobenzenesulfony chloride and superoxide, has been found to have much stronger oxidizing ability than superoxide itself.

Electrophilic epoxidation of olefins,[15] oxidative desulfurization of thiocarbonyl substances to their corresponding carbonyl compounds,[16] and oxidation of the active methylene groups to ketones[17] can be explained by a radical mechanism. Here a question had been raised whether the intermediate is involved as a radical **(I)** or an anion **(I')** character. The spin trapping studies with the use of 5,5-dimethyl-1-pyrroline-1-oxide (DMPO) reveals that 2-NB-PSI has radical species.[18]



2 **(I)** **(I')**

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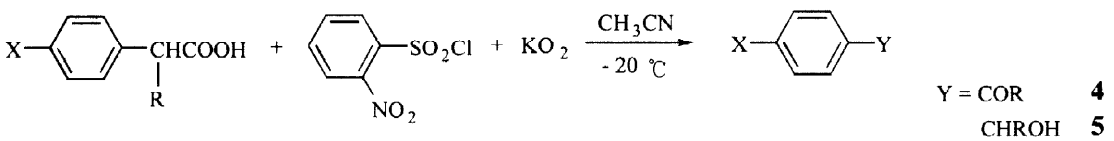
In order to obtain further information concerning the radical character of 2-NB-PSI and to extend the utility of this intermediate, oxidation of arylacetic acids have been examined. We now report that various arylacetic acids undergo the decarboxylative elimination smoothly to yield the degraded aldehydes or ketones **4** in good yield together with alcohols **5** under mild conditions by the 2-NB-PSI, generated *in suit* from 2-nitrobenzenesulfony chloride and potassium superoxide at -20 ℃ in dry acetonitrile. Decarboxylation dose not take place with superoxide in the absence of **2** at 25 ℃ for 24 h: starting material is recovered quantitatively. The results obtained are summarized in Table 1.

Table 1. Oxidative Decarboxylation of Arylacetic Acids with 2-Nitrobenzene Peroxysulfur Intermediate.[a]



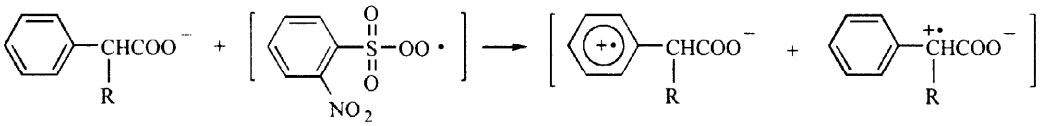
1 **2** **3**

Entry	X	R	Time(h)	Products	Yields(%)[b]		
					4	**5**	**6**
1	H	H	7	**4a, 5a**	55	20	trace
2	NO_2	H	8	**4b, 5b**	52	25	trace
3	Cl	H	8	**4c, 5c**	55	21	trace
4	CH_3	H	5	**4d, 5d**	57	17	trace
5	OCH_3	H	4	**4e, 5e**	62	15	trace
6	H	Ph	5	**4f, 5f**	84	13	
7	H	CH_3	5	**4g, 5g**	83	13	
8	H	ethyl	5	**4h, 5h**	85	13	
9	H	cyclopentyl	5	**4i, 5i**	84	12	
10	H	cyclohexyl	5	**4j, 5j**	84	13	

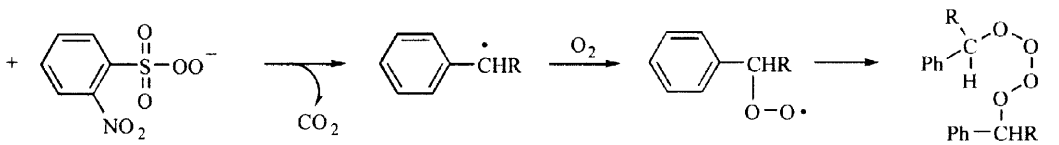
a) Mole ratio **1** : **2** : **3** = 0.5 : 3 : 9. b) Isolated yields.

In a typical experiment, to the heterogeneous potassium superoxide solution (639 mg, 9 mmole, CH_3CN, 5 ml) was added a solution of 2-nitrobenzenesulfonyl chloride (663 mg, 3 mmole) and diphenylacetic acid (106 mg, 0.5 mmole, CH_3CN, 5 ml) at ca. -20 ℃ with good stirring. After stirring for 5 h at -20 ℃, the reaction mixture was poured into cold water, and extracted with dichloromethane (25 ml × 3). The dichloromethane solution was dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure to give benzophenone **4f** (84%) and benzhydrol **5f** (13%), which were purified by column chromatography (silicagel : 35-70 mesh, elution: CH_2Cl_2/n-Hexane = 1/1). The products obtained were identified by comparing their IR, ^1H NMR, ^{13}C NMR, mp and mass spectra[19] with those of literature data.

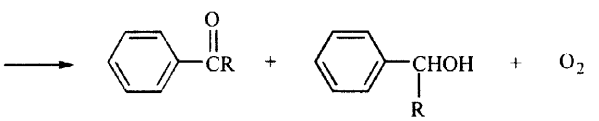
In order to see the effect of *p*-substituted groups for the oxidation of a series of arylacetic acids, competitive oxidation of *p*-substituted arylacetic acids with 2-NB-PSI was carried out. 2-NB-PSI has been found to be an electrophilic oxidant **(I)** toward arylacetic acids, giving Hammett's ρ value -0.408 (r = 0.9996).[20] It is noteworthy that 2-NB-PSI shows an electrophilic character under strong alkaline conditions of $O_2^{-\cdot}$.[14] The possible reaction mechanism of oxidative decarboxylation with **(I)** can be postulated as shown below.



7 **(I)** **8** **9**



(I') **10** **11** **12**



4 **5**

The reaction appears to be initiated *via* formation of a cation radical **8** by one electron transformation from the benzene ring to **(I)** before heterolytic fragmentation (CO_2 evolution) of the carboxylate side chain.[7a] It has been reported that the carboxylate anions are oxidized by the sulfate anion radical ($SO_4^{-\cdot}$) more slowly than the aromatic rings and one electron transfer from the benzene ring to $SO_4^{-\cdot}$ are well studied in mechanisms.[7a] The benzyl radical **10** may couple with molecular oxygen to form peroxy radical **11**. The peroxy radicals **11** may be coupled to form unstable tetraoxide **12** which decomposes to give **4**, **5** and molecular oxygen presumably like the case of the autoxidation of ethylbenzene to the corresponding ketone and alcohol.[21] It was found that benzyl alcohols are converted into the corresponding benzaldehydes and small amount of benzoic acids under same reaction conditions. The reaction mechanism and scope are under investigation.

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19. **4a**; GC/MSD m/z 106, 105, 77, 51. **5a**; GC/MSD m/z 108, 107, 91, 79, 77. **4b**; GC/MSD m/z 151, 150, 100, 99, 77, 51. **5b**; GC/MSD m/z 153, 152, 135, 101, 77. **4c**; GC/MSD m/z 140, 111, 75, 50. **5c**; GC/MSD m/z 142, 107, 79, 77. **4d**; GC/MSD m/z 120, 119, 105, 91. **5d**; GC/MSD m/z 122, 107, 93, 79, 65. **4e**; GC/MSD m/z 136, 135, 107, 92, 77. **5e**; GC/MSD m/z 138, 121, 109, 94, 77. **4f**; GC/MSD m/z 182, 152, 126, 105, 77. **5f**; GC/MSD m/z 184, 165, 105, 77. **4g**; GC/MSD m/z 120, 105, 77. **5g**; GC/MSD m/z 122, 107, 79, 77. **4h**; GC/MSD m/z 134, 107, 106, 77. **5h**; GC/MSD m/z 136, 118, 117, 105, 92, 91. **4i**; GC/MSD m/z 174, 145, 133, 105, 77. **5i**; GC/MSD m/z 176, 158, 129, 107, 79. **4j**; GC/MSD m/z 188, 170, 147, 133, 105, 77. **5j**; GC/MSD m/z 190, 172, 141, 129, 107, 79, 77.
20. r = Correlation coefficient.
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