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OXYGENATION OF SUBSTITUTED 2'-HYDROXYACETOPHENONE 4-BROMOPHENYLHYDRAZONES PROMOTED BY COBALT(II) SCHIFF BASE COMPLEX

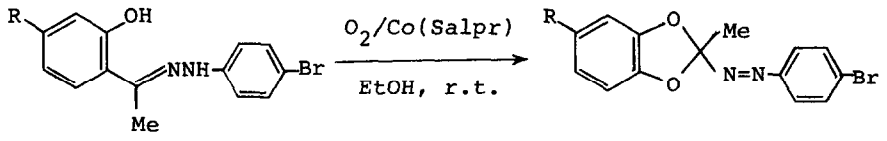
Akira NISHINAGA,* Shigekazu YAMAZAKI, and Teruo MATSUURA
Department of Synthetic Chemistry, Faculty of Engineering,
Kyoto University, Kyoto, Japan

Substituted 2'-hydroxyacetophenone 4-bromophenylhydrazones are oxygenated readily in the presence of Co(Salpr) in ethanol to give 2-(4-bromophenylazo)-1,3-benzodioxoles in good yield. The results are rationalized in terms of the decomposition of a peroxy cobalt(III) complex intermediate by a mechanism similar to the Darkin oxidation.

Oxidations of organic molecules with dioxygen transition metal complexes have extensively been studied in view of exploitation of new synthetic methodologies and of the understanding of biological oxidation mechanisms.[1-3] We have previously reported that cobalt(II) Schiff base complexes, which are capable of binding dioxygen reversibly promote dioxygen incorporation into phenols,[4] flavonols,[5] indoles,[6] and hydrazones,[7] providing good chemical models for dioxygenase reactions. In this communication, we describe that Co(Salpr) promotes the oxygenation of substituted 2'-hydroxyacetophenone 4-bromophenylhydrazones (**1**) in ethanol unexpectedly to give 2-(4-bromophenylazo)-1,3-benzodioxoles (**2**) in good yield.

When oxygen was bubbled through a solution of 2'-hydroxy-4'-methoxyacetophenone 4-bromophenylhydrazone (**1a**) in ethanol containing 1.2 equivalents of Co(Salpr) at room temperature, the reaction was complete in 10 min to give a sole product as detected by tlc. After evaporation of the solvent, the residue was dissolved in a small volume of dichloromethane and filtered through a short

column of silica gel to remove the metal complex. Evaporation of the solvent gave 2-(4-bromophenylazo)-2-methyl-5-methoxy-1,3-benzodioxole (2a) in 94% yield. Similar results were obtained with other compounds 1 indicating that the present oxidation is of general. The reaction also took place in other alcohols with similar results, although a complex mixture was obtained in dichloromethane (Table 1). The spectral and analytical data of 2 are in good agreement with



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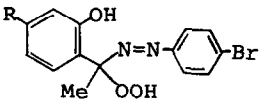
a; R = MeO b; R = Me c; R = H d; R = Cl e; R = NO_2

Table 1. Co(Salpr) Promoted Oxygenation of 1.[a]

1	Solvent	Reaction Time (min)[b]	Yield of Product (%)[c] 2	4
1a	EtOH	10	94	0
1b	EtOH	20	87	3
1c	EtOH	20	75	2
1c	i-PrOH	10	71	-[d]
1c	t-BuOH	20	77	-[d]
1c	CH_2Cl_2[e]	30	24	-[d]
1d	EtOH[f]	10	71	8
1e[g]	Py	150	35	-[d]



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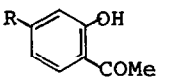

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[a] Reaction conditions: 1 (0.5 mmol), Co(Salpr) (0.6 mmol), EtOH (30 ml). [b] Required for the completion of the reaction. [c] Products were isolated by tlc (silica gel) developed with CH_2Cl_2. The reaction mixtures from 1b-d seemed to contain hydroperoxide 3, which decomposed to 4 during work-up. [d] Not determined. [e] A complex reactoion mixture was obtained. [f] EtOH (60 ml) was used because of slight solbility of 1d. [g] Since 1e was not soluble in EtOH, the reaction was carried out in pyridine (15 ml) with Co(MeOSalen) instead of Co(Salpr).

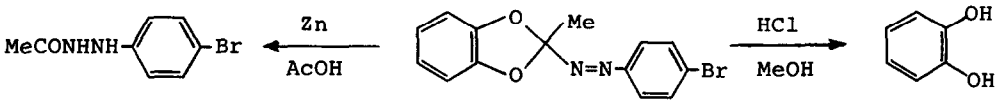
the structure (Table 2). The structure of 2c was further supported by its chemical reactions. Thus, reflux of a solution of 2c in methanol containing 5 equivalents of hydrochloric acid for 30 min gave catechol in 85% yield, and

Table 2. Physical Data of 2.[a]

2	M.p. (°C)	^{1}H NMR ($CDCl_3$) δ (ppm) Me	R	Oxole ring	-N=N-C_6H_4Br
2a	61-62	1.95	3.70	6.25-6.93[b]	7.65[c]
2b		1.92	2.24	6.53-6.93[b]	7.67[c]
2c	67-68	1.93	-	6.82[c]	7.56[c]
2d	82-83	1.94	-	6.69-7.00[b]	7.64[c]
2e	111-112	2.00	-	6.8-8.3[b]	7.66[c]

[a] Satisfactory analytical data were obtained. [b] m, 3H. [c] s, 4H.

treatment of 2c with zinc dust in acetic acid at room temperature for 1 h gave 1-acetyl-2-(4-bromophenyl)hydrazine[8] in 91% yield along with catechol. The



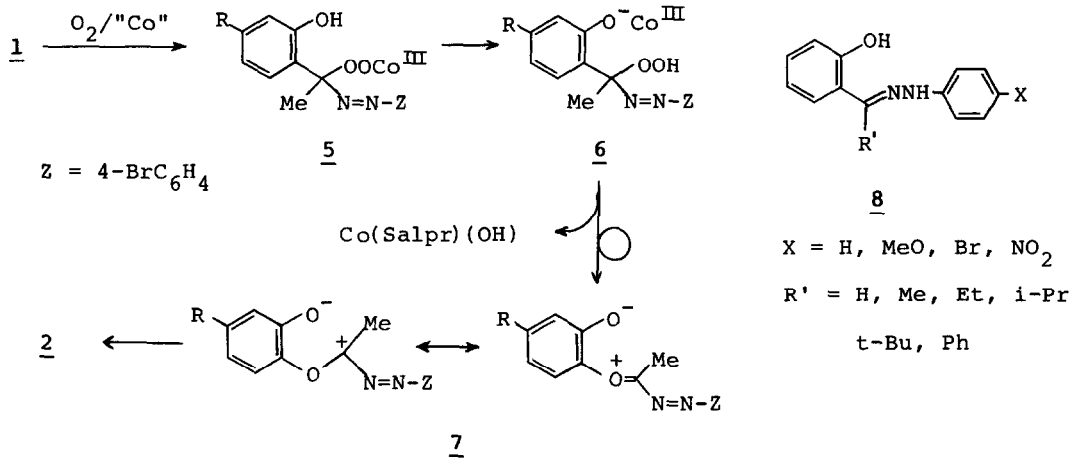
91% 2c 85%

formation of catechol by the acid hydrolysis of 2c provides a new method for the specific formation of catechol from phenol.

Taking into account the results obtained in the oxygenation of hydrazones with Co(Salpr),[7] in the present oxygenolysis of 1, it is reasonable to assume that peroxy complex 5 is formed as the primary intermediate, which can undergo an intramolecular proton transfer to give hydroperoxy phenolate species 6 analogous to the intermediate in the Dakin oxidation reaction.[9] Elimination of hydroxy anion as Co(Salpr)(OH) followed by a migration reaction in 6 gives 2 possibly via a zwitterionic transition state 7 as depicted in Scheme 1. The high yield of 2 obtained from 1 in which the substituent R is an electron-releasing group is due to the stabilization of the cationic center in 7 by the electron-releasing group. According to the mechanism shown in Scheme 1, the oxidation of 1 should proceed catalytically, becasue Co(Salpr)(OH) formed during the course of the reaction is the reactive species for the oxygenation of hydrazones.[7]

Actually, the oxygenolysis of 1 took place with a catalytic amount (0.1 eq.) of Co(Salpr) giving rise to the similar results, although a longer reaction time

Scheme 1



was required. The oxygenation of 1 was also promoted by Co(3-MeOSalen) in pyridine to give similar results, whereas with Co(Salen) in ethanol, the main product was the corresponding acetophenone derivative. Preliminary experiments in order to find out substituent effects on the formation of the product of type 2 in the Co(Salpr) promoted oxygenation of 8 showed that any substituent X did not affect the yield of product of type 2, whereas the substituent R' other than the methyl group made the reaction complicated.

References and Notes

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8) Colorless prisms (EtOH); m.p. 161.5-162.5 °C; ^{1}H NMR ($CDCl_3$ + DMSO-d_6) δ 1.87 (s, 3H), 6.64 (d, 2H, J = 9 Hz), 7.21 (d, 2H, J = 9 Hz), 7.78 (s, 1H, NH), 10.61 (s, 1H, NH); IR(Nujol) 3460, 3285, 3220, 3100, 1645, 1635 cm^{-1}. Anal. Calcd for $C_8H_9BrN_2O$: C, 41.95; H, 3.96; N, 12.23; Br, 34.88. Found: C, 41.65; H, 3.89; N, 12.02; Br, 34.85.
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