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REACTION OF 9-t-BUTYL-10-METHYL-9,10-ENDOTRIOXY-9,10-DIHYDROANTHRACENE WITH TRANSITION METAL COMPOUNDS

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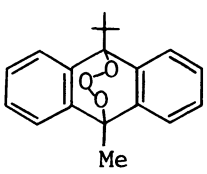
9-t-butyl-10-methyl-9,10-endotrioxy-9,10-dihydroanthracene underwent reductive decomposition readily with transition metal compounds having one-electron reducibility to result unexpectedly in the specific cleavage of the shorter O-O bond close to the t-butyl group in the trioxide finally giving rise to 10-methyloxanthrone and t-butyl alcohol. A plausible mechanism is discussed.

Considerable attention has been focused in recent years on the chemistry of organic polyoxides including peroxides as key intermediates in low-temperature oxidations, atmospheric and stratospheric chemistry, combustion, flames, and biological oxidation process.[1] However, little has been known about the chemical reactivity of trioxides because no stable trioxides have been isolated, although trioxides are primary intermediates in ozonization of organic compounds and it is therefore important to know their chemical reactivities. We have recently reported the first strucurally well-defined 9-t-butyl-10-methyl-9,10-endotrioxy-9,10-dihydroanthracene (1), which can be derived from the ozonization of 9-t-butyl-10-methylanthracene, and its some chemical reactivities.[2,3] In general, dialkyl peroxides including endoperoxides are unsusceptible at room temperature to transition metal compounds possessing one-electron reducibility such as VO(II), Fe(II), and Co(II) complexes,[1] whereas endoperoxides undergo reductive cleavage with Ru(II) and Pd(0) complexes.[4] We now find that endotrioxide 1, contrary to the behavior of endoperoxides towards transition metal compounds, undergoes reductive decomposition readily with transition metal compounds having one-electron reducibility resulting unexpectedly in the specific cleavage of the shorter O-O bond close to the t-butyl group whereas it is not susceptible to Ru(II) and Pd(0) complexes.

The trioxide 1 was quite stable in a dichloromethane solution at room temperature. However, when 1 was added to a solution of $VO(acac)_2$ in dichloromethane, the greenish color of the solution turned to brown, indicating that the oxidation of V(IV) to V(V) took place. The reaction mixture gave 10-methyloxanthrone (2) resulting from the reductive decomposition of 1 as the main product. The reductive decomposition of 1 also took place with other transition metal compounds, and the nature and ratio of products depended on the reaction conditions (Table 1). As seen from Table 1, with more than two equivalents of $VO(acac)_2$ compound 2 and $VO(acac)_2(OH)$[5] were obtained in quantitative yield. In addition, t-butyl alcohol



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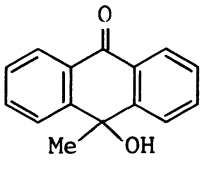

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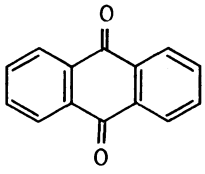

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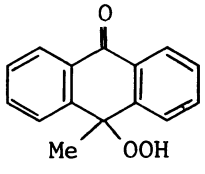

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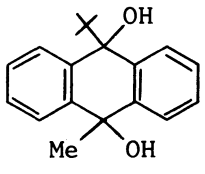

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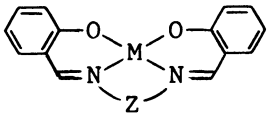
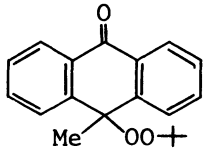


Co(salen); M = Co, Z = CH_2CH_2

Co(salpr); M = Co, Z = $(CH_2)_3NH(CH_2)_3$



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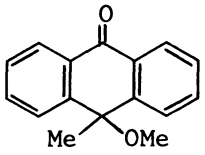

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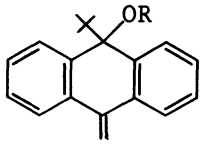

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a; R, Me
b; R, H

Table 1. Reaction of 1 with Transition Metal Compounds [a]

Run	Metal Comp.	[M]/[1]	Solvent	Reaction time/h[b]	Conv./%	Product yield/%[c] 2	3	4	5
1	None	-	CH_2Cl_2	30	0	-	-	-	-
2	$VO(acac)_2$	4	CH_2Cl_2	1	100	100	-	-	-
3	$VO(acac)_2$		CH_2Cl_2	5	100	97	-	-	-
4	$VO(acac)_2$	1.5	CH_2Cl_2	24	100	89	6	-	-
5	$VO(acac)_2$	1	CH_2Cl_2	26	100	87	12	-	-
6	$VO(acac)_2$	0.05	CH_2Cl_2	89	47	49	23	-	-
7	$VO(acac)_2$	2	CH_2Cl_2(NMeIm)[d]	24	44	89	6	-	-
8	$VO(acac)_2$	2	DMF	12	100	90	2	-	-
9	$VO(acac)_2$	2	CH_3COOH	5	100	93	-	-	-
10	VO(salen)	2	CH_2Cl_2	49	83	13	57	-	-
11	Co(salen)	2	CH_2Cl_2(NMeIm)[e]	4	100	61	-	-	27
12	Co(salpr)	2	CH_2Cl_2	25	51	27	-	36	-
13	$Co(acac)_2$	2	CH_2Cl_2	40	73	72	-	-	-
14	$RuCl_2(PPh_3)_3$	0.05	CH_2Cl_2	66	77	62	26	-	-
15	$Pd(PPh_3)_4$	1	CH_2Cl_2	102	100	72	-	-	-

a) Reaction conditions: 1 (0.35-7 mmol), solvent (10 cm^3) at room temperature.
b) Reaction time required for the conversion indicated. c) Isolated yield.
d) Ten equivalents of 1-methylimidazole (NMeIm) to the metal were added.
e) One equivalent of NMeIm was added.

was isolated in 61% yield in an equimolar reaction of 1 with $VO(acac)_2$. When the amount of $VO(acac)_2$ was reduced, the reaction became slow and anthraquinone (3) was formed (Table 1, Runs 4-6). The time course of the reaction of 1 with $VO(acac)_2$ showed that with less than two equivalents of $VO(acac)_2$ the reaction proceeded in two phases: a fast stoichiometric and slow catalytic reactions (Fig. 1). Nevertheless, at low conversion stages, compound 2 was the sole product and the rate of the formation of 2 was proportional to the amount of $VO(acac)_2$. These results evidently indicate that the trioxide 1 is converted to 2 quantitatively

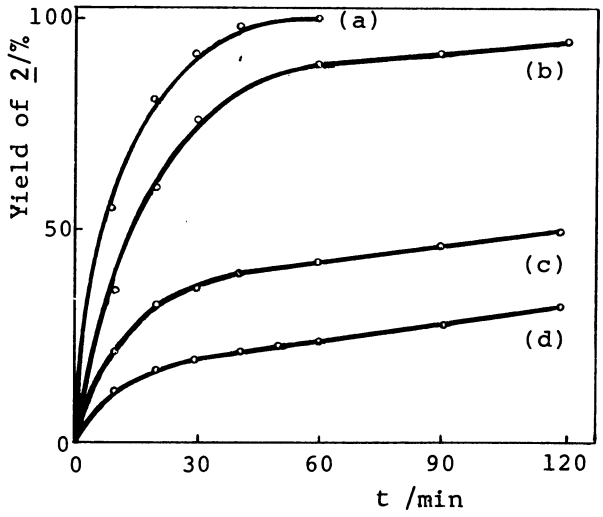
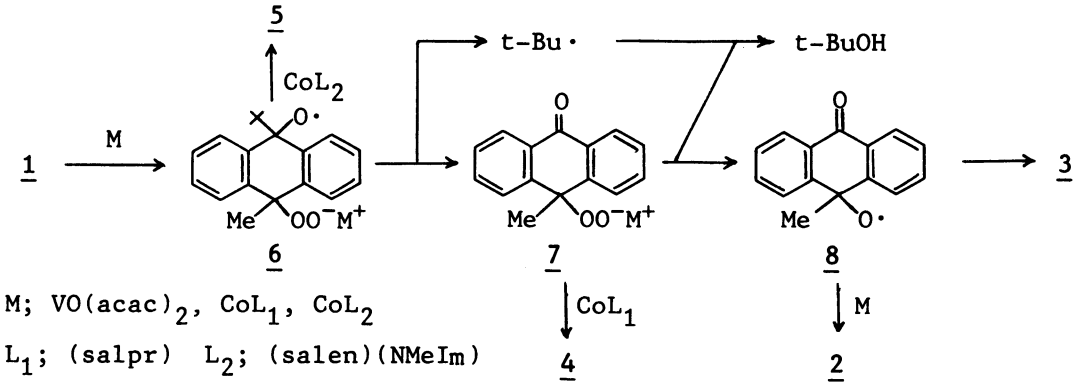


Fig. 1. Time course of the reaction of 1 with $VO(acac)_2$. $[VO(acac)_2]/[1]$: (a), 4.0; (b), 2.0; (c), 1.0; (d), 0.5. 1; 0.6 mmol in CH_2Cl_2 (10 cm^3) at 30 °C under N_2.

in a rapid reaction at the expense of two molecules of $VO(acac)_2$ accompanied by the formation of t-butyl alcohol. When 1-methylimidazole (NMeIm) was added as a sixth ligand, the reaction was retarded (Run 7). Similar retardation was observed in a coordinative solvent (Run 8), although in a polar solvent such as acetic acid no retardation was took place (Run 9), indicating that the coordination of 1 to vanadyl complex is essential. Interestingly, VO(salen) was not effective, but five coordinate cobalt(II) Schiff base complexes, Co(salen)(NMeIm) and Co(salpr), acted as efficient reducing agents giving rise to informative products for elucidation of the mechanism of the present reductive cleavage of the O-O bond in 1. Thus, the reaction of 1 with Co(salen)(NMeIm) gave 9-t-butyl-9,10-dihydroxy-10-methyl-9,10-dihydroanthracene (5), whereas with Co(salpr) 10-hydroperoxy-10-methyl-9-anthrone (4) was obtained in addition to 2. These results strongly suggest that the mechanism of the present reductive decomposition of 1 involves attack by the metal compounds on the O-O bond close to the t-butyl group at the initial stage resulting in one-electron reduction to give intermediate 6, which is partly trapped by Co(salen)(NMeIm) but normally undergoes rapid β-scission.[6] The resulting peroxyquinolato complex intermediate 7, which is stabilized by Co(salpr) to some extent,[7] undergoes further reactions in the case with $VO(acac)_2$. Taking into account the 1 : 2 stoichiometry for the reductive decomposition of 1 with $VO(acac)_2$ acompanying the formation of t-butyl alcohol and anthraquinone (3) in catalytic reactions, the mechanism of the reaction of 1 with transition metal compounds shown in Table 1 may be rationalized by the diagram depicted in the following scheme.[8] When hydroperoxide 4[9] was reacted with an equimolar $VO(acac)_2$ in dichloromethane at room temperature, 2 and 3 were obtained in 30% and 55% yield, respectively,



whereas with two equivalents of $VO(acac)_2$ compound 2 was obtained quantitatively, supporting also the involvement of 7 in the mechanism shown in the scheme.

The reaction of 1 with $FeCl_3$(1 equiv.) in methanol at 50°C, on the other hand, gave 10-t-butyldioxy-10-methyl-9-anthrone (9) (8%), 10-methoxy-10-methyl-9-anthrone (10) (53%), and 9-t-butyl-9-methoxy-10-methylene-9,10-dihydroanthracene (11a) (20%) in addition to 2 (17%). Similar results were obtained with $CuCl_2$. These results are rationalized by assuming the homolysis of either O-O bond in 1: that is, 2, 9, and 10 would result from the homolysis of the O-O bond close to the t-butyl group, whereas 11a from that of the other O-O bond followed by deoxygenation, oxidation with the metal ion, hydrogen abstraction from methanol, and dehydration. Actually, the homolysis of 1 took place even only in methanol at 50°C to give 9 in 59% yield, and the acidic dehydration of 5 gave 11b in 88% yield.

$RuCl_2(PPh_3)_3$ and $Pd(PPh_3)_4$ are known to catalyze the cleavage of the O-O bond in 1,4-endoperoxides in a redox manner.[4] Interestingly, however, these complexes were not much effective for the decomposition of 1 (Table 1, Runs 14,15), indicating that the reactivity of endotrioxide 1 towards transition metal compounds is considerably different from that of endoperoxides.

References

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5) Analytical data were consistent with this complex being contaminated with about 5% of 2, which was detected by TLC, but attempts for purification of the complex by reprecipitation or recrystallization were unsuccessful.
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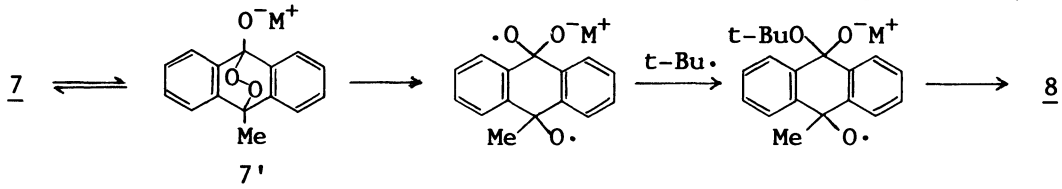
8) Peroxyquinolato Co^{III}(salpr) complexes of type 7 are normally stable and are not susceptible to direct one-electron reduction by Co^{II}(salpr).[7] Therefore, in order to elucidate the formation of 2 in the reaction of 1 with Co(salpr) as well as the results obtained in the reaction of 1 with $VO(acac)_2$, it may be reasonable to assume the intramolecular nucleophilic addition of the peroxy anion to the carbonyl group in 7 to form 7', which would undergo readily homolysis of the endoperoxy bond under the influence of the geminal oxy anion.[6]



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