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BASE-CATALYZED DECOMPOSITION OF 3,5-DI-t-BUTYL-4-HYDROXYBENZOIC ESTERS OF p-PEROXYQUINOLS DERIVED FROM 2,6-DI-t-BUTYLPHENOLS

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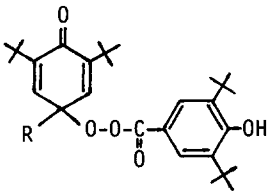
In a previous paper,[1] we reported a novel base-catalyzed rearrangement of p-peroxyquinol esters derived from 2,6-di-t-butylphenols leading to quinoxyacetic acid derivatives, where the peroxy bond cleaves even below -60 °C. Nature of the peroxy bond cleavage has been remained obscure. Leffler et al[2] have argued heteroltic cleavage of peroxy bond for the base-catalyzed decomposition of t-butyl 3,5-di-t-buytl-4-hydroxyperbenzoate. However, insufficient search for the fate of the t-butoxy moiety of the peroxy ester has made their argument uncertain. We have therefore investigated the base-catalyzed reaction of 1-alkyl-3,5-di-t-butyl-4-oxo-2,5-cyclohexadienyl 3,5-di-t-butyl-4-hydroxyperbenzoates (1) with the expectaion of easy finding of nature of the peroxy bond cleavage by seeking for the fate of quinoxy moiety in the peroxy esters. This will in turn give a significant clue to elucidate mechanism of the base-catalyzed rearrangement of the p-peroxyquinol esters as an analogous electronic system.

We now find that the peroxy esters 1 readily undergo homolysis of the peroxy bond by catalysis with t-BuOK in DMF even at -78 °C and that the resulting quinoxy radicals undergo intramolecular rearrangement with ring expansion.

The peroxy esters 1 were synthesized in good yield by the Schotten-Baumann acylation with 3,5-di-t-butyl-4-hydroxybenzoyl chloride[3] of 1-alkyl-3,5-di-t-butyl-4-oxo-2,5-cyclohexadienyl hydroperoxides which are easily obtained by the base-catalyzed oxygenation of 4-alkyl-2,6-di-t-butylphenols.[4] A solution of 1 (2 mmol) in a mixture of petroleum ether (12 ml) and benzene (3 ml) was added in 30 min to a stirred solution of t-BuOK (8 mmol) in DMF (20 ml) and petroleum ether (10 ml) at -78 °C under nitrogen atmosphere. After additional stirring at the same temperature for 30 min, the reaction mixture was acidified with cold dilute hydrochloric acid and extracted with ether. From the extract products 2 - 10 were isolated by silica gel colmn chromatography.[5] The results are given in Table. The structures of 2a and 3a are in good agreement with spectral and analytical data.[5]



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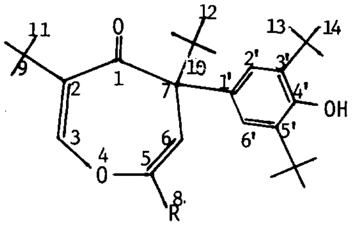

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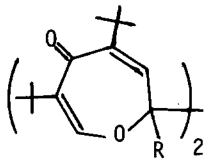

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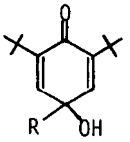
a; R = Me   c; R = i-Pr

b; R = Et   d; R = t-Bu



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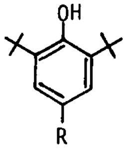

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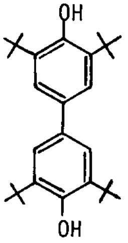

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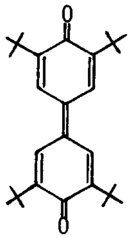

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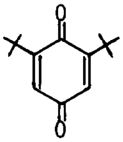

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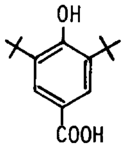

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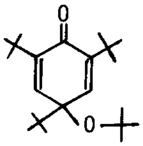

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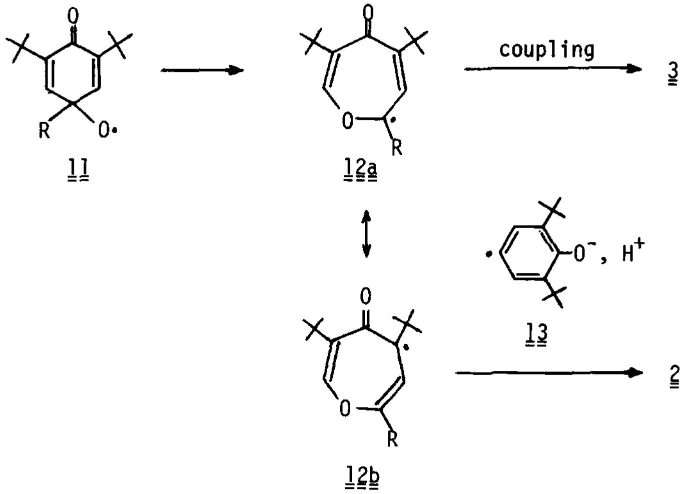
Table. The Base-Catalyzed Decomposition of 1

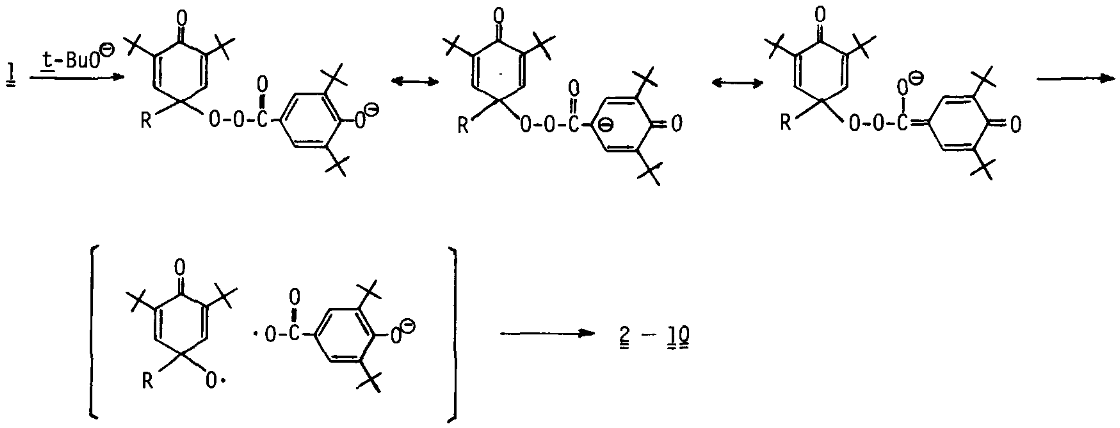
Substrate	Yield of Product (mol/mol of 1)[a]								
1	2	3	4	5	6	7	8	9	10
1a	46	22	3	0	5	7	4	24	-
1b	38[b]	20[b]	12	0	10	3	8	29	-
1c	0	0	10	9	16	3	80	52	-
1d	0	0	13	21	11	0	45	58	21

[a] Yields were determined by ^{1}HNMR. [b] Not isolated in pure form but clearly confirmed by the ^{1}HNMR of crude product.

Undoubtedly, the dimer 3 is the homo-coupling product of the ring expanded isomeric form (12a) of quinoxy radical (11). Similarly, the formation of 2 is reasonably interpreted by coupling between the other ring expanded radical(**12b**) and 3,5-di-t-butyl-4-hydroxyphenyl radical



(**13**) resulted from decarboxylation of carboxy radical of the ester moiety in **1**. Neither coupling product between **12a** and **13** nor **12b** itself was detected in the reaction mixture. In the cases of **1c** and **1d**, no such radical coupling products were obtained. Instead, **8** and **9** became the main products, indicating that quinoxy radicals **11c** and **11d** readily undergo β-scission and the carboxy radical is reduced under the reaction conditions. The formation of **5d** and **10** may be interpreted by coupling of t-butyl radical with **13** and **11d**, respectively. Since **1** exists as phenolate anion under the reaction conditions, all these findings strongly suggest that the peroxy bond of **1** is susceptible to homolysis even at -78 °C when the hydroxy group is dissociated to phenolate anion.



Direct interaction between the peroxy bond and t-BuOK leading to the cleavage of the peroxy bond is not the case.[1] Quinolate anions are not oxidized to the quinoxy radicals under the reaction conditions. Our present observations are contrary to the argument of Leffler et al.[2]

The extreme instability of the phenolate anion of **1** is due to the generation of carbanion adjacent to the carbonyl group through resonance structure, which is analogous to the case of the base-catalyzed rearrangement of *p*-peroxyquinol esters leading to quinoxyacetic acids.[1]

References and Notes

1) A. Nishinaga, K. Nakamura, and T. Matsuura, *Chem. Lett.*, 303 (1977).

2) A. M. Hucek, J. T. Barbas, and J. E. Leffler, *J. Am. Chem. Soc.*, **95**, 4698 (1973).

3) E. Muller, A. Rieker, R. Mayer, and K. Scheffler, *Justus Liebigs Ann. Chem.*, **645**, 36 (1961).

4) A. Nishinaga, T. Itahara, and T. Matsuura, *J. Am. Chem. Soc.*, **100**, 1820 (1978). **1a**: mp 126-128 °C; yield, 74%. **1b**: mp 118-120 °C; yield, 85%. **1c**: mp 101-103 °C; yield, 75%. **1d**: mp 101-103 °C; yield, 73%. All the products gave satisfactory elemental analyses (C ±0.25%, H ±0.26%).

5) Compounds **4** - **10** are known and were identical with authentic samples. **2a**: colorless needles, mp 141-143 °C; IR(Nujol) 3600(OH), 1690(CO) cm^{-1}; ^{1}HNMR($CDCl_3$) δ 1.04(s, 9H), 1.20(s, 9H), 1.44(s, 18H), 2.16(d, 3H, J=0.67 Hz), 5.17(s, 1H (OH)), 5.68(q, 1H, J=0.67 Hz), 7.94(s, 1H), 7.17(s, 2H); ^{13}CNMR($CDCl_3$) δ 204.6(C_1), 135.8(C_2), 170.3(C_3), 140.3(C_5), 121.9(C_6), 95.8(C_7), 18.3(C_8), 127.6(C_1'), 122.9(C_2',C_6'), 135.4(C_3',C_5'), 153.3(C_4'), 34.27(C_9), 40.1(C_{10}), 28.3(C_{11}), 24.5(C_{12}), 29.6(C_{13}), 30.2(C_{14}). Anal. Calcd for $C_{29}H_{44}O_3$: C, 79.04; H, 10.07. Found: C, 78.75; H, 10.03. The assignment of the ^{13}CNMR has been made by comparison of decoupled, off-resonance, and full coupled spectra with the analogous systems.[6,7] We thank Prof. A. Rieker and Dr. K. Albert, Tübingen University, for measurement of the ^{13}CNMR and for their helpful discussions.
3a: colorless needles, mp 230-232 °C(decomp.); m/e(M^+) 470; IR(Nujol) 1640, 1655(cross conjugated dienone) cm^{-1}; λ_{max}(CH_2Cl_2) 248, 292 (logε 3.90, 3.75); ^{1}HNMR($CDCl_3$) δ 1.20(s, 18H), 1.24(s, 18H), 1.54(s, 6H), 5.93(s, 2H), 6.79(s, 2H). Anal. Calcd for $C_{30}H_{46}O_4$: C, 76.55; H, 9.85. Found: C, 76.38; H, 10.15.

6) A. Nishinaga, T. Itahara, T. Matsuura, A. Rieker, D. Koch, K. Albert, and P. Hitchcock, *J. Am. Chem. Soc.*, **100**, 1826 (1978).

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