BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 47(3), 712—714 (1974)

Radical Addition Reactions to the Carbonyl Group. I. The Reaction of Aliphatic Aldehydes with Di-*t*-butyl Peroxide

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(Received September 22, 1973)

The thermal decomposition of di-*t*-butyl peroxide in aliphatic aldehydes has been carefully examined. *n*-Aldehydes and β-substituted aldehyde gave appreciable amounts of *sec*-alcohols in the reactions. *sec*-Alcohol arose from the addition of the alkyl radical to the carbonyl group of aldehyde. α-Substituted aldehydes, however, did not give *sec*-alcohol, but instead gave considerable amounts of enol ether-aldehydes and dialdehydes. The addition of the alkyl radical to the carbonyl group and the decarbonylation of aldehydes were influenced remarkably by the structures of the aldehydes.

The cleavage reaction of the *t*-alkoxy radical to form ketone and the alkyl radical has been extensively studied. The relative ease of the bond scission of the *t*-alkoxy radical has been determined quantitatively by various methods.[1] On the other hand, only a few studies have been reported on the addition of the alkyl radical to the carbonyl groups of aldehyde and ketone, which is considered to be the reverse of the well-known cleavage reaction of the *t*-alkoxy radical.[2] However, no quantitative investigation has been published.

In this work, the formation of *sec*-alcohols by the reaction of aliphatic aldehydes with di-*t*-butyl peroxide has been examined in order to ascertain the possibility of the radical addition reaction to carbonyl groups.

Results and Discussion

The thermal decomposition of di-*t*-butyl peroxide in *n*-aldehydes yielded considerable amounts of *sec*-alcohols, accompanied by paraffin hydrocarbons and carbon monoxide. The yields of the reaction products were determined by gas chromatography. The reproducibility of the experimental results was fairly good: same typical experimental results are summarized in Table 1. The *sec*-alcohols, obtained in *ca.* 8% yields based on the aldehydes consumed (Table 1), were isolated by distillation and were identified by a comparison of the retention times in gas chromatography, and by a comparison of the IR, NMR, and mass spectra, with those of authentic samples. The main products obtained from the reaction of *n*-aldehydes with di-*t*-butyl peroxide can be explained by the mechanism shown in Eqs. (1)—(6):[2a]

$$(CH_3)_3COOC(CH_3)_3 \longrightarrow 2(CH_3)_3CO\cdot \qquad (1)$$

$$(CH_3)_3CO\cdot + RCHO \longrightarrow (CH_3)_3COH + R\dot{C}O \qquad (2)$$

TABLE 1. TYPICAL EXPERIMENTAL RESULTS OBTAINED IN THE REACTION OF ALDEHYDES WITH DI-*t*-BUTYL PEROXIDE (REACTION TIME 6 hr)

	Aldehyde used						
	Heptanal	Octanal	Nonanal	Decanal	2-Ethyl-heptanal	2-Methyl-octanal	3-Ethyl-heptanal[a]
Reactants, m mol							
Aldehyde	87.5	87.5	87.3	87.3	87.3	87.3	87.3
Di-*t*-butyl peroxide	26.6	26.6	26.6	26.6	26.6	26.6	26.6
Products, m mol							
t-Butyl alcohol	2.8	7.5	6.8	6.4	8.1	10.6	4.0
Paraffin hydrocarbon	29.1	46.6	62.0	60.2	33.7	18.0	70.2
Di-*t*-butyl peroxide	25.3	23.2	22.4	22.2	22.0	21.4	24.0
Aldehyde	39.9	22.3	11.5	10.4	43.2	56.7	7.4
sec-Alcohol	1.8	2.6	2.9	3.4			1.5
Enol ether-aldehyde					1.0	1.7	
Dialdehyde					0.3	0.7	
Carbon monoxide	48.8	65.0	72.4	74.0	41.5	26.4	80.6
Conversion, %							
Aldehyde	54.4	74.5	86.8	88.1	50.5	35.0	91.5
Di-*t*-butyl peroxide	4.9	12.8	15.8	16.5	17.3	19.5	9.8
Product Yields, mol/100 mol of aldehyde consumed							
Paraffin hydrocarbon	61.2	71.5	81.8	78.3	76.5	58.9	88.0
sec-Alcohol	7.6	8.0	7.7	8.9			3.8
Enol ether-aldehyde					4.5	11.1	
Dialdehyde					1.4	4.6	
Carbon monoxide	102.0	99.7	95.5	96.3	94.0	86.3	101.0

a) Reaction was carried out in 4 hr.

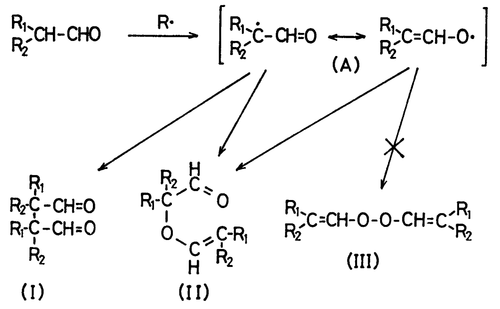
$$R\dot{C}O \longrightarrow R\cdot + CO \qquad (3)$$

$$R\cdot + RCHO \longrightarrow R_2CHO\cdot \qquad (4)$$

$$R\cdot + RCHO \longrightarrow RH + R\dot{C}O \qquad (5)$$

$$R_2CHO\cdot + RCHO \longrightarrow R_2CHOH + R\dot{C}O \qquad (6)$$

The main products—*t*-butyl alcohol, carbon monoxide, paraffin hydrocarbons, and *sec*-alcohols—are formed by Reactions 2, 3, 5, and 4—6 respectively. Reaction 4 implies the addition of the alkyl radical to the carbonyl group and is the reverse reaction of the decomposition of the *t*-alkoxy radical. Thus, the yield of *sec*-alcohol is a measure of the facility of the addition of the alkyl radical to the carbonyl group. β-Substituted aldehyde also yielded *sec*-alcohol, but its yield was considerably lower than those of *n*-aldehydes (Table 1). On the other hand, the reaction of α-substituted aldehydes with di-*t*-butyl peroxide led to the formation of enol ether-aldehydes and dialdehydes, much as in the oxidative coupling of α-substituted aldehydes by activated manganese dioxide.[3] In spite of our efforts, no *sec*-alcohol was detected in the products of these reactions. The formation of enol ether-aldehydes and dialdehydes may be explained by the following scheme:



α-Substituted aldehydes may suffer hydrogen abstraction on the α-carbon by a radical to a significant degree, thus giving the resonance-stabilized hybrid radicals (A). The hybrid radicals are considered to be fairly well stabilized by the hyperconjugation of two alkyl groups. However, with *n*-aldehydes and β-substituted aldehyde, an analogous conjugation would not be so important, because the radicals derived from α-hydrogen abstraction have only one alkyl group which contributes to such a stabilization. This would be the reason why the hybrid radical (A) plays an important role in the reaction of α-substituted aldehydes. Dialdehyde (I) and enol ether-aldehyde (II) can be produced through the dimerization of the radical (A). None of the other symmetrical coupling product, the divinyl peroxide (III), was found in the products. Moreover, 2-methyloctanal yielded quite large amounts of enol ether-aldehydes and dialdehyde compared with 2-ethylheptanal (Table 1). This can be explained by the greater capacity for the hyperconjugation effect of the methyl group, because it is well-known that this effect is much greater in the methyl group than in the ethyl group.[4] The lack of *sec*-alcohol may be interpreted in terms of steric factors. That is to say, the alkyl radicals derived from α-substituted aldehydes are *sec*-radicals, while the radicals from *n*-aldehydes and β-substituted aldehyde are prim-radicals. Thus, in adding to the carbonyl group, the radicals derived from α-substituted aldehydes are more sterically inhibited than those from *n*-aldehydes and β-substituted aldehyde. Similarly, the alkyl radical derived from β-substituted aldehyde is more sterically crowded than those from *n*-aldehydes. This would cause the lower yield of *sec*-alcohol in the reaction of β-substituted aldehyde (Table 1). As the other products, carbon monoxide was formed almost quantitatively except in the cases of α-substituted aldehydes, in which considerable amounts of enol ether-aldehydes and dialdehydes were formed: paraffin hydrocarbons were obtained in yields ranging from *ca.* 60 to 90%, depending on the structures of the aldehydes used. *t*-Butyl alcohol was obtained almost quantitatively with respect to the peroxide decomposed. Finally, in comparison with the rate of the decarbonylation of the three isomers of nonanal (Table 1), it was found that their rates were remarkably influenced by the structures of the aldehydes, decreasing in the following order: β-substituted aldehyde>*n*-aldehydes>α-substituted aldehydes. Therefore, the radical-induced decarbonylation of aliphatic aldehydes does not depend only on the structure of the attacking radical, but also on the structure of aldehydes.

Experimental

Materials. The heptanal, octanal, 2-ethylhexanal, nonanal, decanal, and di-*t*-butyl peroxide were all purchased from commercial sources. The 2-methyloctanal and 3-ethylheptanal were prepared by the Grignard procedure from the corresponding halides and ethyl orthoformate: 2-methyloctanal: bp 65—67 °C/18 mmHg; $n_D^{25.8}$ 1.4180: 3-ethylheptanal: bp 74—76 °C/18 mmHg; $n_D^{29.0}$ 1.4213. Their purities were confirmed by gas chromatography. The aldehydes were purified by vacuum distillation under nitrogen immediately before use.

Apparatus. The product analyses were performed by means of Yanagimoto Model GCG-220 and G-8 chromatographs equipped with thermal conductivity detectors. A Varian Model 920 aerograph was used in the preparations. The product identifications were carried out by a comparison of retention times in gas chromatography, and, if necessary, by a comparison of the IR spectra (Perkin-Elmer 521 spectrometer), the NMR spectra (Varian A-60 spectrometer), and the mass spectra (JMS-01SG spectrometer) of the products with those of authentic specimens.

Procedure. A three-necked reaction flask was equipped with a thermometer, a reflux condenser, and a gas inlet tube. The inlet tube was connected to a cylinder of nitrogen of 99.99 mol% purity. The reflux condenser was connected to a dry ice-acetone trap and then in turn to a water gas holder. A mixture of aldehyde and di-*t*-butyl peroxide was added to the reaction flask. The air in the reaction apparatus was then replaced by nitrogen prior to heating. The flask was heated to 120 °C in an oil bath. The reaction time was determined after the temperature of the oil bath had reached 120 °C. The gas liberated in the reaction was passed through the cold trap (−78 °C) and collected over water in the gas holder. The quantity of carbon monoxide was determined by means of the gaseous volume collected in the gas holder. At given time intervals, the oil bath was removed and the reaction flask was cooled by standing in air in order to quench the reaction. The reaction mixture in the flask and the volatile products found in the cold trap were then combined. The resultant mixture was analyzed quantitatively by gas chromatography, using a suitable substance as an internal standard. The analyses of the products were mainly carried out, for lower-boiling materials by the use of a Model GCG-220 gas chromatograph equipped with a column (2.5 m) packed with 25% of Squalane on Firebrick C-22, 60—80 mesh, at 80 and 140 °C: for higher-boiling materials, we used a Model G-8 gas chromatograph equipped with a column (0.75 m) packed with 5.0% of Silicone Gum SE-30 on Chromosorb W, 60—80 mesh, at temperatures from 100 to 160 °C.

Preparation of Enol Ether-aldehydes and Dialdehydes by the Oxidative Coupling of α-Substituted Aldehydes. As a typical example, the procedure for the oxidative coupling of 2-ethylhexanal will be described. Activated manganese dioxide was prepared by a modified Attenburrow procedure[5] and activated by the azeotropic distillation of the excess water with benzene.[6] 2-Ethylhexanal (18.0 g) was added under nitrogen to a stirred mixture of activated manganese dioxide (69.5 g) in dioxane (150 ml). Then, the resultant mixture was heated for 24 hours at the reflux temperature of dioxane. The reaction mixture was subsequently filtered, and the filtrate evaporated. The residue was vacuum distilled under nitrogen. 2-Ethyl-2-(2′-ethyl-1′-hexenyloxy)hexanal (enol ether-aldehyde) and 2,3-diethyl-2,3-dibutyl-succinaldehyde (dialdehyde) were obtained in yields of 31 and 21% respectively. Essentially the same results were obtained from 2-methyloctanal.

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