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Abstract

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SYNTHESIS OF ALKYLATED HYDROPEROXIDES OF THE 1,1-DIPHENYLETHANE SERIES USING A CHROMATOGRAPHIC METHOD FOR THEIR ISOLATION

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The chemistry of organic peroxide compounds has recently been enriched by many new hydroperoxides obtained by autoxidation of hydrocarbons of almost all series. As a result of a number of studies (1-3), certain regularities of the autoxidation process have also been established, namely, that peroxidation occurs predominantly at the site of the C—H bond, and that the reactivity of the latter increases both in the series primary, secondary, and tertiary C atom, and under the influence (through the α-carbon atom) of other structural factors: ether oxygen, benzene nucleus, double bond, system of double bonds, etc. In our previous works (4,5) it was found that the rate of thermal decomposition and the sympathetically changing initiating activity of hydroperoxides in the series: purely alkyl $(CH_3)_3COOH$, alkyl-aryl $C_6H_5(CH_3)_2COOH$, $(C_6H_5)_2CH_3COOH$, and purely aryl $(C_6H_5)_3COOH$—increase under the influence of phenyl radicals and reach optimal values for 1,1-diphenylethane hydroperoxide.

In connection with the above, it was of interest to determine the influence on the autoxidation process and on the properties of hydroperoxides of various alkyl radicals acting on the C—H bond and on the hydroperoxide group —OOH through the benzene nucleus. Thus, the task arose of synthesizing several hydroperoxides of the 1,1-diphenylethane series with introduction into one of the benzene nuclei, in the para position, of the following alkyl radicals: CH_3 (I), C_2H_5 (II), $CH(CH_3)_2$ (III), and $C(CH_3)_3$ (IV), as well as with n-C_3H_7 (V) at the central C atom (formulas are given below):

$$C_6H_5 - C(CH_3)(OOH) - C_6H_4Alk \qquad C_6H_5 - C(H)(C_3H_7)(OOH) - C_6H_5$$

The listed hydroperoxides were obtained by autoxidation of the corresponding hydrocarbons with the use of a chromatographic method for their isolation and purification, owing to the impossibility of applying distillation and crystallization.

Hydrocarbons: n-$CH_3C_6H_4CH(CH_3)C_6H_5$ (1), n-$C_2H_5C_6H_4CH(CH_3)C_6H_5$ (2), $n(CH_3)_2CHC_6H_4CH(CH_3)C_6H_5$ (3), and n-$(CH_3)_3CC_6H_4CH(CH_3)C_6H_5$ (4) were synthesized according to Kramer et al. (6) by condensation of styrene with the corresponding alkylbenzenes: toluene, ethylbenzene, isopropylbenzene, and tert-butylbenzene in the presence of sulfuric acid. The hydrocarbons were purified with concentrated sulfuric acid, 30% alkali, and water, and were distilled in vacuum. Of those not described in the literature, (2), (3), and (4), the last two, for purposes of verification, were also obtained by organomagnesium synthesis: (3) from n-bromocumene and acetophenone, with formation of phenyl-n-cumylphenylmethylcarbinol and its subsequent reduction to the hydrocarbon; the synthesis of (4) was described in the preceding paper (7). The hydrocarbon 1,1-diphenyl-n-butane for hydroperoxide V was obtained by a Grignard synthesis according to Klages and Hellmann (8) from propyl bromide and benzophenone via diphenylpropylcarbinol, followed by reduction. Table 1 gives data characterizing the synthesized hydrocarbons.

Table 1

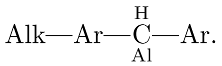
Hydrocarbons	B.p., °C (2–3 mm Hg)	d_4^{20}	n_D^{20}	MR found	MR calc.	C, % found	C, % calc.	H, % found	H, % calc.
1	115–116	0.9850	1.5660	64.77	64.27	–	–	–	–
2	118–119	0.9743	1.5610	68.89	69.89	91.06	91.38	8.78	8.63
3	137–139	0.964	1.5530	75.24	73.50	90.76	91.01	9.16	8.99
4	148–150	0.960	1.5508	78.88	78.12	84.82	84.99	8.70	8.72
5	86m.p. 27	–	–	–	–	–	–	–	–

Autoxidation of the hydrocarbons was carried out in a glass flask at a temperature of 80–82° in the presence of 0.1 N sodium hydroxide solution at a phase ratio of 1 : 1 and with bubbling of pure oxygen at 6–8 ml/min. The rate and level of accumulation of hydroperoxide (HP) are characterized by the data given in Table 2.

Table 2

Hydrocarbons	Sample 1 duration, h	Sample 1 HP, %	Sample 1 accumulation rate, %/h	Sample 2 duration, h	Sample 2 HP, %	Sample 2 accumulation rate, %/h	Sample 3 duration, h	Sample 3 HP, %	Sample 3 accumulation rate, %/h	Sample 4 duration, h	Sample 4 HP, %	Sample 4 accumulation rate, %/h
1	24	3.56	0.15	48	11.84	0.36	67	16.17	0.23	96	25.0	0.30
2	24	4.6	0.19	48	13.0	0.36	72	20.5	0.31	–	–	–
3	46	3.6	0.08	88	15.5	0.30	158	44.4	0.41	222	53.4	0.14
4	48	5.2	0.11	96	23.0	0.16	165	42.2	0.28	214	53.3	0.23
5	48	7.0	0.15	72	12.7	0.24	120	15.0	0.05	–	–	–

From the results obtained it is seen that, under these conditions, the autoxidation of the hydrocarbons proceeds at approximately the same rate, namely, at a maximum formation rate of 0.25-0.35% hydroperoxide per hour. These observations are consistent with the uniformity of the structure (I) of the hydrocarbons studied:



$$\mathrm{Alk{-}Ar{-}}\overset{\mathrm{H}}{\underset{\mathrm{Al}}{\mathrm{C}}}\mathrm{{-}Ar.}$$

It follows from these results that the nature of the alkyls introduced into the para position in one of the benzene rings does not substantially affect the process of peroxidation at the site of the tertiary C—H bond. The only peculiarity is that, during the autoxidation of hydrocarbons 3-4, a longer induction period is observed, which is apparently connected with purification rather than with the structure of these hydrocarbons. Hydrocarbon 5 behaves differently: in its autoxidation, the accumulation of hydroperoxide can be brought only to 14-15%, since on further oxidation it undergoes almost complete decomposition. Evidently the lowering of the thermal stability of the hydroperoxide is associated with lengthening of the aliphatic chain at the tertiary carbon atom.

From the oxidized hydrocarbons the hydroperoxides were isolated and purified by a chromatographic method (7); alumina of reduced activity (between groups II and III according to Brockmann) was used as the adsorbent, and petroleum ether (35-70°) and desorbent was diethyl ether. The oxidized hydrocarbons were first washed with 5% caustic soda solution and with water, and dried in vacuo until clarified. The oxidized purified hydrocarbon was then diluted with petroleum ether to a hydroperoxide content of 5-6% and passed through a chromatographic column at a rate of 0.30-0.35 ml/min until saturation (monitoring was carried out by the iodometric method). After washing with pure solvent, the hydroperoxides were desorbed with diethyl ether; after distilling off the latter, 97-98% hydroperoxides were obtained, and after repeated passage through the column, pure hydroperoxides. Table 3 gives data characterizing the newly obtained hydroperoxides.

Table 3

Hydroperoxides	M.p., °C	d_4^{20}	n_D^{20}	MR found	MR calc.	C, % found	C, % calc.	H, % found	H, % calc.	O_2, % found	O_2, % calc.
I	Liquid	1.123	1.5820	67.80	67.98*	78.82	78.91	7.38	7.09	7.01	7.01
II	Liquid	1.101	1.5755	72.82	72.60	79.10	79.31	7.68	7.46	6.63	6.61
III	Liquid	1.079	1.5670	77.41	77.22	79.63	79.15	7.92	7.86	6.24	6.24
IV	47	–	–	–	–	80.38	79.96	8.15	8.20	5.91	5.92
V	39	–	–	–	–	79.25	79.33	7.50	7.43	6.60	6.61

* The increment for the peroxide group —OO—is 3.715 ([1,9]).

The hydroperoxides obtained were also characterized by chemical methods from their decomposition products. On decomposition of (I) over highly active alumina, acetophenone was obtained (semicarbazone, m.p. 195.5°) and *p*-cresol (bromo derivative, m.p. 48–49°). On decomposition of (II) according to Kharasch ([10]) in glacial acetic acid in the presence of hydrochloric acid, acetophenone and *p*-ethylphenol (m.p. 44–47°) were obtained. Decomposition of (III) over active alumina gave acetophenone and *p*-isopropylphenol. Reduction of (IV) with potassium iodide in glacial acetic acid gave the corresponding carbinol (m.p. 86°), through which the starting hydrocarbon was obtained by organomagnesium synthesis. Decomposition of (IV) over alumina gave acetophenone and *p*-tert-butylphenol (bromo derivative, m.p. 49–50°). Reduction under the same conditions of (V) gave the carbinol (m.p. 65°, as for the starting compound). It is of interest that on decomposition of (V) over active alumina, phenol is not formed at all, and the hydroperoxide decomposes completely to benzophenone.

The data obtained lead to the conclusion that the peroxide compounds synthesized by us are tertiary hydroperoxides, whose structure is expressed by the formulas given above, and they may be named as follows. I: 1-phenyl-1-*p*-tolylethane hydroperoxide-1; II: 1-phenyl-1-*p*-ethylphenylethane hydroperoxide-1; III: 1-phenyl-1-*p*-cumylethane hydroperoxide-1; IV: 1-phenyl-1-4-tert-butylphenylethane hydroperoxide-1; V: 1,1-diphenyl-*n*-butane hydroperoxide-1.

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