FREE RADICALS IN THE PERIMIDINE SERIES.
2-TERT-BUTYLPERIMIDYL RADICALS

V. Kh. Sabanov, E. S. Klimov, I. V. Bogdanova
E. P. Trub, N. T. Berberova, and O. Yu. Okhlobistin

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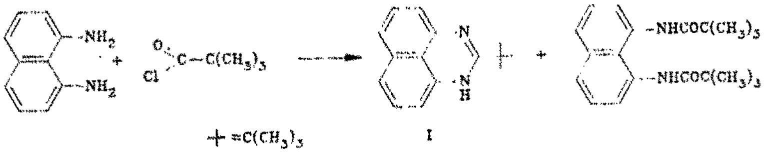
Electrochemical and EPR methods have been applied to a study of perimidyl free radicals containing a bulky tert-butyl substituent in the 2-position. A stepwise mechanism is proposed for the dehydrogenation of 1,3-dimethyl-2-tert-butyl-2,3-dihydroperimidine; the mechanism involves formation of a cation-radical from the substrate in the first step. Shielding of the nitrogen atoms seems to be an important factor in increasing the stability of free perimidyl radicals.

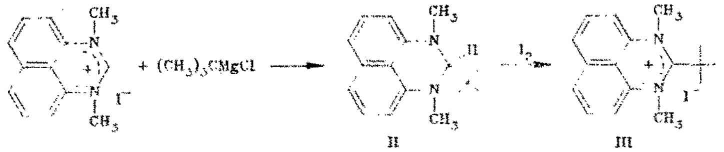
The anion-radical of 1-methylperimidine is a known derivative in the perimidine series [1]. Several perimidines have been studied in the crystalline state by EPR and have given EPR signals of ∿7 Oe width [2].

Reduction of heteroaromatic cations which are not sterically hindered generally leads to rapid dimerization of the intermediate free radicals which are formed (cf. [3]). For this reason, it was of interest to us to study perimidines containing tert-butyl groups, which block the potential reactive site, in the 2-position.

2-tert-Butylperimidine (I) was prepared from 1,8-diaminonaphthalene and trimethylacetyl chloride in 74% yield; 1,8-di(pivaloylamino)naphthalene was obtained as a side product in 14% yield:



Reaction of tert-butylmagnesium chloride with 1,3-dimethylperimidinium iodide gave 1,3-dimethyl-2-tert-butyl-2,3-dihydroperimidine (II), which was further reacted to give 1,3-dimethyl-2-tert-butylperimidinium iodide (III):



Assuming that dehydrogenation of the 2H-perimidine II can not take place via a synchronous mechanism, i.e., by a one-event transfer (cf. [4]), we have studied the electrochemical oxidation of II and have also attempted to isolate and identify its corresponding cation radical, formed during chemical oxidation, by EPR, as has been done previously in the case of 4H-pyrans [5, 6].

Two oxidation waves were obtained during the oxidation of dihydroperimidine II on a stationary platinum electrode in anhydrous dimethylformamide.

Scientific-Research Institute of the Chemistry of Free Radicals, K. L. Khetagurov Severo-Osetinsk University, Ordzhonikidze 362040. Scientific-Research Institute of Physical and Organic Chemistry, M. A. Suslov Rostov University, Rostov-Don 344090. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 970-972, July, 1986. Original article submitted March 3, 1985. Revised article submitted June 17, 1985.

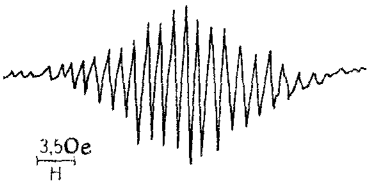
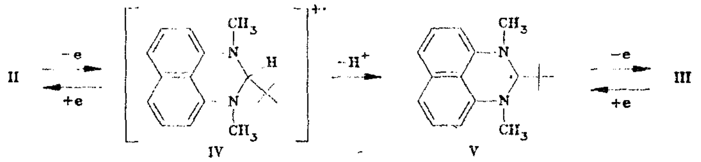


Fig. 1. EPR spectrum of 1,3-dimethyl-2-tert-butyl-perimidyl radical in DMF at 25°C.

The first wave is a one-electron wave which is partially reversible (E_{pa} = 0.73 V) relative to silver chloride electrode ($\alpha = 0.67$), and corresponds to formation of the unstable cation-radical IV. Its subsequent fragmentation can be followed by cyclic voltemmetry: it loses a proton and generates the cation III, which was identified by addition of an authentic sample ($-E_{pa}$ = 1.72 V). Electrochemical dehydrogenation of II apparently proceeds according to the scheme -e, $-H^+$, -e:



The second irreversible, two-electron wave which is observed during oxidation of compound II is probably due to decomposition of the molecule (E_{pa} = 1.32 V).

The cation radical IV could also be formed during chemical oxidation of dihydroperimidine II with aluminum chloride in nitrobenzene; in this case an unresolved singlet of width ΔH = 30 Oe was detected by EPR. Reduction of the cation III with zinc metal in DMF or oxidation of the dihydroperimidine II with silver oxide in the same solvent both led to the same perimidyl free radical, namely V; its spectrum is shown in Fig. 1. Analysis of the hyperfine structure of this spectrum yielded the following values of the hyperfine splitting constants: $a_N^{1,3} = a_H^{1,3\text{-}CH_3}$ = 4.2 Oe; a_H = 1.4 Oe (for the proton in the naphthyl fragment).

Oxidation of dihydroperimidine II with 3,5-di-tert-butyl-1,2-benzoquinone did not permit us to trap either the cation radical stage IV or the free radical V, although even in this circumstance the presence of one-electron transfer was established without doubt by the observation of the EPR signal for the well-known o-semiquinolate radical [7], (doublet, a_H = 2.5 Oe).

Oxidation of perimidine I with lead dioxide in benzene gave rise to a signal for the unstable 2-tert-butylperimidyl radical, whose spectrum was interpreted in a manner similar to that described above: $a_N^{1,3}$ = 4.2 Oe; a_H = 1.4 Oe (for the naphthyl fragment proton). Electrochemical oxidation of perimidine I occurred as a one-electron, incompletely reversible wave, E_{pa} = 0.64 V; decomposition of the molecule was observed beginning at a potential of E_{pa} = 1.24 V.

The relatively low stability of the 2-tert-butylperimidyl radical is probably related to the relatively high spin density on the unhindered nitrogen atom.

EXPERIMENTAL

EPR spectra were recorded on a modified RE-1301 radiospectrometer under vacuum ($5 \cdot 10^{-4}$ mm); PMR spectra were obtained on a Tesla BS-487-C spectrometer (80 MHz) versus HMDS is internal standard. Electrochemical experiments were carried out on a P-5827-M potentiostat with a trigonal impulse generator [8] in a three-electrode cell. The anode consisted of a Pt needle, with auxiliary Pt spiral electrode, and a silver chloride reference electrode separated by a waterproof membrane. DMF was used as solvent and was purified according to a general procedure [9]; 0.1 M lithium perchlorate was used as background electrolyte and the working depolarizer concentration was $5 \cdot 10^{-3}$ mole/liter.

2-tert-Butylperimidine (I) and 1,8-Di(pivaloylamino)naphthalene. A solution of 8 g (50 mmole) of 1,8-diaminonaphthalene in 50 ml of benzene was treated with stirring with 8.5 g (70 mmole) of trimethylacetyl chloride; a colorless, voluminous precipitate was obtained. The mixture was heated on a water bath for 0.5 h with continued stirring; the residue remaining after removal of the benzene was worked up with 100 ml of boiling water. The aqueous solution was filtered to remove insoluble material, cooled, and neutralized with 25% aqueous ammonia to pH 8. The resulting precipitate was recrystallized from toluene. Yield of compound I, 8.2 g (74%); coarse yellow-green crystals, mp 155°C. IR spectrum: 3400 cm^{-1} (NH). PMR spectrum (in DMSO-D_6): 1.28 t (t-C_4H_9), 5.28 (NH), 8.62 ppm (H_{arom}). Found: C 80.2; H 7.3; N 12.2%. $C_{15}H_{16}N_2$. Calcd.: C 80.3; H 7.1; N 12.5%.

The solid which was not soluble in water was recrystallized from toluene. Yield of 1,8-di(pivaloylamino)naphthalene, 1.2 g (14%); colorless needles, mp 274°C. IR spectrum (vaseline mull): 3300, 3370 (NH), 550, 1670 cm^{-1} (amide group). Found: C 73.2; H 8.1; N 8.4%. $C_{20}H_{26}N_2O_2$. Calcd.: C 73.6; H 8.0; N 8.6%.

1,3-dimethyl-2-tert-butyl-2,3-dihydroperimidine (II). An ethereal solution of tert-butylmagnesium chloride (40 mmole) was treated with stirring with 6.48 g (20 mmole) of powdered 1,3-dimethylperimidinium iodide [10]. The mixture was stirred under reflux until it was completely decolorized (2 h), and was then decomposed by the addition of saturated ammonium chloride solution; the ether extracts were dried over sodium sulfate. Yield of compound II, 4.8 g (94%); colorless crystals, mp 144°C (from ethanol). PMR spectrum (in acetone-D_2): 1.25 (t-C_4H_9), 2.95 (CH_3), 6.52, 7.12 ppm (H_{arom}). Found: C 80.2; H 8.5; N 11.1%. $C_{17}H_{22}N_2$. Calcd.: C 80.3; H 8.7; N 11.0%.

1,3-Dimethyl-2-tert-butylperimidinium Iodide (III). A mixture of 2.5 g (10 mmole) of dihydroperimidine II in 20 ml of ethanol was treated with a solution of 2.5 g of I_2 in 20 ml of ethanol. After 10 min the mixture was worked up with $Na_2S_2O_5$ and the precipitate was recrystallized from water to give yellow crystals, mp 259-260°C, with a yield of 3.5 g (92%). PMR spectrum (in acetone-D_6): 1.26 (t-C_4H_9), 3.52 (CH_3), 7.2, 7.60 ppm (H_{arom}). Found: C 53.4; H 5.6; N 7.5, I 33.5%. $C_{17}H_{22}IN_2$. Calcd.: C 53.6; H 5.5; N 7.3; I 33.4%.

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