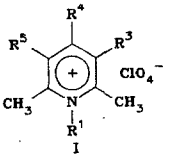
ELECTROCHEMICAL PREPARATION OF PYRIDINYL RADICALS, SUBSTITUTED BY ELECTRON ACCEPTORS IN THE β-POSITION

R. A. Gavar, L. Kh. Baumane, Ya. P. Stradyn', V. K. Lusis, G. Ya. Dubur, and D. Kh. Mutsenietse

UDC 547.821.3:541.515'138.3:543:422.27

In the electrochemical oxidation of 1,2-dihydropyridines, containing electron-acceptor substituents in positions 3 and 5, we have obtained relatively stable cation-radicals which deprotonated and transformed into pyridinyl radicals [1]. However, under the conditions of electrochemical generation at positive potentials the latter rapidly undergo further electrooxidation; as a result of this, the EPR spectra cannot be recorded. For the preparation and study of pyridinyl radicals we have therefore used the opposite processes: electroreduction in aprotic solvents (dimethylformamide, acetonitrile) of the corresponding pyridinium salts of type I:



I

$R^1 = CH_3$, p-$CH_3C_6H_4$, C_6H_5; $R^3 = R^5 = COOC_2H_5$, $COCH_3$, CN; $R^4 = H$, CH_3, C_6H_5, p-$CH_3C_6H_4$

The first stage of the polarographic reduction of these compounds ($E_{1/2}$ in the interval from −0.6 to −1.1 V against the saturated calomel electrode) is a one-electron process. The reduction potentials as function of the nature of the substituents and their position in the pyridinium ring are given by the equations

$$E_{1/2} = 0.82\sigma^+_p(R^4) - 0.93 \text{ (B)}, \quad r = 0.999;$$
$$E_{1/2} = 1.11 \cdot 2\sigma_m(R^{3,5}) - 1.85 \text{ (B)}, \quad r = 0.993.$$

Cyclic voltammetry on a mercury drop or on a graphite electrode showed that the reversibility of this one-electron process also depends on the nature of the substituent and the place of substitution by decreasing when the substituents R^1, R^3 (R^5), and R^4 decrease in the following order:

$$p\text{-}CH_3C_6H_4 \approx C_6H_5 \gg CH_3 \quad (\text{for } R^1);$$
$$C_6H_5 \approx CH_3 \approx H \quad (\text{for } R^4);$$
$$COCH_3 > COOC_2H_5 > CN \quad (\text{for } R^3, R^5).$$

Electrochemical generation [2] at the potentials of the first polarographic wave leads to the formation of pyridinyl radicals which are sufficiently stable for recording by EPR. The stability of these radicals is due to the reversibility of the primary one-electron process of electroreduction of the initial compounds. The EPR spectra of the pyridinyl radicals have a complex hyperfine structure (HFS) which is difficult to interpret. For instance, the HFS constants for the pyridinyl radical with the substituents $R^1 = R^4 = C_6H_5$, $R^{3,5} = COOC_2H_5$ have the following values (mT):

$$a_N = a_{6\text{-}H} = 0.50 \pm 0.02; \quad a_{II} = 0.33 \pm 0.01; \quad a_{2\text{-}H} = 0.315 \pm 0.005;$$
$$a_H = 0.145 \pm 0.005; \quad a_{2\text{-}H'} = 0.074 \pm 0.005; \quad a_{2\text{-}H} = 0.04 \pm 0.01.$$

Thus, at room temperature relatively stable pyridinyl radicals have been recorded, in which the electron-acceptor substituent is not in the position 4 (in conjugation with the nitrogen atom), but in the positions 3 and 5 of the pyridinium ring.

Institute of Organic Synthesis, Academy of Sciences of the Latvian SSR, Riga. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 5, pp. 708-709, May, 1986. Original article submitted November 13, 1985.

0009-3122/86/2205-0581$12.50

LITERATURE CITED

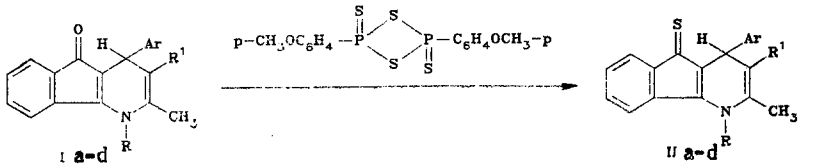
1. Ya. V. Ogle, L. Kh. Baumane, R. A. Gavar, V. P. Kadysh, Ya. P. Stradyn', V. K. Lusis, D. Kh. Mutsenietse, and G. Ya. Dubur, Khim. Geterotsikl. Soedin., No. 5, 651 (1984).
2. Ya. P. Straydyn', R. A. Gavar, and L. Kh. Baumane, Izv. Akad. Nauk LatvSSR, No. 2, 73 (1986).

SYNTHESIS OF 4-ARYL-5-THIOXO-4,5-DIHYDROINDENO[1,2-b]PYRIDINES

V. K. Lusis, D. Kh. Mutsenietse, and G. Ya. Dubur

UDC 547.836'665.07

We have found that 4-aryl-5-oxo-4,5-dihydroindeno[1,2-b]pyridines Ia-d react easily with Lawessons's reagent (dimeric sulfide of p-methoxyphenylthionophosphine) to form the hitherto unknown 5-thioxo-derivatives IIa-d; they are not accessible via cyclocondensation [1] since the corresponding thioketones of the indane series are not known so far.



I, II a—c R=H, d R=CH_3; **a**, b, d R'=$COOC_2H_5$, c R'=CN; **a**, c, d Ar=C_6H_5, b Ar=$C_6H_4NO_2$-4

5 mmoles of ketone I and 1.01 g (2.5 mmoles) of Lawesson's reagent are refluxed in 250 ml dry benzene for 15-20 min (Ic for 40 min). The solvent is evaporated and the thioketones II isolated by preparative TLC (L 40/100 silica gel, eluent chloroform—hexane—acetone 9:7:1) or column chromatography [2] (L 100/160 silica gel, eluent first benzene then benzene—acetonitrile 10:1). All compounds obtained are dark blue crystalline substances which absorb in the visible region of the spectrum around 370 and 580 nm.

2-Methyl-3-ethoxycarbonyl-4-phenyl-5-thioxo-1H-4,5-dihydroindeno[1,2-b]pyridine (IIa). Yield 55%, mp 158-160° (from ethanol); IR spectrum (nujol): 3295 (NH), 1680 (C=O), 1218 cm^{-1} (C=S). PMR spectrum ($CDCl_3$): 5.11 (s, 1H, 4-H), 6.77 ppm (s, 1H, NH). ^{13}C NMR spectrum (DMSO): 167.9 (C=O), 217.1 ppm (C=S). Mass spectrum: M^+ 361.1139. $C_{22}H_{19}NO_2S$. Calculated: M 361.1136.

In the same way were prepared the thioketones IIb (mp 171-173° from ethanol), IIc (mp 182-184° from chloroform, CN 2203 cm^{-1}), and IId (mp 145° from ethanol; signal of the N—CH_3 group in the PMR spectrum ($CDCl_3$) at 373 ppm).

LITERATURE CITED

1. V. Petrow, J. Saper, and B. Sturgeon, J. Chem. Soc., No. 9, 2134 (1949).
2. B. S. Pedersen, S. Scheibye, N. H. Nilsson, and S. O. Lawesson, Bull. Soc. Chim. Belges, 87, 223 (1978).

Institute of Organic Synthesis, Academy of Sciences of the Latvian SSR, Riga. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 5, p. 709, May, 1986. Original article submitted November 1, 1985.

0009-3122/86/2205-0582$12.50