radical adducts with the above trap under experimental conditions.[12,13]

References

1. R. W. Murray, *Chem. Rev.*, 1989, **89**, 1187.
2. W. Adam, Y. Chan, D. Cremer, J. Gauss, D. C. Scheutzow, and M. Schindler, *J. Org. Chem.*, 1987, **52**, 2800.
3. W. Adam, R. Curci, and J. O. Edwards, *Acc. Chem. Res.*, 1989, **22**, 205.
4. J. C. Stowell, *J. Org. Chem.*, 1975, **36**, 3055.
5. V. E. Zubarev, *Metod spinovykh lovushek* [*The Spin Traps Method*], Izd-vo MGU, Moscow, 1984, 29 pp. (in Russian).
6. E. Niki, S. Yokoi, J. Tsuchiya, and Y. Kamiya, *J. Am. Chem. Soc.*, 1983, **105**, 1498.
7. M. Singh and R. W. Murray, *J. Org. Chem.*, 1992, **57**, 4263.
8. P. Neta, R. E. Hull, and A. B. Ross, *J. Phys. Chem. Ref. Data*, 1990, **19**, 423.
9. V. A. Roginskii, *Fenol'nye antioksidanty* [*Phenolic Antioxidants*], Nauka, Moscow, 1988, 68 pp. (in Russian).
10. B. Plesnicar, F. Kovac, and M. Schara, *J. Am. Chem. Soc.*, 1988, **110**, 214.
11. W. A. Pryor, D. G. Prier, and D. F. Church, *J. Am. Chem. Soc.*, 1983, **105**, 2883.
12. J. Pfab, *Tetrahedron Lett.*, 1978, **9**, 843.
13. V. E. Zubarev, V. N. Belevskii, and L. T. Bugaenko, *Usp. Khim.*, 1979, **48**, 1365 [*Russ. Chem. Rev.*, 1979, **48** (Engl. Transl.)].

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O,N-Dimethylation of 5,6-dihydroxynicotinic acid

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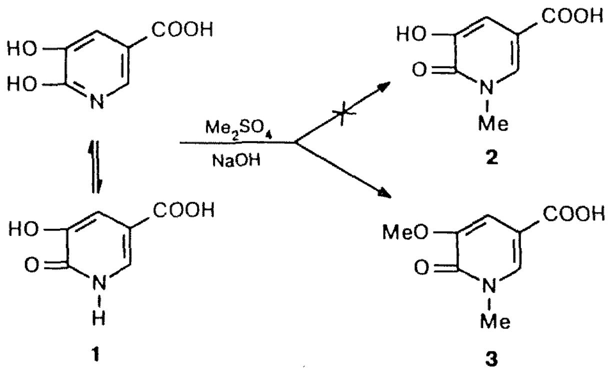
An *O,N*-dialkylation product, 1-methyl-5-methoxy-6-oxo-1,6-dihydropyridine-3 carboxylic acid, is formed in the reaction of 5,6-dihydroxynicotinic acid with dimethylsulfate.

Key words: 5,6-dihydroxynicotinic acid, dimethyl sulfate, *O,N*-dialkylation.

Studies of the alkylation of 3-hydroxypyridine derivatives containing functional groups are not only of theoretical interest, but are also of practical interest. *O*- or *N*-alkylation of 3-hydroxypyridine is known to be possible, depending on the reaction conditions and the type of alkylating agent.[1] Thus, the *N*-alkylation of non-substituted 3-hydroxypyridine occurs if dimethyl sulfate is used,[2] while 3-methoxypyridine is formed in the reaction with diazomethane.[3] Only *N*-methylation[4] occurs in the reaction of 5-hydroxynicotinic acid and its methyl ether with dimethylsulfate. Alkylation of 4,5-dihydroxypicolinic acid and 3,4-dihydroxy-6-methylpyridine with dimethyl sulfate in a basic medium results in the formation of an *O,N*-dimethyl derivative.[5] Taking into account the above data, one could expect either a product of monoalkylation at the N atom (**2**) or an *O,N*-dialkyl derivative (**3**) produced in the reaction of 5,6-dihydroxynicotinic acid (**1**) with Me_2SO_4.



Alkylation **1** with dimethyl sulfate in a basic medium was performed following the known procedure.[4] It was established that *O,N*-methylation with the formation of compound **3** proceeds under these conditions. The structure of **3** was confirmed by mass spectrometry and NMR spectroscopy.

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The mass spectrum (EI) of compound 3 contains a molecular ion peak with m/z = 183 (100 %). Its ^{1}H NMR spectrum contains two doublets of aromatic H(2) (δ 8.08) and H(4) (δ 7.07, $J_{2,4}$ = 2.1 Hz) protons along with two singlets at δ 3.74 and 3.51, which were assigned to MeO and MeN protons, respectively. More detailed information on the structure of compound 3 is obtained from the ^{13}C NMR spectrum, where the line assignments were based on the chemical shifts[6,7] and $J_{\mathrm{C,H}}$[8] values for related compounds. The MeN signal is observed at δ 38.20. In this case the quartet components (^1J = 141.6 Hz) are additionally split into doublets due to interaction with the H(2) proton (^3J = 3.7 Hz). MeO gives a quartet with δ 56.61 (^1J = 145.3 Hz). A MeO group in position 5 is characterized by the quartet splitting of the doublet components of the C(5) signal registered at δ 148.89 as a quintet because of equal ^3J and ^2J constants (3.7 Hz). The protons of the MeN group cause additional quartet splitting of the doublet-doublet components of the C(2) signal (δ 136.72, ^3J = 3.7 Hz); the doublet components (^1J = 187.8 Hz) manifest themselves as quintets because of equal ^3J constants (3.7 Hz).

Experimental

The mass spectrum (EI, 70 eV) was recorded on an MKh-1321A spectrometer by the direct inlet of the sample into the ionization chamber of the evaporator (100 °C). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker WH-90 (90 MHz and 22.62 MHz, respectively) spectrometer in DMSO-d_6 at 40 °C. Concentrations of substances in solutions were 2 % and 10 %, respectively. Chemical shifts (δ) were measured relative to $SiMe_4$ (^{1}H) and ane (^{13}C).

1-Methyl-5-methoxy-6-oxo-1,6-dihydro-3-pyridine carboxylic acid (3). Me_2SO_4 (2 g, 15.9 mmol) was added portionwise to a solution of acid **1** (0.5 g, 3.2 mmol) in 10% aqueous NaOH (5 mL). The mixture was stirred for 3 h at ~20 °C, the excess Me_2SO_4 was extracted with ether, and the water layer was neutralized with dilute H_2SO_4 to pH 4. The precipitate that formed upon cooling was filtered off, dried, and recrystallized from water with the addition of carbon. Compound **3** (0.23 g, 39 %) was obtained; m.p. 257—258 °C. Found (%): C, 52.61; H, 4.95; N, 7.72. $C_8H_9NO_4$. Calculated (%): C, 52.50; H, 4.91; N, 7.65.

References

1. R. A. Abramovitch, *Pyridine and its Derivatives*, 1974, Pt. III, 745.
2. S. L. Shapiro, K. Weinberg, and L. Freedman, *J. Am. Chem. Soc.*, 1959, **81**, 5140.
3. D. A. Prins, *Rec. Trav. Chim. Pays-Bas*, 1957, **76**, 58.
4. M. Kawazu, T. Kauno, S. Saito and H. Tomaki, *J. Med. Chem.*, 1972, **15**, 914.
5. US pat. 2.212, Swiss pat. 212.521: *Chem. Abstrs.*, 1941, **35**, 4665.
6. E. Breitmaier and W. Voelter, *^{13}C NMR Spectroscopy*, Verlag Chemie, Weinheim—New York, 1978, 200.
7. E. Breitmaier, G. Haas, and W. Voelter, *Atlas of Carbon-13 NMR Data*, Heyden, 1979, **2**, 2364, 2365, 2367.
8. E. Breitmaier and W. Voelter, *^{13}C NMR Spectroscopy*, Verlag Chemie, Weinheim—New York, 1978, Chap. 3.2.2.

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Formation of azulene and naphthalene from piperylene

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Piperylene mixed with air is converted into a mixture of aromatics containing azulene and naphthalene on contact with bismuth oxide at ~600 °C. The yield of azulene and naphthalene is 6—8 %. The reaction is accompanied by burning of some of the piperylene and by the reduction of Bi_2O_3 to Bi metal. When the initial mixture is diluted with steam no reduction occurs. The reaction is believed to involve elimination of the allylic hydrogen, formation of dienyl radicals, their dimerization, and subsequent aromatization.

Key words: azulene, naphthalene, piperylene, dehydrodimerization.

It has been reported previously[1] that in the presence of some dehydrogenation catalysts, piperylene is converted into azulene (0.2—0.5 %) and naphthalene (0.3—0.7 %). Since the yields of these products from 1-decene are markedly higher, we suggested that the transformation of piperylene into them occurs *via* a linear interme-

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