Materials of Conference

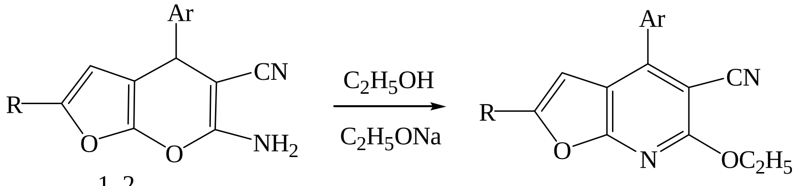
RECYCLIZATION OF 6-AMINO-5-CARBONITRILEFUROPYRANES UNDER THE ACTION OF NUCLEOPHILS

Anis'kova T.V., Timofeyeva Z.Yu., Yegorova A.Yu.
Saratov State University named after N.G. Chernyshevsky
Saratov, Russia

6-Amino-4-aryl-2R-4H-furo[2,3-b]pyrane-5-carbonitriles are an important class of heterocyclic compounds of significant interest owing to their various chemical transformations and many opportunities of practical application (1, 2). These bifunctional compounds with cyano and amino groups in the vicinal position are promising initial substances for synthesis of sophisticated annealed heterocyclic systems.

The synthesis of the said compounds is based on Michael's condensation of 5-aryl-3-arylmethylene-3H-furan-2-ones with malonic acid dinitrile under basic catalysis /1/.

The behavior of furopyranes 1, 2 under the action of a strong nucleophilic reagent (sodium alcoholate) was studied. The reaction was carried out at heating of equimolar amounts of sodium alcoholate and furopyranes in an ethanol solution during 4 hr.

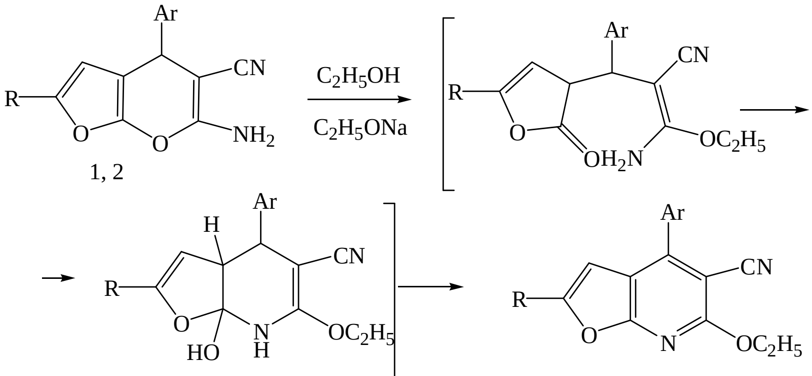


1,3 R=C_6H_5, Ar =C_6H_4-Cl-2; **2, 4** R=C_6H_4-CH_3-3, Ar =C_6H_4-Cl-2;

The reaction products were identified as 4-aryl-6-ethoxy-2R-furo [2,3-b] pyridine - 5-carbonitriles (3, 4) by their physicochemical and spectral characteristics.

The IR spectra of compounds 3, 4 contain the absorption bands of a cyano group (2215-2210 cm^{-1}), the absorption band of a -C-O-C- bond within 1130-1120 cm^{-1}, and no amino group absorption band. In the NMR^{1}H spectrum a series of signals in a strong field is observed within 1.40-1.45 ppm and 3.90-4.00 ppm, corresponding to the protons of an ester fragment, the singlet of a furan ring proton is shown at 6.3-6.4 ppm, the signal of the methyl group protons of the aromatic substituent (for compound 4) is about 2.35 ppm.

The formation of a pyrane cycle of compounds 1, 2 due to intramolecular interaction of the hydroxylic and cyano groups is a reversible process [2]; under certain conditions the pyrane cycle may open with subsequent cyclization.



First, nucleophilic addition of an alcoholate anion by the α carbon atom of the pyrane cycle occurs with subsequent opening of the heteroring. Further attack of the unshared electronic pair of the nitrogen atom by the electron-deficient carbon atom of the lactonic system, cyclization, and aromatization result in formation of a pyridine structure.

EXPERIMENTAL

IR spectra were recorded on an FSM-1201 Fourier spectrometer in KBr tablets, the spectral range being 400-4000 cm^{-1}. NMR1H spectra were obtained on a Bruker MSL-400 spectrometer within 20-25°C in $CDCl_3$, TMS being the internal reference. The working frequency was 400 MHz.

4-Aryl-6-ethoxy-2R-[2,3-b]-pyridine-5-carbonitriles (3, 4). A mixture of 0.01 mol of 6-amino-4-aryl-2R-4H-furo[2,3-b]pyrane-5-carbonitrile (1, 2) and 0.01 mol of sodium alcoholate in an ethanol solution was heated for 2-3 hr, poured out in cold water, and neutralized with diluted HCl. The precipitated crystals were filtered out on a Schott filter and recrystallized from a hexane-IPA 1:1 mixture.

For **3**: yield 75%; mp 160-162^{0}C; ^{1}H NMR, δ: 6.50 (1H, s), 1.42 (3H, t, $OCH_2\underline{\mathbf{CH_3}}$), 4.20 (2H, m, $O\underline{\mathbf{CH_2}}CH_3$), 7.25-7.68 (9H, m, Ar). Found (%) C, 70.24; H, 4.33; N, 7.53. Calc. for $C_{22}H_{15}ClN_2O_2$ (%) C, 70.50; H, 4.03; N, 7.47

For **4**: yield 68%; mp 157-159^{0}C; ^{1}H NMR, δ: 6.64 (1H, s), 1.47 (3H, t, $OCH_2\underline{\mathbf{CH_3}}$), 4.30 (2H, m, $O\underline{\mathbf{CH_2}}CH_3$), 7.15-7.50 (8H, m, Ar). Found (%) C, 70.86; H, 4.60; N, 7.05. Calc. for $C_{23}H_{17}ClN_2O_2$ (%) C, 71.04; H, 4.41; N, 7.20

The work was supported by grant No MK-2952.2007.3 of President of Russian Federation for state support of young Russian scientists.

References:

1. T.V. Anis'kova, A.Yu. Yegorova, and Z.Yu. Timofeyeva. Reactions of 3-arylmethylene-3H-furan-2-ones with malononitrile, a design method of furopyrane systems. Carbonylic Compounds in Heterocycle Synthesis. Coll. Book / Ed. Prof. A.P. Kriven'ko. Saratov, 2008. P. 36-38.

2. F.S. Babichev, Yu.Ya. Sharanin, V.P. Litvinov, V.K. Promonenkov, Yu.M. Volovenko. Intramolecular interaction of nitrile and C-H, O-H, and S-H groups. Naukova dumka, Kiev, 1985.

The work was submitted to international scientific conference «Prospects for the development of university science», Dagomys (Sochi), 20-23 September 2008, came to the editorial office on 08.08.2008.

Materials of Conferences

PROGRESSIVE METHOD OF CUTTING STAINLESS AND HEATPROOF STEELS AND ALLOYS

Krainev D.V., Norchenko P.A., Ingemansson A.R.
Volgograd State Technical University
Volgograd, Russia

Stainless and heatproof steels and alloy (steels of austensite class) find more and more application in modern machine-building industry. Machine and constructions' parts made of these materials are characterized by durability and high service performance.

The steels of austensite class refer to hard-to-treat ones; their characteristic is the formation of cyclic chips, the increased wear of the instrument and the machined part surface coating low quality.

For the solution of the abovementioned problem it is offered to use the method of cutting with advanced plastic deformation. At the plastic materials machining process the intensive plastic deformation precedes the separation of the cut-down layer material from the blank part, i.e. the principle cutting work part is spent on the plastic deformation of the metal taken off. The essence of the cutting with advanced plastic deformation of the cut-down layer material consists in combining two processes – the preliminary plastic deformation and cutting itself. Thereat by the moment of the cutting instrument action on the cut-down material layer a part of the work spent on plastic deformations in the process of chip formation at usual cutting action is already performed by a supplementary rolling device making the depth and cold work degree necessary for the maximal efficiency of the following process.

It provides the cutting force, temperature, specific work decrease, process cyclicity, that results in the instrument's durability and processing capacity increase. The chip making process if treated with cutting the preliminary cold-worked layer cut down results in surface roughness decrease, some chip shrinkage reduction and friction conditions change.

The work was submitted to international scientific conference «Manufacturing Technology» (Italy - Rome, Florence, September, 9-16, 2008, came to the editorial office on 14.07.2008.

THYRISTOR INVERTERS WITH AN IDLE LIMITER FOR TRANSFORMER LOADS

Magazinnik L.T.
Ulyanovsk State Technical University
Ulyanovsk, Russia

Electroarc welding sets of an inverter type, i.e. welders in which a welding transformer is operated from the inverter with frequency till 100 kHz, are widely used [1]. Inverters in such welders may be realized as the single-ended circuit as well as the push-pull circuit. Single-ended inverters use the core of the welding transformer slightly worse than push-pull inverters. But push-pull bridge inverters form the supply voltage asymmetry of the welder transformer. When frequency increases this asymmetry increase too and result in the saturation of the transformer core that minimize advantages of bridge (push-pull circuit) inverters to single-ended inverter. The asymmetry is eliminated in push-pull circuits if condensers are used in the power circuit. Specifically, the asymmetry is lacked in the half-bridge inverter shown in [2]. The deficiency of such inverter is poor utilization of capacitor capacity. Utilization of the condenser is better fourfold, but a surge voltage is possible in the diagonal of the bridge load at the quiescent condition and light loads.

The general deficiency of half-bridge inverters as well as bridge inverters is the need to use gate-turn-off (GTO) keys, i.e. transistors or GTO thyristors. Transistors constraint a power range of welders, and GTO thyristors have the more complicated control system, and main, have large losses and lesser permissible switching frequency in comparison with ordinary (SCR) thyristors.

Inverters using ordinary (SCR) thyristors with coercive commutation by means of condensers ("C"-commutation) or of a combination of condensers and inductor ("L-C"-commutation) are known too. But coercive commutation complicates the power circuit of the inverter. A "classic" thyristor inverter using gate-turn-off thyristors or ordinary thyristors with coercive commutation is described in [3]. The circuit provides for the series condenser turn on with the primary winding of the transformer welder that may result in voltage surges in the condenser and the primary winding at the quiescent condition and light loads. Gate-turn-off thyristors are much expensive than ordinary thyristors and it losses are greater. The control system of it is more complex too. Frequency behaviors of gate-turn-off thyristors are worse than of ordinary thyristors too. Therefore such decision may used only for comparatively low frequencies that increase integrally the mass and gabarit characteristics of the device.

Decisions described in [4] permit to optimize the device. Specifically, gate-turn-off thyristors of the inverter are substitute for ordinary (SCR) thyristors; the inverse diode bridge is excluded from the thyristor inverter circuit, and a standard control circuit has in addition a current sensor, a resistance transducer of the "welding die - welding surface" gap, a delay cell, an AND element, a gate-tape diode and four keys. After primary winding current of the transformer welder was dropped the delay cell provided the interval was required to restore locking properties of the conducting current diagonal thyristor pair. If the welding electrode don't contact with a welding surface at the same time then current was missed in the circuit of the resis-