Isomer (IX + X), bp 56-57°C/mm, n_D^{20} 1.4720. IR spectrum (ν, cm^{-1}): 890, 3090 ($C=CH_2$), 920, 1000, 3090 ($-CH=CH_2$). PMR spectrum (δ, ppm): 1.13 s (3H, CH—); 1.55 m (4H, $-CH_2-$); 1.67 s (3H, $CH_3-C=$); 3.06-3.83 m (3H, $-CH_2-O-$, CH—O—); 4.69-6.01 m (5H, $-CH=CH_2$); m/e 166. Found: C 79.3; H 10.5%. $C_{11}H_{18}O$. Calculated: C 79.5; H 10.4%.

CONCLUSIONS

It has been shown for the first time that 1-(2,7-octadienyl)-2,5-divinyl- and 1-(2,7-dimethyl-2,7-octadienyl)-2,5-diisopropenylpiperidine can be prepared by reacting urotropin with butadiene or isoprene in the presence of a $Pd(acac)_2—PR_3—Al(C_2H_5)_3—H_2SO_4$ catalyst (1:3:2:1.5).

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CATALYTIC CONVERSION OF FURAN AMINES INTO PYRIDINE AND PYRAZINE DERIVATIVES

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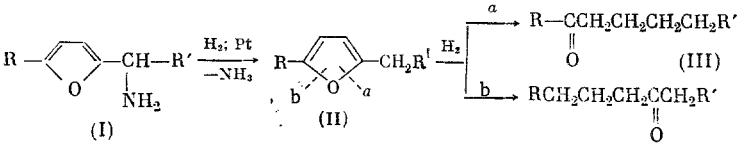
UDC 542.97:547.722.6:547.821:547.861

The catalytic hydrogenation of furan compounds containing functional groups (hydroxyl, carbonyl, or amino) in the 1, 3, or 5 position of the side chain with respect to the furan ring may initially result in the formation of γ-, δ-, or ε-type bifunctional compounds. New five-, six-, and seven-membered heterocyclic compounds have been prepared by hydrogenation of furan alcohols, ketones and amines [1-8].

In the present work, we have investigated the hydrogenation of 2-aminoalkyl- and 2-aminoalkyl-5-alkylfurans (I) in a continuous-flow system in the presence of Pt and Raney Cu—Al catalysts. Compounds (I) are easily prepared by reductive amination of α-acylfurans in the presence of a Ni—Al catalyst. The hydrogenation of (I) follows routes (1)-(3)



(I) (II) (III) (1)

Route (2), in which the amino group in the side chain is retained and the furan ring is hydrogenolyzed through the C—O bond not adjacent to the aminoalkyl side chain, results in the formation of pyrazines (Table 1)

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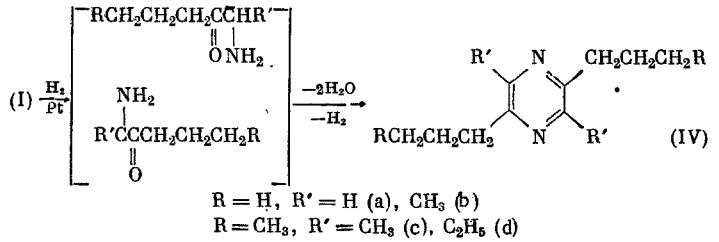
Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 6, pp. 1364-1366, June, 1977. Original article submitted March 2, 1976.

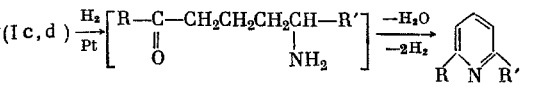


R = H, R′ = H (a), CH_3 (b)
R = CH_3, R′ = CH_3 (c), C_2H_5 (d)

(2)

By this route, 2,5-dipropylpyrazine (IVa) is obtained from furfurylamine (Ia), and 2,5-dimethyl-3,6-dipropylpyrazine (IVb) is obtained from 1-furyl-1-aminoethane (Ib) [9]. Hydrogenolysis of the furan ring in the 2-aminoalkylfurans (Ia and Ib) takes place selectively at the C—O bond not adjacent to the side chain, giving ~50% yields of the pyrazine homologs (IV), the remainder being products formed by elimination of the amino group followed by hydrogenolysis of the furan ring, i.e., compounds (II) and (III).

The yields of pyrazine homologs (IV) are lower in the case of the 2-aminoalkyl-5-alkylfurans (Ic and Id) because the latter, as well as undergoing reaction (2), also undergo hydrogenolysis of the furan ring at the C—O bond adjacent to the aminoalkyl substituent (3). This results in the formation of 2,6-dialkylpyridines [10]

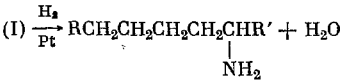


R = CH_3; R′ = CH_3, C_2H_5

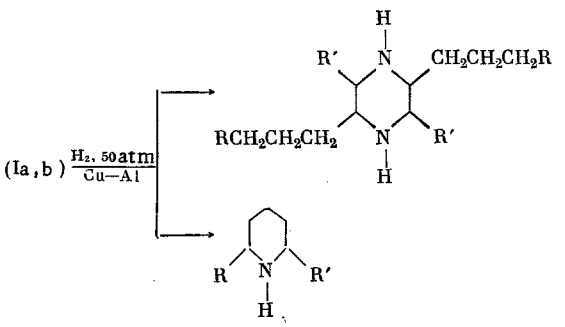
(3)

The relative amounts of the products formed from the 2-aminoalkyl-5-alkylfurans depends on the temperature. At 220°C compounds (Ic) and (Id) give 40% 2,6-dialkylpyridines, 35% 2,5-dialkylfurans, 10-15% pyrazine homologs, and ~10% aliphatic ketones, while at 300°C they give 25% 2,6-dialkylpyridines, 40% 2,5-dialkylfurans, 10% pyrazine homologs and 20% aliphatic ketones.

Small amounts (5-10%) of aliphatic amines are also formed by hydrogenolysis of the furan ring and elimination of the oxygen atom



The furan amines can also be converted into piperazine and piperidine homologs by altering the hydrogenation conditions, primarily the H_2 pressure. Thus, hydrogenation of furfurylamine and 1-furyl-1-aminoethane under flow conditions in the presence of a Raney Cu—Al catalyst at 230-250°C and an H_2 pressure of 50 atm gives the corresponding homologs of piperazine (70-80% yield) and piperidine (15-20% yield) (see Table 1)



EXPERIMENTAL

The Raney Ni—Al catalyst was prepared by incomplete (50%) removal of aluminum from a Ni—Al alloy by leaching with 10% NaOH while cooling with ice. The catalyst was washed with water to remove alkali and stored under alcohol. The Raney Cu—Al catalyst was prepared similarly from an alloy comprising 45% Cu and 55% Al. A 10% Pt catalyst was prepared by impregnating BAU carbon with a solution of H_2PtCl_6. The catalyst was reduced with H_2 at 250-300°C for 15 h. We prepared 2-acetylfuran, 2-propionylfuran, 2-methyl-5-acetyl-, and 2-methyl-5-propionylfuran by acylating furan or 2-methylfuran respectively with acetic or

TABLE 1. Properties of Furan Amines, Pyrazines, and Piperazines

Compound	bp, °C (p, mm Hg)	n_D^{20}	d_4^{20}
Furfurylamine	144–145 (750)	1,4893	1,0506
1-Furyl-1-aminoethane	146–147 (750)	1,4780	1,0024
1-(5-Methylfuryl)-1-aminoethane	66 (14)	1,4800	0,9750
1-(5-Methylfuryl)-1aminopropane	77–80 (17)	1,4764	0,9639
2,5-Dipropylpyrazine	106 (18)	1,4828	0,9272
2,5-Dimethyl-3,6-dipropylpyrazine	100–102 (4)	1,4862	0,9205
2,5-Dimethyl-3,6-dibutylpyrazine	143–145 (2)	1,4882	0,9000
2,5-Diethyl-3,6-dibutylpyrazine	157–160 (10)	1,4852	0,8922
2,5-Dipropylpiperazine	112–113 (15) mp 80°	–	–
2,5-Dimethyl-3,6-dipropylpiperazine	60–62 (5)	1,4540	0,9102

propionic anhydride in the presence of H_3PO_4, and converted them to amines (I) by reductive amination in an autoclave in the presence of a Raney Ni—Al catalyst [11] (see Table 1).

The hydrogenation of the furan amines was carried out under flow conditions by passing them in an H_2 stream through a catalyst bed at 220-250°C with a space velocity of 0.1 h^{-1}. The catalyzates, which were yellow or orange in color, were saturated with KOH, separated from the aqueous phase, dried with anhydrous KOH, and distilled in a rectification column at atmospheric and then reduced pressure, giving successively the 2-alkylfurans (25%), aliphatic ketones (15%), and pyridines and pyrazine homologs (50%). The pyrazine homologs after distillation were pale-yellow liquids which turned dark-orange on standing; their constants and elementary analyses were determined soon after distillation. The elementary analysis data were in good agreement with the calculated data. The pyridine fractions contained small amounts of aliphatic ketones and amines.

Hydrogenation of 2-methyl-5-aminoethylfuran on Pt—C gave 2-methyl-5-ethylfuran, bp 117-118°C/750 mm, n_D^{20} 1.4460, d_4^{20} = 0.8935; 2,6-dimethylpyridine [12] (which was freed of 2-heptanone and 3-heptanone impurities either by boiling with Na for ~10 h or by converting into the hydrochloride, extracting an aqueous solution of this with ether to remove the ketones, and treating the salt with conc. KOH to isolate the 2,6-dimethylpyridine), bp 142-143°C/750 mm (after distilling over Na), n_D^{20} 1. 4940, d_4^{20} 0.9169, picrate, mp 163°C (from alcohol); a fraction with a bp of 146-150°C/750 mm, n_D^{20} 1.4120 (semicarbazone, mp 117°C, from alcohol) comprising a mixture of 2-heptanone and 3-heptanone; and 2,5-dimethyl-3,6-dibutylpyrazine (see Table 1).

Hydrogenation of 2-methyl-5-aminopropylfuran on Pt—C gave 2-methyl-5-n-propylfuran, bp 138-139°C/750 mm, n_D^{20} 1. 4464, d_4^{20} 0.8829; 2-methyl-6-ethylpyridine [13], bp 160-162°C/750 mm, n_D^{20} 1.4850, d_4^{20} 0.8945 (after distillation over Na), picrate, mp 127°C (from alcohol); a fraction with a bp of 167-172°C, n_D^{20} 1.4150 (semicarbazone, mp 120°C) comprising a mixture of 2-octanone and 4-octanone; and 2,5-diethyl-2,6-dibutylpyrazine (see Table 1).

The conversion of furfurylamine and 1-furyl-1-aminoethane into piperazine and piperidine homologs was carried out in a flow system in the presence of Raney Cu—Al at 220-250°C and an H_2 pressure of 50 atm with a space velocity of 0.1-0.15 liter·h^{-1}. The catalyzates were distilled in a rectification column to give respectively 2,5-dipropylpiperazine and 2,5-dimethyl-3,6-dipropylpiperazine (70-80% yield), and also piperidine and 2-methylpiperidine (15-20% yield). The properties of the latter are in accord with literature data.

CONCLUSIONS

1. The hydrogenation of furan amines containing an amino group in the side chain adjacent to the furan ring in the presence of a Pt catalyst under continuous-flow conditions at 220-250°C proceeds via two parallel routes, viz., elimination of the amino group in the form of ammonia to form furan homologs, and primary hydrogenolysis of the furan ring without elimination of the amino group to form pyridine and pyrazine homologs.

2. Hydrogenation of furan amines under continuous-flow conditions in the presence of a Raney Cu—Al catalyst under a pressure of hydrogen results in the formation of piperazine and piperidine homologs.

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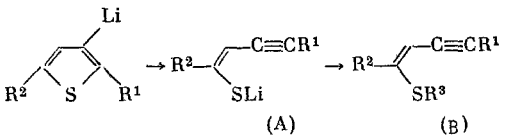
REACTION OF ARYLSULFONYL COMPOUNDS WITH EXCESS ORGANOLITHIUM REAGENT

10. OPENING OF THE THIOPHENE RING IN β-LITHIUM DERIVATIVES OF 2,5-BIS(tert-BUTYLSULFONYL)THIOPHENE*

F. M. Stoyanovich, G. B. Chermanova, and Ya. L. Gol'dfarb

UDC 542.957:547.73

It is known that the thiophene skeleton remains unchanged under conditions of electrophilic and nucleophilic (protophilic) attack. Because of this and other factors, the thiophene system was at one time regarded as aromatic. It has recently been shown, however, that the β-lithium derivatives of 2,5-substituted thiophenes undergo cleavage [2] to form lithium thiolates (A), which give alkylthio derivatives (B) when treated with alkylating agents

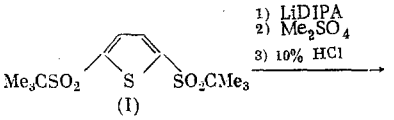


(A) (B)

The motive force for this reaction is evidently the formation of an acetylenic bond as a result of ring opening by trans 1,2 elimination. This fact is of considerable importance, since ring opening does not occur in the case of α-lithium derivatives. All observations made hitherto relate to β-lithium derivatives containing electron-donor substituents in the 2 and 5 positions.

It has recently been reported that the β-lithium derivatives of 2,5-bis(t-butylsulfonyl)thiophene, i.e., compounds with electron-acceptor substituents, undergo some reaction which evidently involves the kind of ring opening characteristic of β-lithium-substituted thiophenes [3].

In the present work we will present data confirming this hypothesis. Treatment of 2,5-bis(t-butylsulfonyl)thiophene (I) with 5 equivalents of lithium diisopropylamide (LiDIPA) at −40°C and then 20°, followed by methylation with dimethyl sulfate and treatment with 10% HCl gives N,N-diisopropyl-γ-methylthio-β-chlorovinylacetamide (II) and 1,4-bis(t-butylsulfonyl)-1-methylthio-3-diisopropylamino-1,3-butadiene (III)



(I)

* See [1] for communication 9.

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 6, pp.1367-1370, June, 1977. Original article submitted May 19, 1976.