

3. V. G. Kul'nevich and Yu. M. Shapiro, "Investigation of reactions of furanaldehydes in nonaqueous medium when catalyzed by strong bases. Review," Krasnodar (1982), Deposited in ONIITÉKhim, Cherkassy, 10.05.82, No. 550-khp-D82; *Ref. Zh. Khim.*, 18Zh186 (1982).
4. T. A. Geisman, in: *Organic Reactions*, Vol. 2, R. Adams (ed.) [Russian translation], IL, Moscow (1950) p. 106.
5. A. A. Ponomarov, *Syntheses and Reactions of Furanic Substances* [in Russian], Izd. Saratov Univ. (1960).
6. Yu. M. Shapiro, *Khim. Geterotsikl. Soedin.*, No. 9, 1168 (1977).
7. Yu. M. Shapiro, *Zh. Obshch. Khim.* 58, 947 (1988).
8. Yu. M. Shapiro, 31st Int. Congress of Pure and Applied Chemistry, Abstracts of Poster Commun., Vol. 2, Sofia, Bulgaria (1987), p. 6168.
9. Z. N. Parnes and D. N. Kursanov, *Hydride Shift Reactions in Organic Chemistry* [in Russian], Nauka, Moscow (1969), p. 84.
10. W. J. Scott, W. J. Bower, K. Bratin, and P. Zuman, *J. Org. Chem.* 41, 1952 (1976).
11. Yu. M. Shapiro, in: 1st Regional Conference on Physical and Organic Chemistry with the Participation of Northern Caucasus Institutions of Higher Education, Izd. Rostov Univ., Rostov-on-Don (1989), p. 51.

## REDUCTION OF ALDEHYDES OF THE FURAN SERIES BY THE METHOD OF CATALYTIC HYDROGEN TRANSFER

Zh. G. Yuskovets and M. V. Shimanskaya

UDC 542.941.7:547.724.1'724.2

*The intermolecular transfer of hydrogen from donor molecules to aldehydes of the furan series is studied in the presence of homogeneous, complex  $[Ru(PPh_3)_3Cl_2]$  and heterogeneous (Pd/C) catalysts. A linear correlation is obtained between the reactivity of the furan aldehydes and the nature of the substituent.*

Catalytic, intermolecular hydrogen-transfer reactions have been very often used recently along with the familiar method of catalytic hydrogenation with molecular hydrogen in order to reduce organic compounds.

The basic results of reducing unsaturated bonds and functional groups by the use of different hydrogen donors, solvents, and catalysts have been generalized in several reviews [1-3].

Alcohols are most widely used as hydrogen donors. With their help, for example, in the presence of Raney nickel [4] and zirconium oxychloride [5], the carbonyl group of aldehydes and ketones is reduced. In [6], the reduction of aldehydes and ketones with 2-propanol in the liquid phase using zirconium oxide was described. At the boiling point of 2-propanol, which is simultaneously the solvent and hydrogen donor, furfural, together with other aldehydes and ketones, is reduced to furfuryl alcohol, which is formed in 99% yield when the reaction is prolonged for 6 h. Hydrogen transfer took place on the reduction of dimethyldi(2-furyl)germane in the presence of Raney Ni at 120°C. When a Pd/C catalyst was used, transfer was effected only from cyclohexene [7]. The reduction of aldehydes and ketones by alcohols is also effectively catalyzed by the metal complexes  $Co(PPh_3)_3H_3$  [8],  $Ru(PPh_3)_3Cl_2$  [9-12],  $Rh(PPh_3)_3Cl$  [12, 13], and  $Ru(PPh_3)_3H_2$  [14, 15].

In the presence of heterogeneous, palladium catalysts for the reduction of aromatic carbonyl compounds, cyclohexene, along with alcohols, can serve as a hydrogen donor [16-18].

One of the extremely effective hydrogen donors for the reduction of the carbonyl group is formic acid, at the carbon atom of which there is a hydrogen that possesses marked hydridic mobility. The reduction of carbonyl compounds with the aid of formic acid in the presence of ruthenium complexes as catalysts, is described in [19]. Aliphatic, alicyclic, and aromatic ketones and aldehydes under hydrogen transfer conditions are also reduced in the presence of excess formic acid, a tertiary amine, and compounds of Group IVA metals –  $Cp_2ZrCl_2$ ,  $Cp_2TiCl_2$ ,  $Cp_2HfCl_2$ ,  $CpZrCl_3$ ,  $ZrCl_4$ , and  $Cp_2ZrH$  – as catalysts [20]. According to [21], the system  $HCOOH-(C_2H_5)_3N-Ru(PPh_3)_3Cl_2$  selectively reduced aldehydes to the corresponding al-

---

Institute of Organic Synthesis, Academy of Sciences of the Latvian SSR, Riga 226006. Translated from *Khimiya Geterotsiklicheskich Soedinenii*, No. 6, pp. 745-749, June, 1990. Original article submitted February 16, 1989.

TABLE 1. Hydrogenation of Aldehydes in the Presence of Ru(PPh<sub>3</sub>)<sub>3</sub>Cl<sub>2</sub>\*

Starting compound	Degree of conversion	Selectivity of alcohol formation %	Starting compound	Degree of conversion	Selectivity of alcohol formation %	Starting compound	Degree of conversion	Selectivity of alcohol formation
VII	0,77	89	VIII	0,38	93	IV	0,99	100
I	0,62	92	V	0,35	92	IX	0	0
II	0,37	91	VI	0,31	90	X	0	0
III	0,99	99						

\*Reaction conditions: a mixture of 0.25 mmole aldehyde, 0.5 mmole formic acid, and 0.025 mmole Ru(PPh<sub>3</sub>)<sub>3</sub>Cl<sub>2</sub> catalyst in distilled toluene is heated at 90°C in an argon atmosphere for 2 h.

TABLE 2. Catalytic, Liquid-Phase Reduction of 5-Methylfurfural\*

Expt. No.	Catalyst	Hydrogenation agent	Solvent	Yield of 5-methylfurfuryl alcohol, %
1	Rh(PPh <sub>3</sub> ) <sub>3</sub> HCO	H <sub>2</sub>	EtOH	0
2	Rh(PPh <sub>3</sub> ) <sub>3</sub> HCO	NaBH <sub>4</sub> + H <sub>2</sub>	EtOH	0
3	Rh(PPh <sub>3</sub> ) <sub>3</sub> Cl	H <sub>2</sub>	EtOH	0
4	Ru(PPh <sub>3</sub> ) <sub>3</sub> Cl <sub>2</sub>	H <sub>2</sub>	2-PrOH	0
5	Ru(PPh <sub>3</sub> ) <sub>3</sub> Cl <sub>2</sub>	HCOOH	Toluene	95
6	Raney Ni	H <sub>2</sub>	EtOH	25**
7	RhCl <sub>3</sub> ·4H <sub>2</sub> O	H <sub>2</sub>	EtOH	86***
8	10% Pd/C	H <sub>2</sub>	EtOH	0

\*Reaction conditions: we heated 0.025 mmole of catalyst, 0.25 mmole of 5-methylfurfural, and 2.5 ml of solvent at 50°C in a hydrogen atmosphere at 0.3 MPa pressure for 5 h. Experiment 5 was carried out in the presence of 0.5 mmole of HCOOH; experiment 2, with 0.025 mmole of NaBH<sub>4</sub>.

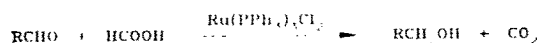
\*\*The yield of tetrahydrofurfuryl alcohol was 60%.

\*\*\*The yield of 2-methylfuran was 3%.

cohols. The use of such systems, selectively operating under mild conditions, is necessary for the reduction of furan aldehydes, because their hydrogenation into alcohols by molecular hydrogen occurs at high temperatures and pressures.

In order to determine the most selective system of hydrogen transfer to furan aldehydes and to establish the basic laws of this process, we have investigated the conversion of furfural (I), 5-methylfurfural (II), furan-2,5-dialdehyde (III), 5-bromofurfural (IV), 5-trimethylsilylfurfural (V), 5-trimethylgermylfurfural (VI), and also benzaldehyde (VII), thiophene-2-carbaldehyde (VIII), pyridine-3-carbaldehyde (IX), and pyridine-4-carbaldehyde (X) to the corresponding alcohols in the presence of Ru(PPh<sub>3</sub>)<sub>3</sub>Cl<sub>2</sub> and 10% Pd/C catalysts at 20-90°C. Formic acid, cyclohexene, indoline, 2,5-dihydrofuran, and bromobenzene served as hydrogen donors.

The reduction of aldehydes by formic acid (Table 1) can be represented by the scheme:

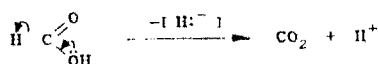


A comparison of the data on the conversion of aldehydes I, VII, and VIII shows that no basic differences due to the nature of the radical bound to the carbonyl group are observed, although the aldehydes are ordered VII > I > VIII according to the degree of conversion. The pyridine aldehydes do not react under analogous conditions. This is due to the inhibition of the

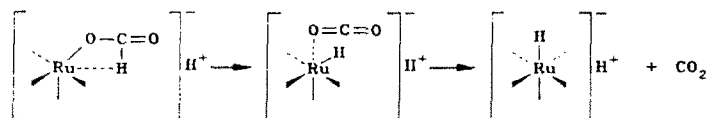
reaction because of the deactivation of the catalyst by the substrate molecules which form stable complexes with the ruthenium catalyst. The inhibiting effect of pyridine has also been observed by other investigators [21].

The introduction of different substituents in the 5 position of the furan ring has a substantial influence on the conversion of the carbonyl group. Thus, under comparable conditions, aldehydes II, V, and VI are converted in the range of 37, 35, and 31%, respectively. The introduction of bromine or a carbonyl group enables conversion to rise to 99%. The rate of the transfer of hydrogen to the aldehydes decreases in the order: IV > III > I > II > V > VI. We attempted to reveal a correlation between the reactivities of the furan aldehydes and their structures with the help of two independent parameters, Hammett's  $\sigma$ - and  $\rho$ -equations. If it is assumed that there is no change in the mechanism of the hydrogen transfer, that the corresponding reactions are first-order, and that the reaction conditions are constant, then  $\rho$  describes only the structural features of the reacting aldehydes. Using Hammett  $\sigma$ -constants [22, 23], we find  $\rho = +5.9$  for substituents located in the 5 position of the furan ring. The correlation coefficient, which characterizes the deviation from linearity, was calculated by the method of least squares and is  $r = 0.9531$ . The large positive value of constant  $\rho$  is evidence of a strong acceleration of the hydrogen transfer reaction on the introduction of such electron-accepting substituents as  $-\text{Br}$  and  $-\text{CHO}$  into the furan molecule. The presence of electron-donating substituents  $-\text{H}$ ,  $-\text{CH}_3$ ,  $-\text{Si}(\text{CH}_3)_3$ , and  $-\text{Ge}(\text{CH}_3)_3$  leads to the redistribution of electron density at the reaction center and thereby decreases the rate of reduction of the furan aldehydes.

The hydridic lability of the C-H bond in the donor molecule is of special importance for the occurrence of the reduction reaction. The ease of splitting off a hydride ion from formic acid is explained not only by the effect of the free pair of electrons on the adjacent oxygen, but also by the considerable stability of the resulting carbon dioxide molecule:



Apparently, decomposition of formic acid under the influence of  $\text{Ru}(\text{PPh}_3)_3\text{Cl}_2$  is possible through the formation of a formate complex with a subsequent hydride transfer from the C-H bond according to the scheme:



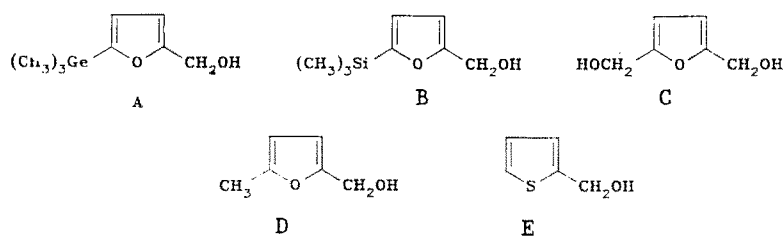
It is quite probable that the presence of electron-accepting substituents in the molecule of the furan aldehydes, which decrease the electron density on the aldehyde group, facilitates the coordination of the substrate molecule to the ruthenium complex, enriched with a hydride ion hydrogen. The reverse effect of electron-donating groups decreases the rate of reduction of the aldehyde.

An increase in the rate of reduction of the aldehydes is observed on the addition of triethylamine to the mixture of formic acid and  $\text{Ru}(\text{PPh}_3)_3\text{Cl}_2$ . After only 30 min at room temperature, all of the aldehydes are selectively converted into the corresponding alcohols. This property of  $(\text{C}_2\text{H}_5)_3\text{N}$  is obviously the result of an increase in the rate of elimination of  $\text{CO}_2$  and the formation of the hydrido complex. The use of such hydrogen donors as 2,5-dihydrofuran, bromobenzene, and indoline in conjunction with the complex catalyst  $\text{Ru}(\text{PPh}_3)_3\text{Cl}_2$  is not effective for the transfer of hydrogen to aldehydes of the furan series.

The aldehyde group of aromatic compounds was reduced to the methyl group by means of the transfer reaction in the presence of heterogeneous palladium catalysts [16]. However, the use of such a catalyst in conjunction with formic acid to reduce aldehyde I at  $90^\circ\text{C}$  did not lead to the formation of the alcohol. Replacing the formic acid with cyclohexene in this system does allow small amounts of the alcohols to be isolated: 0.6% 5-methylfurfuryl alcohol (from aldehyde II), 0.5% furfuryl alcohol (from aldehyde I), and 14% benzyl alcohol (from benzaldehyde VII). Moreover, a subsequent reduction of the alcohol group to a methyl group takes place, the yield of the alkyl derivative being: 2.0 (from aldehyde I), 0.6 (from aldehyde II), and 3.0% (from VII). We compare the results (Table 2) of the liquid-phase reduction of 5-methylfurfuryl alcohol with molecular hydrogen using homogeneous (experiments 1-4) and heterogeneous (experiments 6-8) catalysts and under the conditions for a catalytic hydrogen transfer to the carbonyl group (experiment 5). The catalytic transfer of hydrogen from the donor molecules of  $\text{HCOOH}$  to the aldehyde II is characterized by a high yield of alcohol compared the contact hydrogenation with molecular hydrogen taking place at the elevated hydrogen pressure of 0.3 MPa.

Thus, the high selectivity and rate of the process of hydrogen transfer to furan aldehydes, the mild conditions, and the accessibility of applicable catalysts and reductants, allow this reaction to be used for the preparation of alcohols of the furan series.

TABLE 3. Mass Spectra of the Products of the Reduction of the Aldehydes



Compound	m/z ( $I_{\text{rel}}$ , %)*
A	216 ( $M^+$ , 20), 201 ( $M^+ - \text{Me}$ , 100), 121 (60), 89 (25)
B	170 ( $M^+$ , 35), 155 ( $M^+ - \text{Me}$ , 85), 139 (10), 99 (15), 75 (100), 45 (13)
C	112 ( $M^+$ , 90), 95 ( $M^+ - \text{OH}$ , 100), 84 (20), 55 (25)
D	128 ( $M^+$ , 45), 111 ( $M^+ - \text{OH}$ , 15), 97 ( $M^+ - \text{MeOH}$ , 100), 69 (30), 55 (15), 41 (25)
E	114 ( $M^+$ , 100), 97 ( $M^+ - \text{OH}$ , 55), 81 (25), 45 (40)

\*Ion peaks with an intensity  $\geq 10\%$  are shown.

## EXPERIMENTAL

The catalysate was analyzed on a Varian Aerograph-2800 chromatograph with a flame ionization detector and a steel column 2 mm in diameter and 2 m long packed with 10% SE-30 + 2.5% Reoplex on Chromosorb W-AW carrier. The temperature was raised from 40 to 150°C at a rate of 8 deg/min. The rate of the carrier gas, helium, was 20 ml/min.

The mass spectra of the compounds were taken on Kratos MS-25 chromato-mass spectrometer with ionizing electrons of 70 eV energy. Temperature of the ionization chamber, 200°C. Glass column with an OV-17 phase (5%) supported on Chromosorb W-HP (80-100 mesh). Column temperature 60-200°C; programmed rate 15 deg/min. Carrier gas, helium. Table 3 shows the mass spectra of the reduction products. These mass spectra of the germanium and silicon derivatives of furfuryl alcohols agree with the spectra in [24].

The reduction of the aldehydes was carried out in a Pierce reaction tube of 5 cm<sup>3</sup> capacity.

The amounts of reactants, the conditions and duration of the experiments, and the spectral characteristics are presented in Tables 1-3. The results in Table 2 were obtained in a Parr hydrogenation unit.

We thank L. M. Ignatovich for making the aldehydes samples available.

## LITERATURE CITED

- I. S. Kolomnikov, V. P. Kukolev, and M. E. Vol'nin, *Usp. Khim.* **43**, 903 (1974).
- G. Brieger and T. J. Nestruck, *Chem. Rev.* **74**, 567 (1974).
- R. A. Johnstone, A. H. Wilby, and J. D. Entwistle, *Chem. Rev.* **85**, 129 (1985).
- M. J. Andrews and C. N. Pillat, *Indian J. Chem.*, No. 5, 465 (1978).
- H. Matsushita, S. Ishiguro, H. Ichinose, A. Izumi, and S. Muzusaki, *Chem. Lett.*, No. 6, 731 (1985).
- M. Shibagaki, K. Takahashi, and H. Matsushita, *Bull. Chem. Soc. Jpn.* **61**, 3283 (1988).
- É. Lukevits, L. M. Ignatovich, Zh. G. Yuskovets, O. L. Golender, and M. V. Shimanskaya, *Zh. Obshch. Khim.* **57**, 1294 (1987).
- E. Malunowicz, S. Tyrlik, and Z. Lasocki, *J. Organomet. Chem.* **72**, 269 (1974).
- Y. Sasson, P. Albin, and J. Blum, *Tetrahed. Lett.* **10**, 833 (1974).
- V. Z. Sharf, L. Kh. Freidlin, V. N. Krutii, and T. V. Lysyak, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 10, 2195 (1972).
- L. Kh. Freidlin, V. Z. Sharf, V. N. Krutii, and S. N. Shcherbakova, *Zh. Org. Khim.* **8**, 979 (1972).

12. V. Z. Sharf, L. Kh. Freidlin, and V. N. Krutii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 10, 2264 (1973).
13. L. Kh. Freidlin, V. Z. Sharf, V. N. Krutii, and T. P. Prokopenko, *Kinet. Katal.* 14, 601 (1973).
14. H. Imai, T. Nishiguchi, and K. Fukuzumi, *Chem. Lett.*, No. 8, 807 (1975).
15. H. Imai, T. Nishiguchi, and K. Fukuzumi, *J. Org. Chem.* 41, 665 (1976).
16. G. Brieger and T. H. Fu, *Chem. Commun.*, No. 19, 757 (1976).
17. M. A. Aramendia, V. Borau, C. Jiménez, I. M. Marinas, M. E. Sempere, and P. Urbano, *Appl. Catal.* 43, 41 (1988).
18. G. Brieger, T. J. Nestrick, and T. H. Fu, *J. Org. Chem.* 44, 1876 (1979).
19. Y. Watanabe, T. Ohta, and Y. Tsuji, *Bull. Chem. Soc. Jpn.* 55, 2441 (1982).
20. N. Tatsuya, A. Ioichi, I. Yasutaka, and O. Masaya, *Technol. Rep. Univ. Kansas*, No. 29, 69 (1987).
21. B. T. Khai and A. Arcelli, *Tetrahedron Lett.* 26, 3365 (1985).
22. D. H. McDaniel and H. C. Brown, *J. Org. Chem.* 23, 420 (1959).
23. A. N. Egorochkin and G. A. Razuvaev, *Usp. Khim.* 61, 1480 (1987).
24. L. M. Ignatovich, Dissertation, Candidate of Chemical Sciences, Riga (1985).

## ADDITION OF THIOPHENOLS TO N-VINYLPYRROLES

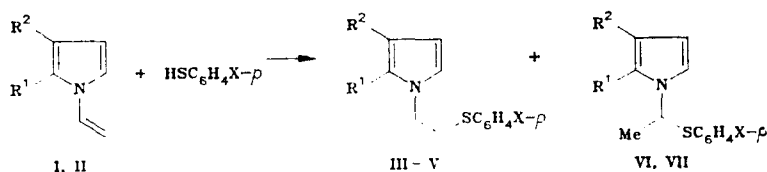
I. A. Aliev, A. I. Mikhaleva, and B. R. Gasanov

UDC 547.742'753'569.1.07:542.945.22

*Thiophenols add to 1-vinyl-4,5,6,7-tetrahydroindole and 1-vinyl-2-phenylpyrrole in the presence of azobisisobutyronitrile to form 1-(2-arylthioethyl)pyrroles. The major products in the absence of initiator are the isomeric 1-(1-arylthioethyl)pyrrole  $\alpha$ -adducts. NH-Pyrroles inhibit the radical process and form selectively the  $\alpha$ -adducts.*

N-Vinylpyrroles have become available via a new and effective method from ketoximes and acetylene in the superbase system KOH–DMSO [1, 2] and readily add hydrosilanes [3, 4], alcohols [5, 6], phenols [7], and thiols [8]. Alkane thiones add to N-vinylpyrroles in the presence of azobisisobutyronitrile (AIBN) and in the absence of the initiator to form N-( $\beta$ -alkylthioethyl)pyrroles in high yields. Thus, N-vinylpyrroles can act as precursors to a large family of previously unknown N-ethyl pyrroles with different heteroatoms in the ethyl radical which show promise in terms of potential biological activity.

This publication continues our systematic study of the reactivity of N-vinylpyrroles with respect to the addition of thiophenols. It has been found that thiophenols add to pyrroles I and II under conditions of free radical initiation to form the 1-(2-arylthioethyl)pyrrole  $\beta$ -adducts III–V selectively. Analogous conditions without initiator lead to a mixture of only 20% of the  $\beta$ -adduct but up to 80% of 1-(1-arylthioethyl)pyrrole  $\alpha$ -adducts VI and VII.



I R<sup>1</sup>-R<sup>2</sup>=(CH<sub>2</sub>)<sub>4</sub>; II R<sup>1</sup>=Ph, R<sup>2</sup>=H; III R<sup>1</sup>-R<sup>2</sup>=(CH<sub>2</sub>)<sub>4</sub>, X=H; IV R<sup>1</sup>-R<sup>2</sup>=(CH<sub>2</sub>)<sub>4</sub>, X=F; V R<sup>1</sup>=Ph, R<sup>2</sup>=H, X=F; VI R<sup>1</sup>-R<sup>2</sup>=(CH<sub>2</sub>)<sub>4</sub>, X=H; VII R<sup>1</sup>-R<sup>2</sup>=(CH<sub>2</sub>)<sub>4</sub>, X=F

Irkutsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR, Irkutsk 664033. S. M. Kirov State University, Baku 370073. Translated from *Khimiya Geterotsiklicheskikh Soedinenii*, No. 6, pp. 750-752, June, 1990. Original article submitted November 3, 1988; revision submitted June 16, 1989.