

HYDROGENATION OF HETEROCYCLIC ANALOGS OF β -NITROSTYRENE OVER PALLADIUM CATALYST

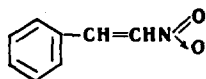
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A study is made of the liquid phase hydrogenation of α -(α' -furyl)- and α -(α' -thienyl)- β -nitroethylenes over Pd black. It is shown that the nature of the substituent (phenyl, furyl, thienyl) does not affect the mode of addition of the hydrogen to the nitrovinyl group. Conditions are found for catalytic synthesis of high yields of heterylacetaldehyde oximes from nitroalkenes.

We previously [1] studied the catalytic hydrogenation of β -nitrostyrene, which contains a conjugated system of double bonds.



The present work deals with the reduction of heterocyclic analogs of β -nitrostyrene, viz. α -(α' -furyl)- and α -(α' -thienyl)- β -nitrostyrene. A number of papers have described the reduction of those compounds by various chemical methods [2-4], but their catalytic hydrogenation has not been investigated. We have investigated the hydrogenation of heterylnitroalkenes over Pd black using various solvents at atmospheric pressure and 25° C.

Table 1 gives the average rates of hydrogenation of α -(α' -furyl)- (I) and α -(α' -thienyl)- β -nitroethylene (II) compared with that of β -nitrostyrene (III). Under identical conditions the furylnitroalkene is hydrogenated at the same high speed as β -nitrostyrene. The rate of reduction of the thiophene analog is considerably less. We previously showed [1, 5] that the reaction is of zero order with respect to the β -nitrostyrene. The same order is observed for furylnitroethylene (Fig. 1). The rate of hydrogen absorption remains constant till the unsaturated nitro compound is fully converted. At the instant when the α -(α' -furyl)- β -nitroethylene vanishes from the reaction mixture, the process slows down sharply.

α -(α' -Thienyl)- β -nitroethylene hydrogenates at decreasing speed (Fig. 1), but the initial reaction velocity is independent of the initial concentration of thienyl-nitroalkene (Fig. 2). It can be assumed that the peculiarities in the kinetics of the hydrogenation of the thiophene derivative are due to the known poisoning effect of compounds containing a sulfur atom with a free pair of electrons [6]. Actually the presence of 5 mole thiophene, when hydrogenating β -nitrostyrene over 0.2 g Pd black in 25 ml acetic acid, cuts the rate of hydrogen absorption from 61.5 to 11 ml/min. However, despite the sharp drop in speed in the presence of large amounts of poison, reaction proceeds to complete conversion of the β -nitrostyrene to phenylacetaldehyde oxime. Similarly in [7] it is shown that the degree of poisoning of Raney nickel in the presence of 1 mmole thiophene when hydrogenating nitromethane is only 20%. This is probably because nitro compounds can be hydrogenated by hydrogen with varied energy of linking to the catalyst [8]. Unsaturated nitro compounds are hydrogenated much more easily than saturated ones. Thus in a binary mixture with 1-phenyl-2-nitroethane β -nitrostyrene is first hydrogenated. From 1 g palladium black, β -nitrostyrene extracts up to 100 ml hydrogen [1].

It is of interest that when hydrogenating binary mixtures of β -nitrostyrene and α -(α' -thienyl)- β -nitroethylene (1.25:1.0), hydrogen is absorbed at the same rate as when hydrogenating β -nitrostyrene in the presence of thiophene, when the thienylnitroalkene is preferentially hydrogenated. Figure 3 shows the change in the ratio α -(α' -thienyl)- β -nitroethylene/ β -nitrostyrene during the process. Apparently the preferential hydrogenation of the thiophene derivative is due to its being more strongly absorbed on the catalyst.

Table 1
Comparison of Hydrogenation Rates for β -Nitrostyrene and its Heterocyclic Analogs

Solvent	dv/dt, ml/min (mean)		
	α -(α' -furyl)- β -nitroethylene (I)	α -(α' -thienyl)- β -nitroethylene (II)	β -nitrostyrene (III)
Ethanol	87	1.4	70
Acetic-sulfuric acid mixture (15:1 by volume)	59	10	61
Acetic acid-ethanol mixture (1:1 by volume)	57	18	50
Dioxane	72	7.5	60

Analysis of the catalyzates in the hydrogenation of α -(α' -furyl)- and α -(α' -thienyl)- β -nitroethylenes shows the reduction proceeds to complete conversion of the starting nitro compounds, after which reaction practically ceases. The main reaction products are the oximes of the corresponding heterylacetaldehydes and hydrodimers (Table 2).

The proportions of these products in the catalyzate is a function of the nature of the solvent (Table 2). The total amount of hydrogen absorbed is determined by those proportions. Insignificant amounts of saturated nitroalkanes and amines are formed.

It is known that when hydrogenating β -nitrostyrene, strong mineral acids repress the dimerization reaction [9]. However, thiophene and furan derivatives are unstable under such conditions. We have shown [5] that the presence of weak organic acids is sufficient to repress dimerization and raise the yield of oxime. We have hydrogenated α -(α' -furyl)- and α -(α' -thienyl)- β -nitroethylene in ethanol mixed with acetic acid (1:1 by volume) or oxalic acid (0.005 mole per 25 ml ethanol), when high yields (up to 90%) of oximes were obtained. To obviate their being resinfied at the end of the reaction, the catalyzate was neutralized under hydrogen with sodium bicarbonate solution. This method of preparing furyl- and thienylacetoximes can be recommended preparatively.

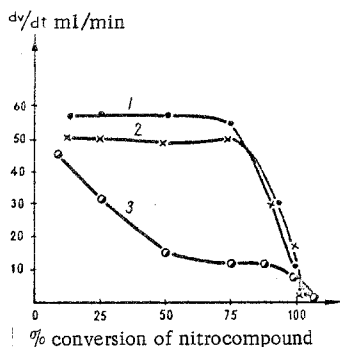
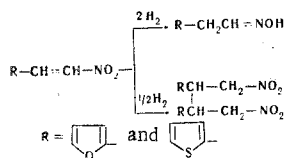


Fig. 1. Kinetic plots for hydrogenation of unsaturated nitro compounds over Pd in an EtOH+AcOH mixture (1:1): 1) α -(α' -Furyl)- β -nitroethylene; 2) β -nitrostyrene; 3) α -(α' -thienyl)- β -nitroethylene.

Thus the experimental results show that the kind of aromatic substituent at the β -carbon atom in the group



is without effect on the mode of addition of hydrogen to the conjugated system in the presence of Pd catalyst. Introduction of the thiophene ring increases the ad-

sorbability of the nitroalkene, and leads to a decrease in the rate of reaction due to self-poisoning of the process.

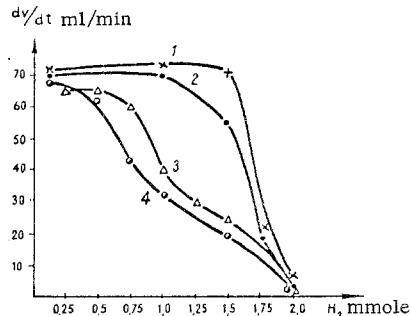


Fig. 2. Kinetic plots for hydrogenation of α -(α' -thienyl)- β -nitroethylene at different concentrations: 1) 1.6 mmole; 2) 2.5 mmole; 3) 7.5 mmole; 4) 10 mmole (0.2 g Pd, 25 ml EtOH+AcOH (1:1)).

EXPERIMENTAL

The starting α -(α' -furyl)- β -nitroethylene was prepared by condensing furfural with nitromethane in the presence of KOH; mp 74-76°. The literature gives [10] mp 75-76°.

α -(α' -Thienyl)- β -nitroethylene was synthesized from α -thiophene aldehyde and nitromethane. MP 78.5-81° (ex EtOH), the literature gives [11] mp 79-80°.

Hydrogenation was carried out at atmospheric pressure and 25°, in a thermostatted long-necked hydrogenation vessel, shaken 700-800 times a minute. Each run used 0.005 mole nitrocompound, 25 ml solvent, and 0.2 g palladium black, prepared by reducing PdCl₂ with formaldehyde in alkaline solution. During the hydrogenation catalyzate samples (about 0.15 ml) were withdrawn for analysis. Polarography was used for quantitative determination of the starting heterylnitroalkenes and the oximes formed from them. The polarographic behavior of these compounds and the method for determining them resembled those previously described for β -nitrostyrene and phenylacetoxime [12]. Inside the 0.1-2 mmole range investigated, wave heights were proportional to the concentrations of the compounds being determined. Table 3 gives the polarographic properties.

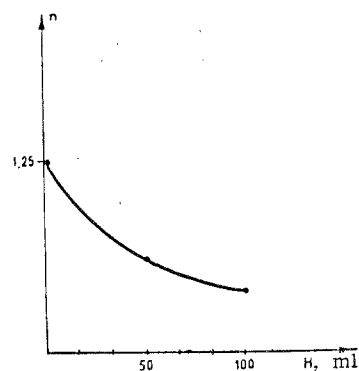


Fig. 3. Change in the ratio α -(α' -thienyl)- β -nitroethylene/ β -nitrostyrene = n when hydrogenating binary mixtures of these.

Table 2
Catalyzate Compositions in the Hydrogenation of Unsaturated Nitro Compounds over Pd Black

Compound hydrogenated	Solvent	H ₂ absorbed, moles	Yields of reaction products, %			
			Oxime	Saturated nitro compound	Amine	Occurrence of hydro-dimers
I	EtOH	1.2	25	—	—	+
II		0.9	26	—	—	+
III		0.9	27	3	—	+
I	Dioxane	1.8	54	—	—	+
II		1.6	43	—	—	+
III		1.6	47	4.5	—	+
I	EtOH+AcOH(1: 1)	2.0	97	—	3	—
II		1.6	82.8*	—	—	—
III		2.0	86	—	5	—
I	EtOH+(COOH) ₂ (0.005 mole)	2.5	75	—	7	—
II		1.8	66.7**	—	traces	—
III		2.3	73	—	8—9	—

*Found 15% unreacted α -(α' -thienyl)- β -nitroethylene

**Found 21% unreacted α -(α' -thienyl)- β -nitroethylene

Table 3
Half-Wave Potentials and Diffusion Current Constants of Heteryl-nitroalkenes and the Corresponding Oximes*

Polarographic constants	α -(α' -Thienyl)- β -nitroethylene		α -Thienyl-acetoxime	α -(α' -Furyl)- β -nitroethylene		α -Furyl-acetoxime
	wave I	wave II		wave I	wave II	
$E_{1/2}(b)$	-0.24	-1.14	-1.18	-0.26	-1.12	-1.18
$k = id/c \cdot m^{2/3} \cdot t^{1/6}$	5.51	4.34	4.28	5.66	4.06	4.18

*Buffer solution pH = 1.65 (HCl+KCl), containing 10% EtOH, concentration = 2 mmole, temperature 25°.

As in the hydrogenation of β -nitrostyrene, saturated nitro compounds and amines in the catalyzate were checked by GLC. A column of Apiezon L on Chromosorb W was used for the nitroalkanes, and one of polyethylene glycol 4500 on NaCl for the amines.

α -Furylaceroxime was obtained by hydrogenating α -(α' -furyl)- β -nitroethylene in ethanol-acetic acid (1:1). A mixture of oil and crystals was obtained. The oxime is unstable in air. After filtering off the crystals, mp 63.5° (ex 50% EtOH), Found: C 51.16, 51.45, H 5.28, 5.08, N 10.13, 10.03, S 22.98, 23.01%. Calculated for C_6H_7ONS : C 51.03, H 5.00, N 9.91, S 22.71%.

As in the case of β -nitrostyrene, hydrogenation of heteronitroalkenes in the absence of acid gave hydropolymers. After recrystallizing from glacial acetic acid the furan derivative dimer had mp 213–214° (decomp), while the thiophene derivative dimer had mp 236–239° (decomp).

REFERENCES

1. L. Kh. Freidlin, E. F. Litvin, and V. M. Chursina, DAN, 155, 1144, 1964.
2. A. P. Terent'ev and R. P. Gracheva, ZhOKh, 32, 2231, 1962.
3. R. T. Gilsdorf and F. F. Nord, J. Org. Chem., 15, 807, 1950.
4. R. Takamota, J. Pharm. Soc. Japan., 48, 136, 1928.
5. L. Kh. Freidlin, E. F. Litvin, and V. M. Chursina, Kinetics and Catalysis [in Russian], 1967 (in press).
6. E. B. Maxted, Advances in Catalysis, 3, 129, 1951.
7. L. Horner, H. Renter, and E. Hermann, Lieb. Ann., 660, 1, 1962.
8. D. V. Sokol'skii, Hydrogenation in Solution [in Russian], Alma-Ata, 1962.
9. O. Schales, Chem. Ber., 68, 1579, 1935.
10. Z. N. Nazarova, ZhOKh, 24, 275, 1954.
11. W. J. King and F. F. Nord, J. Org. Chem., 14, 405, 1949.
12. V. M. Chursina, E. F. Litvin, and L. Kh. Freidlin, ZhAKh, 21, 3, 365, 1966.
13. V. Asahina and A. Fujita, J. Pharm. Soc. Japan, 490, 1084, 1922.

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