Studies on Heteroaromaticity. XIV.[1] Ring-opening Reaction of *N*-[β-(5-Nitro-2-furyl)vinyl]- and *N*-(2-Furyl)-*N*′-ethyleneurea

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(Received October 25, 1967)

In the previous paper[2] we reported the ring-opening reaction of β-(5-nitro-2-furyl)acryloyl- and furoyl aziridine. In this paper the similar ring-opening reaction and nucleophilic rearrangement reaction of *N*-[β-(5-nitro-2-furyl)vinyl]- and *N*-(2-furyl)-*N*′-ethyleneurea will be described.

N-[β-(5-Nitro-2-furyl)vinyl]-*N*′-ethyleneurea (I) was easily prepared in 90% yield by the Curtius rearrangement of β-(5-nitro-2-furyl)acryloyl azide[3] in boiling benzene, followed by treatment with aziridine. β-(5-Nitro-2-furyl)vinyl isocyanate (II), the Curtius rearrangement product, could be isolated in quantitative yield by removing benzene prior to addition of aziridine in the former reaction. Compound I was treated with *p*-toluidine or *p*-phenetidine at room temperature for one month to give the corresponding ring-opened compounds, III or IV, in yields of 18% or 12% respectively. Compound I was refluxed in acetone or acetonitrile in the presence of sodium iodide to afford the rearranged imidazolidine-2-one (V) in 85% or 90% yield. The structure of V was confirmed by the following spectral data: the IR spectrum showed characteristic absorptions at 3420 (ν_{NH}) and 1730 cm^{-1} (ν_{CO} of five-membered ureide[3]), the UV spectrum showed $\lambda_{max}^{\mathrm{DMSO}}$ 440 mμ ($\varepsilon=13800$), somewhat shifted bathochromically

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[1] Part XIII of this series: T. Sasaki and K. Shoji, *Yuki Gosei Kagaku Kyokai-shi* (*J. Soc. Org. Synth. Chem. Japan.*), **26**, 432 (1968).

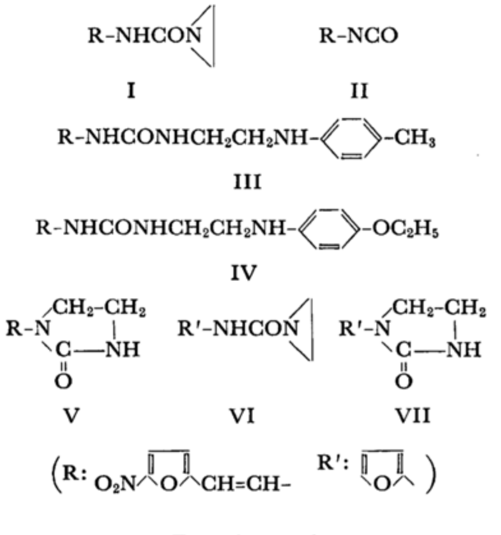
[2] T. Sasaki and T. Yoshioka, *ibid.*, **25**, 658 (1967).

[3] A. Sugihara and M. Ito, *Yakugaku Zasshi* (*J. Pharm. Soc. Japan*), **86**, 269 (1966).

compared with that of I, and the NMR spectrum in DMSO-d_6 showed singals at 6.04 τ (multiplet, 4 H, methylene protons) and at 2.20 and 4.31 τ (each doublet, 1 H, $J=14.5$ cps, methine protons in a trans-configuration) and at 2.40 τ (broad, 1 H, N*H*, disappeared by deuteration) besides those due to furan ring protons.

Similarly, *N*-furyl-*N'*-ethyleneurea (VI) was prepared in 60% yield from furoyl azide.[4] This somewhat lower yield compared with that of I may be explained by the different stability of the intermediate isocyanates.[4] Compound VI was refluxed in acetone with sodium iodide to give 1-(2'-furyl)imidazolidine-2-one (VII) in 50% yield.

The mechanism of these rearrangements of I and VI to the corresponding imidazolidine-2-ones, V and VII, will be explained by Heine's theory about the rearrangement of the corresponding phenyl derivatives.[5] All attempts to isomerize I or VI with hydrochloric acid, hydrobromic acid and acetic acid failed and resulted in the formation of intractable tars.



Experimental

***N*-[β-(5-Nitro-2-furyl)vinyl]-*N'*-ethyleneurea (I).** A solution of 5.0 g (0.025 mol) of β-(5-nitro-2-furyl) acryloyl azide[3] in 40 m*l* of dry benzene was refluxed in an oil bath at 105°C for 7 hr until the evolution of nitrogen had perfectly ceased. After filtering off a small amount of an insoluble material, the filtrate was cooled to 10°C and a solution of 2.0 m*l* of aziridine in 10 m*l* of dry benzene was added dropwise to the cooled solution and the resulting reaction mixture was stirred at 10°C for 1 hr and then, at room temperature for 1 day. Precipitated crystals were collected and washed with a small amount of benzene to afford I as red crystals, mp 181—182°C (EtOH–C_6H_6).

Found: C, 48.06; H, 3.96; N, 18.66%. Calcd for $C_9H_9O_4N_3$: C, 48.43; H, 4.06; N, 18.85%.

UV: λ_{max}^{DMF} mμ (ε) 421 (17900). IR: (KBr) cm^{-1} 3350 (ν_{NH}), 1678 (ν_{CO}).

β-(5-Nitro-2-furyl)vinyl Isocyanate (II). The above experiment was repeated and after filtering off a small amount of an insoluble material, benzene used as a solvent was removed under reduced pressure at room temperature and the residual yellow crystals were recrystallized from a small amount of benzene to give II of mp 88—89°C, indicating a characteristic IR absorption at 2260 cm^{-1} (ν_{NCO}).

Found: C, 46.58; H, 2.19; N, 15.63%. Calcd for $C_7H_4O_4N_2$: C, 46.67; H, 2.24; N, 15.55%.

Reaction of I with *p*-Toluidine. I, 0.5 g (0.002 mol), was melted with 0.5 g (0.004 mol) of *p*-toluidine at 50°C and the mixture was kept standing at room temperature for 1 month. Solidified masses were dissolved in chloroform and chromatographed on a silica gel column, using chloroform as an eluent. From the first and second fractions of the chromatography there obtained a small amount of intractable red oils, which were not further investigated and discarded; from the third fraction there obtained 0.15 g of purple-red crystals of mp 179—180°C (EtOH), the structure of which was confirmed as III by the following spectral data: IR spectrum (KBr disk), 3380 (ν_{NH}), 1687 (ν_{CO}) cm^{-1} and UV spectrum, λ_{max}^{EtOH} 412 ($\varepsilon=13400$) and 253 ($\varepsilon=17200$) mμ, shifting hypsochromically compared with I.

Found: C, 58.38; H, 5.39%. Calcd for $C_{16}H_{18}O_4N_4$: C, 58.17; H, 5.49%.

Reaction of I with *p*-Phenetidine. Similarly, red crystals of mp 194—195°C were obtained in 12% yield. The structure was confirmed as IV, considering from the similar spectral patterns as III.

Found: C, 56.34; H, 5.73%. Calcd for $C_{17}H_{20}O_5N_4$: C, 56.66; H, 5.59%.

1-(5'-Nitro-2'-furyl)vinylimidazolidine-2-one (V). I, 0.38 g (0.0015 mol), was dissolved in 20 m*l* of acetone and 0.22 g (0.0014 mol) of sodium iodide was added to this solution. The mixture was refluxed for 17 hr. During this period of time a crystalline substance was separated. After cooling, it was collected and recrystallized from a mixture of DMF and EtOH to give V as red crystals, mp 237—239°C (decomp).

Found: 48.41; H, 4.22; N, 18.58%. Calcd for $C_9H_9O_4N_3$: C, 48.43; H, 4.06; N, 18.83%.

***N*-Furyl-*N'*-ethyleneurea (VI).** Similarly as for the preparation of I, from furyl isocyanate, which was prepared in 70% yield from furoyl azide by the known procedure,[4] bp 111°C, and aziridine there obtained VI as white needles (petroleum ether + benzene), mp 98—99°C.

Found: C, 55.26; H, 5.16; N, 18.00%. Calcd for $C_7H_8O_2N_2$: C, 55.25; H, 5.30; N, 18.41%.

UV: λ_{max}^{EtOH} mμ (ε) 250 (13300). IR: (KBr) cm^{-1} 3200 (ν_{NH}), 1700 (ν_{CO}).

1-(2'-Furyl)imidazolidine-2-one (VII). VI, 0.4 g (0.0034 mol), was dissolved in 20 m*l* of dry acetone and 0.32 g (0.002 mol) of sodium iodide was added to this solution. After refluxing the reaction mixture for 11 hr, the solvent was removed under reduced pressure, 50 m*l* of water was added to the residue and the solution was extracted with ether. The ether extract was dried over anhydrous sodium sulfate and the ether was removed. The residue was recrystallized from benzene - petroleum ether to give VII as colorless crystals, mp 124—126°C.

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[4] H. M. Singleton and W. R. Edwards, Jr., *J. Am. Chem. Soc.*, **60**, 540 (1938).

[5] H. W. Heine, *Angew. Chem.*, **60**, 540 (1962).

Found: C, 55.08; H, 4.96; N, 18.20%. Calcd for $C_7H_8O_2N_2$: C, 55.25; H, 5.30; N, 18.41%.

UV: λ_{max}^{EtOH} mμ (ε) 253 (13500). IR: (KBr) cm^{-1} 3230 (ν_{NH}), 1710 (ν_{CO}).

The authors wish to thank Mr. Akiho Ishihara at their laboratories for microanalyses and the Ueno Pharmaceutical Co. for kind supply of some starting materials. For the NMR spectral measurements the authors are much indebted to the Dainippon Pharmaceutical Co.