in a mixture of 5 ml of dioxane and 5 ml of methanol. Imidazolidine IVb crystallized after refluxing reagents I and IIIb for 8 h in a mixture of 5 ml of dioxane, 5 ml of methanol, and 5 ml of water. The product was isolated by treatment with methanol. The yield was 0.014 g (5.2%).

X-Ray Diffraction Analysis of Methyl (1-Allyl-5-oxo-2-thioxoimidazolidin-4-ylidene) acetate (IVa). The light-yellow single crystals of IVa ($C_9H_{10}N_2O_3S$), which were grown from methanol, were characterized by the following crystallographic parameters: $a = 9.068(2)$, $b = 5.062(2)$, $c = 23.624(7)$ Å, $\beta = 105.44(2)°$, $V = 1045.3(5)$ Å^3, $M = 226.24$, $d_{calc} = 1.44$ g·cm^{-3}, $Z = 4$, space group $P2_1/c$. The cell parameters and the intensities of 1700 reflections were measured with a Syntex $P2_1$ automatic diffractometer (Cu Kα emission, graphite monochromator, θ/2θ scanning up to $2\theta_{max}$ 150°). To decode the structure we used 1215 independent reflections with $I \geq 2\sigma_I$. The calculations were made with a Nova-1200 minicomputer by means of programs of the XTL system. The structure was decoded by the direct method by means of the MULTAN program and was refined by the total-matrix method of least squares within the anisotropic approximation for the nonhydrogen atoms and within the isotropic approximation for the hydrogen atoms (the coordinates of which were localized from differential synthesis) with the use of the weight scheme $I/W = \sigma_F^2 + (0.01F_0)^2$ up to a final value $R = 0.068$.

The coordinates of the atoms thus obtained are presented in Table 1.

LITERATURE CITED

1. G. A. Bremanis, I. Ya. Kalvin'sh, M. P. Gavars, P. T. Trapentsier, and É. Lukevits, Izv. Akad. Nauk Latv. SSR, No. 5, 586 (1986).
2. G. A. Bremanis, I. Ya. Kalvin'sh, É. Lukevits, and É. É. Liepin'sh, Izv. Akad. Nauk Latv. SSR, No. 5, 591 (1986).
3. A. N. Kost and S. I. Suminov, Zh. Org. Khim., 1, 1341 (1965).
4. G. V. Rutkovskii, B. A. Ivin, E. G. Sochilin, and I. Yu. Tsereteli, Zh. Obshch. Khim., 40, 389 (1969).
5. C. Thieme and E. Hädicke, Annalen, No. 2, 227 (1978).
6. K. S. Dragonette and I. L. Karle, Acta Crystallogr., 19, 978 (1965).

1,2,4-TRIAZOL-3-ONE IN REACTION WITH ACETYLENE

B. V. Trzhtsinskaya, E. V. Rudakova, A. V. Afonin,
V. V. Keiko, and V. K. Voronov

UDC 547.792'314.2.07:
543.422.25

Depending on the conditions, the reaction of 1,2,4-triazol-3-one with acetylene leads to the addition of one or two molecules of acetylene to give, in the latter case, a mixture of divinyl isomers, $N_{(2)}N_{(4)}$, $N_{(1)}O$, and $N_{(2)}O$.

1,2,4-Triazole-3-thione and its 5-methyl(phenyl)-substituted derivatives react with acetylene in the presence of an alkaline catalyst primarily at the more nucleophilic sulfur atom to form the corresponding triazolyl vinyl sulfides [1-4]. The use of cuprous chloride or cadmium acetate promotes the addition of a second molecule of acetylene to one of the nitrogen atoms to give a mixture of isomers with respect to the $N_{(1)}$ and $N_{(2)}$ atoms.

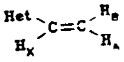
In the present research we studied the behavior of the oxygen analog of the thione – 1,2,4-triazol-3-one (I) – in the reaction with acetylene. Under the usual conditions for the synthesis of triazolyl vinyl sulfide (KOH, 180°C) the reaction of triazole I with acetylene proceeds with the formation of a very small amount of 4-vinyl-1,2,4-triazol-3-one (IIa). Increasing the reaction temperature to 240°C leads to a certain increase in the yield of IIa to 15%, but starting I remains unchanged. We were able to accomplish the complete conversion

---

Irkutsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR, Irkutsk 664033. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 9, pp. 1224-1226, September, 1987. Original article submitted May 19, 1986.

0009-3122/87/2309-0978$12.50

TABLE 1. PMR Spectra of Vinyl Derivatives of 1,2,4-Triazol-3-one

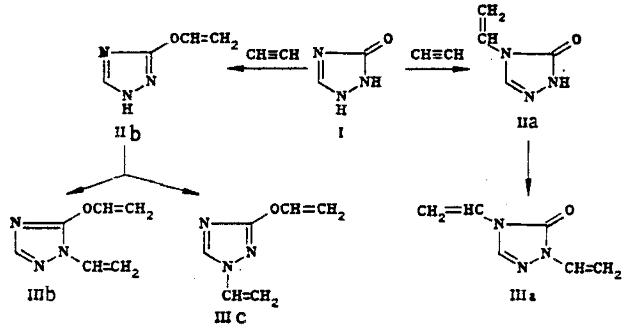


Compound	Position of the vinyl group in the ring	Chemical shifts, ppm			SSCC, Hz			
		A	B	X	$^3J_{AB}$	$^3J_{AX}$	$^3J_{BX}$	$^3J_{5X}$
IIa	4	4,91	5,29	6.68	−1,6	9,2	16,0	—
IIb	3	4,44	4,85	7,11	−1,9	6,0	13,6	—
IIIa	2	4,77	5,46	6,92	−0,4	9,1	15,7	0,7
	4	4,95	5,36	6,70	−1,7	9,2	16,2	—
IIIb	2	4,95	5,68	6.92	−0.9	9,1	15,6	0,7
	3	4.68	5,05	7.19	−2,5	5,9	13,6	—
IIIc	1	4,98	5,70	6.68	−1,3	8,6	15,3	—
	3	4,54	4,96	7,23	−1,9	5,9	13,6	—

of triazolone I when we used cadmium acetate as the catalyst at 240°C. Exhaustive vinylation is accompanied by the formation of products of the addition of two molecules of acetylene. The overall yield of the vinylation products in this case reaches 60%.

On the basis of an analysis of the PMR spectra of the individual fractions obtained by vacuum fractionation of the reaction products it was established that the low-boiling fraction is almost individual 2-vinyl-3-vinyloxy-1,2,4-triazole (IIIb). 2,4-Divinyl-1,2,4-triazol-3-one (IIIa) is characterized by the highest boiling point. From the intermediate fraction, which is a mixture of isomers, by gas–liquid chromatography (GLC) we were able to isolate 1-vinyl-3-vinyloxy-1,2,4-triazole (IIIc) in addition to divinyltriazole IIIa.

Decreasing the reaction temperature to 200°C leads to a sharp decrease in the yield of the divinyl derivatives and retention of monovinyltriazole IIa in the reaction products.



An analysis of the reaction products makes it possible to assume that the addition of acetylene to triazolone I initially takes place at the nitrogen atom in the 4 position of the heteroring and that a second molecule of acetylene "prefers" to attack the $N_{(2)}$ atom rather than the oxygen atom. Evidence for this is provided by the fact that monovinyltriazole IIa was detected, in addition to divinyl compounds IIIa-c, in the reaction products under more mild conditions. The formation of the O-monovinyl isomer of 3-vinyloxy-1,2,4-triazole (IIb), which was detected in one of the fractions in very small amounts only by means of PMR spectroscopy, evidently also proceeds simultaneously. It should be assumed that, as in the case of 1,2,4-triazole-3-thione [1], the addition of a second molecule of acetylene to IIb leads to isomers IIIb, c.

The reactivity of triazolone I in the reaction with acetylene is decreased significantly as compared with the reactivity of its sulfur analog. In the latter the addition of acetylene takes place primarily at the more nucleophilic center – the sulfur atom – and under milder conditions [1]. The acceptor effect of the carbonyl group predominates in triazolone I, and the attack by acetylene is directed to the nitrogen atom with the formation of primarily monovinyl product IIa.

As a consequence of the comparable activities of the two nucleophilic centers in cyclic amide I, exhaustive vinylation to give divinyl products occurs, and monovinyl products therefore could not be isolated in high yields.

Data from the PMR spectra of IIa, b and IIIa-c are presented in Table 1. In the spectra of IIa and IIIa the vicinal spin-spin coupling constants (SSCC) in the vinyl group are 9.1-9.2 Hz ($^3J_{AX}$) and 15.7-16.2 Hz ($^3J_{BX}$); this indicates the presence of only N-vinyl groups in these compounds [5]. In the spectrum of the IIb molecule $^3J_{AX}$ and $^3J_{BX}$ are 6.0 and 13.6 Hz, respectively. This constitutes evidence for the formation of an O-vinyl derivative [5]. Compounds IIIb, c have two vinyl groups for which the $^3J_{AX}$ and $^3J_{BX}$ values differ substantially. The values of the indicated SSCC of one of the vinyl groups lie in the region that is characteristic for N-vinyl derivatives, while they lie in the region that is characteristic for the O-vinyl derivatives in the case of the other group (see Table 1).

Long-range spin-spin coupling (LRSSC) between the ring protons and the H_X proton of the N-vinyl group (0.7 Hz) is observed in the PMR spectrum of the IIIb molecule, whereas it is absent in the spectrum of IIIc. The analogy with the products of the vinylation of triazolethione makes it possible to assign the IIIb molecule to the $N_{(2)}$O vinyl derivative and IIIc to the $N_{(1)}$O-divinyl derivative.

The presence of LRSSC of the ring proton with the H_X proton of one of the vinyl groups in IIIa indicates that it belongs to the $N_{(2)}$ atom. All of the spectral parameters of the second vinyl group of the N,N-divinyl derivative (IIIa) virtually coincide with those for N-monovinyl product IIa; this denotes the identical character of their location in the ring. In addition, it follows from this that the introduction of a vinyl group into the $N_{(2)}$ position does not have a steric effect on the second vinyl group, since otherwise this would cause a change in its spectral parameters [6]. It might therefore be assumed that the vinyl groups in IIIa are spatially remote from one another; this is possible only in the case of an $N_{(2)},N_{(4)}$-divinyl derivative.

The IR spectrum of monovinyl compound IIa contains an absorption band at 1650 cm^{-1}, which characterizes the $CH{=}CH_2$ group, intense absorption of a carbonyl group at 1715 cm^{-1}, and absorption bands of associated NH groups at 3100-3200 cm^{-1}. The IR spectrum of divinyl derivative IIIa is also characterized by the presence of the intense absorption of carbonyl (1720 cm^{-1}) and N-vinyl (1640 cm^{-1}) groups. The absorption of a carbonyl group is absent for isomers IIIb, c, but their spectra do contain a broad band at 1640-1650 cm^{-1}, which characterizes the overall absorption of the N- and O-vinyl groups, and absorption at 1140 cm^{-1}, which is due to stretching vibrations of a $C{-}O{-}C$ group.

EXPERIMENTAL

The PMR spectra of solutions of the compounds in $CDCl_3$ (5.0% solutions) were recorded with a Tesla BS-497 (100 MHz) spectrometer with hexamethyldisiloxane (HMDS) as the internal standard. The IR spectra of thin layers and KBr pellets of the compounds were recorded with a Specord IR-75 spectrometer. Preparative GLC was carried out with a 1 m × 10 mm column packed with 15% polyphenyl ether. The column temperature was 140°C, and the carrier gas was helium.

4-Vinyl-1,2,4-triazol-3-one (IIa). A steel rotating autoclave was charged with 5 g (0.06 mole) of triazole I, 1 g (20%) of KOH, 1 ml of water, and 300 ml of dioxane, and acetylene was fed in from a cylinder at an initial pressure of 9 atm. The reaction mixture was heated at 240°C for 4 h, after which the dioxane was removed by distillation, and the residue was passed through a column packed with Al_2O_3 [using chloroform—benzene—alcohol (10:2:1)]. The substance was purified by recrystallization from a mixture of acetone and hexane to give 0.9 g (15%) of a product with mp 150°C. Found: C 43.2; H 4.3; N 38.3%. $C_4H_5N_3O$. Calculated: C 43.2; H 4.5; N 37.8%.

Divinyl Derivatives (IIIa-c) of Triazolone. A mixture of 10 g (0.12 mole) of triazolone I, 2 g (20%) of cadmium acetate, and 300 ml of dioxane was saturated with acetylene, and the mixture was heated in an autoclave at 240°C for 4 h. The dioxane was removed, and the residue was distilled in vacuo to isolate isomer IIIb with bp 60-70°C (0.5 mm) and n_D^{20} 1.4930; the yield was 1.5 g (9%). We used GLC to isolate 1.8 g (11%) of isomer IIIc, with mp 35°C, and 6.5 g (40%) of isomer IIIa, with mp 43°C, from the fraction with bp 70-170°C (0.5 mm). Found: C 53.0; H 5.1; N 30.1%. $C_6H_7N_3O$. Calculated: C 52.5; H 5.2; N 30.6%.

LITERATURE CITED

1. G. G. Skvortsova, B. V. Trzhtsinskaya, L. F. Teterina, V. K. Voronov, and M. M. Popova, Khim. Geterotsikl. Soedin., No. 11, 1561 (1977).

2. B. V. Trzhtsinskaya, G. G. Skvortsova, Yu. A. Mansurov, P. I. Buchin, and M. G. Viderker, Khim.-Farm. Zh., No. 12, 58 (1982).
3. B. V. Trzhtsinskaya, E. V. Rudakova, A. V. Afonin, V. K. Voronov, and B. Z. Pertsikov, Izv. Akad. Nauk SSSR, Ser. Khim., No. 12, 2745 (1986).
4. B. V. Trzhtsinskaya, E. V. Rudakova, A. V. Afonin, B. Z. Pertsikov, and V. P. Aksenov, Izv. Akad. Nauk SSSR, Ser. Khim., No. 7, 1674 (1986).
5. A. Gordon and R. Ford, The Chemist's Guide [Russian translation], Mir, Moscow (1976), p. 303.
6. M. V. Sigalov, B. A. Trofimov, A. I. Michaleva, and G. A. Kalabin, Tetrahedron, 37, 3051 (1981).

FORMATION OF FURO- AND DIFURO-1,4-DIHYDROPYRIDINES IN THE BROMINATION OF 2,6-DIMETHYL -3,5-DIMETHOXYCARBONYL-4-(o-NITROPHENYL)-1,4-DIHYDROPYRIDINE

I. P. Skrastin'sh, V. V. Kastron, G. Ya. Dubur,
I. B. Mazheika, and V. P. Kadysh

UDC 547.728'828.04:
542.944'953:543.422

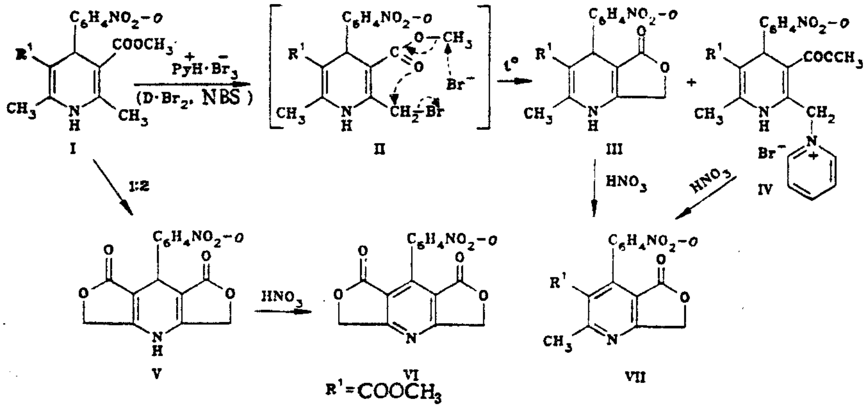
Furo- and difuro-1,4-dihydropyridines were obtained by bromination of 2,6-dimethyl-3,5-dimethoxycarbonyl-4-(o-nitrophenyl)-1,4-dihydropyridine with mild brominating agents (pyridinium bromide perbromide, N-bromosuccinimide, and dioxane dibromide).

Relatively little study has been devoted to the bromination of 1,4-dihydropyridines. The 2,6-methyl groups are brominated in the action of bromine on 4,4-disubstituted 1,4-dihydropyridines [1, 2], while 4-aryl-1,4-dihyropyridines are oxidized in this case and form unidentified substances [3-5]. It has been shown [6] that the action of a mild brominating reagent — pyridinium bromide perbromide — on 4-aryl-1,4-dihydropyridines does not lead to oxidation, and Young isolated lactones of the III type.

We have studied the action of pyridinium bromide perbromide, as well as dioxane dibromide and N-bromosuccinimide, on 2,6-dimethyl-3,5-dimethoxycarbonyl-4-(o-nitrophenyl)-1,4-dihydropyridine (I) (also known as nifedipine and fenigidin).

Bromination of the methyl group evidently occurs initially in the action of pyridinium bromide perbromide ($\mathrm{Py^{+}H\cdot Br_3^{-}}$) on I in an equimolar ratio in solution in chloroform. The

Scheme 1



Institute of Organic Synthesis, Academy of Sciences of the Latvian SSR, Riga 226006. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 9, pp. 1227-1232, September, 1987. Original article submitted May 16, 1986.