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1,3-DIPOLAR CYCLOADDITION OF 3-IMIDAZOLINE-3-OXIDE NITROXYL

RADICAL TO DIPOLAROPHILES CONTAINING CARBON-CARBON DOUBLE BONDS*

UDC 542.91:541.515:547.782:547.786

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Paramagnetic derivatives of 3-imidazoline-3-oxide incorporating a nitroxyl radical center and a nitronic group in one heterocyclic ring, are used as spin tracers in molecular biology and in analytical chemistry [2, 3]. Because of the reactivity of the nitronic group in these compounds with respect to electrophilic and nucleophilic agents, it was possible to synthesize an extensive group of functional derivatives [2]. In continuation of the study of the chemistry of 3-imidazoline-3-oxide, we turned our attention to 1,3-dipolar cycloaddition reactions [4]. It is known that the use of nitrons as additive groups in 1,3dipolar cycloaddition reactions gives heterocyclic derivatives, which can be converted into various classes of compounds [5].

In the present work, we studied the reaction of the nitroxyl radical, 2,2,5,5-tetramethyl-3-imidazoline-3-oxide-1-oxyl (I), which has an aldonitronic group in the composition of the heterocyclic ring, with dipolarophiles containing a C=C group. The aim of the present investigation was to establish the range of the possible addenda in 1,3-dipolar cycloaddition for this paramagnetic heterocyclic nitron and the stereochemistry of the reaction. It was also desired to investigate the possibility of using this reaction for introducing spin tracers into molecules of compounds containing a C=C bond, and also to synthesize new heterocylcic nitroxyl radicals.

When radical (I) is held for 3 h at 20°C in an excess of methyl acrylate, compound (II) is formed in quantitative yield, in the IR and UV spectra of which absorption of the nitronic grouping is absent. This indicates that compound (II) is an adduct in a 1,3-dipolar cycloaddition of methyl acrylate to the nitronic group, a derivative of isoxazolidine. However, with these data it is impossible to establish whether the radical formed is a 5- or 4-substituted isoxazolidine. To establish the stereochemistry of cycloaddition by the PMR

*For previous communication, see [1].

Novosibirsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR. Lenin Komsomol Novosibirsk State University. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 8, pp. 1875-1882, August, 1988. Original article submitted March 2, 1987.

 R^{4} ³ TABLE 1. PMR Spectral Data of Diamagnetic Cycloadducts H^{4}

Å2

 H^2

CH ₃	m SSCC, Hz	$R^{1} \qquad R^{2} \qquad R^{3} \qquad H^{1} - H^{2} \qquad H^{1} - R^{1} \qquad R^{1} - R^{2} \qquad H^{2} - R^{3} \qquad R^{1} - R^{3}$	2,44 3,74 4,32 6,9 6,5 6,8 - 4,8 8,7	2,67 - 4,67 7,9 4,7 7,9 - 4,9 8,5	2,64 7,30 5,04 7,5 5,5 13,1 - 5,3 8,7	3,69 3,72 4,90 8,5 ~ - 9,6 -	3,78 3,78 4,81 4,0 8,1
	SS	H ¹ H ² H ¹	6,9	7,9	7,5	8,5	4,0
		R3	4,32	4,67	5,04	4,90	4,81
CH ₃		R ²	3,74	1	7,30	3,72	3,78
	mq	Ъ	2,44	2,67	2,64	3,69	3,78
	, δ, F	H2	2,28	2,53	2,14	4,04	4,00
	shifts	iΗ	3,31	3,62	3,52	3,58	3,62
	nical	cH,	2,13	2,22	2,23	2,19	2,26
	Chei	-CH ₃ N	1,01 2,13	1,08 1,27	$1.12 \\ 1.27$	1,16 1,23	1,15 1,37
		4,4,6,6	0,94, 1,05,	0,96, 1,16,	1,07, 1,19,	1,06, 1,18,	1.08, 1.20,
		R ³	н	н	н	Н	COOCH
						H ₃	
	tructure	R²	COOCH	CN	C ₆ H5	C00CI	II
	Structure	R' R ²	H COOCH	II CN	II C ₆ H ₅	COOCH ₃ COOCI	COOCII2 II

method, we carried out a similar reaction with a diamagnetic analog of radical (I), 1,2,2,-5,5-pentamethyl-3-imidazoline-3-oxide (III). The reaction of compound (III) with excess methyl acrylate leads to adduct (IV), the IR spectrum of which is similar to that of radical (II), so that we can assume a similar structure for these two compounds. In the PMR spectrum of compound (IV) (Table 1), beside the signals of the gem-CH₃ groups at the 4- and 6positions of the imidazolidine ring and the signal of the N-CH_a group, three groups of multiplets are observed: those with 2H intensity in the 2.36 ppm region (the center of gravity of the multiplet; the calculated value of the chemical shifts of protons are 2.28 and 2.44 ppm) and those with 1H intensity in the 3.31 ppm and 4.32 ppm region, respectively. The methine protons have no relative spin-spin interaction (J = 0), which indicates that the signal of none of them changes when another proton is irradiated. This means that here is a -CH-CH2-CH2 fragment in the molecule, and this unequivocally indicates the presence of a 5-substituted isoxazolidine structure, so that a structure of 4,4,5,6,6-pentamethyl-2methoxycarbonylperhydroimidazo[1,5-b]isoxazole can be assigned to compound (IV), and that of 4,4,6,6-tetramethyl-2-methoxycarbonyl-5-hydroxyperhydroimidazo[1,5-b]isoxazole to radical (II).



The reaction of nitrons with monosubstituted olefins usually proceeds with the formation of mixtures of diastereomers, the ratio between which is determined by the preferentiality of an endo or exo transition state of the reaction [6]. Numerous examples of these reactions indicate that nitrons with an acyclic structure react preferentially via the endo transition state with favorable secondary orbital interactions, while the cyclic nitrons react via the sterically less strained exo transition state [4]. In the case of the 3imidazoline-3-oxide derivatives (I) or (III), the reaction leads to a single product (II) or (IV), respectively. By comparing the SSCC values in the PMR spectrum of compound (IV) with the values given in the literature for the exo adducts of nitrons [6-8], we were able to ascribe to compounds (II) and (IV) the structures with a cis coupling of the heterocyclic rings and a trans disposition of protons at C^2 and C^{3a} (cf. [8]). Thus, the addition of methyl acrylate to aldonitronic groups of 3-imidazoline-3-oxides (I) and (III) proceeds, as expected, at the less hindered side, i.e., via the exo transition state. The stereospecificity of the reaction may be explained by the presence of gem-methyl groups, flanking the nitronic grouping of 3-imidazoline-3-oxides and strengthening the steric requirements in the transition state (cf. [6, 9])



Radical (I) similarly adds other monosubstituted ethylenes: ethyl acrylate, methyl vinyl ketone, acrylonitrile, styrene, 4-vinylpyridine, and also N-vinylphthalimide, with the formation of 5-substituted isoxazolidines: 2-ethoxycarbonyl-(V), 2-acetyl-(VI), 2-cyano-(VII), 2-phenyl-(VIII), 2-(4-pyridyl)-(IX), 2-phthalimido-(X), 4,4,6,6-tetramethyl-5-oxyl-perhydroimidazo[1,5-b]isoxazoles. In the reaction of the diamagnetic compound (III) with acrylonitrile and styrene, cycloadducts (XI), (XII) are formed. The study of the PMR spectra of these compounds by the double resonance method confirms the stereochemistry proposed for the cycloaddition.

Addition of cis- and trans-1,2-disubstituted olefins, dimethyl maleate and dimethyl fumarate to 3-imidazoline-3-oxides (I) and (III) leads to the formation of cycloadducts (XII)-(XVI) as the only reaction products. Analysis of the PMR spectrum of the diamagnetic product (XIV) of the addition of dimethyl maleate at the nitronic group of compound (III), 4,4,5,6,6-pentamethyl-2,3-dimethoxycarbonylperhydroimidazo[1,5-b]isoxazole, shows that in this case, the reaction proceeds via a less hindered exo transition state. It is known that in the case of cycloaddition of trans-1,2-disubstituted olefins, the steric requirements of the carbon-carbon, and not of the carbon-oxygen bond are the most important [10]. From this fact, and also from the PMR spectral data of the diamagnetic adduct of dimethyl fumarate (XVI), structures with a trans diposition of protons at C³ and C^{3A} were ascribed to compounds (XV), (XVI) (cf. [8]).



According to the literature data [4], 1,2-disubstituted olefins with an acyclic structure, which have no electron-accepting activating substituents, practically do not enter into 1,3-dipolar cycloaddition reactions with nitrons. On prolonged heating of the paramagnetic nitron (I) with excess of methyl oleate, a cycloadduct (XVII) can be obtained, but the yield of the reaction is low. Compound (XVII) comprises a mixture of isomers (regioisomers or diastereomers), which is indicated by the splitting of the peak shown by HPLC analysis. In contrast, the cycloaddition of norbornene to radical (I) proceeds rapidly and leads to cycloadduct (XVIII) in a high yield. Comparison with the literature data [4] indicates that the addition of imidazoline oxide (I) proceeds at the least hindered exo side of norbornene.

	UV Spec	trum	IR Spec	trum (.v, cm ⁻¹)
Compound	λ, nm	lg ε	C=0	other bands
(II) (IV)	235 *	3,69	1740	1210 (C-O) 1210 (C-O)
(V) (VI)	236 230	$3,71 \\ 3,45$	1740	1210 (C-O)
(VII)	235 240	3,53		2250 (C=N)
(IX)	235	3,80 4,00	1730	
	*	3 83	1150	2250 (C=N)
(XIII) (XIII) (XIV)	235	3,48	1760	1220 (C-O)
(XIV) (XV)	238	3,52	1730, 1740	1220 (C-0) 1220 (C-0) 1220 (C-0)
(XVII) (XVIII)	2 30 220	3.30 3.77	1730. 1740	$ \begin{array}{c} 1220 & (C-0) \\ 1210 & (C-0) \end{array} $

TABLE 2. IR and UV Spectra of Synthesized Compounds

*There is no absorption above 220 nm.

elting Points and Data of Elemental Analysis of	
Yields,	
Conditions of Preparation,	
BLE 3.	1400+0

$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	3										
method transform transform			Reaction con	ditions				Found	d/Calculated		Hmnirica1
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$		method	tween the addenda, molar	T, °C	time, h	Yield, %	Mp, °C	υ	Ш	Z	formula
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$		A B	1:5	20 20	84	100	101-103 a	54,4	2'9	10,5	C ₁₁ H ₁₉ N ₂ O ₄
B 1:2 20 10 76 $\frac{34.3}{560}$ $\frac{31.4}{560}$ $\frac{10.6}{560}$ C ₁ H ₃ NO ₀ A 1:5 20 10 76 $\frac{56.0}{560}$ $\frac{34.3}{560}$ $\frac{10.6}{50}$ C ₁ H ₃ NO ₀ A 1:5 20 10 91 $125-127^a$ $\frac{56.0}{560}$ $\frac{8.5}{8.5}$ $\frac{11.7}{11.2}$ C ₁ H ₄ NO ₀ B 1:7 20 25 82 77.7 $\frac{8.6}{8.6}$ $\frac{8.5}{8.5}$ $\frac{11.1}{11.2}$ C ₁ H ₄ NO ₀ A 1:5 20 10 58 110-112 $\frac{64.1}{64.1}$ $\frac{7.3}{7.2}$ $\frac{10.1}{10.7}$ C ₁ H ₄ NO ₀ A 1:5 20 10 97 $\frac{7.3}{7.8}$ $\frac{10.1}{10.7}$ C ₁ H ₄ NO ₀ A 1:5 20 10 97 $\frac{7.3}{7.8}$ $\frac{10.5}{10.7}$ C ₁ H ₄ NO ₀ B 1:3 50 10 93 $\frac{10.3}{7.7}$ C ₁ H ₄ NO ₀ B 1:3 50 10 11 $\frac{7.5}$		V	1:3	20	10	100	3235 b	59,5 59,5	9,2 9,2	11,5	C ₁₂ H ₂₂ N ₂ O ₃
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$		В	1:2	20	10	76	84-86 a	59,5 56,2	9,1	11,6	C ₁₂ H ₂₁ N ₂ O ₄
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$		V	1:5	20	2	60	59 -60 a	56,0 56,2	8.2 8.2	10,8	C11H19N2O3
B 1:7 20 25 82 77-79a $\frac{53}{63}$ $\frac{7}{3}$ $\frac{101}{107}$ C ₁ H ₁₃ N ₂ O ₂ B 1:1.5 20 10 58 110-112 c $\frac{63}{644}$ $\frac{7}{73}$ $\frac{101}{107}$ C ₁ H ₁₃ N ₂ O ₂ B 0.5:1 50 15 37 178-179 c $\frac{61}{641}$ $\frac{7}{72}$ $\frac{100}{107}$ C ₁ H ₁₃ N ₃ O ₁ A 1:5 20 10 97 78-80 a $\frac{63}{643}$ $\frac{61}{3}$ $\frac{61}{3}$ $\frac{7}{7}$ $\frac{100}{9}$ C ₁ H ₁₃ N ₃ O ₁ A 1:5 20 10 97 73 $\frac{91}{93}$ $\frac{101}{93}$ C ₁ H ₁₃ N ₃ O ₁ B 1:3 50 10 93 $\frac{100}{101}$ C ₁ H ₁₃ N ₂ O ₂ B 1:3 50 10 93 $\frac{101}{106}$ C ₁ H ₁₃ N ₂ O B 1:3 50 10 60 $\frac{71}{75}$ $\frac{91}{93}$ C ₁ H ₁₃ N ₂ O B 1:3 50 10 60<		V	1:5	20	10	91	125-127 в	56,0 57,3	8,8 7,7	11,1	C10H18N3O2
B 1:1,5 20 10 58 110-112 63.9 80.0 10.7 C_{414} 7.8 10.7 C_{414} 7.0 10.7	_	ß	1:7	20	25	82	77-79 a	57,1 68,6	7,6 8,3	19,1 10,5	$C_{15}H_{21}N_2O_2$
B $0.5:1$ 50 15 37 $178-179c$ 64.1 7.2 160 G_1 T_1 T_2 160 G_1 1.7 G_1 <		ß	1:1,5	20	10	58	110–112 c	68,9 64,4	2,80	10,7	$C_{14}H_{19}N_8O_2$
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$		B	0.5:1	50	15	37	178–179 c	64,1 61,7	6.2	16.0	$\mathrm{C}_{17}\mathrm{H_{18}N_3O_4}$
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$		V	1:5	20	10	6	78—80 a	62,8 62,8	0,3	12,7	C ₁₁ II ₁₉ N ₃ O
B 1:3 50 4 70 100-102 c $\frac{7_{4}}{51.5}$ $\frac{8.9}{7.0}$ $\frac{10.6}{9.1}$ C ₁₃ H ₂ N ₂ O ₆ B 1:3 50 10 60 100-102 c $\frac{7.4}{51.6}$ $\frac{8.9}{7.0}$ $\frac{10.6}{9.2}$ C ₁₃ H ₂ N ₂ O ₆ B 1:3 50 10 60 106-108 c $\frac{51.6}{52.0}$ $\frac{8.0}{8.0}$ $\frac{9.4}{9.3}$ C ₁₃ H ₂₁ N ₂ O ₆ B 1:3 50 10 60 106-108 c $\frac{51.6}{52.0}$ $\frac{8.3}{7.0}$ $\frac{9.4}{9.3}$ C ₁₃ H ₂₁ N ₂ O ₆ B 1:3 50 16 60 35-38d $\frac{56.3}{56.3}$ $\frac{8.3}{8.3}$ $\frac{9.3}{9.3}$ C ₁₄ H ₂₁ N ₂ O ₆ B 1:10 50 60 12 Liquid d $\frac{70.1}{7.0}$ $\frac{9.3}{9.3}$ C ₁₄ H ₂₁ N ₂ O ₆ B 1:11/2 50 20 12 Liquid d $\frac{70.1}{7.0}$ $\frac{9.4}{9.3}$ C ₁₄ H ₂₃ N ₂ O ₂ B 1:11/2 50 2 72 126-128 a $\frac{67.1}{67.1}$		V	1:5	20	10	98	Liquid b	74.5	1.0	10.6	$C_{16}H_{24}N_2O$
B 1:3 50 10 62 96–98 ^a $\frac{51,8}{55,8}$ $\frac{7,0}{8,2}$ $\frac{9,2}{9,3}$ C ₁ /H ₂ /N ₂ O ₅ B 1:3 50 10 60 106–108 c $\frac{55,6}{51,8}$ $\frac{8,2}{8,2}$ $\frac{9,4}{9,3}$ C ₁ /H ₂ /N ₂ O ₅ B 1:3 50 10 60 106–108 c $\frac{55,6}{51,8}$ $\frac{8,2}{3,3}$ $\frac{9,4}{9,3}$ C ₁ /H ₂ /N ₂ O ₅ B 1:10 50 16 60 35–38d $\frac{56,3}{56,3}$ $\frac{8,3}{8,3}$ $\frac{9,3}{9,3}$ C ₁ /H ₂ /N ₂ O ₅ B 1:10 50 60 12 Liquid $\frac{70,1}{66,1}$ $\frac{11,3}{8,2}$ $\frac{9,3}{9,3}$ C ₁ /H ₂ /N ₂ O ₅ B 1:1,12 50 2 72 126–128 ^a $\frac{67,1}{67,1}$ $\frac{9,4}{9,4}$ C ₁ /H ₂ ₃ N ₂ O ₃		£	1:3	50	4	20	100–102 c	51.5	5.4 1.7	9,1	$\mathrm{C}_{13}\mathrm{H}_{21}\mathrm{N}_{2}\mathrm{O}_{6}$
B 1:3 50 10 60 106–108 c $\frac{50,0}{51,8}$ $\frac{3,0}{7,0}$ $\frac{3,3}{9,3}$ C ₁₃ H ₂₁ N ₂ O ₆ B 1:3 50 16 60 35–38 d $\frac{51,8}{51,3}$ $\frac{7,0}{7,0}$ $\frac{9,3}{9,3}$ C ₁₃ H ₂₁ N ₂ O ₆ B 1:3 50 16 60 35–38 d $\frac{56,0}{56,13}$ $\frac{8,3}{8,2}$ $\frac{9,3}{9,3}$ C ₁₃ H ₂₁ N ₂ O ₆ B 1:10 50 12 Liquid d $\frac{70,1}{10,13}$ $\frac{9,3}{5,8}$ C ₁₄ H ₂₄ N ₂ O ₅ B 1:1,12 50 2 72 126–128 a $\frac{67,1}{67,1}$ $\frac{9,4}{9,4}$ C ₁₄ H ₂₄ N ₂ O ₃		В	1:3	50	10	62	96—98 a	51,8 55,8	8,2	8'7 6'7	C141124N2O5
B 1:3 50 16 60 35-38 d $\frac{51,8}{56,3}$ $\frac{7,0}{8,3}$ $\frac{9,3}{9,3}$ C ₁₁ II ₂₄ N ₂ O ₅ B 1:10 50 60 12 Liquid d $\frac{70,1}{70,1}$ $\frac{9,3}{11,0}$ C ₁₄ II ₅₄ N ₂ O ₅ B 1:1,2 50 60 12 Liquid d $\frac{70,1}{10,1}$ $\frac{11,3}{11,0}$ $\frac{5,8}{6,2}$ C ₁₄ II ₅₆ N ₂ O ₅ B 1:1,2 50 2 72 126-128 ^a $\frac{67,1}{67,1}$ $\frac{9,3}{4,4}$ C ₁₄ H ₅₈ N ₂ O ₅		В	1:3	50	10	60	106–108 c	56,0 52,0	7.30	9.4	$\mathrm{C_{13}H_{21}N_2O_6}$
B 1:10 50 60 12 Liquid d 70.1 8.2 9.3 5.8 $C_{26}H_{50}N_2O_4$ B 1:1,2 50 2 72 126-128 ^a 67.1 11.3 5.8 $C_{26}H_{50}N_2O_4$ B 1:1,2 50 2 72 $126-128^{a}$ 67.1 9.4 11.3 $G_{14}H_{28}N_2O_2$		8	1:3	50	16	60	35–38 đ	01,X	0,7	0,0	C141124N2O5
B 1:1,2 50 2 72 $126-128^{a}$ $67,1$ $9,4$ $11,0$ $0,2$ $C_{14}H_{2s}N_2O_2$		B	1:10	50	60	12	Liquid d	1,07 1,07	11,3	5 0 0 0 0 0 0 0 0	C26H50N2O4
		В	1:1,2	20	5	72	126–128 a	67,1	9,4	11.3	$C_{14}H_{23}N_2O_2$

aFrom hexane. bWithout purification. cFrom a hexane-ethyl acetate, 3:1, mixture. dPurified chromatographically. .



The data obtained show that 2,2,5,5-tetramethyl-3-imidazoline-3-oxide-1-oxyl can be used as a spin tracer for introducing the radical fragment into molecules containing multiple bonds. It should be emphasized that introduction of a spin tracer into the substrate by cycloaddition, has obvious advantages from the standpoint of fixation of a radical fragment simultaneously at the two atoms at the multiple bonds. This enables exclusion of an intrinsic movement of radical [11]. This approach was used to synthesize spin-labeled rubbers in order to study the movement of the macro molecules by the EPR method [12].

EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrophotometer in KBr tablets and in CCl_4 solutions. The UV spectra were run in ethanol on Specord UV-VIS spectrophotometer. The PMR spectra were obtained in deuterochloroform on Bruker WP-200SY and Bruker CXP-300 spectrophotometers, using the double resonance method for the determination of SSCC. The uniformity of the reaction products was established by analysis of the PMR spectra of the reaction mixtures in the case of the diamagnetic compound and by HPLC method in the case of the paramagnetic compounds. The HPLC analysis was carried out on an Ob'-4 apparatus, using a nucleosil- C_{18} filled column with an efficiency of 4000 theoretical plates, with aqueous methanol (50-80%) as the mobile phase. The spectral characteristics of the products are given in Tables 1, 2; the conditions of preparation, yields, melting points and data of the elemental analysis are given in Table 3. The diamagnetic aldonitron (III) was synthesized according to [13].

2,2,5,5-Tetramethyl-3-imidazoline-3-oxide-1-oxyl (I). A 10-g portion of MnO₂ was added to a suspension of 3 g of 1-hydroxy-2,2,5,5-tetramethyl-3-imidiazoline-3-oxide [14] in 50 ml of CHCl₃, and the mixture was stirred for 2 h. It was then filtered, the filtrate evaporated, and the residue was purified by flash chromatography on a SiO₂ column (eluent -CHCl₃). The yield of radical (I) was 80% (according to [14], 32%). The paramagnetic aldonitron (I) can be stored for several days at 0°C, without decomposition.

<u>Reaction of 3-Imidazoline-3-oxides (I), (III) with Dipolarophiles. a) In Excess Di-</u> <u>polarophile</u>. Aldonitron (I) or (III) was dissolved in dipolarophile and the solution was held at a given temperature. The reaction mixture was evaporated, the residue was chromatographed on a SiO₂ column (eluent-CHCl₃) or recrystallized (compounds (II), (V), (VII), (VIII)).

<u>b.</u> In Solution. A dipolarophile was added to a solution of 1 g of aldonitron (I) or (III) in 10 ml of $CHCl_3$ and the mixture was held at a given temperature, and then was treated in a similar way as described above.

CONCLUSIONS

1. Derivatives of 3-imidazoline-3-oxide react with dipolarophiles containing a C=C bond to form perhydroimidazo[1,5-b]isoxazoles. The reaction proceeds regio- and stereo-specifically with the formation of 5-substituted isoxazolidines via a less hindered transition state.

2. The paramagnetic heterocyclic aldonitron, 2,2,5,5-tetramethyl-3-imidazoline-3-oxidel-oxyl, can be used as a spin tracer for compounds containing a C=C bond.

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REACTION OF AZOLONES WITH ACETYLENE

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An investigation of the reaction of benzimidazole-2-, 4,5-diphenylimidazole-2-, and 1,2,4-triazole-3-thiones with acetylene in the presence of KOH showed that regardless of the structure of the starting azole the reaction occurred primarily at the more nucleophilic sulfur atom. The use of copper monochloride as a catalyst led to addition of acetylene at a second center, the nitrogen atom [1-4].

In the present paper, we used 4,5-diphenylimidazol-2-one (I) and benzimidazol-2-one (II) and also indazol-3-one (III) in the reaction with acetylene. Under the conditions of [1-4], azolones (I)-(III) do not react with acetylene, or they form vinyl derivatives in significant amounts. When the reaction temperature was increased to 240°C, it was possible, in the presence of KOH, to obtain the N,N-divinyl derivative of azolone (I) in 36% yield and the N²,O-divinyl derivative of azolone (III) in 10% yield. In the presence of CuCl, the azolones do not react with acetylene.

It was determined that the most efficient catalyst for the vinylation of azolones is $Cd(OAc)_2$. Apparently, because of the comparable activity of both nucleophilic centers (N, O) in cyclic amides (I)-(III), we were unable to direct the reaction toward the formation of only the monovinyl product. In almost all cases, we observed exhaustive vinylation at the two reaction centers. However, in the reaction of azolone (I) with acetylene, we were able to recover all the possible mono- and divinyl derivatives.

Previously only azolone (VIII) was obtained by the reaction of (II) with acetylene under the conditions of alkaline catalysis [5]. We determined that in the presence of $Cd(OAc)_2$



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