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HEXAHYDROPYRIDAZINE DERIVATIVES.

3.* SYNTHESIS OF HEXAHYDRO-4-PYRIDAZINONES

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UDC 547.852.2

The reaction of azodicarboxylic acid esters with 2-methoxy- or 2-trimethylsilyloxy-1,3-butadienes gave a number of 1,2-bis(alkoxycarbonyl)-4-methoxy(trimethylsilyloxy)-1,2,3,6-tetrahydropyridazines, which were hydrolyzed to the corresponding hexahydro-4-pyridazinones.

The Diels—Alder reaction is widely used for the synthesis of six-membered heterocycles [2, 3]. Various combinations of heterodienes and heterodienophiles have been proposed [4, 5]. The possibilities of this reaction for the synthesis of heterocycles are far from having been exhausted.

We have previously reported the synthesis of 1,2-bis(methoxycarbonyl)-4-piperidazines by the [4 + 2]-cycloaddition of azodicarboxylic acid esters to 2-methoxy-1,3-butadiene with subsequent hydrolysis of the resulting 1,2-bis(alkoxycarbonyl)-4-methoxy-1,2,3,6-tetrahydropyridazines [1, 6]. To obtain new ketones of the hexahydropyridazine series with various substituents we studied the reaction of a number of other dienes (Ia-e) with azodicarboxylic acid esters IIa, b. In particular, 1,2-bis(ethoxycarbonyl)-4-methoxy-5-methyl-1,2,3,6-tetrahydropyridazine (III) was obtained from 2-methyl-3-methoxy-1,3-butadiene (Ia) [7]. The most convenient starting compounds for the synthesis of 6-substituted hexahydropyridazines are 2-trimethylsilyloxybutadienes Ib-d, which are readily accessible from α,β-unsaturated ketones [8-10]. The 1,2-bis(alkoxycarbonyl)-4-trimethylsilyloxy-1,2,3,6-tetrahydropyridazines IV-VII obtained in the reaction of Ib-d with esters IIa, b, like pyridazine III, are readily hydrolyzed by dilute hydrochloric acid at room temperature to give ketones VIII-XI in high yields. Evidence for this is provided by the absence in the PMR spectra of signals of OCH_3 and $OSi(CH_3)_3$ groups and the presence of 5-CH (VIII) and 5-CH_2 (VIII-XI) signals, as well as by the retention of the signals of protons of CO_2CH_3 (IX, X) and $CO_2C_2H_5$ (VIII, XI) groups (Table 1) (see scheme below).

1-Ethoxy-3-trimethylsilyloxy-1,3-butadiene (Ie) [11] behaves somewhat differently in this reaction. The 1,2-bis(alkoxycarbonyl)-3-ethoxy-5-trimethylsilyloxy-1,2,3,6-tetrahydropyridazines (XIIa, b) formed in the cyclization of Ie with azodicarboxylic acid esters IIa, b cannot be isolated. Fractional distillation of the reaction products gave 1,2-

*See [1] for Communication 2.

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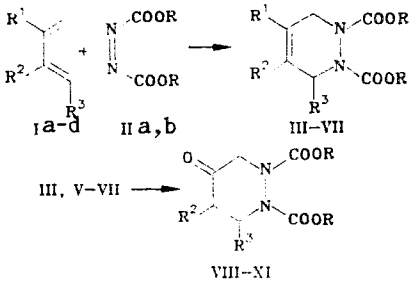
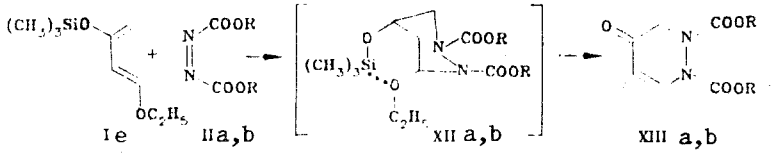
TABLE 1. Characteristics of the Synthesized III-XI and XIIIa, b

Compound	Empirical formula	bp, °C (mm)	R_f	IR spectrum, cm^{-1}		PMR spectrum, δ, ppm (J, Hz)	Yield, %
				$\nu_{C=C}$	$\nu_{C=O}$		
III	$C_{12}H_{20}N_2O_5$	152...154 (1)	0,55	1650	1710...1740	4,33...3,96 (4H, q, $2OCH_2CH_3$, $J=7$); 3,50 (3H, s, OCH_3); 3,83...3,33 (4H, m, $2NCH_2$); 1,60 (3H, s, CH_3); 1,35...1,01 (6H, t, $2OCH_2CH_3$, $J=7$)	90 76
IV	$C_{11}H_{20}N_2O_5Si$	132...135 (1,5)	0,51	1675	1725 (ester)	4,44...4,40 (1H, m, =CH); 4,22...3,45 (4H, m, $2NCH_2$); 3,40 (6H, s, $2OCH_3$); 0,15 (9H, s, $OSi(CH_3)_3$)	83
V	$C_{12}H_{22}N_2O_5Si$	125...130 (2)	0,48	1650, 1675	1720 (ester)	5,00...4,83 (1H, m, =CH); 3,83 (6H, s, $2OCH_3$); 2,30...1,70 (3H, m, CH, CH_2); 1,40...1,16 (3H, d, CH_3, $J=6$); 0,20 (9H, s $OSi(CH_3)_3$)	83
VI	$C_{17}H_{24}N_2O_5Si$	170...172 (1)	0,43	1625, 1635, 1670	1720, 1725, 1730	7,25 (5H, s, C_6H_5); 5,75 (1H, m, PhCH); 5,00 (1H, m, =CH); 3,73 (6H, s, $2OCH_3$); 3,07 (2H, s, NCH_2); 0,22 (9H, s, $OSi(CH_3)_3$)	88
VII	$C_{19}H_{28}N_2O_5Si$	180...181 (1)	0,41	1630 (arom) 1670	1720 (ester)	7,32 (5H, s, C_6H_5); 5,25...5,07 (1H, m, PhCH); 4,45...3,20 (7H, m, =CH, NCH_2, $2OCH_2CH_3$); 1,20 (6H, t, $2OCH_2CH_3$, $J=7$), 0,15 (9H, c, $OSi(CH_3)_3$)	95
VIII	$C_{11}H_{18}N_2O_5$	165...170 (1)	0,49		1680 (ketone) 1730 (ester)	4,60...3,66 (5H, m, CH, $2NCH_2$); 1,48...1,24 (6H, t, $2OCH_2CH_3$, $J=7$); 1,23...1,10 (3H, d, CH_3, $J=5$); 4,37...4,03 (4H, q $2OCH_2CH_3$, $J=7$)	79
IX	$C_9H_{14}N_2O_5$	155...157 (2)	0,37		1705, 1710 (ketone) 720, 725 (ester)	4,73...4,20 (2H, m, NCH_2); 3,76 (6H, s, $2OCH_3$); 2,66...1,90 (3H, m, CH, CH_2); 1,40...1,26 (3H, d, CH_3, $J=6$)	78
X	$C_{14}H_{16}N_2O_5$	180...185 (1)	0,47	1600 (arom) 1620	1710 (ketone) 1725 (ester) 740	7,30 (5H, s, C_6H_5); 5,70 (1H, t, PhCH); 4,35...3,40 (4H, m, $2CH_2$); 3,41 (3H, s, OCH_3); 3,38 (3H, s, OCH_3)	71
XI	$C_{16}H_{20}N_2O_5$	170...172 (2)	0,53	1600 (arom), 1620	1710 (ketone) 1725 (estern)	7,30 (5H, s, C_6H_5); 5,43 (1H, PhCH, $J=8$); 4,80...3,33 (6H, m, NCH_2, $2OCH_2CH_3$); 2,85...2,70 (2H, d, CH_2, $J=7$); 1,20 (6H, t, $2OCH_2CH_3$, $J=7$)	
XIIIa	$C_8H_{10}N_2O_5$	140...141 (3)	0,45	1600	1675, 1740	8,11...7,96 (1H, d, —CH=, $J=8$); 5,5...5,35 (1H, d, =CH—, $J=8$); 3,93 (3H, s, OCH_3); 3,83 (3H, s, OCH_3); 4,33...3,66 (2H, m, NCH_2)	89
XIIIb	$C_{10}H_{14}N_2O_5$	130...132 (1)	0,43	1600	1680 (ketone) 1690, 1725, 1740, 1750	8,10...7,95 (1H, d, —CH=, $J=8$); 5,45...5,31 (1H, d, =CH—, $J=8$); 4,50...3,56 (6H, m, NCH_2, $2OCH_2CH_3$); 1,40...1,10 (3H, t, OCH_2CH_3, $J=8$); 1,33...1,07 (3H, t, OCH_2CH_3, $J=8$)	77



IIb IV—VI, IX, X R=CH_3; IIa III, VII, VIII, XI R=C_2H_5; Ia III R^1=OCH_3, Ib–d, IV—VII R^1=$OSi(CH_3)_3$; Ia, III, VIII R^2=CH_3, Ib–d, IV—VII, IX—XI R^2=H; Ia,b, III, IV, VIII R^3=H, Ic, V, IX R^3=CH_3; Id, VI, VII, X, XI R^3=C_6H_5

bis(alkoxycarbonyl)-1,2,3,4-tetrahydro-4-pyridazinones XIIIa, b, as well as ethyl trimethylsilyl ether; this evidently attests to intramolecular transetherification.



II—XIII a R=CH_3; b R=C_2H_5

In the PMR spectra of XIIIa, b signals of 5H and 6H protons appear in the form of doublets at 5.35-5.51 and 7.96-8.11 ppm.

Thus the schemes presented above make it possible to obtain hexahydro-4-pyridazinones with substituents in various positions of the ring.

EXPERIMENTAL

The IR spectra of suspensions of the compounds in mineral oil were recorded with a UR-20 spectrometer. The PMR spectra of solutions in $CDCl_3$ were obtained with a Varian T-60 spectrometer (60 MHz) with tetramethylsilane (TMS) as the internal standard. Thin-layer chromatography was carried out on Silufol UV-254 plates in a hexane—acetone (2:1) system.

The results of elementary analysis for C, H, and N were in agreement with the calculated values.

1,2-Bis(alkoxycarbonyl)-4-methoxy- and 1,2-Bis(alkoxycarbonyl)-4-trimethylsilyloxy-1,2,3,6-tetrahydropyridazines III-VII. A 0.1-mole sample of the corresponding diene Ia-d was added dropwise with stirring and cooling to 20°C to a solution of 0.1 mole of azodicarboxylic acid ester IIa, b in 50 m of chloroform. At the end of the exothermic reaction (~0.5 h) the mixture was stirred for 1 h at 20°C. The chloroform was then removed by distillation, and the residue was subjected to fractional distillation.

1,2-Bis(alkoxycarbonyl)-1,2,3,4-tetrahydro-4-pyridazinones XIIIa, b. These compounds were similarly obtained.

1,2-Bis(alkoxycarbonyl)hexahydro-4-pyridazinones VIII-XI. A solution of 0.1 mole of the corresponding vinyl ether III-VII in 50 ml of 20% HCl was stirred for 4 h at 20°C, after which the mixture was extracted with chloroform (3 × 50 ml). The extract was dried with $MgSO_4$, the solvent was removed by distillation, and the residue was subjected to fractional distillation.

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RESEARCH IN THE CHEMISTRY OF HETEROCYCLIC QUINONE IMINES.
11.* EFFECT OF BENZANNELATION ON THE OXIDATIVE CYCLIZATION OF DIARYLAMINO-N-ARYL-1,4-BENZOQUINONE MONOIMINES TO PHENAZINONE DERIVATIVES

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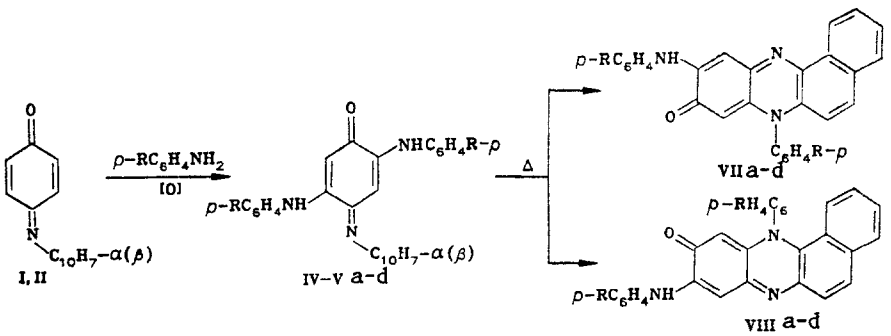
2'567.5.07:542.943:543.422

2,5-Diarylamino-N-α(β)-naphthyl-1,4-benzoquinone monoimines undergo oxidative cyclization to give benzannelated phenazinone derivatives. The effect of an N-aryl fragment on the ease of cyclization decreases in the order N-β-naphthyl > N-α-naphthyl > N-phenyl. 2-Arylamino-N-phenyl-1,4-naphthoquinone monoimines do not undergo oxidative cyclization to phenazinones.

It has been previously shown [2] that the cyclization of diarylamino-N-phenyl-1,4-benzoquinone monoimines is a simple and convenient method for the synthesis of phenazinone derivatives, which may be of interest as biologically active compounds [3]. Arylamino derivatives of benzannelated phenazinones can be obtained by the oxidative cyclization of the corresponding N-aryl-1,4-benzo(naphtho)quinone monoimines.

In the present research we examined the effect of annelation of the aromatic and quinone imine fragments in arylamino derivatives of quinone monoimines on oxidative cyclization to phenazinones. Arylamino derivatives of quinone monoimines are formed in the reaction of aromatic amines with N-α-naphthyl-1,4-benzoquinone monoimine (I), N-β-naphthyl-1,4-benzoquinone monoimine (II), and N-phenyl-1,4-benzoquinone monoimine (III). The reactions of the benzologs I and II of N-phenyl-1,4-benzoquinone monoimine with an annelated aromatic fragment with arylamines proceeds without pronounced differences from the reactions with nonannelated quinone imine. In the case of refluxing in ethanol the only products of nucleophilic arylamination of I and II are 2,5-diarylamino-N-α(β)-naphthyl-1,4-benzoquinone monoimines IVa-d and Va-d, which correspond to addition of the nucleophile to the C=C—C=N and C=C—C=O conjugated systems. The formation of the reduced form of the substrates indicates their participation in oxidation of the intermediately obtained adducts.



IV, V, VII, VIII a R=H, b R=CH_3O, c R=Br, d R=Cl

The PMR spectra of IVa-d and Va-d are similar to the spectra of the nonannelated analogs [2] and contain two singlet signals (1H, 1H) at 5.9-6.3 ppm belonging to the quinone imine 3-H and 6-H protons (compare with the PMR spectra of unsubstituted quinone imines I and II [4]), a multiplet of aromatic protons, and weak-fields signals of protons of amino groups. The structural similarity of the amino derivatives is also manifested in the common character of their electronic spectra (see Table 1).

*See [1] for Communication 10.
†Deceased.

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