SYNTHESIS OF 1-BENZOXEPINES FROM DICHLOROCARBENE ADDUCTS OF CHROMENES

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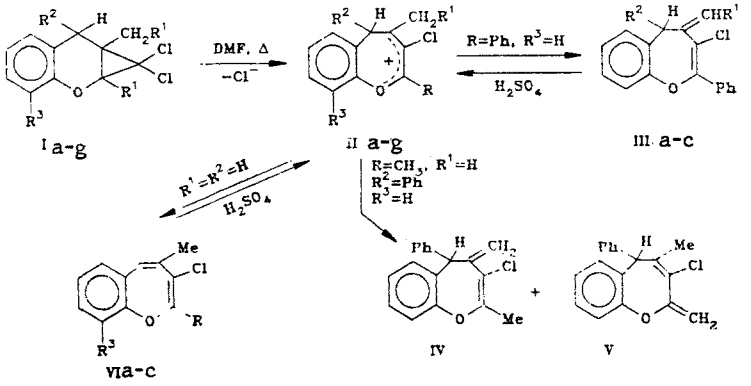
Synthesis of 1-benzoxepines by dehydrochlorination of carbene adducts of chromenes has been carried out. Different alkyl-, alkylidene-, alkoxy-, aryl- and hetaryl-substituted 1-benzoxepines were obtained.

The practical significance of benzoxepines [1, 2] dictates the necessity of a search for effective methods for their preparation [3, 8]. These include the expansion of pyran to an oxepine ring, starting from gem-dihalocyclopropane derivatives of pyrans and benzopyrans, which attracts particular attention, since the ability of bicyclic halocyclopropanes to undergo an expansion of the ring annelated with a trimembered ring is well known [9, 10]. This reaction was used for the preparation of 6,7-dihydrooxepines [11-14], 6-oxooxepine [15], and 1,3-dihydro-2-benzoxepines [16]. Attempts to synthesize 1-benzoxepines from gem-dihalocyclopropane derivatives of unsubstituted 2H- and 4H-chromenes wre not successful [17, 18]. The aim of the present work was to explore the possibilities of obtaining 1-benzoxepines from dichlorocarbene adducts of chromenes and to study the influence of the nature of the substituent in the dichlorocyclopropane ring in promoting the ring opening. The dehydrochlorination of the starting dichlorocyclopropanes was carried out by boiling them in DMFA (pyridine is ineffective because of its low boiling point, which the use of quinoline at 150°C leads to lowering of the yield of the reaction products). We were unable to obtain 1-benzoxepines from 2-phenyl-3-unsubstituted dichlorocyclopropane derivatives of 4H-chromenes (their synthesis is described in [19]), but compounds Ia-g having an alkyl group at the 3-position of the pyran ring rearrange into 1-benzoxepine derivatives IIIa-c, IV, V, VIa-c:



I a-g II a-g III a-c VIa-c IV V

I, II **a** R=Ph, R^1=H, R^2=Ph, R^3=H; **b** R=Ph, R^1=CH_3, R^2=Ph, R^3=H; **c** R=Ph, R^1=R^2=R^3=H; **d** R=Ph, R^1=H, R^2=CH_3, R^3=H; **e** R=CH_3, R^1=R^2=R^3=H; **f** R=Ph, R^1=R^2=H, R^3=CH_3; **g** R=CH_3, R^1=H, R^2=Ph, R^3=H; III **a** R^1=H, R^2=Ph; **b** R^1=CH_3, R^2=Ph; **c** R^1=H, R^2=CH_3; VI **a** R=Ph, R^3=H; **b** R=Ph, R^3=CH_3; **c** R=CH_3, R^3=H

As is known, the first stage in the mechanism of opening of the dichlorocyclopropane ring is the ionization of the halogen atom and a disrotatory cleavage of the C–C bond, with the formation of an allyl cation of type II [20]. By increasing the electron density in the cyclopropane ring, the alkyl groups promote the successful course of this process. Deprotonation of the intermediate cations IIa-g leads to the reaction products IIIa-c, IV, V, and

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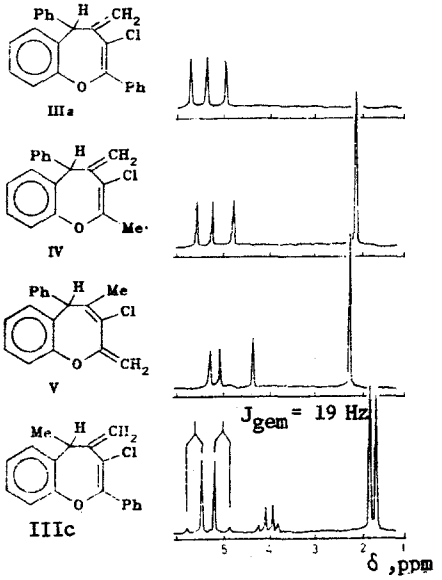


Fig. 1. PMR spectra of 1-benzoxepines IIIa, c, IV, and V. Multiplets of aromatic protons are not shown here.

VIa-c*. The direction of the deprotonation is determined by the presence or absence of a substituent at the 5-position of cations II. Thus, in the 5-substituted cations IIa, b, d, g, the proton splits off from the alkyl group, and in the 5-unsubstituted compounds, from the cyclic carbon atom. This can be explained by the presence of steric hindrances, created by the substituent at the 5-position of cations IIa, b, d, g when the solvent approaches the proton being eliminated. Dimethylamine hydrochloride was isolated from the reaction mixture, which corresponds to the interaction of the split-off proton with DMFA.

The protonation of compounds IIIa and VIa,c (their dissolution in 98% H_2SO_4 at 20°C) makes it possible to reconstruct the intermediate cations IIa,c,e which we observed by the PMR method (see the experimental part), which serves as confirmation of the proposed reaction scheme.

The structure of the 1-benzoxepines synthesized was proven by spectral methods. In the PMR spectra of compounds IIIa, IV, V, the signals of the diastereotopic protons of the methylene group [21] appear in the form of two lines, which corresponds to an AB-quartet, whose external lines cannot be seen. As is known, this phenomenon occurs when the inner lines are close to one another and the value of SSCC is fairly high [22]. In the PMR spectrum of compound IIIc, recorded at a higher concentration, the outer lines can be seen, so that the geminal SSCC, equal to 19 Hz, can be measured (see Fig. 1). The signals of tertiary protons of 1-benzoxepines IIIa, c, IV, V are present at 4.85, 3.88, 4.75, and 4.45 ppm, respectively. As expected, in the case of compound IIIb, a quartet of an olefinic proton (6.30 ppm) and a doublet of the methyl group proton (1.85 ppm) are observed [23]. Dichlorocyclopropane Ig converts into a mixture of two products with mp 80 and 129°C and at an overall yield of 33%. These compounds have a similar character of the PMR spectra with different CS of the methylene protons, which corresponds to two isomers IV and V. As is known, the CS value of the β-protons of vinyl esters is lower than that of the usual alkenes [24] due to the electron-donor influence of the oxygen atom. Therefore structure IV can be ascribed to the compound with mp 129°C, for which lower CS values of the olefinic protons are characteristic than for its isomer, since in this case the electron-donor influence of the oxygen atom should be more strongly evident than in compound V (see Fig. 1). This is confirmed by the data in [25], wherein the PMR spectra of different alkoxy-1,3-dienes are discussed.

In the IR spectra of compounds IIIa-c, IV, and V, a band appears at 1625-1600 cm^{-1}, which we assign to the double bond vibrations, rather than to the vibrations of the aromatic rings, since in the IR spectra of the corresponding dichlorocyclopropane derivatives, the

*During the opening of the three-membered ring of compounds Ic,e,f, other products are formed besides benzoxepines, whose structure is now being clarified.

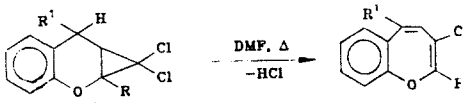
TABLE 1. IR Spectra, Elemental Analysis and Yields of Dichlorocyclopropane Derivatives

Compound	IR spectrum, cm^{-1}		Found, %			Empirical formula	Calculated, %			Yield, %
	benzene rings	C—O—C	C	H	Cl (S)		C	H	Cl (S)	
Ia	1585	1240	72,6	4,5	18,6	$C_{23}H_{18}Cl_2O$	72,5	4,8	18,6	77
Ib	1595	1235	72,9	5,1	17,9	$C_{24}H_{20}Cl_2O$	72,8	5,2	17,8	76
Ic	1580	1220	66,9	4,7	23,3	$C_{17}H_{14}Cl_2O$	66,9	4,6	23,2	52
Id	1585	1215	68,0	5,1	22,1	$C_{18}H_{16}Cl_2O$	67,7	5,0	22,2	73
Ie	1530	1240	59,3	5,1	29,0	$C_{12}H_{12}Cl_2O$	59,3	5,0	29,2	61
If	1595	1205	67,5	5,1	22,3	$C_{18}H_{16}Cl_2O$	67,7	5,0	22,2	54
Ig	1590	1265	67,4	4,9	22,2	$C_{18}H_{16}Cl_2O$	67,7	5,0	22,2	80
VIIa	1610, 1595	1240	69,5	4,6	17,9	$C_{22}H_{18}Cl_2O_2$	69,8	4,4	17,7	80
VIIb	1610, 1585	1245	62,5	4,0	17,6 (8,0)	$C_{21}H_{18}Cl_2O_2S$	62,7	4,1	17,6 (7,9)	74
VIIc	1580	1250	64,4	3,6	19,0 (8,6)	$C_{19}H_{14}Cl_2OS$	64,4	3,8	19,0 (8,6)	74
IXb	1610, 1580	1220	65,3	5,5	20,1	$C_{19}H_{19}Cl_2O_2$	65,2	5,5	20,2	84

1585-1595 cm^{-1} frequency, also retained in the spectra of 1-benzoxepines IIIa-c, IV, V, corresponds to the benzene rings. The presence of a conjugated system of double bonds is also indicated by the absorption at 292 nm in the UV spectrum of compound IIIa. The molecular weight of this 1-benzoxepine was confirmed mass-spectrometrically.

In the PMR spectra of compounds VIa-c methyl group proton signals are observed at 1.75-2.10 ppm. The singlet of the olefinic proton of 1-benzoxepine VIc is present at 6.35 ppm, and of compounds VIa, b in the aromatic multiplet region. In the IR spectra, the vibration band of the C=C bond is observed at 1620-1640 cm^{-1}. The molecular weight of 1-benzoxepine VIa was measured mass-spectrometrically, and corresponds to the calculated value.

In order to carry out the synthesis of 1-benzoxepines successfully, not only alkyl groups can be used as electron donors promoting the opening of the dichlorocyclopropane ring. The anticipated 1-benzoxepines VIIIa, b can be obtained by introducing a methoxy group into the para-position of the 2-phenyl ring. Dichlorocyclopropane VIIc having a π-excessive thienyl substituent at the 2-position also converts into 1-benzoxepine VIIIc:



VII a-c VIII a-c

VII, VIII a R=$C_6H_4OCH_3$-*p*, R^1=Ph; b R=$C_6H_4OCH_3$-*p*, R^1=2-thienyl, c R=2-thienyl R^1=Ph

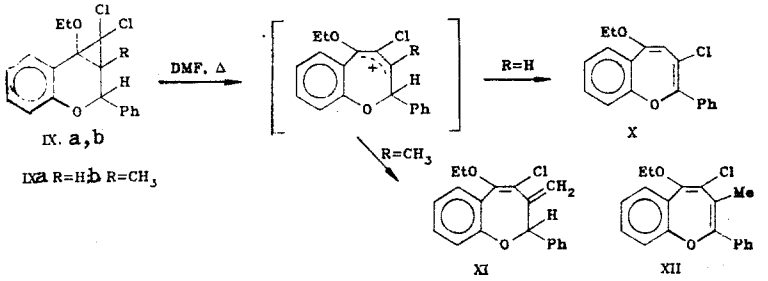
In the PMR spectra of compounds VIIIa, c, signals of the oxepine ring proton are observed at 6.45 and 6.42 ppm, respectively. An oxepine proton signal of the 5-thienyl-substituted compound VIIIc lies in an aromatic multiplet region. In the IR spectra, a double bond vibration band is noted at 1615 cm^{-1}. The presence of a double bonds system conjugated with benzene rings is indicated by absorption at 348, 360 and 362 nm, respectively, in the UV spectrum of compounds VIIIa-c. These bands are shifted in the direction of longer wavelengths, compared with the band of 1-benzoxepine IIIa (292 nm), in which, in contrast to the $C_{(4)}$—$C_{(5)}$ double bond in compounds VIIIa-c, the double bond of the exomethylene group is not conjugated with phenyl substituent at $C_{(5)}$ and the benzene ring condensed with the seven-membered ring. Moreover, it is known that homoannular dienes absorb at higher values than the heteroannular dienes [26]. The molecular weights of compounds VIIIa, b were measured mass-spectrometrically and coincide with the calculated values.

The formation of 1-benzoxepines proceeds also from adducts of dichlorocarbene and 4-ethoxy-2H-chromenes IXa, b. In the case of compound IXb, a deprotonation of the tertiary carbon atom and the methyl group takes place with the formation of a mixture of isomeric 1-benzoxepines XI and XII in a 5:2 ratio, respectively, as determined by the PMR method.

TABLE 2. Melting Points and PMR Spectra of Dichlorocyclopropane Derivatives

Compound	mp, deg C	PMR spectrum, δ, ppm (J, Hz)
Ia	135—137	1,15 (3H, s, 3-CH_3); 4,5 (1H, s, 4-H); 6,6—7,8 (14H, m, H_{arom})
Ib	203	1,0 (3H, t, J=5,3, CH_3); 1,15—1,6 (2H, m, CH_2); 4,35 (1H, s, 4-H); 6,45—7,6 (14H, m, H_{arom})
Ic	109—110	1,25 (3H, s, 3-CH_3); 2,8 (1H, d, J=16, 4-H_{endo}; 3,19 (1H, d J=16, 4-H_{exo}); 6,4—7,6 (9H, m, H_{arom})
Id	75—77	1,3 (3H, s, 3-CH_3); 1,55 (3H, s, 2-CH_3); 2,6 (1H, d, J=16,5, 4-H_{endo}); 3,05 (1H, d, J=16,5, 4-H_{exo}); 6,65—7,23 (4H, m, C_6H_4)
Ie	85—86	1,28 (3H, s, 3-CH_3); 1,8 (3H, s, 8-CH_3); 2,8 (1H, d, 4-H_{endo}); 3,2 (1H, d, J=16, 4-H_{exo}); 6,5—7,5 (8H, m, H_{arom})
Ig	156—157	0,9 (3H, s, 3-CH_3); 1,65 (3H, s, 2-CH_3); 4,1 (1H, s, 4-H); 6,3—7,5 (9H, m, H_{arom})
VIIa	122—124	2,4 (1H, d, J=1,5, 3-H); 3,6 (3H, s, OCH_3); 4,2 (1H, d, J=1,5, 4-H); 6,4—7,5 (13H, m, H_{arom})
VIIb	111—112	2,55 (1H, d, J=1,5, 3-H); 3,7 (3H, s, OCH_3); 4,6 (1H, d, J=1,5, 4-H); 6,5—7,6 (11H, m, H_{arom})
VIIc	120—121	2,45 (1H, d, J=1,8, 3-H); 4,15 (1H, d, J=1,8, 4-H); 6,45—7,4 (12H, m, H_{arom})
IXd	114—116	0,8—1,4 (6H, m, 3-CH_3 and OCH_2CH_3); 2,9—3,7 (2H, m, OCH_2CH_3); 5,3 (1H, s, 2-H); 6,6—7,6 (9H, m H_{arom})

*Solvent for recrystallization of compounds Ia, g, VIIc – 1-propanol; for IVb, VIIa, b – butanol; for Ic, e, f, IXb – ethanol.



Thus, to carry out successfully a synthesis of 1-benzoxepines from dichlorocarbene adducts of chromenes, the presence of electron-donor substituents in the cyclopropane ring is necessary. These can be of different nature: they can be alkyl and ethoxy groups, a p-methoxyphenyl substituent, or a π-excessive heterocycle, which shows a fairly broad latitude of the proposed method for the synthesis of 1-benzoxepines.

EXPERIMENTAL

The PMR spectra were run on a Tesla BS-487 spectrometer (80 MHz), using HMDS as internal standard; solvent – CCl_4 (for compound VIIIb, CH_2Cl_2 was used as solvent). The IR spectra were recorded on a Specord IR-71 spectrophotometer in mineral oil, using NaCl prism. The UV spectra were obtained on a Specord UV-vis spectrophotometer, and the mass spectra on a MS-30 spectrometer.

2,3-Dichloromethylene-1-benzodihydropyrans (Ia-g, VIIIa-c) and 3,4-dichloromethylene-2-phenyl-3-methyl-4-ethoxy-1-benzodihydropyran (IXb) are obtained by treating the corresponding chromenes with dichlorocyclopropane by the method of interphase catalysis [19]. A solution of 5 g of chromene in 100 ml of chloroform is stirred for 2 h with 50 ml of a 50% aqueous solution of NaOH and 0.1 g of triethylbenzylammonium chloride. The mixture is diluted with water, the organic layer is separated, washed with 10% HCl, and chloroform is distilled off on a water bath. The solid residue is recrystallized* (Tables 1, 2). The method of preparation and characteristics of compound IXa are given in [19].

1-Benzoxepines IIIa-c, IV, V, VIa-c, VIIIa-c, XI, XII. The dichlorocyclopropane derivative of chromene Ia-g, VIIa-c, or IXa, b is boiled in dry DMFA. When cool, dimethylamine

*Compound Id is a liquid which is purified by passing its hexane solution through a layer of aluminum oxide.

TABLE 3. Preparation of 1-Benzoxepines

Starting compounds: dichlorocyclopropane compound	amt., g	DMFA, amt., ml	Time of reaction, h	Data on purification: lgth. Al_2O_3 layer, cm	column diam., cm	eluent	R_f	solvent for recrystallization	Reaction products: compound	mp, deg C	yield: g	%
Ia	1,0	6	6	Purified by recrystallization only			—	1-propanol	IIIa	157	0,44	49
Ib	0,5	3	6	„	„	„	—	As above	IIIb	127—129	0,24	53
Id	4,5	25	1	35	1,8	Hexane	0,6	Ethanol	IIIc	108—109	0,83	22
Ig	6,0	36	5	69	3,8	As above	0,7 0,5	As above 1-propanol	IV V	80—82 129—130	0,75 0,20	14* 4*
Ic	5,0	15	1,2	23	3,3	Benzene—hexane, 1:2	0,8	Methanol	VIa	86—87	2,54	58
If	3,4	10	1	28	1,8	As above	0,9	—	VIb	Liquid material	1,87	64
Ie	1,0	6	2	24	1,8	Hexane	0,6	—	VIc	Liquid material	0,51	60
VIIa	0,5	3	6	47	1,8	Benzene—hexane, 1:1	0,8	1-propanol	VIIIa	145—146	0,13	29
VIIb	1,0	8	6	40	1,8	As above 1 : 2	0,7	As above	VIIIb	144—146	0,44	48
VIIc	0,7	4	6	37	1,8	As above 1 : 1	0,8	As above	VIIIc	126—128	0,20	32
IXa	1,0	6	2	28	1,8	Benzene	0,9	—	X	54—55	0,75	84
IXb	0,5	3	3	37	1,8	As above	0,8	—	XI XII	A liquid mixture of compounds isolated	0,20	32 13

*The total yield of the mixture of isomers was 33%, but they could be separated in yields of 14 and 4% only, since during the elution of products from the columns, the intermediate fraction contained a mixture of compounds.

TABLE 4. Characteristics of 1-Benzoxepines

Compound	IR spectrum, cm^{-1}: C=C	benzene ring	UV spectrum, λ_{max}, nm (EtOH)	Mass spectrum, M^+	Elemental analysis: Found, %: C	H	Cl (S)	Empirical formula	Calculated, %: C	H	Cl (S)
IIIa	1620	1585	292	344	79,9	5,1	10,2	$C_{23}H_{17}ClO$	80,1	5,0	10,3
IIIb	1600	1590	—	—	80,5	5,2	9,7	$C_{24}H_{19}ClO$	80,3	5,3	9,9
IIIc	1610	1575	—	—	76,4	5,2	12,4	$C_{18}H_{15}ClO$	76,5	5,4	12,5
IV	1625, 1615	1590	—	—	76,6	5,3	12,6	$C_{18}H_{15}ClO$	76,5	5,4	12,5
V	1610	1580	—	—	76,7	5,4	12,6	$C_{18}H_{15}ClO$	76,5	5,4	12,5
VIa	1620	1595, 1575	—	268	76,1	4,7	13,2	$C_{17}H_{13}ClO$	76,0	4,9	13,2
VIb	1630	1580	—	—	76,4	5,6	12,6	$C_{18}H_{15}ClO$	76,5	5,4	12,5
VIc	1640	1570	—	—	69,9	5,3	17,0	$C_{12}H_{11}ClO$	69,7	5,4	17,2
VIIIa	1615	1580	348	360	76,5	5,0	10,0	$C_{23}H_{17}ClO_2$	76,6	4,8	9,8
VIIIb	1615	1580	360	366	68,7	4,0	9,7 (8,6)	$C_{21}H_{13}ClO_2S$	68,8	4,1	9,7 (8,7)
VIIIc	1615	1580	362	—	71,4	3,7	10,5 (9,8)	$C_{20}H_{13}ClOS$	71,3	3,9	10,5 (9,5)
X	1640	1610	334	—	72,2	5,1	11,7	$C_{18}H_{15}ClO_2$	72,4	5,1	11,9
Mixture XI XII	—	—	—	—	72,8	5,6	11,6	$C_{19}H_{17}ClO_2$	73,0	5,5	11,4

hydrochloride separates out from the reaction mixture (which for identification, was filtered, washed with dry ether, mp 171°C, agrees with data given in [27]). The mixture is then poured into water and the reaction products are extracted by ether. The ether extract is dried over sodium sulfate and the solvent is distilled on a water bath. The residue is purified by chromatography on aluminum oxide and by recrystallization (Tables 3-5).

5H-1-Benzoxepinium cations IIa, c, e. A 0.1 g portion of 1-benzoxepine IIIa, VIa, or VIc is dissolved in 0.4 ml of 98% H_2SO_4 at 20°C. A red solution is formed whose PMR spectrum is

TABLE 5. PMR Spectra of 1-Benzoxepines

Compound	PMR spectrum, δ ppm (J, Hz)
IIIa	4,85 (1H, s, 5-H); 5,28 s, 5,62 (1H and H, two s, $=CH_2$); 6,85—7,40 (14H, m, H_{arom})
IIIb	1,88 (3H, d, J=6,7; CH_3); 5,20 (1H, s, 5-H); 6,30 (1H, qt, J=6,7, =CH—); 6,45—7,40 (14H, m, H_{arom})
IIIc	1,58 (3H, d J=7, CH_3); 3,88 (1H, qt, J=7, 5-H); 5,20 (2H, AB qt, J_{AB}= =19, $=CH_2$); 6,60—7,70 (9H, m, H_{arom})
IV	2,00 (3H, s, 2-CH_3); 4,75 (1H, s, 5-H); 5,10 and 5,45 (1H and 1H, two s, $=CH_2$); 6,75—7,50 (9H, m, H_{arom})
V	2,25 (3H, s, 4-CH_3); 4,45 (1H, s, 5-H); 4,90 and 5,35 (1H and 1H, two s, $=CH_2$); 6,70—7,51 (9H, m, H_{arom})
VIa	2,05 (3H, s 4-CH_3); 6,30—7,80 (10H, m 5-H and H_{arom})
VIb	1,75 (3H, s, 9-CH_3); 2,10 (3H, s, 4-CH_3); 6,45—7,80 (9H, m, 5-H and H_{arom})
VIc	2 00 (3H, s, 4-CH_3); 2,08 (3H, s, 2-CH_3); 6,38 (1H, s, 5-H); 6,50—7,25 (4H, m, H_{arom})
VIIIa	3,75 (3H, s, OCH_3); 6,45 (1H, s, 4-H); 6,60—8,00 (13H, m, H_{arom})
VIIIb	3,75 (3H, s, OCH_3); 6,60—8,00 (12H, m, 4-H and H_{arom})
VIIIc	6,42 (1H, s, 4-H); 6,75—7,90 (12H, m, H_{arom})
X	1,23 (3H, t, J=5,3, CH_3); 3,83 (2H, qt, J=5,3, CH_2); 5,10 (1H, s, 3-H); 6,80—7,75 (9H, m, H_{arom})
Mix. of XI XII:	
XI	1,40 (3H, t, CH_3); 3,80 (2H, qt, CH_2); 4,70 (1H, s, 2-H); 5,36 and 5,8 (1H and 1H, two s $=CH_2$)
XII	1,30 (3H, t, OCH_2CH_3); 1,95 (3H, s, 3-CH_3); 3,85 (2H, qt, OCH_2CH_3)*

*The aromatic multiplets coincide and lie in the 6.70-7.60 ppm region.

recorded using HMDS as external standard:

cation IIa: 3.17 (3H, s, 4-CH_3); 5.52 (1H, s, 5-H); 6.83-8.65 (14H, m, H_{arom});

cation IIc: 3.08 (3H, s, 4-CH_3); 4.18 (2H, s, 5-H and 5-H); 7.70-9.00 (9H, m, H_{arom});

cation IIe: 3.10 (3H, s, 4-CH_3); 3.60 (3H, s, 2-CH_3); 4.20 (2H, s, 5H and 5H); 7.20-8.50 (4H, m, H arom).

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SYNTHESIS OF NITROGEN-CONTAINING HETEROCYCLES OF AN IRON CATALYST. 2.* THE CONVERSIONS OF 1,4-BUTANEDIOL AND DIETHYLENE GLYCOL IN THE PRESENCE OF AMMONIA AND HYDROGEN

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The gas-phase interaction of 1,4-butanediol and diethylene glycol with ammonia and/or hdyrogen on a reduced, fused, iron catalyst has been investigated.

The higher activity and selectivity of a reduced, fused, iron catalyst (RFC) towards the amination of alcohols of various structures to the corresponding amines with ammonia was established previously [2-4]. One would expect the involvement of diols in this reaction to lead to the formation of the corresponding aminoalcohols, diamines, and heterocyclic amines. Such a possibility is indicated, in particular, by work on the synthesis of pyrrolidine from 1,4-butanediol (I) and of morpholine from diethylene glycol (II) on some oxide [5, 6] and metal [7-9] catalysts.

We have studied the possibility of using RFC for the gas-phase synthesis of aminoalcohols, diamines, and heterocyclic amines from compounds I, II, NH_3, and H_2.†

We carried out the investigation with a linear, gas-flow rate of no less than 0.6 cm/sec and a catalyst grain size of no more than 2-3 mm. This guaranteed that the reaction took place in the kinetic region.

It was established by GLC and chromatography-mass spectrometry that at a temperature of 250-310°C, partial pressures of ammonia (P_{NH_3}) of 0.64-2.5 MPa, of hydrogen (P_{H_2}) of 0.9-4.2 MPa, and of diol (P_I, P_{II}) of 0.06-0.24 MPa, and a specific feed rate of the diol of 220-1880 g/liter·h, compound I forms primarily pyrrolidine, N-butylpyrrolidine, n-butylamine, and, in smaller amounts, n-butanol, 4-(pyrrolidyl-1)butanol, 1,4-dipyrrolidyl-butane, di-n-butylamine, pyrrole, N-butylpyrrole, and N-(4-pyrrolidylbutyl)pyrrole (a total of 10-15%). Under these conditions, II is converted to morpholine, diethyl ether, ethanol, ethylene glycol, and N-ethylmorpholine. It should be noted that within the limits of the analytical error, no aminoalcohols or diamines were found among the conversion products of compounds I and II.

Table 1 presents the data on the effect of the reaction conditions on the yield of the basic products formed in the reaction of compound I with an ammonia/hydrogen mixture. It is clear from Table 1 that the greatest yield of pyrrolidine (71%) is achieved at 260°C and v_l = 560 g/liter·h and P_{NH_3}, P_{H_2}, and P_I equal to 2, 2.8, and 0.1 MPa, respectively. Under these

*For Report 1, see [1].
†We need hydrogen in the reaction zone to preserve the stability of the RFC in the presence of water [10].

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