B. A reactor was charged with 12.5 g (0.05 mole) of isocyanurate I and 14.55 g (0.05 mole) of isocyanurate IV, and the mixture was heated to 190-200°C and maintained at that temperature for 5 h. It was then cooled, and the resulting partially polymerized mass was pulverized and extracted with toluene. According to GLC, the toluene extract contained 23.3% isocyanurate II, 24.0% isocyanurate V, 31.6% isocyanurate VI, and 21.1% isocyanurate VII.

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TRANSFORMATION OF DIHYDRO-1,5-BENZODIAZEPIN-2-ONES UNDER THE INFLUENCE OF ACETIC ANHYDRIDE

B. A. Puodzhyunaite, R. A. Yanchene, and P. B. Terent'ev

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The acylation of 4-R-2,3-dihydro-1H-1,5-benzodiazepin-2-ones leads to isomerization or opening of the heteroring with subsequent acylation. 1-Acyl-2,3-dihydro-1,5-benzodiazepin-2-ones are not formed.

We have previously synthesized 1,5-diacyl-2,3,4,5-tetrahydro-1H-1,5-benzodiazepin-2-ones, which are of interest from both chemical and biological points of view [1]. Continuing our research in this area we have studied the reaction of 4-methyl- and 4-phenyl-2,3-dihydro-1H-1,5-benzodiazepin-2-one (I, II) [2, 3] with acetylating agents.

The reaction of I with a 4.5-fold excess of acetic anhydride in toluene by the method in [1] led only to pronounced resinification. At the same time, carrying out the reaction in chloroform gave a mixture of substances, the principal component of which was acetoacetic acid N-(2-acetamidophenyl)-amide (III).

Institute of Biochemistry, Academy of Sciences of the Lithuanian SSR, Vilnius 232,021. M. V. Lomonosov Moscow State University, Moscow 119,899.

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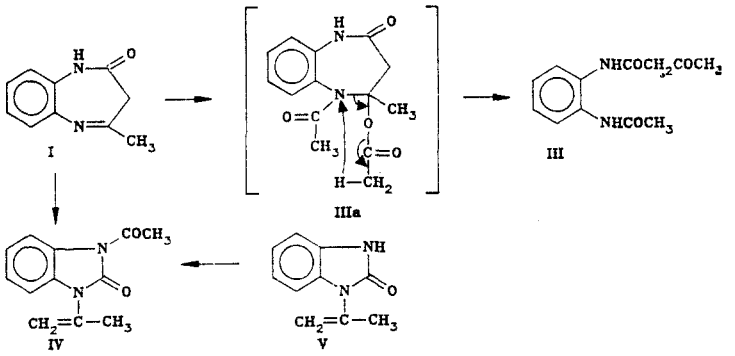


In addition, 1-isopropenyl-3-acetylbenzimidazol-2-one (IV) was identified along with starting I in the reaction mixture by TLC. An intense absorption band of a ketone carbonyl group at 1725 cm^{-1}, a broad absorption band of amide carbonyl groups at 1660 cm^{-1}, and a weak band at 1615 cm^{-1}, which is apparently related to the stretching vibrations of the multiple bond of the enol form, are observed in the IR spectrum of anilide III (Table 1). In addition to the absorption bands of amide N–H bonds (3220 cm^{-1}), a less intense but broad band at 3400-3450 cm^{-1} of stretching vibrations of the O–H bond of the enol form is observed in the higher-frequency region. Two singlets of methyl groups (1.92 and 2.01 ppm), a singlet of a methylene group at 3.35 ppm, a broad multiplet of four aromatic protons at 6.85-7.51 ppm, and two broad singlets of amide protons centered at 8.40 and 8.92 ppm are observed in the PMR spectrum of III (Table 2). In addition to this, a weak (with an intensity of 0.2 H) singlet of the olefin proton of the enol form at 4.85 ppm is also noted in the spectrum. Like other acetylated arylamines, the molecular ion of III (M^+ 234) (Table 3) that is formed under the influence of electron impact successively eliminates three molecules of ketone (ions 192, 150, and 108*) and also loses an acetonyl residue (ion 177) in one step, which is characteristic for acetoacetic acid derivatives [4]. The formation of III is probably explained by the initial addition of acetic anhydride to the azomethine bond of diazepinone I with subsequent cleavage of the resulting hemiaminal diacetate IIIa. A similar process was described in the case of 5H-2,3-benzodiazepines [5].

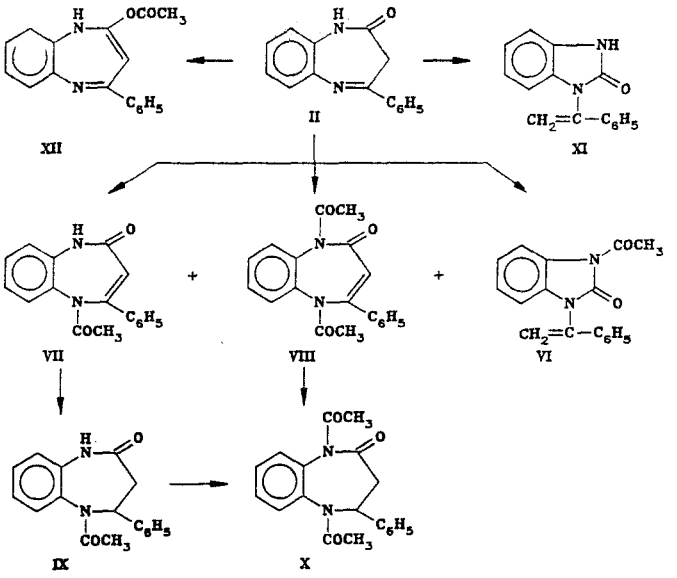
The acetylation of I in solution in pyridine led to the formation, as the chief product (44%), of benzimidazolone IV, the structure of which was confirmed unequivocally by, in addition to the spectral data, alternative synthesis – by acetylation of 1-isopropenylbenzimidazol-2-one (V), obtained by the method in [2]. The formation of IV is explained by primary characteristic thermal isomerization of benzodiazepinone I to benzimidazolone V [6] with subsequent acylation of it.

A similar compound VI† (see the scheme) was isolated from the reaction mass obtained in the acetylation of benzodiazepinone II in pyridine. In addition to this, products of mono- (VII) and diacetylation (VIII) of starting II, the formation of which is accompanied by migration of the multiple bond in the latter under the influence of pyridine [7], were detected in the reaction medium. Judging from the yields of VII and VIII (24% and 14%), this isomerization is the predominant process. The structures of the two compounds were confirmed by catalytic reduction of the C=C bond, which led to substances with known structures – 5-acetyl-4-phenyl-2,3,4,5-tetrahydro-1H-1,5-benzodiazepin-2-one (IX) [8] and the corresponding 1,5-diacyl derivative X, which we also synthesized by acetylation of IX in pyridine by the method in [1] (see top of following page).

The character of the mass-spectrometric behavior of VII does not contradict the structure proposed for it. Its molecular ion initially eliminates a molecule of ketone (ion 236), thereby confirming the presence of a C_6H_5–N–$COCH_3$ fragment [4], after which an NHCO fragment (ion 193) and a phenyl residue (ion 159) or a molecule of phenylacetylene (ions 134 and 102) are lost.

It was established that thermal rearrangement to 1-phenylvinylbenzimidazol-2-one (XI) [9] also occurs in the reaction of II with acetic anhydride in acetic acid in the presence of sodium acetate at 80°C, whereas N-acetylation of II and benzimidazolone XI does not occur.

*Here and subsequently, the m/z values are given for the ion peaks.
†The structure was confirmed by spectral data (Tables 1-3).



In the case of prolonged refluxing in toluene of II with a sixfold excess of acetic anhydride, from the reaction mixture, in addition to unchanged benzodiazepinone II, we isolated only XII (in greater than 60% yield), which is also formed in the reaction of the sodium salt of II with acetyl chloride in tetrahydrofuran (THF). In addition to a molecular ion (278), intense peaks of $[M - CH_2CO]^+$ (236) and $[M - CH_3CO]^+$ (235) ions are observed in the mass spectrum. In addition to these, there is also a low-intensity peak of an $[M - CH_3COO]^+$ ion (219), which was not observed in the mass spectra of III-XI. In addition, the ion with m/z 236, which probably has the 2-hydroxy-4-phenyl-1,5-benzodiazepine structure, loses a formyl residue (metastable ion; found 181.8, calculated 181.6), which is characteristic for hydroxyarenes [4], as well as a second molecule of ketene (ion 194 [10]). In addition to a singlet of a methyl group (2.11 ppm) and a multiplet of nine aromatic protons (7.20-7.83 ppm), a broad singlet of one amide proton (10.22 ppm) and a distinct doublet of an olefin proton attached to the $C_{(3)}$ atom with a center at 5.24 ppm and a long-range SSCC with respect to the amide proton of 2 Hz are observed in the PMR spectrum of XII. Signals of the carbon atoms of an acetyl group (168.90 and 22.75 ppm) and signals of $C_{(2)}$ (166.84 ppm), $C_{(3)}$ (96.70 ppm), and $C_{(4)}$ (158.40 ppm) atoms [11, pp. 89, 129] were observed in the ^{13}C NMR spectrum of XII at weak field.

The acidic hydrolysis of XII is complete in 2 h and leads to o-phenylenediamine and acetophenone, which was identified in the form of the hydrazone. It is known that dihydrobenzodiazepinone derivatives undergo decomposition to the corresponding aromatic o-diamines under the influence of acids [12].

According to the widely accepted mechanism, the acylation of amides occurs with the formation of O-acyl intermediates [13]. In our case the enol form of II is formed through the 3-H proton; this is evidently associated with the greater degree of conjugation as compared with the lactim form, and rearrangement of the O-acetyl derivative to the N-acetyl compound is not realized.

Thus in the case of benzodiazepinones I and II it was shown that, because of the tendency of these compounds to undergo isomerization, 1-acyl-substituted derivatives of 2,3-dihydro-1,5-benzodiazepinones, in contrast to tetrahydro-1,5- [1] and dihydro-1,4-benzodiazepin-2-ones [14], cannot be obtained in reactions with acylating agents.

EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were recorded with a Specord 71 IR spectrometer. The PMR spectra of solutions in $CDCl_3$ were obtained with a Hitachi R-22 spectrometer (90 MHz) with hexamethyldisiloxane as the internal standard (d_6-DMSO was used as the solvent for XII). The ^{13}C NMR spectra were recorded with a Tesla BS-567 A spectrometer (25.14 MHz) with complete suppression of coupling with the protons in d_6-DMSO with tetramethylsilane as the internal standard. The mass spectra were obtained with Varian MAT-212

TABLE 1. Constants of the Products of Isomerization of 4-R-Dihydro-1,5-benzodiazepin-2-ones

Compound	mp, °C*	R_f	IR spectrum, ν, cm^{-1}	Found, %			Empirical formula	Calc., %		
				C	H	N		C	H	N
III	120—122	0,08	1615 (C=C), 1660 (CO), 1725 (CO), 3220 (NH), 3400—3450 (OH)	61,9	6,0	12,1	$C_{12}H_{14}N_2O_2$	61,5	6,0	12,0
IV	108—110	0,85	—	66,8	5,8	13,2	$C_{12}H_{12}N_2O_2$	66,7	5,6	13,0
VI	179—181	0,75	—	73,5	5,1	10,2	$C_{17}H_{14}N_2O_2$	73,4	5,1	10,1
VII	215—217	0,25	1630 (CO), 1660 (CO), 3220 (NH)	73,6	5,2	10,2	$C_{17}H_{14}N_2O_2$	73,4	5,1	10,1
VIII	175—177	0,65	1660 (CO), 1680 (CO)	71,4	5,1	8,3	$C_{19}H_{16}N_2O_3$	71,2	5,0	8,7
X	198—199**	—	—	70,7	6,0	8,3	$C_{19}H_{18}N_2O_3$	70,8	5,6	8,6
XI***	165—167	0,49	—	76,0	5,3	11,7	$C_{15}H_{12}N_2O_2$	76,3	5,1	11,9
XII	209—211	0,43	1570 (C=N), 1610 (C=C), 1660 (CO), 3280 (NH)	73,5	5,1	10,0	$C_{17}H_{14}N_2O_2$	73,4	5,1	10,1

*The compounds were recrystallized: III and VI-VIII from benzene, IV from ether, XI from ethyl acetate, and XII from THF.

**The boiling point at 1.3-2.7 hPa.

***The formation of XI was described in [9], but the constants were not presented.

TABLE 2. PMR Spectra of III, IV, VI-VIII, and X-XII

Compound	Chemical shifts, δ, ppm (SSCC, J, Hz)
III	1,92; 2,01 (6H, two s, CH_3); 3,35 (2H, s, CH_2); 4,85 (1H, s, CH enol form); 6,85-7,51 (4H m, arom); 8,40 and 8,92 (2H, br.s NH)
IV	2,07 (3H, s, CH_3); 2,65 (3H, s, $COCH_3$); 5,17 and 5,36 (2H, two q, $=CH_2$); 6,93—7,22 (3H, m, arom.); 8,05—8,20 (1H, m, arom)
VI	2,73 (3H, s, CH_3); 5,52 and 5,95 (2H, dd, ^2J=0,75, $=CH_2$); 6,45—7,05 (3H, m, arom); 7,15 (5H, m, arom.); 8,01 (1H, m, arom)
VII	1.92 (3H, s, CH_3); 6,28 (1H, s, =CH); 7,10—7,76 (9H, m arom); 9,94 (1H, br. s, NH)
VIII	1,91 (3H, s, 5-$COCH_3$); 2,54 (3H, s, 1-$COCH_3$); 6,02 (1H, s, =CH); 7,10—7,62 (9H, m, arom)
X	1,70 (3H, s, 5-$COCH_3$); 2,60 and 2,66 (5H, 1-$COCH_3$ overlapped with $COCH_2$); 6,12 (1H, m, CH); 6,84—7,64 (9H, m. arom)
XI	5,46 и 6,02 (2H, two s, $=CH_2$); 6,42—7,41 (4H, m, arom); 7,26 (5H, m, arom); 10,02 (1H, br.s, NH)
XII	2,13 (3H, s $OCOCH_3$); 5,22 (1H, d, ^4J=2, =CH); 7,22—7,86 (9H, m, arom); 10,22 (1H, br.s, NH)

TABLE 3. Characteristic Ions in the Mass Spectra of III, IV, VI, VII, and XII

Compound	m/z values (relative intensities, %)
III	234 (39), 192 (18), 177 (9), 150 (45), 135 (33), 134 (55), 133 (30), 108 (100), 107 (30), 80 (25), 28 (38)
IV	216 (19), 174 (100), 159 (42), 134 (24), 132 (13), 131 (31), 119 (5), 106 (8), 105 (6), 90 (9), 77 (1)
VI	278 (53), 236 (100), 221 (54), 134 (80), 106 (5), 103 (19), 91 (5), 90 (5), 77 (19), 51 (6), 43 (17)
VII	278 (14), 236 (31), 195 (12), 194 (10), 193 (26), 133 (18), 104 (11), 102 (14), 77 (18), 51 (24), 43 (100)
XII	278 (28), 236 (100), 235 (28), 207 (13), 195 (41), 194 (91), 193 (24), 133 (7), 104 (7), 77 (13), 43 (18)

and MAT-44S spectrometers at an ionizing-electron energy of 70 eV with introduction of the samples into the ion sources at 10-12°C below the melting points. The course of the reaction and the purity of the compounds were monitored on Silufol UV-254 plates in chloroform–ethyl acetate (2:1). The separation and purification of the substances were carried out with columns packed with silica gel L 40/100 μ with elution by benzene. The yields of the compounds are presented for chromatographically pure samples.

Acetoacetic Acid N-(2-Acetamidophenyl)amide (III). A solution of 3.5 g (20 mmole) of I and 8.6 ml (90 mmole) of acetic anhydride in absolute chloroform was refluxed for 7 h, after which it was cooled and washed with Na_2CO_3 solution, the solvent was evaporated, and the residue was chromatographed with a column packed with silica gel to give 0.6 g (13%) of product.

3-Acetyl-1-isopropenylbenzimidazol-2-one (IV). A. A solution of 3.5 g (20 mmole) of I and 8.6 ml (90 mmole) of acetic anhydride in 15 ml of dry pyridine was refluxed for 4 h, after which it was poured over ice, and the resulting precipitate was removed by filtration and recrystallized to give 1.9 g (44%) of product.

B. A solution of 3.5 g (20 mmole) of V, obtained by the method in [2], and 8.6 ml (90 mmole) of acetic anhydride in 15 ml of dry pyridine was refluxed for 6 h, after which it was worked up as described above to give 2.9 g (67%) of product. The samples of IV obtained by the two methods did not produce melting-point depressions.

3-Acetyl-1-phenylvinylbenzimidazol-2-one, 5-Acetyl-4-phenyl-1,5-dihydro-1H-1,5-benzodiazepin-2-one, and 1,5-Diacetyl-4-phenyl-1,5-dihydro-1,5-benzodiazepin-2-one (VI-VIII). A solution of 7.08 g (30 mmole) of II and 12.9 ml (135 mmole) of acetic anhydride in 25 ml of dry pyridine was refluxed for 12 h, after which it was poured into 200 ml of water. The

aqueous mixture was neutralized with dilute hydrochloric acid and extracted with chloroform. The extract was concentrated, and the residue was chromatographed with a column to give 1.17 g (14%) of benzimidazolone VI, 2 g (24%) of benzodiazepinone VII, and 1.3 g (14%) of VIII.

5-Acetyl-4-phenyl-2,3,4,5-tetrahydro-1H-1,5-benzodiazepin-2-one (IX). A solution of 0.5 g (1.8 mmole) of VII in 80 ml of absolute ethanol was hydrogenated over palladium black. After the calculated amount of hydrogen had been absorbed, the catalyst was removed by filtration, the solvent was evaporated, and the residue was recrystallized from ethyl acetate to give 0.36 g (71%) of a product with mp 205-207°C. A sample of this product did not depress the melting point of the substance obtained by the method [8].

1,5-Diacetyl-4-phenyl-2,3,4,5-tetrahydro-1H-1,5-benzodiazepin-2-one (X). A. A 3.2-g (10 mmole) sample of VIII was hydrogenated under similar conditions. After evaporation of the solvent, the residue was distilled in vacuo to give 2 g (62%) of a product with bp 198-199°C (1.3-2.7 hPa).

B. A mixture of 1.35 g (5 mmole) of IX, 10 ml of dry pyridine, and 2.4 ml (25 mmole) of acetic anhydride was refluxed for 12 h, after which it was poured into water. The aqueous mixture was neutralized with hydrochloric acid and extracted with chloroform. The solvent was evaporated, and the residue was distilled in vacuo to give 0.8 g (50%) of a product with bp 197-199°C (1.3-2.7 hPa).

1-Phenylvinylbenzimidazol-2-one (XI). A mixture of 4.7 g (20 mmole) of II, 1.9 ml (20 mmole) of acetic anhydride, and 1.65 g (20 mmole) of sodium acetate in 30 ml of glacial acetic acid was maintained at room temperature for 24 h, after which it was heated at 80°C for 16 h. The solution was poured into 200 ml of water, and the resulting precipitate was removed by filtration and crystallized from ethyl acetate to give 1.7 g of starting II. The aqueous solution was extracted with chloroform, and the extract was washed with NaOH solution and concentrated. The residue was recrystallized to give 0.5 g (17%) of benzimidazolone XI, which did not depress the melting point of a sample obtained by the method in [9].

2-Acetoxy-4-phenyl-1H-1,5-benzodiazepine (XII). A. A solution of 5.7 g (24 mmole) of II in 60 ml of absolute toluene was refluxed with 13.6 ml (144 mmole) of acetic anhydride for 8 h, after which it was cooled, and the resulting precipitate was recrystallized to give 2.65 g (61% based on the converted II) of XII. The toluene solution was washed with Na_2CO_3 solution and evaporated, and the residue was recrystallized to give 1.85 g of starting II.

B. A suspension of 4.72 g (20 mmole) of II and 0.9 g of 55% NaH in absolute THF or absolute benzene was refluxed with stirring for 1 h, after which 1.4 ml (20 mmole) of acetyl chloride was added, and refluxing was continued for another 3 h. The precipitated NaCl was removed by filtration, the solvent was evaporated, and the residue was subjected to fractional crystallization or chromatographed with a column to give 1.2 g (30% based on the converted II) of XII and 1.4 g of starting II. No melting-point depression was observed for the samples of XII obtained by methods A and B.

Hydrolysis of XII. A mixture of 1.17 g (4.2 mmole) of XII, 30 ml of methanol, and 3 ml of 5 N H_2SO_4 was refluxed for 2 h, after which the solvent was evaporated, and the residue was dissolved in chloroform. The chloroform solution was washed with Na_2CO_3 solution and concentrated, and the residue was treated with hot water to give 0.3 g of o-phenylenediamine with mp 99-101°C. The filtrate was evaporated to dryness, and the residual oil was treated with solution of 2,4-dinitrophenyl-hydrazine by the method in [15]. The precipitated hydrazone (mp 237-239°C) did not depress the melting point of a sample synthesized from acetophenone and 2,4-dinitrophenylhydrazine.

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CONDENSED IMIDAZO-1,2,4-AZINES.

19.* SYNTHESIS OF 4-IMINO DERIVATIVES OF 2-METHYL-7,8-DIPHENYL-5H-IMIDAZO[1,2-b]-1,2,4-TRIAZEPINE

V. P. Kruglenko, V. A. Idzikovskii, N. A. Klyuev, and M. V. Povstyanoi

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A number of new 4-imino-substituted 2-methyl-7,8-diphenyl-5H-imidazo[1,2-b]-1,2,4-triazepines were synthesized by replacing the S atom in 2-methyl-7,8-diphenyl-5H-imidazo[1,2-b]-1,2,4-triazepine-4-thione by the action of nitrogen-containing nucleophiles. It is shown that the imine form is characteristic for the synthesized compounds.

To study the reactivities of 4-oxo and 4-thioxo derivatives of imidazo[1,2-b]-1,2,4-triazepine (ITA) [2] we carried out nucleophilic substitution reactions with primary and secondary amines, hydroxylamine, hydrazine hydrate, p-bromobenzoic acid hydrazide, aminoacetic acid, and 1,2-diamino-4,5-diphenylimidazole.

The starting components were isolated in the reaction with 2-methyl-7,8-diphenyl-5H-imidazo[1,2-b]-1,2,4-triazepin-4-one [2] in various solvents (alcohols, acetic acid, DMF), while refluxing imidazotriazepin-4-one with hydroxylamine hydrochloride in isopropyl alcohol led to destruction of the triazepine ring, the principal product of which was 1,2-diamino-4,5-diphenylimidazole. A negative result was also obtained in carrying out the synthesis by the method in [3] with use of triethylamine and phosphorus oxychloride. In this connection we used another representative of ITA – 2-methyl-7,8-diphenyl-5H-imidazo[1,2-b]-1,2,4-triazepine-4-thione (I) – as the starting substrate.

Thione I reacts with monoethanolamine, aniline, morpholine, hydroxylamine, hydrazine hydrate, or p-bromobenzoic acid hydrazide in the case of refluxing in alcohols. Substitution with aminoacetic acid and 1,2-diamino-4,5-diphenylimidazole was observed only when the process was carried out in refluxing DMF (see top of following page).

The $\nu_{C=S}$ absorption band at 1145 cm^{-1} that is specific for the IR spectrum of starting thione I [2] is absent in the IR spectra of substitution products II-IX. The ν_{NH} absorption at 3045-3220 cm^{-1}, which is also observed in the spectrum of the starting imidazotriazepine-4-thione I, is characteristic for the IR spectra of II-IV and VI-VIII. This similarity shows that the compounds under consideration, like substituted imidazo[1,2-b]-1,2,4-triazepin-4-

*See [1] for communication 18.

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