2α-R¹-4α-R²-cis-1-Thiadecalin-1-oxides (IX, XII, XIII). Sulfide II, V, or VI, [2], 4 mmole, is dissolved in 10 ml of glacial acetic acid, and a 5-10% molar excess of 30% hydrogen peroxide is added dropwise with stirring. The mixture is kept at 20°C for 24 h, then poured dropwise on 200 g of crushed ice. Sulfoxides IX, XII, XIII are filtered off, dried, and reprecipitated from chloroform by hexane.

2α-R¹-4α-R²-cis-1-Thiadecaline-1-dioxides (XVI, XX). A mixture of 2 mmole of sulfide II, VI [2], 5 ml of glacial acetic acid, and 1.4 ml of 30% hydrogen peroxide is heated in a water bath 7 min at 60° until the sulfide dissolves, then left for 24 h at 20°. Then the mixture is poured on 100 g of ice, and sulfones XVI, XX are filtered off, dried, and recrystallized from 1:1 ethanol–acetone.

The purity of the sulfones and sulfoxides was monitored by TLC (Silufol, elution by 3:2 ethyl acetate–hexane).

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SYNTHESIS OF AZETIDIN-3-ONES. STRUCTURE OF N-TOSYL-2-ETHYLAZETIDIN-3-ONE

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A one-step synthesis of azetidin-3-ones by intramolecular cyclization of 1-diazo-3-arenesulfamoylalkan-2-ones was developed. The yield of cyclic product increases to 70% in the presence of an alkyl or benzyl substituent in the hydrocarbon chain of the diazoketone. The structure of N-tosyl-2-ethylazetidin-3-one was studied by x-ray diffraction analysis and it was shown that the four-membered ring has 15° inflection.

Uncondensed azetidines with a keto group in position 3 are difficultly accessible derivatives of this heterocyclic system. Two basic synthesis routes to these compounds are known, that consist of formation of the azetidine ring followed by introduction of the carbonyl group; these are oxidation of 3-hydroxy-3-azetidinecarboxylic acid derivatives by lead tetra-

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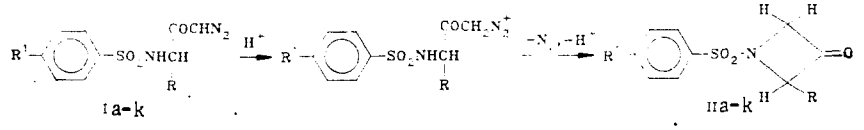
TABLE 1. Spectral Properties of Azetidines IIa-k

Compound	PMR spectrum, δ, ppm (number of protons, J, Hz)					IR spectrum, ν, cm^{-1}	UV spectrum, λ_{max} (log ε), nm
	R^1	Ar	3-H	1,2-H	R		
IIa	—	7,58—7,92 m (5H)	4,65 s (4H)		—	1810, 1140	204 (3,99), 224 (3,90)
IIb	2,45 s (3H)	7,52 d (2H, 8); 7,84 d (2H, 8)	4,62 s (4H)			1810, 1580, 1150	205 (4,0), 230 (4,13)
IIc	3,89 s (3H)	7,05 d (2H, 9); 8,50 d (2H, 9)	4,60 s (4H)		—	1810, 1580, 1140	204 (4,41), 243 (4,29)
IId	—	7,42 d (2H, 9); 7,80 d (2H, 9)	4,64 s (4H)		—	1810, 1580, 1140	203 (4,36), 228 (4,32)
IIe	—	8,02 d (2H, 8); 8,45 d (2H, 8)	4,65 s (4H)		—	1810, 1580, 1140	203 (4,11), 210 (3,97) sh
IIf	2,10 s (3H)	7,88 m (4H)	4,66 s (4H)		—	3290, 1810, 1640, 1580, 1140	207 (4,19), 266 (4,27), 278 (4,12) sh
IIg	2,43 s (3H)	7,40 d (2H, 8); 7,78 d (2H, 8)	4,77 m (1H; 1,5; 2,7; 6,75)	4,50 m (2H, 1,5; 2,7; 15,6)	1,42 d (3H, 6,75)	1805, 1580, 1140	206 (3,94), 231 (4,10)
IIh	2,10 s (3H)	7,85 m (4H)	4,80 m (1H)	4,55 s (2H)	1,40 d (3H, 7)	3320, 1800, 1680, 1580, 1140	207 (4,15), 267 (4,22), 278 (4,08) sh
IIi	2,45 s (3H)	7,39 d (2H, 8); 7,77 d (2H, 8)	4,72 m (1H, 3,63; 6,22) 4,74 m (1H)	4,45 q (1H, 3,63; 16,32); 4,51 d (1H, 16,32)	1,01 t (3H, 7); 1,84 m (2H, 6,22; 7)	1805, 1580, 1140	203 (4,21), 230 (4,16)
IIj	2,10 s (3H)	7,80 m (4H)		4,50 m (2H)	1,0 t (3H, 7); 1,90 m (2H)	3325, 1800, 1680, 1580, 1140	206 (4,70), 267 (4,15), 278 (4,02) sh
IIk	2,43 s (3H)	7,36 d (2H, 8); 7,78 d (2H, 8)	4,97 m (1H, 4,05; 4,42; 7,05)	4,19 q (1H, 4,05; 16,5); 4,43 d (1H, 16,5)	3,10 q (1H, 4,42; 14,4); 3,18 q (1H, 7,05; 14,4); 7,25 m (5H)	1805, 1580, 1140	204 (4,28), 230 (4,08)

acetate [1, 2], and oxidation of N-substituted azetidin-3-ols by chromic anhydride [3] or by Py—SO_3 complex in DMSO [4].

We have synthesized azetidin-3-ones (II) in one step by intramolecular acidic cyclization of 1-diazo-3-arenesulfamoylalkan-2-ones (I). The diazoketones (I) are easily obtained by acylation by arenesulfonylaminoacyl chlorides of diazomethane [5], or by the reaction of 1-diazo-3-aminoalkan-2-ones with the respective sulfonyl chloride [6]. Subsequent treatment of diazoketones Ia-f with concentrated sulfuric acid and aqueous sodium bicarbonate yielded two products. One is the arenesulfonyl derivative of azetidin-3-one (II), the other is an acyclic α-hydroxy-methyl ketone. The IR spectra of the latter show NH and OH absorption at 3250, and C=O absorption at 1730 cm^{-1}; the PMR spectra show an NH proton signal at 5.3 ppm, a doublet of CH_2 protons at 4.11 ppm (J = 4.5 Hz), and a $COCH_2$ singlet at 4.06 ppm. It should be noted that the proportions of cyclic and linear product in the reaction mixture are approximately the same, and are independent of the nature of the R^1 substituent in the para position of the benzene ring. In the case of compounds Ig-k which contain an alkyl or benzyl substituent R, azetidines II become the main reaction products (yields up to 70%).



I, II a-f R=H, g, h R=CH_3, i, j R=C_2H_5, k R=$CH_2C_6H_5$; a R^1=H, b, g, i, k R^1=CH_3, c R^1=OCH_3, d R^1=Cl, e R^1=NO_2, f, h, j R^1=$NHCOCH_3$

The action of more nucleophilic reagents, e.g., acetic acid and hydrogen chloride, on diazoketones Ia-k yields only linear products, α-acetoxymethyl ketones and α-chloromethyl ketones, respectively; the IR spectra of these show the characteristic NH absorption at 3270-3280 cm^{-1}.

The IR spectra of azetidines IIa-k show the characteristic intense C=O band in the 1800-1810 cm^{-1} region [7]. They also show the less intense benzene-ring C=C bands at 1580, and the symmetrical SO_2 valence vibrations at 1140-1150 cm^{-1}. Compounds IIf,h,j show NH absorption at 3290-3325 and C=O absorption at 1640-1680 cm^{-1}. In the PMR spectra of azetidines IIa-f the $C_{(19)}$* and $C_{(3)}$ protons are symmetrical and give a singlet, in accordance with the intensity

*Numbering in agreement with Fig. 1.

TABLE 2. SSSC Values of Azetidine Ring Protons in PMR Spectra of Compounds IIg,i,k

Compound	J_{gem}, Hz	$^4J_{trans}$, Hz
IIg	15,60	2,70 (1,50)*
IIi	16,32	3,63
IIk	16,50	4,05

*$^4J_{cis}$.

of the respective four protons, in the 4.60-4.66 ppm region. In the case of IIg,i,k the character of the azetidine ring spectrum changes: 1) the $C_{(1)}$ protons become nonequivalent and their signals have geminal SSCC which increase in absolute value as the volume of substituent R increases, while in the IIg,i spectra the AB-system lines are distorted; 2) the AB-system proton, which has a signal in the stronger field, interacts with the 3-H proton through four bonds. The long range ^4J constant increases in absolute value as the bulk of substituent R increases; 3) the AB-system proton that has a signal in the weaker field interacts with the 3-H proton only in the case of IIg, with ^4J constant of 1.5 Hz. As substituent volume increases, this interaction disappears. If we take into account that for the azetidines $^4J_{trans} > {}^4J_{cis}$ [8], the constants can be arranged in the sequence shown in Table 2; 4) the spectrum of IIk shows a 0.2 ppm shift of the 3-H proton signal to the weaker field, and a 0.3 ppm shift of one of the $C_{(1)}$ protons to the stronger field; this can be related to the diamagnetic anisotrophy of the phenyl ring of the benzyl group.

We studied the structure of N-tosyl-2-ethylazetidin-3-one (IIi) by means of x-ray diffraction analysis. This is the first structural study of a four-membered heterocycle containing nitrogen with a carbonyl at position 3. The structural data hitherto accumulated refer to quaternary azetidine salts [9], and monocyclic [10] and condensed [11] β-lactams (penicillins and cephalosporins).

Fig. 1 shows the structure of the molecule. The bond lengths and valence angles are shown in Table 3. The values of the S—C (1.76 Å), S—O (1.44 Å), and S—N (1.60 Å) distances and the O—S—O angle (118°) are the usual ones for sulfamide [12]. The four-membered ring is not planar; the inflection along the C...C line is 15°. The nitrogen atom deviates by 0.35 Å from the plane of the three carbons. The carbonyl oxygen is 0.04 Å outside the same plane. In correspondence with the nonplanar conformation of the heterocycle, the nitrogen has a pyramidal structure. The sum of the valence angles at N is 340°. The nitrogen deviates from the coordination plane by 0.40 Å, and the S—N line makes a 143° angle with the $NC_{(1)}C_{(3)}$ plane. The N—$C_{(1)}$ and N—$C_{(3)}$ bond lengths are 1.509 and 1.505 Å, respectively, and are in good agreement with the analogous values in azetidines [9]. The substituents at N and $C_{(3)}$ are disposed

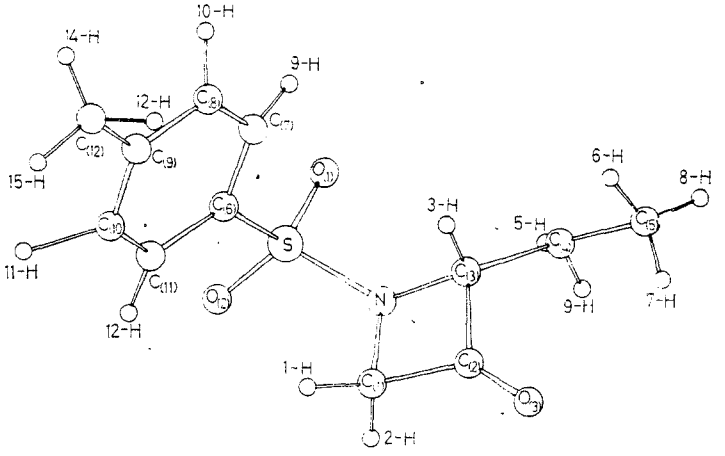


Fig. 1. Structure of N-tosyl-2-ethylazetidin-3-one molecule.

TABLE 3. Bond Lengths, d, in Compound IIi

Bond	d, Å	Bond	d, Å	Bond	d, Å
S—$O_{(1)}$	1,445(6)	$C_{(1)}$—$C_{(2)}$	1,505(12)	$C_{(7)}$—$C_{(8)}$	1,403(14)
S—$O_{(2)}$	1,443(6)	$C_{(2)}$—$C_{(3)}$	1,554(10)	$C_{(8)}$—$C_{(9)}$	1,396(13)
S—N	1,604(7)	$C_{(2)}$—$O_{(3)}$	1,205(11)	$C_{(9)}$—$C_{(10)}$	1,374(12)
S—$C_{(6)}$	1,762(8)	$C_{(3)}$—$C_{(4)}$	1,532(10)	$C_{(9)}$—$C_{(12)}$	1,521(13)
N—$C_{(1)}$	1,509(11)	$C_{(4)}$—$C_{(15)}$	1,500(14)	$C_{(10)}$—$C_{(11)}$	1,397(12)
N—$C_{(3)}$	1,505(11)	$C_{(6)}$—$C_{(7)}$	1,381(12)	$C_{(11)}$—$C_{(6)}$	1,393(10)

in pseudoequatorial positions. Such a conformation is energetically the most favorable. Conformations with pseudoaxial-equatorial and pseudoaxial dispositions of the two substituents are less favorable because of the steric hindrance between either the two cis-disposed bulky substituents or the ethyl and the diagonal proton. Of the two C—C bonds in the heterocycle, $C_{(1)}$—$C_{(2)}$ (1.505 Å) corresponds to a single $C(sp^3)$—$C(sp^2)$ bond, while $C_{(2)}$—$C_{(3)}$ (1.554 Å) is substantially longer. Moreover the $C_{(4)}$...N and $C_{(4)}$...$C_{(2)}$ intramolecular distances are 2.56 and 2.65 Å, respectively, i.e., with allowance for the respective radii the steric interactions between these atoms are the same. The N—$C_{(3)}$ and N—$C_{(1)}$ bond lengths and the $C_{(3)}$—$C_{(2)}$—$O_{(3)}$ and $C_{(1)}$—$C_{(2)}$—$O_{(3)}$ angles are equal. From this it can be concluded that the lengthening of the $C_{(2)}$—$C_{(3)}$ bond does not result from steric hindrance between the ethyl segment and the carbonyl carbon, but is typical of this compound and reflects its electronic structure. It can therefore be presumed that in reactions with ring opening the scission should take place mainly at the $C_{(2)}$—$C_{(3)}$ bond.

The possibility of transannular interaction in small rings is considered in the literature [14]. Therefore aside from establishing the geometry of the molecule we hoped to obtain structural information concerning such an interaction. The distances between atoms in the ring not linked by a valence bond are N...C, 2.08 and C...C, 2.22 Å. In other words the intracyclic N...C distance is substantially shorter than the C...C distance. Moreover the geometry is such that the alignments of the carbonyl π-system and the unshared electron pair of N are nearly parallel. Thus both of these factors are favorable for transannular interaction. But this should inevitably cause a substantial lengthening of the C=O bond. The $C_{(2)}$—O distance is 1.205 Å, which is closer to the lower limit of distances observed in ketones. From this it can be concluded that there is no direct interaction between nitrogen and the carbonyl group. This is a structural confirmation of the calculations that showed the absence (or insignificant presence) of transannular interaction in azetidin-3-one [14].

EXPERIMENTAL

IR spectra were recorded with a Specord 75 IR instrument in mineral oil. PMR spectra were recorded with Bruker WH-360 (360 MHz) and Jeol HL-60 (60 MHz) instruments in $CDCl_3$ solution, with TMS internal standard. UV spectra were obtained with a Specord UV-VIS instrument in methanol. Unit cell parameters were determined in a RKOP camera and refined with a DRON-1.5 diffractometer. To determine the space group, scans of the layer lines were obtained with a KFOR camera. Experimental material in the amount of 838 independent nonzero reflections was

TABLE 4. Valence Angles, ω, in Compound IIi

Angle	ω°	Angle	ω°
S—N—$C_{(1)}$	122,3(5)	$C_{(2)}$—$C_{(3)}$—N	85,7(6)
$C_{(1)}$—N—$C_{(3)}$	93,6(6)	$C_{(2)}$—$C_{(3)}$—$C_{(4)}$	118,1(6)
$C_{(1)}$—$C_{(2)}$—$C_{(3)}$	91,8(7)	N—S—$C_{(6)}$	109,4(4)
$C_{(3)}$—$C_{(2)}$—$O_{(3)}$	133,8(7)	$O_{(2)}$—S—N	105,9(4)
N—$C_{(3)}$—$C_{(4)}$	115,3(7)	$O_{(1)}$—S—$C_{(6)}$	108,5(5)
$C_{(3)}$—$C_{(4)}$—$C_{(5)}$	110,7(8)	S—$C_{(6)}$—$C_{(7)}$	118,8(6)
$O_{(1)}$—S—N	105,9(4)	$C_{(6)}$—$C_{(7)}$—$C_{(8)}$	119,3(8)
$O_{(1)}$—S—$O_{(2)}$	113,0(4)	$C_{(7)}$—$C_{(8)}$—$C_{(9)}$	120,0(9)
$O_{(2)}$—S—$C_{(6)}$	109,0(4)	$C_{(8)}$—$C_{(9)}$—$C_{(12)}$	118,9(9)
S—$C_{(6)}$—$C_{(11)}$	119,6(7)	$C_{(9)}$—$C_{(10)}$—$C_{(11)}$	122,0(7)
S—N—$C_{(3)}$	124,2(5)	$C_{(7)}$—$C_{(6)}$—$C_{(11)}$	121,5(8)
N—$C_{(1)}$—$C_{(2)}$	87,3(6)	$C_{(8)}$—$C_{(9)}$—$C_{(10)}$	119,2(9)
$C_{(1)}$—$C_{(2)}$—$O_{(3)}$	134,4(7)	$C_{(10)}$—$C_{(9)}$—$C_{(12)}$	121,8(8)
		$C_{(10)}$—$C_{(11)}$—$C_{(6)}$	117,9(7)

TABLE 5. Atomic Coordinates ($\times 10^4$) in Compound IIi

Atom	x	y	z	Atom	x	y	z
S	873(2)	3629(1)	5051(6)	1-H	−232	4498	8418
$O_{(1)}$	711(5)	4194(3)	3288(12)	2-H	−1318	4279	6796
$O_{(2)}$	1116(5)	2946(3)	4066(13)	3-H	294	2920	9810
$O_{(3)}$	−1706(5)	3501(3)	11504(14)	4-H	−954	2161	6090
N	−210(5)	3474(3)	6538(15)	5-H	−1546	2251	6928
$C_{(1)}$	−740(7)	4061(4)	7826(19)	6-H	−1636	2056	11282
$C_{(2)}$	−1086(6)	3518(4)	9806(19)	7-H	−355	1815	11201
$C_{(3)}$	−369(6)	2968(4)	8720(17)	8-H	−1354	1279	9710
$C_{(4)}$	−868(7)	2216(4)	8072(18)	9-H	2482	2952	7531
$C_{(5)}$	−1085(8)	1782(4)	10400(22)	10-H	3836	3384	10403
$C_{(6)}$	1864(6)	3947(4)	7164(17)	11-H	3814	4435	14300
$C_{(7)}$	2438(7)	3458(4)	8354(20)	12-H	4820	4462	12095
$C_{(8)}$	3203(7)	3702(5)	10108(23)	13-H	4163	5222	12641
$C_{(9)}$	3360(7)	4431(5)	10681(19)	14-H	3152	5531	9316
$C_{(10)}$	2760(6)	4902(4)	9504(20)	15-H	1601	5051	6758
$C_{(11)}$	2014(6)	4676(4)	7697(18)				
$C_{(12)}$	4149(7)	4676(4)	12702(21)				

TABLE 6. Properties of Azetidines IIa-k

Compound	mp, °C	Found, %			Empirical formula	Calculated, %			Yield, %
		C	H	N		C	H	N	
II a	127—128	51,0	4,3	6,6	$C_9H_9NO_3S$	51,2	4,3	6,6	35
II b	142—143	53.5	5,0	6,1	$C_{10}H_{11}NO_3S$	53,3	4,9	6,2	45
II c	110—111	49,9	4,6	5,7	$C_{10}H_{11}NO_4S$	49,8	4,6	5,8	42
II d	135—136	44,1	3,1	5,9	$C_9H_8ClNO_3S$	44,0	3,3	5,7	45
II e	198—199	42,1	3,2	10,9	$C_9H_8N_2O_5S$	42,2	3,1	11,0	30
II f	194—195	49,3	4,5	10,4	$C_{11}H_{12}N_2O_4S$	49,3	4,5	10,5	28
II g	75—76	55,3	5,5	6,0	$C_{11}H_{13}NO_3S$	55.2	5,4	5,9	70
II h	127—128	51.1	5,1	9,8	$C_{12}H_{14}N_2O_4S$	51,1	5,0	10,0	70
II i	65—66	57,1	5,8	5,6	$C_{12}H_{15}NO_3S$	56,9	5,9	5,5	70
II j	84—86	52,8	5,4	9,4	$C_{13}H_{16}N_2O_4S$	58,7	5,4	9,5	55
II k	92—93	64,8	5,5	4,6	$C_{17}H_{17}NO_3S$	64,8	5,4	4,4	57

obtained with a DAR-UM automatic diffractometer with monochromatic CuK_α irradiation. Maximum $\sin\theta/\lambda$ is 0.55. The structure was decoded by the direct method with the Rentgen-75 system of programs [15] according to 160 reflections with [E] > 1.28. Depiction of the structure model under automatic conditions was unsuccessful; the origin was not determined by the reflections from the group of the most intense. Manual assignment of coordinate and reference reflections enabled us to obtain to a first approximation the coordinates of all 16 nonhydrogen atoms. The structure was refined by a full-matrix anisotropic approximation. The hydrogen atoms were revealed by a differential synthesis. Positional and thermal parameters of the H atoms were not refined. B_{iso} of the hydrogen atoms was taken as one unit more than for the corresponding carbon atom. The final R-factor value was 0.065. Table 5 gives the coordinates of the atoms.

Crystallographic data for IIi: colorless needles, $C_{12}H_{15}NO_3S$, monoclinic, a = 12.834(3), b = 18.735(4), c = 5.335(1) Å, γ = 95.2(2)°, V = 1277.5 Å, M = 253.3, d_{xr} = 1.325 g/cm^3, Z = 2, $P2_1/n$ space group.

General Procedure for Synthesis of N-Arenesulfonyl-azetidin-3-ones (IIa-k). Diazoketone I, 2.5 mmole, was dissolved in 20 ml of chloroform, 4 mmole of conc. H_2SO_4 was added, and the mixture was vigorously shaken. Nitrogen was evolved and the solution became colorless. The mixture was washed with saturated aqueous sodium bicarbonate solution, and the chloroform layer was separated and dried with sodium sulfate. The solvent was removed, and chromatography on a SiO_2 column ($L_{40/100}$ μ, eluent 5:1 benzene—ethyl acetate) separated azetidines IIa-f. Azetidines IIg-j were obtained analogously, but after removal of chloroform the residue was recrystallized from hexane. The properties of compounds IIa-k are given in Table 6.

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PREPARATION OF N-ARYLAMINO-2-PYRROLIDONES FROM ARYLHYDRAZIDES OF γ-CHLOROBUTYRIC ACID

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Intramolecular alkylation of the arylhydrazides of γ-chlorobutyric acid in the presence of sodium ethoxide leads to the formation of N-arylamino-2-pyrrolidones. The direction of the reaction is not altered by the absence of a substituent on the aniline nitrogen atom. In the case of a p-nitrophenyl-hydrazide, O-alkylation is observed.

We have shown previously [1] that reaction of N-methyl-N-phenylamino-2-pyrrolidone with phosphoryl chloride is accompanied by a Kost rearrangement with the formation of 3-(2-arylamino)-2-pyrrolidones. The present work is concerned with the development of a method for the preparation of the difficultly accessible N-arylamino-2-pyrrolidones. 2-Pyrrolidones substituted on the nitrogen atom are generally prepared by the reaction of primary amine salts with γ-butyrolactone [2] or by intramolecular alkylation of amides of γ-halogen-substituted fatty acids [3, 4].

Experiments on the preparation of N-arylaminopyrrolidones by the reaction of arylhydrazine hydrochlorides with γ-butyrolactone were not successful because under these conditions tar formation occurred and the product was a complex mixture from which only the N-arylpyrrolidone could be separated.

The most acceptable method for the preparation of the N-arylamino-pyrrolidones III was the intramolecular alkylation of the arylhydrazides II.

The arylhydrazides IIa-k were prepared by acylation of arylhydrazines Ia-k by means of acid chloride of γ-chlorobutyric acid [5]. In the acylation of arylhydrazines Ia-g which have no substituent on the aniline nitrogen the isomeric arylhydrazide was also obtained together

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