SYNTHESIS OF TRIAZA-2-CYCLOHEXENE DERIVATIVES

G. S. Gol'din and L. S. Baturina

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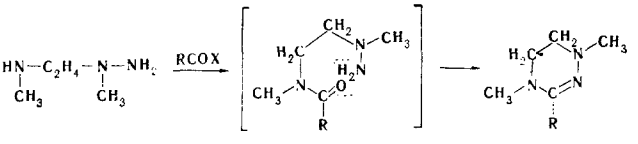
Di- and trialkyl derivatives of 1,3,4-triaza-2-cyclohexene were synthesized by reaction of N,N'-dimethylethyleneaminohydrazine with monocarboxylic acid and their anhydrides, esters, amides, and hydrazides. Alkyl derivatives of α,ω-bis [2-(1,3,4-triaza-2-cyclohexenyl)]alkanes were obtained as a result of the reaction of N,N'-dimethylethyleneaminohydrazine with dicarboxylic acids and their derivatives. 1-Amino-1,3,4-triaza-2-cyclohexene derivatives were obtained from ethylenedihydrazine and monocarboxylic acid esters.

We have previously reported the synthesis of heterocyclic compounds from N,N'-dimethylethyleneaminohydrazine [1], including alkyl derivatives of triazacyclohexane [2]. The present paper is devoted to the synthesis of triazacyclohexene derivatives, which are of interest as additives to improve the properties of oils and other materials.

We obtained 1,3,4-triaza-2-cyclohexene derivatives by reaction of N,N'-dimethylethyleneaminohydrazine with monocarboxylic acids and their esters, anhydrides, amides, and hydrazides.



I-VI

a X = OH, b X = RCOO, c X = OR', d X = NH_2, e X = $NHNH_2$; I R = H; II R = CH_3; III R = C_2H_5; IV R = C_3H_7; V R = C_4H_9; VI R = C_6H_{13}

The formation of 1,4-dimethyl-1,3,4-triaza-2-cyclohexene (I) was followed by gas–liquid chromatography (GLC) in the case of the reaction of N,N'-dimethylethyleneaminohydrazine with ethyl formate at 100°C. The N,N'-dimethylethyleneaminohydrazine is almost completely consumed after the first 3 h of the reaction, during which ethanol and an intermediate, which has a longer retention time than the starting material, are formed. A peak corresponding to 1,4-dimethyl-1,3,4-triaza-2-cyclohexene subsequently appears, and there is a simultaneous sharp decrease in the concentration of the intermediate in the reaction mixture.

Thus the results make it possible to assume that the first step in the reaction of N,N'-dimethylethyleneaminohydrazine with ethyl formate is acylation, after which intramolecular condensation to give 1,3,4-triaza-2-cyclohexene occurs.

TABLE 1. Characteristics of the Synthesized Compounds

Compound	bp, °C (mm Hg), mp, °C	d_4^{20}	n_D^{20}	MR_D found	MR_D calc.	Found, % C	Found, % H	Found, % N	Empirical formula	Calc., % C	Calc., % H	Calc., % N
I	79—80 (10)	0,9921	1,5010	33,55	33,33	52,8	9,9	37,3	$C_5H_{11}N_3$	53,0	9,8	37,1
II	82—83 (10)	0,9854	1,5007	37,94	37,98	56,9	10,4	33,3	$C_6H_{13}N_3$	56,7	10,3	33,0
III	89—90 (10)	0,9727	1,4950	42,70	42,63	59,8	10,8	30,1	$C_7H_{15}N_3$	59,5	10,7	29,8
IV	103—104 (10)	0,9505	1,4898	47,18	47,28	61,7	11,2	28,1	$C_8H_{17}N_3$	61,9	11,0	27,1
V	112—113 (10)	0,9387	1,4869	51,86	51,89	63,6	11,3	24,8	$C_9H_{19}N_3$	63,9	11,3	24,8
VI	134 (8)	0,9083	1,4771	61,29	61,22	67,2	11,7	20,9	$C_{11}H_{23}N_3$	66,9	11,8	21,3
VII	95—96					57,2	9,8	33,4	$C_{12}H_{24}N_6$	57,1	9,6	33,3
VIII	62—63					60,0	9,9	29,7	$C_{14}H_{28}N_6$	59,9	10,0	29,9
IX	110—112					36,2	7,9	55,8	$C_3H_8N_4$	35,9	8,0	56,0
X	106—107					42,3	9,0	48,9	$C_4H_{10}N_4$	42,1	8,8	49,0

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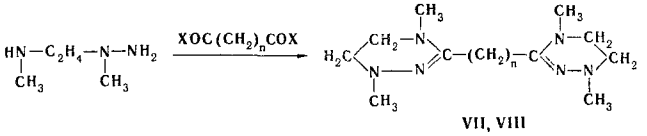
The IR spectra of the alkyl derivatives (I-VI) of 1,3,4-triaza-2-cyclohexene contain a band at 1600-1610 cm^{-1}, which is related to the C = N bond. Bands characteristic for NH and NH_2 groups are absent.

The PMR spectrum of 1,4-dimethyl-2-ethyl-1,3,4-triaza-2-cyclohexene (III) contains two signals of an ethyl group in the form of a triplet (δ 1.03 ppm) and a quartet (δ 2.12 ppm) and two singlets (δ 2.49 and 2.46 ppm), which are related, respectively, to methyl groups attached to amine and hydrazine nitrogen atoms, as well as two triplets of ring methylene groups (δ 2.62 and 3.24 ppm).

We also studied the reaction of N,N'-dimethylethyleneaminohydrazine with succinic and adipic acids and their esters, anhydrides, and hydrazides. As a result, we obtained α,ω-bis[2-(1,4-dimethyl-1,3,4-triaza-2-cyclohexenyl)]alkanes (VII and VIII, Table 1).

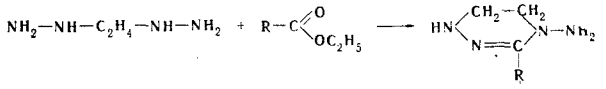


VII, VIII

a X = OH, b X = OC_2H_5, c X = $NHNH_2$, X = O; VII n = 2; VIII n = 4

The IR spectra of the two-ring derivatives are similar to the IR spectra of triazacyclohexenes I-VI.

We were able to obtain 1-amino derivatives of 1,3,4-triaza-2-cyclohexene (IX and X, Table 1) in low yields by heating equimolar amounts of ethylenedihydrazine with monocarboxylic acid esters.



IX R = H; X R = CH_3 IX, X

The IR spectra of IX and X contain bands at 1620 (C = N) and at 1640, 3150, and 3270 cm^{-1} (NH and NH_2).

EXPERIMENTAL

The chromatographic studies were made with a KhL-4 chromatograph. The sorbent was Teflon (0.25-0.50 mm) with 11.5% E-301 silicone elastomer applied to it. The column was 2-m long with a diameter of 6 mm, the carrier-gas (helium) flow rate was 340 ml/min, the column temperature was 140°, and the vaporizer temperature was 200°. The copper gaskets in the working line of the chromatograph were replaced by Teflon.

The IR spectra of mineral oil suspensions of the solid compounds and thin layers of the liquid compounds were recorded with a UR-10 spectrometer with KBr or NaCl prisms.

The PMR spectra of the compounds were recorded with a JNMC-60HL (JEOL) spectrometer at an operating frequency of 60 MHz with hexamethyldisiloxane as the internal standard.

Di- and Trialkyl-1,3,4-triaza-2-cyclohexenes (I-VI, Table 1). A 0.25-mole sample of the monocarboxylic acid anhydride or 0.5 mole of the monocarboxylic acid or its ester, amide, or hydrazide was added with stirring and cooling to 0.5 mole of N,N'-dimethylethyleneaminohydrazine, and the mixture was heated at 100-130° for 16-22 h. The low-boiling reaction products were removed by distillation at atmospheric pressure, and the residue was vacuum fractionated. In the case of valeric acid hydrazide the reaction was carried out with simultaneous removal of the resulting hydrazine by distillation. The products were obtained in 55-78% yields.

α,ω-Bis[2-(1,4-dimethyl-1,3,4-triaza-2-cyclohexenyl)]alkanes (VII and VIII, Table 1). A mixture of 0.5 mole of N,N'-dimethylethyleneaminohydrazine and 0.5 mole of adipic or succinic acid or their diethyl esters, succinic acid dihydrazide (in the presence of 0.5 ml of H_2SO_4), or succinic anhydride was heated at 100-120° for 20 h. When the acids and anhydrides were used, the final products precipitated when the mixtures were cooled; when the esters are used, the resulting alcohol and water should be initially removed by distillation. The reaction of N,N'-dimethylethyleneaminohydrazine with succinic acid dihydrazide was carried out with simultaneous removal of the hydrazine by distillation. The compounds were crystallized from petroleum ether and were obtained in 25-50% yields.

1-Amino-1,3,4-triaza-2-cyclohexenes (IX, X). A 0.25-mole sample of ethylenedihydrazine and 0.25 mole of ethyl formate or ethyl acetate were mixed with cooling, and the mixture was refluxed for 14-18 h. The low-boiling fraction was removed by distillation, and the residue began to crystallize. The amines obtained in this manner were recrystallized from benzene–absolute alcohol to give the products in ~20% yields.

LITERATURE CITED

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2. G. S. Gol'din, T. A. Balabina, A. N. Ushakova, and S. N. Tsiomo, Zh. Org. Khim., 10, 2218 (1974).