SYNTHESES OF SOME SUBSTITUTED sym-TRIAZINES

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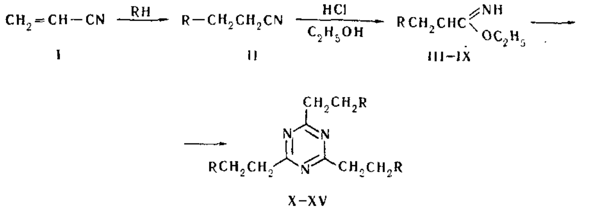
The synthesis of various β-substituted propionimidic esters has been effected and the conditions of their conversion into the corresponding 2,4,6-triethyl-sym-triazine derivatives have been studied.

Recently, a number of authors have described the preparation of some substituted sym-triazines by the trimerization of the corresponding imidic esters in the presence of their hydrochlorides [1,2]. In the present work, we have studied the possibility of using this method for the synthesis of derivatives of sym-triazine in which the functional groups are separated from the ring by a chain of two methylene groups. For this purpose as the starting materials we have used β-substituted propionimidic esters obtained from acrylonitrile in the following way:



The synthesis of the substituted propionitriles (II), which were known previously, was effected by the cyanoethylation of the corresponding reactants [3, 4]. The propionimidic esters III–IX were obtained by Pinner's method [5] by the action on the nitrile II of the calculated amount of dry hydrogen chloride in the presence of absolute ethanol (Table 1).

A study of the trimerization of the imidic esters III–IX showed that it takes place comparatively readily only in the case of the imidic esters having alkoxy and alkylthio groups; the triazines XI, XII, and XV obtained from them (Table 2) undergo fractionation without decomposition and are completely stable substances. The imidic ester III trimerizes without the participation of its hydrochlorides as catalyst, but the triazine X formed from it decomposes on heating. The noncrystallizing triazines XIII and XIV do not distill, either, undergoing far-reaching changes on heating, and therefore they were obtained in the pure form by column chromatography on alumina.

The imidic ester IX, containing a diethylamino group, trimerizes in very small amounts (with pronounced resinification). The presence in the reaction products of the triazine corresponding to it can be judged only from the IR spectra.

We explain the ease with which the triazines X, XIII, and XIV undergo change under the influence of heating by the presence in the side chain of protonated α-hydrogen atoms capable of forming readily polymerized vinyl derivatives of triazine [6, 7].

To characterize the compounds obtained in the present work and also the completeness of their reactions, in addition to analytical methods the use of IR spectra proved extremely convenient. Thus, the

Table 1

Imidic Esters $RCH_2CH_2C(=NH)OC_2H_5$

Compound	R	Bp, °C (pressure, mm)	Mp of the hydrochloride, °C	d_4^{20}	n_D^{20}	Empirical formula	N, % found	N, % calculated	MR_D found	MR_D calculated	Yield, %
III	OH	Does not distill*	60–65	1.0068	1.4560	$C_5H_{11}NO_2$	12.35	12.01	31.590	31.134	68.4
IV	CH_3O	34–35 (3)	65–68	0.9342	1.4170	$C_6H_{13}NO_2$	10.70	10.72**	35.870	35.260	70.5
V	C_2H_5O	49 (4)	59–65	0.9227	1.4200	$C_7H_{15}NO_2$	10.05	9.65	39.850	40.488	86.7
VI	HOC_2H_4O	Does not distill	Oil	1.0009	1.4370	$C_7H_{15}NO_3$	8.88	8.70	42.014	41.860	64.7
VII	ClC_2H_4O	Does not distill	Oil	1.0963	1.4600	$C_7H_{14}ClNO_2$	7.53	7.79	45.000	45.355	75.6
VIII	C_2H_5S	77–79 (3)	75–77	0.9906	1.4790	$C_7H_{15}NOS$	8.40	8.66	46.191	46.918	75.95
IX	$(C_2H_5)_2N$	53–55 (1)	Oil	0.8950	1.4390	$C_9H_{20}N_2O$	14.85	16.26***	51.671	53.021	75.40

*Mp 42.0–42.8°C.

**Found, %: C 54.79; H 9.96. Calculated, %: C 54.9; H 9.98.

***Found, %: C 62.72; H 11.79. Calculated, %: C 62.84; H 11.72.

conversion of the substituted propionitriles II into the corresponding imidic esters is readily followed (Fig. 1) by the fall in the absorption of the nitrile group (2200 cm^{-1}) and the appearance of the absorption band of an imino group (1650 cm^{-1}); the trimerization of the imidic esters is accompanied by the appearance of a band at 1550 cm^{-1} which is characteristic of the triazine aromatic system (Fig. 2).

EXPERIMENTAL

β-Chloroethoxypropionitrile. With stirring, 80.5 g (~1 mole) of ethylene chlorohydrin was added over 30 min to a mixture of 53.0 g (~1 mole) of acrylonitrile and 4.0 g of caustic soda in 4 ml of water, the temperature of the mixture rising to 40–45°C. It was stirred for an hour, after which the precipitate that had deposited was filtered off and the filtrate was fractionated. This yielded 80.1 g (60.0%) of β-chloroethoxypropionitrile with bp 110–115°C (55 mm). Found, %: N 10.30, 10.26. Calculated for C_5H_8ClNO, %: N 10.47.

β-Hydroxypropionimidic ester (III). With dry-ice cooling a mixture of 7.10 g (1.0 mole) of ethylene cyanohydrin and 55.2 g (1.2 mole) of ethanol was saturated with hydrogen chloride until the increase in weight was 40.2 g (1.1 mole). The reaction mixture was left at 0° C until it had crystallized completely. The crystals were filtered off, washed with dry ether, and dried in vacuum. This gave 145.2 g (95.0%) of the hydrochloride of the imidic ester III with mp 57–60°C. Found, %: N 9.20, 9.34. Calculated for $C_5H_{12}ClNO_2$, %: N 9.16.

To liberate the free base, 38.25 g (0.25 mole) of the hydrochloride in 200 ml of methylene chloride was mixed with a solution of 10 g (0.25 mole) of caustic soda in a five-fold amount of water and the aqueous layer was extracted with another 200 ml of methylene chloride. The extracts were combined and dried with magnesium sulfate. After the solvent had been distilled off, the imidic ester was trimerized without further purification. The imidic esters IV and VIII were also obtained by this method. In the synthesis of the imidic ester IX, a double amount of hydrogen chloride was used to form its dihydrochloride and a double amount of caustic soda to decompose the dihydrochloride obtained and liberate the free base.

2,4,6-Tris(β-hydroxyethyl)-sym-triazine (X). A mixture of 11.7 g (0.1 mole) of the imidic ester III and 0.23 g (1.5 mmole) of its hydrochloride was stirred for 2 days at room temperature with the ethanol being distilled off periodically. After the end of the reaction, the product was treated with absolute ether and the part insoluble in the ether was separated off and dried in vacuum. This gave 4.5 g (62.7%) of the triazine X. For analysis, the substance was purified by chromatography in a column of alumina of activity grade II.

2,4,6-Tris(β-methoxyethyl)-sym-triazine (XI). A mixture of 13.1 g (0.1 mole) of the imidic ester IV and 0.5 g (3 mmole) of its hydrochloride was stirred at 40° C for two days with the alcohol being periodically distilled off in vacuum. Vacuum distillation of the reaction mixture yielded 4.9 g of the initial imidic ester IV and 3.18 g (59.2%) of the triazine XI with bp 130–132°C (2 mm).

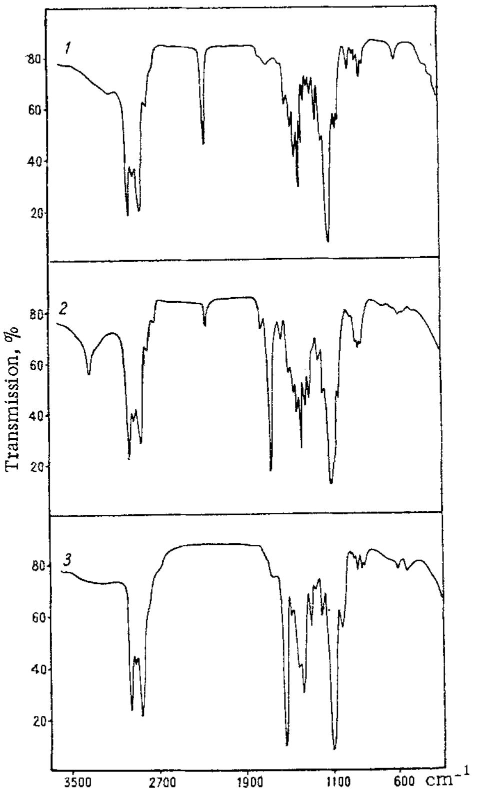


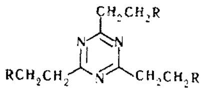
Fig. 1. IR spectra: 1) β-ethoxypropionitrile; 2) β-ethoxypropionimidic ester (VI); 3) 2,4,6-tri-(β-ethoxyethyl)-sym-triazine.

2,4,6-Tris(β-ethoxyethyl)-sym-triazine (XII). A mixture of 14.5 g (0.1 mole) of the imidic ester V and 0.7 g (3.9 mmole) of its hydrochloride was stirred at room temperature for 16 hr and at 70–80°C for 3 hr. Vacuum distillation of the reaction mixture yielded 8.0 g of the initial imidic ester V and 2.2 g of the triazine XII, boiling at 150°–152° C (2 mm).

2,4,6-Tris(β-hydroxyethoxyethyl)-sym-triazine (XIII). A mixture of 16.1 g (0.1 mole) of the imidic ester VI and 0.6 g (3 mmole) of its hydrochloride was left at room temperature for 5 days. Then it was treated in a similar manner to that described in the preceding experiment. The yield of unpurified triazine XIII was 7.6 g (66.3%).

Table 2

Triazines



Compound	R	Bp, °C (pressure, mm)	n_D^{20}	Empirical formula	Found, %			Calculated, %			Yield*, %
					C	H	N	C	H	N	
X	OH	Does not distill	1.5300	$C_9H_{15}N_3O_3$	—	—	19.3	—	—	19.79	62.7
XI	CH_3O	130—132 (2)	1.4776	$C_{12}H_{21}N_3O_3$	56.22	8.26	16.06	56.44	8.23	16.46	59.1
XII	C_2H_5O	150—152 (2)	1.4703	$C_{15}H_{27}N_3O_3$	—	—	13.90	—	—	14.14	78.1
XIII	HOC_2H_4O	Does not distill oil	1.4808	$C_{15}H_{27}N_3O_6$	—	—	11.8	—	—	12.21	66
XIV	ClC_2H_4O	Does not distill gel	1.4943	$C_{15}H_{24}Cl_3N_3O_3$	44.96	6.08	10.44	44.95	6.03	10.53	73
XV	C_2H_5S	216—218 (2)	1.5483	$C_{15}H_{27}N_3S_3$	—	—	12.53	—	—	12.22	89.5

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*Yields calculated on the imidic ester that reacted.

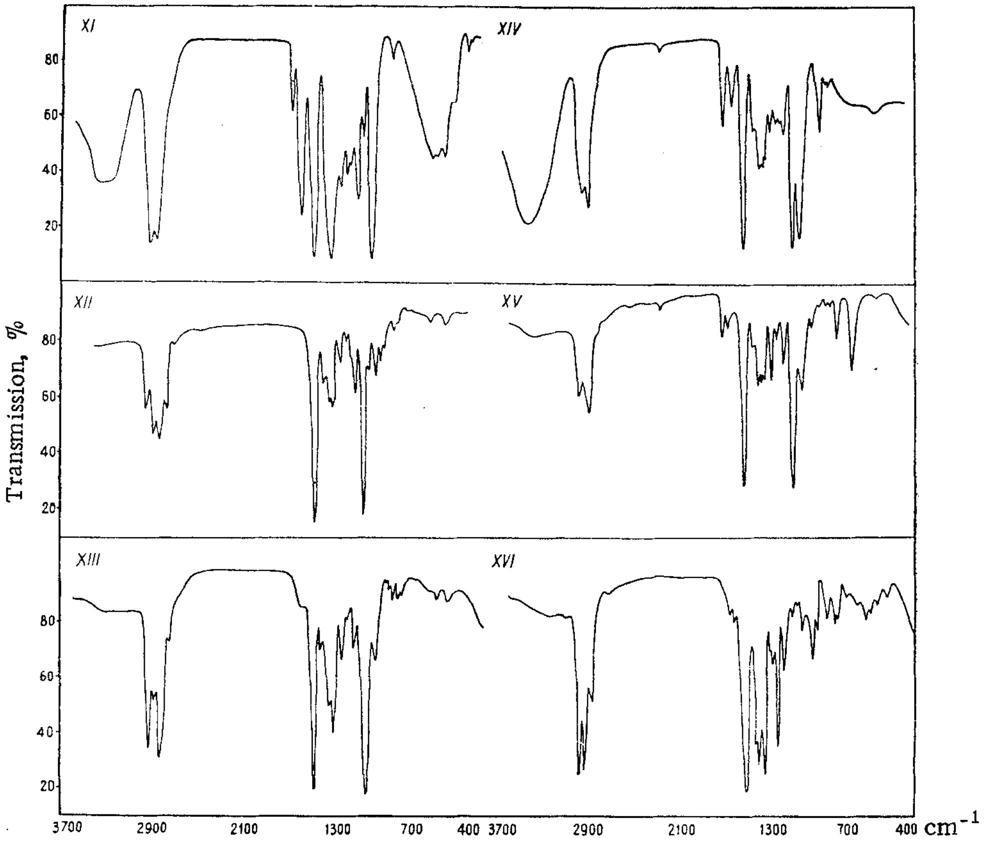

Fig. 2. IR spectra of the sym-triazines synthesized (the numbers of the spectra correspond to the numbers of the compounds given in the text).

For analysis, the substance was purified by chromatography in a column of alumina of activity grade II.

2,4,6-Tris[2-β-chloroethoxy)ethyl]-sym-triazine (XIV). 17.9 g (0.1 mole) of the imidic ester VII was mixed with 0.6 g (~3 mmole) of its hydrochloride. The reaction product was treated as described above. The part of the substance insoluble in ether was purified by additional heating in vacuum to 180°C in order to eliminate the low-boiling components. The yield of the crude triazine XIV was 10.3 g (73.1%). For analysis the triazine was purified by chromatography on a column of alumina of activity grade II.

2,4,6-Tris[2-(β-ethylthio)ethyl]-sym-triazine (XV). A mixture of 16.1 g (0.1 mole) of the imidic ester IX and 0.3 g (1.5 mmole) of its hydrochloride was kept at 40° C for 2 days. Fractionation of the reaction mixture gave 2.8 g of the initial imidic ester IX and 8.5 g of the triazine XV with bp 214–218°C (2 mm).

The IR spectra were recorded on a UR-10 spectrometer in the range of frequencies from 400 to 3600 cm^{-1}, a drop of the substance under investigation being squeezed between plates of potassium bromide.

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