2-Nitro-7-carbamido-7-methyl-6,7-dihydrooxazino[3,2-b]-1,2,4-triazole (V). A 0.5-g (2.4 mmole) sample of III was added in parts with stirring and cooling to 5 ml of concentrated H_2SO_4, after which the mixture was stirred for 3 h. It was then poured into 20 ml of ice water, and the aqueous mixture was allowed to stand for 10 h. The desired product was extracted with ethyl acetate (four 20-ml portions), the extract was washed with water, and the solvent was evaporated. The residue was crystallized from ethanol to give 0.43 g (80%) of a product with mp 162-163°C. IR spectrum (cm^{-1}): 705 m, 750 m, 790 m, 830 w, 860 m, 940 m, 1040 w, 1095 m, 1115 m, 1160 m, 1190 m, 1250 m, 1270 m, 1320 s, 1340 m, 1410 m, 1440 m, 1480 m, 1520 vs, 1570 vs, 1590 vs, 1680 vs, and 1705 vs. PMR spectrum: 2.55 (m, 2H), 4.15 (m, 2H, CH_2), 1.75 (s, 3H, CH_3), and 7.4 ppm (NH_2). Found: C 37.3; H 4.3; N 30.7%; M 222. $C_7H_9N_5O_2$. Calculated: C 37.0; H 4.3; N 30.8%; M 227.

2-Nitro-6-carbamido-6-methyl-5,7-dihydrooxazolo[3,2-b]-1,2,4-triazole (VI). This compound, with mp 156-157°C (from ethanol), was similarly obtained in 70% yield by hydrolysis of VI. IR spectrum (cm^{-1}): 730 s, 750 w, 790 w, 820 w, 865 m, 920 w, 1040 w, 1095 m, 1150 m, 1200 s, 1230 w, 1270 m, 1300 w, 1320 s, 1400 m, 1450 m, 1470 w, 1540 vs, 1570 vs, 1660 s, and 1700 vs. PMR spectrum: 4.60 (d, 1H, H_A), 5.03 (d, 1H, H_B, $J_{H_AH_B}$ = 11 Hz), 2.0 (3H), and 7.83 ppm (2H, NH_2). Found: C 33.7; H 3.4; N 33.1%; M 210. $C_6H_7N_5O_4$. Calculated: C 33.8; H 3.3; N 32.9%. M 213.

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SYNTHESIS OF SOME ESTERS AND AMIDES OF 2-SUBSTITUTED 4,6-BIS(p-CARBOXYPHENOXY)-sym-TRIAZINE

V. K. Pyzhov, V. N. Zaplishnyi,
A. A. Balyan, R. T. Grigoryan,
and G. M. Pogosyan

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A number of corresponding esters and amides were obtained by the reaction of the chlorides of 2-substituted 4,6-bis(p-carboxyphenoxy)-sym-triazines (CPT) with ethanol and some primary amines in the presence of a hydrogen chloride acceptor. It was observed that hydrazine and hydrazine hydrate have a cleavage effect on the C—O bond of chloride of CPT in the 4 and 6 positions even at 0°C. Dihydrazides of CPT were synthesized at -40°C.

We have previously synthesized 2-substituted 4,6-bis(p-carboxyphenoxy)-symtriazines (CPT) and their chlorides. These substances may find application as monomers for polycondensation [2, 3].

Institute of Organic Chemistry, Academy of Sciences of the Armenian SSR, Erevan 375094. A. L. Mndzhoyan Institute of Fine Organic Chemistry, Academy of Sciences of the Armenian SSR, Erevan 375014. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1406-1411, October, 1981. Original article submitted October 30, 1980, revision submitted February 18, 1981.

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TABLE 1. Esters and Amides of CPT (II, III)

Compound	mp, °C	R_f (system)	Found, %			Empirical formula	Calc., %			Yield, %
			C	H	N		C	H	N	
IIa	40—45*	0,77 (A)	59,8	5,2	9,3	$C_{22}H_{21}N_3O_7$	60,1	4,8	9,6	46
IIb	124—125†	0,70 (B)	62,2	6,0	11,7	$C_{25}H_{28}N_4O_6$	62,5	5,9	11,7	40
IIc	104—105*	0,81 (C)	68,7	5,1	9,8	$C_{33}H_{28}N_4O_6$	68,7	4,9	9,7	83
IIIa	228—229‡	0,50 (D)	56,6	4,0	18,4	$C_{18}H_{15}N_5O_5$	56,9	4,0	18,7	74
IIIb	193—195**	0,82 (F)	60,5	5,2	16,2	$C_{22}H_{23}N_5O_5$	60,4	5,3	16,0	58
IIIc	149—150††	0,83 (G)	62,7	5,2	15,0	$C_{24}H_{23}N_5O_5$	62,5	5,0	15,2	67
IIId	222—224‡	0,80 (F)	67,3	4,6	13,0	$C_{30}H_{23}N_5O_5$	67,6	4,3	13,1	96
IIIe	208—209		52,2	4,0	23,7	$C_{18}H_{17}N_7O_5$	52,5	4,2	23,8	92
IIIf	234—235‡	0,43 (F)	59,7	5,5	19,9	$C_{21}H_{22}N_6O_4$	59,7	5,3	19,9	92
IIIg	221—222†	0,78 (D)	63,0	6,6	17,4	$C_{25}H_{30}N_6O_4$	62,7	6,3	17,6	96
IIIh	206—207‡	0,81 (G)	64,6	6,0	16,4	$C_{27}H_{30}N_6O_4$	64,5	6,0	16,7	92
IIIi	230—232‡‡	0,64 (G)	69,3	5,3	14,3	$C_{33}H_{30}N_6O_4$	69,0	5,3	14,6	90
IIIj	243—245***		55,7	5,5	24,6	$C_{21}H_{24}N_8O_4$	55,6	5,3	24,8	98
IIIk	259—260‡	0,64 (D)	67,1	4,5	16,3	$C_{29}H_{22}N_6O_4$	67,2	4,3	16,2	92
IIIl	210—212††	0,75 (D)	68,9	5,3	14,7	$C_{33}H_{30}N_6O_4$	69,0	5,3	14,6	81
IIIm	190—191††	0,81 (D)	69,9	5,3	14,3	$C_{35}H_{30}N_6O_4$	70,2	5,0	14,0	85
IIIn	255—256†††	0,83 (E)	73,8	4,4	12,8	$C_{41}H_{30}N_6O_4$	73,5	4,5	12,5	99
IIIo	229—230‡		63,2	4,5	20,3	$C_{29}H_{24}N_8O_4$	63,5	4,4	20,4	75

*Water-Ethanol (1:2).

†Methanol.

‡Ethanol.

**Acetone.

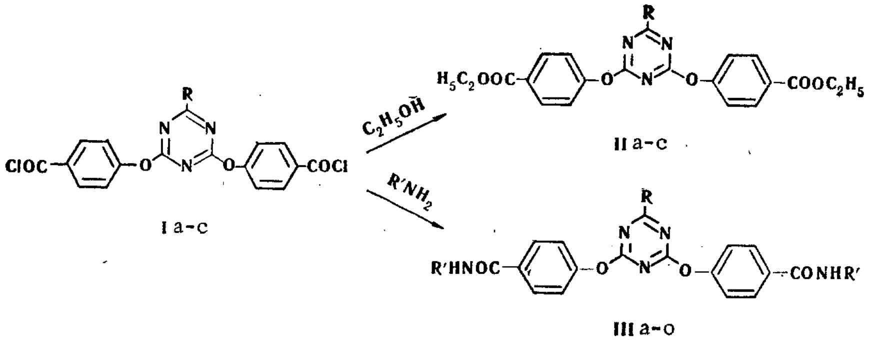
††Toluene.

‡‡Chloroform–ether (4:1).

***DMSO.

†††Chloroform.

In the present research we investigated the possibilities for the synthesis of some esters and amides of CPT:

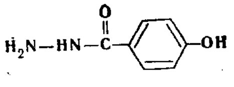


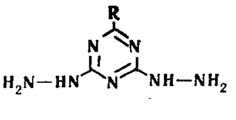
Ia IIa, IIIa-e R=OCH_3; Ib IIb IIIf-j R=$N(C_2H_5)_2$; Ic IIc, IIIk-o R=$N(C_6H_5)_2$;
IIIa,f,k R'=H, b,g,l R'=C_2H_5, c,h,m R'=$CH_2CH{=}CH_2$, d,i,n R'=C_6H_5, e,j,o R'=NH_2

The reaction of chlorides I with ethanol (present in excess amounts) in the presence of triethylamine leads to the corresponding diethyl esters (IIa-c). The reaction of chlorides I with ammonia, which leads to amides IIIa, f, k, also proceeds readily. In the preparation of ethyl-, allyl-, and phenylamides IIIb-d, IIIg-i, and IIIl-n the reaction of the chlorides of CPT with the corresponding amines was realized in benzene in the presence of triethylamine.

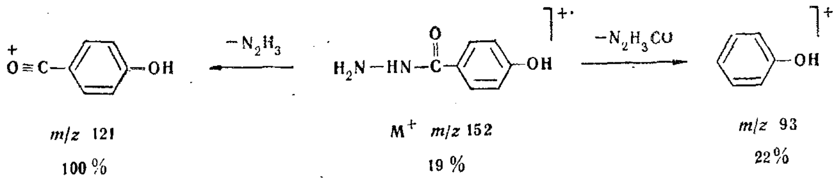
The structures and individuality of the substances obtained were confirmed by the IR and PMR spectra and thin-layer chromatography (TLC) (Tables 1 and 2).

In the synthesis of hydrazides from esters IIa-c, instead of the expected amides IIIe, j, o, we obtained p-hydroxybenzoic acid hydrazide (IV) and 2-substituted 4,6-dihydrazino-sym-triazines (V):


IV


V

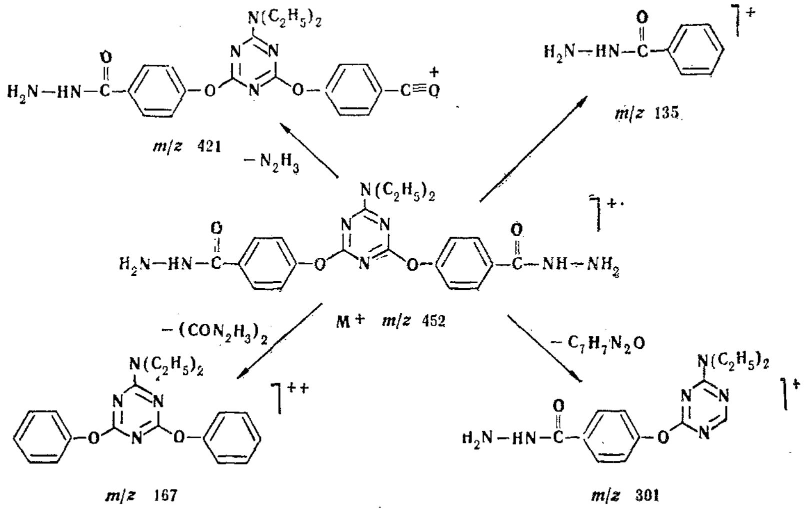
The identification of IV was made on the basis of the results of elementary analysis and the PMR and mass spectra; IV had mp 260°C, in agreement with the value in [4]. The fragmentation of hydrazide IV under the influence of electron impact is represented as follows:



Compound V was identified on the basis of the PMR spectrum and alternative synthesis from 2,4-dichloro-6-diethylamino-sym triazine and hydrazine hydrate by the method in [5].

We found that the acylation of hydrazine or hydrazine hydrate with chlorides I at temperatures above 0°C also leads to IV and V.

Hydrazides IIIe, j, o, were synthesized by the reaction of the chlorides of CPT in excess hydrazine hydrate at -40°C. The structure of IIIe, j, o was confirmed by the IR, PMR (Table 2), and mass spectra. The observed peaks of fragment ions also confirm the IIIj structure:



The synthesized esters and amides of CPT are white, finely crystalline, odorless powders. Diesters II are soluble in ordinary organic solvents. Most amides III are soluble in dimethylacetamide (DMA), dimethylformamide (DMF), dimethyl sulfoxide (DMSO), chlorine-containing hydrocarbons, and alcohols (with heating), slightly soluble in aromatic hydrocarbons, and insoluble in ether and aliphatic hydrocarbons. Thus the solubility of amides III in chloroform as a function of R and R' increases in the order $N(C_2H_5)_2 < N(C_7H_5)_2 < OCH_3$ and $NH_2 < NHC_6H_5 < NHC_2H_5 < NHCH_2CH{=}CH_2$, respectively.

The synthesized compounds may find application as polycondensed monomers, while the amides may find application as modifying additives for thermosetting plastics [6].

EXPERIMENTAL

The starting chlorides of CPT (I) were synthesized by the methods in [1, 2]. The amines used were purified by fractional distillation, while hydrazine and hydrazine hydrate were purified by the method in [7]. All of the solvents used were purified and dried by generally used methods [8]. The IR spectra of mineral oil suspensions (IIc, IIIg-i) and KBr pellets of the compounds were recorded with a UR-20 spectrometer. The PMR spectra of solutions of the compounds in CCl_4 (IIa, b), DMSO (IIIf), $CDCl_3$ (IIIh, i), and d_6-DMSO (the remaining compounds) were recorded with a Perkin-Elmer spectrometer (60 MHz) with tetramethylsilane as the external standard at 30°C. The mass spectra were recorded with an MKh-1320 spectrometer. Thin-layer chromatography was carried out on Silufol UV-254 plates with development with iodine vapors or UV irradiation. The R_f values were found in the following systems: methanol (A), benzene–acetone (4:1) (B), chloroform–methanol (10:1) (C), chloroform–methanol (4:1) (D), chloroform–methanol (8:1) (E), acetone (F), and ethanol (G).

TABLE 2. IR and PMR Spectra of Esters and Amides of CPT(II, III)

Compound	IR spectrum, ν, cm^{-1}						PMR spectrum, δ, ppm (J, Hz)				
	C=O	aromatic C=C and C=N	aromatic CH	C—O—C	N—H	other absorption bands*	N—H	NCH_2CH_3 (J=7,5)	C_6H_4	OCH_3	other groups
IIa	1725	1610, 1600, 1580, 1510	3085	1280, 1220, 1170, 1115		820, 790, 780, 710			8,03 d 7,18 d (9)	3,88 c	4,36 q ; 1,37 t (7,5) (OCH_2CH_3)
IIb	1720	1610, 1585, 1530, 1505	3090, 3075	1290, 1210, 1170, 1100		812, 790, 780, 710		3,35 q ; 0,98 t	7,98 d 7,12 d (9)		4,26 q ; 1,29 t (7,5) (OCH_2CH_3)
IIc	1720	1610, 1575, 1545, 1507	3080, 2995	1275, 1220, 1170, 1110		810, 760, 700			7,83 d 7,21 d (9)		4,25 q ; 1,22 t (7,5) (OCH_2CH_3)
IIIa	1675	1610, 1580, 1510	3080, 3020	1260, 1225, 1175, 1120	3420, 3215	810, 785, 760			7,80 d 7,30 d (9)	3,80 c	
IIIb	1645	1610, 1595, 1555, 1510	3080, 2975	1175, 1110, 1260, 1220	3300, 3150	815	8,35 t (6)	3,05 q; 0,89 t	7,78 d 7,13 d (9)	3,60 c	
IIIc	1645	1610, 1570, 1550, 1505	3085, 3025	1260, 1220, 1175, 1125	3310	818, 980, 925	8,67 t (5,5)		7,96 d 7,35 d (9)	3,87 c	5,87 m, 5,18 t (9,5); 3,93 m ($CH_2CH{=}CH_2$)
IIId	1650	1600, 1580, 1540, 1505	3070, 2970	1265, 1220, 1175, 1115	3335	815, 790, 760, 715	10,24 br s		7—8,1 (C_6H_4+ +C_6H_5)	3,78 c	
IIIe	1620	1600, 1540, 1510	3025, 2970	1178, 1130	3330, 3290	808, 770	9,55 br s		7,78 d 6,86 d (9)	3,42 c	4,45 br s (NH_2)
IIIf	1685	1620, 1595, 1535, 1510	3080, 2990	1268, 1220, 1185, 1120	3440, 3200	812, 780, 710		0,89 t	7,84 d 7,18 d (9)		

IIIg	1650	1615, 1590, 1550, 1500	3085, 3040	1230, 1175, 1145, 1100	3345, 3200	810, 780, 710	8,47 t (6)	3,39 q ; 3,25 q ; 1,0; 1,13 t	7,92 d 7,32 d (9)		
IIIh	1650	1612, 1585, 1540, 1500	3075	1225, 1180, 1155, 1100	3440	812, 790, 770, 980	6,63 br s	3,52 q ; 1,13 t	7,84 d 7,22 d (9)		4,13 t (4); 5,3 t (7,5); 6 m (5) ($CH_2CH{=}CH_2$)
IIIi	1655	1620, 1600, 1540, 1505	3145, 3070	1270, 1225, 1175, 1100	3290, 3200	812, 775, 760, 710	8,72 br s	3,73 q ; 1,13 t	8,07 d 7,38 d (9)		
IIIj	1660	1615, 1585, 1535, 1505	3075, 3010	1270, 1240, 1175, 1125	3410, 3220	810, 780, 760, 710	9,75 br s	3,30 q ; 0,9 t	7,87 d 7,27 d (9)		4,2 s (NH_2)
IIIk	1635	1615, 1587, 1540, 1500	3060	1230, 1180, 1120, 1100	3330, 3300	810, 760, 700			7,84 d 7,22 d (9)		7,28 s (C_6H_5)
IIIl	1645	1610, 1580, 1540, 1505	3075, 3005	1275, 1245, 1210, 1180	3385, 3300	812, 762, 700	8,44 t (6)	3,35 q , 1,12 t	7,85 d 7,25 d (9)		7,34 s (C_6H_5)
IIIm	1643	1619, 1575, 1540, 1500	3080, 3020	1270, 1235, 1215, 1175	3335	810, 760, 700	8,55 t (6)		7,81 d 7,22 d (9)		3,86 t (5,5); 5,12 t 5,78 m (9,5) ($CH_2CH{=}CH_2$)
IIIn	1658	1606, 1580, 1545, 1510	3070, 3010	1265, 1215, 1175, 1110	3335, 3285	810, 760, 700	8,2 br s		7—8 (C_6H_4+ +C_6H_5)		
IIIo	1655	1604, 1570, 1527, 1495	3068, 2985	1240, 1220, 1175, 1110	3320, 3290	810, 760, 700	8,7 br s		7,78 d 7,20 d (9) 7,29 s (C_6H_5)		4,3 br s (NH_2)

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*The absorption regions that are characteristic for the deformation vibrations of p-substituted benzenes, monosubstituted benzenes, the allyl group, and the sym-triazine ring are presented.

2-Diphenylamino-4,6-bis(p-carboxyphenoxy)-sym-triazine Diethyl Ester (IIc). A solution of 2.2 g (4 mmole) of chloride Ic in 30 ml of acetone was added with stirring to a mixture of 15 ml of ethanol and 1.3 ml (9.35 mmole) of triethylamine, and the mixture was refluxed for 2 h. The precipitated triethylamine hydrochloride was removed by filtration and washed with 5 ml of ethanol. The combined filtrates were evaporated to dryness, and the residue was washed thoroughly with water, crystallized from methanol, and dried to constant weight at 60°C to give 1.9 g (83%) of IIc.

Esters IIa and IIb were similarly obtained in solutions in toluene and CCl , respectively.

2-Diethylamino-4,6-bis(p-carboxyphenoxy)-sym-triazine Diallylamide (IIIh). A solution of 2 g (4.4 mmole) of chloride Ib in 30 ml of benzene was added with stirring to a solution of 0.5 g (9 mmole) of triethylamine in 50 ml of dry benzene, after which the mixture was stirred at 20-30°C for 2 h. The resulting precipitate was removed by filtration, washed with hot water, and dried. Recrystallization from ethanol gave 2 g (92%) of IIIh.

The synthesis of the other diamides was accomplished similarly. In the case of IIIa, f, k dry gaseous ammonia was bubbled through the reaction medium until it was saturated completely. The calculated amount of ethylamine hydrochloride was used in the synthesis of ethylamides IIIb, g, l; the ethylamine was liberated with an equimolar amount of sodium hydroxide directly in the reaction medium.

2-Diethylamino-4,6-bis(p-carboxyphenoxy)-sym-triazine Dihydrazide (IIIj). A 1-g (2.2 mmole) sample of chloride Ib was added in very small portions with stirring at -40°C to 10 ml of 100% hydrazine hydrate at -40°C, after which the mixture was stirred at this temperature for 30 min. The resulting precipitate was removed rapidly by filtration, washed successively with water, alcohol, and petroleum ether, and dried to give 0.93 g (98%) of dihydrazide IIIj.

The other dihydrazides were similarly obtained.

p-Hydroxybenzoic Acid Hydrazide (IV) and 2-Diethylamino-4,6-dihydrazino-sym-triazine (V). A solution of 1 g (2.2 mmole) of chloride Ib in 15 ml of dioxane was added with stirring to 20 ml of 60% hydrazine hydrate, and the mixture was refluxed for 2 h. It was then cooled, and the hydrazine layer was separated and evaporated. The dry residue was crystallized from water to give 0.67 g (98%) of IV with mp 260°C. PMR spectrum, $(CD_3)_2SO$: 3.60 (1H, broad s, OH); 4.35 (2H, broad s, NH_2); 7.30, 6.30 (4H, d, J = 8.5 Hz, C_6H_4); 9.52 ppm (1H, broad s, NH). Found: C 55.5; H 5.6; N 18.2%. $C_7H_8N_2O_2$. Calculated C 55.3 H 5.3 N 18.5 .

The dioxane layer was also evaporated, and the residue was washed with ice water and dried to give 0.3 g (55%) of V with mp 85°C. PMR spectrum, $(CD_3)_2SO$: 0.92 (6H, t, CH_3), 3.36 (4H, q, CH_2), 3.94 (4H, broad s, NH_2), and 7.65 ppm (2H, broad s, NH). Found: C 39.6; H 7.5; N 53.0%. $C_7H_{16}N_8$. Calculated: C 39.6; H 7.6; N 52.8%.

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