Ethyl 3,4,5-trimethoxymandelate (IV) (1). A solution of 3 grams (0.0134 mole) of (I) (vacuum dried) in 20 ml. of anhydrous ethanol was saturated with dry hydrogen chloride at 0–5° and refrigerated (4°) over night. Excess solvent was removed from the purple semi-solid mass at the water pump and 50 ml. of water added. Solid barium carbonate was added in excess to neutralize the acid, the mixture kept for 2 hours in the dark, filtered, and the filtrate extracted with four 30-ml. portions of ethyl acetate, using the first two portions of solvent to extract also the filter cake. The combined extracts were dried with sodium sulfate, and the solvent was removed under vacuum to give a yellow oil which crystallized slowly on standing. Recrystallization from ethanol-water gave 1.91 grams (53%) of (IV), m.p. 83–5°.

Anal. Calcd. for $C_{13}H_{18}O_6$: C, 57.77; H, 6.71. Found: C, 57.22; H, 6.20.

3,4,5-Trimethoxymandelic acid (III) by hydrolysis of the ethyl ester, (IV). A mixture of 1 gram (0.0037 mole) of (IV) and 20 ml. of 5% sodium hydroxide solution was refluxed for one hour, cooled, acidified with 6*N* hydrochloric acid, saturated with sodium chloride, and extracted with five 25-ml. portions of ethyl acetate. Isolation as previously described gave 0.74 gram (81%) of (III), m.p. 120–121°. Mixed m.p. and infrared spectra indicated that this compound was identical with (III) obtained through the acetoxynitrile, (II).

3,4,5-Trimethoxyphenylacetic acid (V). Using the method of Rapoport (2), (I), labelled with C-14 on the nitrile group, was easily reduced with tin (II) chloride to (V), m.p. 117–18° (lit. m.p. 117–118°), labelled in the carboxyl group.

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Some Ethers and Amino-Derivatives of *s*-Triazine

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A number of methyl- and phenyl- substituted phenoxy- and amino-derivatives of *s*-triazines have been prepared by reaction of the corresponding chloro-derivatives with phenol and with amines in the melt and in solution.

A NUMBER of new methyl- and phenyl- substituted phenoxy- and amino-derivatives of *s*-triazines have been prepared, Table I. The phenoxy-derivatives were obtained by heating the corresponding chlorotriazines with equivalent amounts of phenol over a period of several hours. The anilino-derivatives resulted from refluxing the chlorotriazines with excess of aniline in a solvent, such as dioxane or benzene, and separating the reaction product from the aniline hydrochloride formed. The methyl- and ethylaminotriazines were prepared by introducing an excess of methyl- and ethylamine gas into benzene solutions of chlorotriazines at controlled temperatures.

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Several dimers, trimers and tetramers were obtained from the melt reaction of chlorotriazines with anilinotriazines under nitrogen at temperatures of 200° to 220° C. over several hours. One of these (Compound 12) has also been prepared in solution (diphenylether as solvent).

The trimers and tetramers were subjected to thermogravimetric analysis under nitrogen (ΔT = 150° C./hour). As Figure 1 shows, breakdown begins to occur in the range of 350° to 460° C., the compounds containing methyl groups being less stable than those without. The dimer (Compound 11) was subjected to a decomposition study in a high pressure isoteniscope (Monsanto Chemical Company under Air Force contract.) The value found for a decomposition of approximately 1% per hour was 382° C.

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Table I. Compounds

No.	Compound	Formula	Recryst. From	Yield, %	M.P. (Uncorr.), °C.		Analysis C	H	N	Cl
1	2-phenyl-4,6-diphenoxy-*s*-triazine	$C_{21}H_{15}N_3O_2$	Methanol		110	Calcd.	73.90	4.40	12.32	
						Found	74.26	4.69	12.21	
2	2,4-diphenyl-6-phenoxy-*s*-triazine	$C_{21}H_{15}N_3O$	Ligroin	63	138–41	Calcd.	77.54	4.62	12.92	
						Found	77.59	4.64	12.73	
3	2-methyl-4,6-diphenoxy-*s*-triazine	$C_{16}H_{13}N_3O_2$	Ethanol	59	74–77	Calcd.	68.81	4.66	15.05	
						Found	68.77	4.52	15.15	
4	2-phenyl-4,6-dianilino-*s*-triazine	$C_{21}H_{17}N_5$	Chloroform		210	Calcd.	74.34	5.02	20.64	
						Found	73.93	5.13	20.37	
5	2-methyl-4,6-dianilino-*s*-triazine	$C_{16}H_{15}N_5$	Isopropanol	81	244	Calcd.	69.31	5.41	25.28	
						Found	69.35	5.72	25.04	
6	2-phenyl-4-chloro-6-methylamino-*s*-triazine	$C_{10}H_9N_4Cl$	Ligroin	55	198	Calcd.	54.43	4.11	25.39	16.07
						Found	54.83	4.54	24.65	15.92
7	2-phenyl-4,6-dimethylamino-*s*-triazine	$C_{11}H_{13}N_5$	Ligroin	58	133	Calcd.	61.37	6.09	32.54	
						Found	61.54	5.79	32.65	
8	2,4-diphenyl-6-methylamino-*s*-triazine	$C_{16}H_{14}N_4$	Ligroin	30	143	Calcd.	73.26	5.38	21.36	
						Found	73.29	5.38	21.32	
9	2-phenyl-4,6-diethylamino-*s*-triazine	$C_{13}H_{17}N_5$	Ligroin	77	164	Calcd.	64.17	7.04	28.79	
						Found	64.03	7.00	28.62	
10	2-methyl-4,6-diethylamino-*s*-triazine	$C_8H_{15}N_5$	Ligroin	51	166	Calcd.	53.01	8.34	38.65	
						Found	52.98	8.27	38.55	
11	*N*,*N*-bis(4,6-diphenyl-*s*-triazinyl-2)aniline	$C_{36}H_{25}N_7$	Ligroin	60	258	Calcd.	77.80	4.51	17.69	
						Found	77.75	4.19	18.01	
12	Bis-[*N*-phenyl-*N*-(4′,6′-diphenyl-*s*-triazinyl-2′)]-2,4-diamino-6-phenyl-*s*-triazine	$C_{51}H_{33}N_{11}$	Ligroin	90	238	Calcd.	76.39	4.35	19.22	
						Found	76.56	4.59	19.08	
13	Bis-[*N*-phenyl-*N*-(4′,6′-diphenyl-*s*-triazinyl-2′)]-2,4-diamino-6-methyl-*s*-triazine	$C_{45}H_{31}N_{11}$[a]	Ethanol-benzene 2:1	50	247	Calcd.	74.69	4.46	20.83	
						Found	76.09	4.73	19.20	
14	Tris-[*N*-phenyl-(4′,6′-diphenyl-*s*-triazinyl-2′)]-2,4,6-triamino-*s*-triazine	$C_{66}H_{45}N_{12}$[a]	Benzene	93	258	Calcd.	75.64	4.33	20.05	
						Found	75.47	4.16	19.68	
15	Tris-[*N*-methyl-*N*-(4′,6′-diphenyl-*s*-triazinyl-2′)]-2,4,6-triamino-*s*-triazine	$C_{51}H_{39}N_{15}$[a]	*n*-amylacetate	75	287	Calcd.	70.70	5.09	24.21	
						Found	70.26	4.66	24.09	

[a] Figure 2.

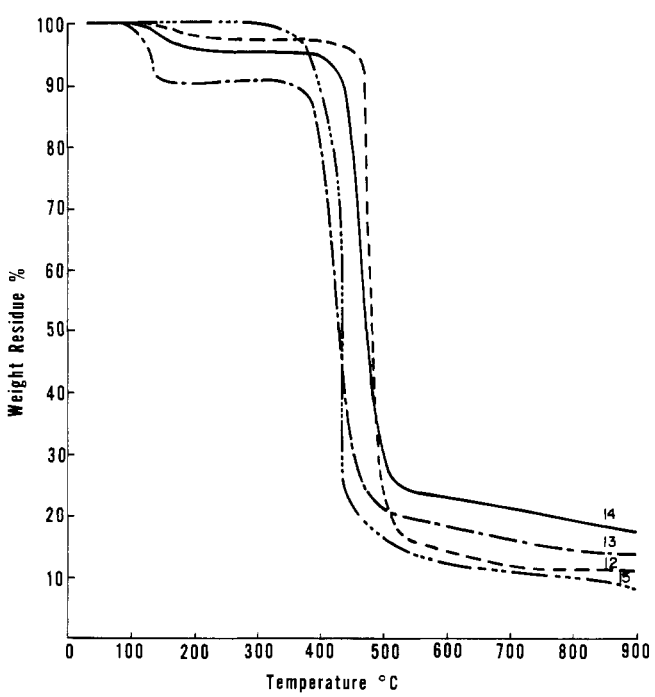

Figure 1. Thermogravimetric analysis of 1,3,5-triazine derivatives

Compound 12: — — —
Compound 13: — · — ·
Compound 14: ————
Compound 15: — · · ·

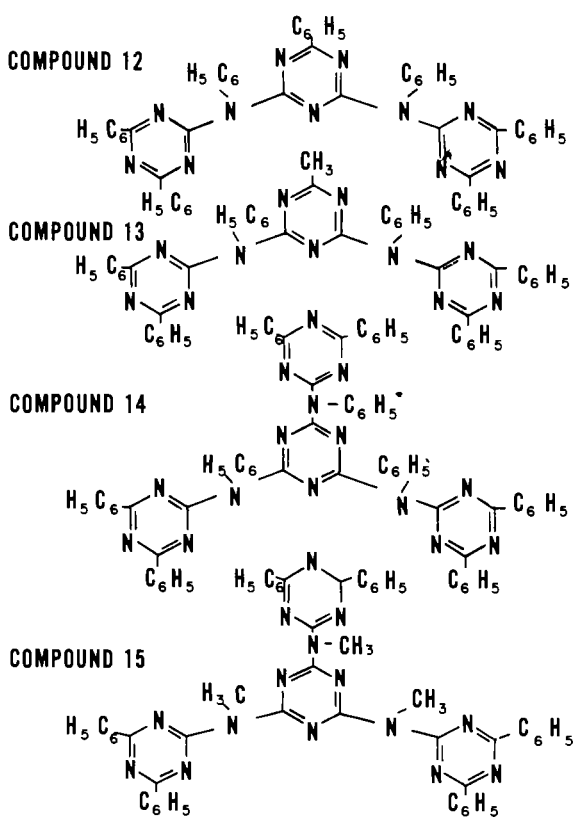

Figure 2. Structure of compounds 12, 13, 14, and 15