195. *Some Substituted* 1,3,5-*Triazines.*

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The preparation and properties of some substituted 1,3,5-triazines are described. Replacement of 1, 2, or 3 of the chloro-groups of cyanuric chloride by bromo-groups during the preparation of monoalkyldichlorotriazine from cyanuric chloride and alkylmagnesium bromide has been demonstrated. Differences in the ease of transesterification of some esters of cyanuric acid are described.

THE need for lubricants of thermal and oxidative stability greater than those of currently available materials led to the preparation and characterisation of the substituted 1,3,5-triazines (listed in Tables 1 and 2), which form the subject of this Paper.

1,3,5-Triazines substituted in the 2,4,6-positions were studied since 2,4,6-triphenoxy-1,3,5-triazine was shown [1] to be thermally stable up to 465°. It was considered that substituents could be selected so that the compounds prepared would possess other properties necessary in lubricating oils, *e.g.*, low volatility, low pour point, and satisfactory viscosity/temperature characteristics.

Alkyl intermediates used in the preparation of the 1,3,5-triazines were prepared by the replacement of a chloro-group in cyanuric chloride by a methyl,[2] ethyl,[2] or t-butyl group. Difficulty was experienced during the purification of the 2,4-dichloro-6-methyl-1,3,5-triazine which hydrolysed under atmospheric conditions whereas the 6-ethyl analogue was stable. Furthermore, during 7 days in a stoppered bottle, 2,4-dichloro-6-methyl-1,3,5-triazine was converted into its 2,4-dihydroxy-analogue, (m. p. 272—274°, lit.,[3] 275—276°) whereas the 6-ethyl analogue was unchanged even after 6 months.

Evaporation of the mother-liquors obtained during crystallisation of the 2,4-dichloro-6-ethyl- and the 2,4-dichloro-6-methyl-1,3,5-triazines gave residues which were examined by mass spectroscopic techniques. m/e Values of peaks in the mass spectrum of the residue from the 6-methyl derivative indicated the presence of 2-bromo-4-chloro-6-methyl-, 2-bromo-4,6-dichloro-, 2,4-dibromo-6-methyl-, 2,4-dibromo-6-chloro-, and 2,4,6-tribromo-1,3,5-triazines. Furthermore, the mass spectrum of the residue from the preparation of the 6-ethyl derivative was consistent with the presence of 2-bromo-4-chloro-6-ethyl-1,3,5-triazine. Ratios of the heights of the peaks grouped in the region of each parent peak, in both spectra, equalled the ratios calculated from the natural abundance of the isotopes present, thus confirming the assignments. It was not possible to determine whether the bromo-groups which entered the triazine nucleus came from the Grignard reagent, or from the magnesium bromide obtained from the reaction of the Grignard reagent with cyanuric chloride. However, 2-bromo-4,6-dichloro-1,3,5-triazine was shown by mass spectroscopy to be present in the product obtained after a mixture of magnesium bromide dietherate and cyanuric chloride had been kept under conditions similar to those used in the preparation of 2,4-dichloro-6-methyl-1,3,5-triazine.

Under the conditions used for the preparation (60%) of its 6-ethyl- and 6-methyl-analogues, no detectable yield of 2-t-butyl-4,6-dichloro-1,3,5-triazine was obtained. Even the use of a higher temperature in the reaction did not increase the yield above 32% based on the cyanuric chloride unrecovered.

2,4-Dichloro-6-ethoxy-1,3,5-triazine was obtained after cyanuric chloride had been stirred with ethanol in aqueous sodium hydrogen carbonate; the temperature was kept below 25°. Replacement of only one of the chloro-groups by a 2,2,3,3-tetrafluoropropoxy-group occurred on warming cyanuric chloride and the fluoroalcohol in dioxan at

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[1] Rice and Kirk, "The Development of Nuclear Radiation Resistant Fluids and Lubricants." Wright Air Development Division Technical Report 59—244, Vol. II.

[2] Hirt, Nidecker, and Berchtold, *Helv. Chim. Acta*, 1950, 1365.

[3] Ostrogrovick, *Annalen*, 1895, **288**, 318.

TABLE 1.

Known 1,3,5-triazines.

Substituent		M. p.		Yield	Found (%)			Formula	Calc. (%)		
6	2,4	Found	Lit.	(%)	C	H	N		C	H	N
Me	Cl	97—98°	98° [2]	—	—	—	—	$C_4H_3Cl_2N_3$	—	—	—
Et	Cl	35—36·5	35 [2]	60	33·2	3·1	23·1	$C_5H_5Cl_2N_3$	33·7	2·8	23·6
EtO	Cl	31—32·5 [a]	113—114^5/14 mm Hg [b]	13	—	—	—	$C_5H_5Cl_2N_3O$	—	—	—
Me$_2$N	Cl	122—123	122·5—123·5 [6]	55	31·4	3·4	28·6	$C_5H_6Cl_2N_4$	31·1	3·1	29·0
PhS	Cl	71—72	72—73 [7]	30	42·5	2·15	16·2	$C_9H_5Cl_2N_3S$	41·8	2·0	16·3
PhO	PhO	234·5—236	232—235 [8]	88	70·5	4·2	11·4	$C_{21}H_{15}N_3O_3$	70·6	4·2	11·75
H·[CF$_2$]$_6$·CH$_2$·O	H·[CF$_2$]$_6$·CH$_2$·O	46—48	46—48 [9]	79	27·1	0·9	3·9	$C_{24}H_9F_{36}N_3O_3$	26·9	0·85	3·9

[a] This compound has a b. p. of 87—90°/2·5 mm. Hg. [b] Boiling point.

TABLE 2.

New 1,3,5-triazines.

6	2,4	M. p.	B. p. (°/mm. Hg)	Yield (%)	Found (%) C	H	N	Formula	Reqd. (%) C	H	N
Bu^t	Cl	—	62/1·5	32	40·75	4·5	—	$C_7H_9Cl_2N_3$	40·8	4·4	—
H·[CF$_2$]$_2$·CH$_2$·O	Cl	—	57—62/0·08	45	25·95	1·4	14·8	$C_6H_3Cl_2F_4N_3O$	25·7	1·1	15·0
Me	PhO	87°	—	—	68·8	4·75	15·0	$C_{16}H_{13}N_3O_2$	68·8	4·7	15·0
Et	PhO	117—118	—	60	69·2	4·95	14·3	$C_{17}H_{15}N_3O_2$	69·6	5·2	14·3
Et	*o*-Me C$_6$H$_4$O	—	162—168/0·08	73	71·2	6·0	13·05	$C_{19}H_{19}N_3O_2$	71·0	5·95	13·1
Et	*o*-Bu^{t}C$_6$H$_4$O	—	190—197/0·1	80	73·4	7·1	10·0	$C_{29}H_{31}N_3O_2$	74·0	7·05	10·4
Bu^t	PhO	65—66	—	82	71·15	5·6	13·2	$C_{19}H_{19}N_3O_2$	71·0	5·95	13·1
EtO	PhO	135—136	—	87	66·4	5·2	13·4	$C_{17}H_{15}N_3O_3$	66·0	4·9	13·6
Me$_2$N	*o*-Me C$_6$H$_4$O	112·5—113	—	60	67·9	6·0	16·7	$C_{19}H_{20}N_4O_2$	67·9	5·9	16·7
Me$_2$N	H(CF$_2$)$_6$CH$_2$O	66—67	—	55	29·5	1·5	6·8	$C_{19}H_{12}F_{24}N_4O_2$	29·1	1·5	7·1
H·[CF$_2$]$_2$·CH$_2$·O	*o*-Me C$_6$H$_4$O	85—86	—	80	56·8	4·1	10·1	$C_{20}H_{17}F_4N_3O_3$	56·7	4·1	9·9
o-Me C$_6$H$_4$O	*o*-Me C$_6$H$_4$O	159—160	—	—	71·95	5·4	10·4	$C_{24}H_{21}N_3O_3$	72·2	5·3	10·5
H·CMe$_2$·CH$_2$·CMe$_2$·CH$_2$·O	HCMe$_2$·CH$_2$·CMe$_2$·CH$_2$·O	82—83	—	61	69·4	11·0	8·9	$C_{27}H_{51}N_3O_3$	69·7	11·0	9·0

65° in the presence of sodium carbonate; a 45% yield was obtained. Dudley and his co-workers [4] showed that under similar conditions, when ethanol was used, replacement of all of the chloro-groups by ethoxy-groups occurred.

Preparation of the trialkoxy- and triaryloxy-1,3,5-triazines was carried out by warming cyanuric chloride with an excess of the corresponding hydroxylic compound in aqueous alkali or with the anhydrous sodium salt of the hydroxylic compound in an organic solvent. 2,4,6-Tri-*o*-tolyloxy-1,3,5-triazine was also obtained, by transesterification, during an attempted preparation of 2-(2,2,3,3-tetrafluoropropoxy)-4,6-di-*o*-tolyloxy-1,3,5-triazine when the mixture was heated under reflux. When the temperature was lowered to 25° the required compound was isolated in 80% yield. This contrasts with the result obtained from the attempted preparation of 2-phenylthio-4,6-di-*o*-tolyloxy-1,3,5-triazine which showed that, even at 20°, transesterification occurred to give 2,4,6-tri-*o*-tolyloxy-, 2-phenylthio-4,6-di-*o*-tolyloxy-, and the 2,4-diphenylthio-4,6-di-*o*-tolyloxy-1,3,5-triazines.

EXPERIMENTAL

Dichloro-1,3,5-*triazines*.—(*a*) 2-*t-Butyl*-4,6-*dichloro*-1,3,5-*triazine*. After attempts to prepare this compound in a manner similar to the preparations of the 2-methyl and 2-ethyl analogues had failed, the following method gave the *compound*, m. p. 23—25°, although in small yield (32%): to a stirred mixture of magnesium turnings (5·0 g.) and a crystal of iodine was slowly added a solution of t-butyl chloride (23 ml.) in ether (55 ml.). The mixture was heated under reflux for 1 hr., cooled, and quickly filtered. To the filtered solution was added, over 15 min., a solution of cyanuric chloride (18·0 g.) in toluene (50 ml.). The solution was then heated, and the temperature rose to 112° as ether evaporated off; toluene (35 ml.) was added to compensate for the loss of ether. After the solution was heated under reflux at 112° for 3·5 hr. it was cooled, filtered, and evaporated to small bulk to leave a residue (5 ml.). During the evaporation, cyanuric chloride (4·6 g.) was removed at intervals by filtration. Distillation of the residue gave 2-t-butyl-4,6-dichloro-1,3,5-triazine.

(*b*) 2,4-*Dichloro*-6-(2,2,3,3-*tetrafluoropropoxy*)-1,3,5-*triazine*. A mixture of cyanuric chloride (15·0 g.), sodium carbonate (4·3 g.), 2,2,3,3-tetrafluoropropanol (30 ml.), and dioxan (10 ml.) was stirred for 3 hr. at 65°. After this time the mixture was cooled to 0° and poured into an ice–water mixture. The colourless oily paste which formed was separated from the aqueous phase and dried in a desiccator. Distillation of the oily filtrate obtained from the paste gave the *compound*.

Alkyldiaryloxy- and Alkoxydiaryloxy-1,3,5-*triazines*.—(*a*) 2-*Methyl*-4,6-*diphenoxy*-1,3,5-*triazine*. To a solution of 2,4-dichloro-6-methyl-1,3,5-triazine [5·0 g., shown by g.l.c. to contain cyanuric chloride (17%)] in acetone (20 ml.) at 18° was added during 20 min., with stirring, a solution of phenol (8·0 g.) in aqueous sodium hydroxide (4·5 g. NaOH; 30 ml. water). The heterogeneous mixture which formed was stirred at 25° for 6 hr. and the solid was filtered off. Fractional crystallisation of the residue from ethanol gave a product (4·6 g.) which was examined by g.l.c. The retention volumes of two peaks, accounting for 52% and 26% of the sample, respectively, were 2·2 and 12·1 relative to nonadecane at 257°, " Embaphase Silicone Oil " being used as stationary phase and nitrogen as the eluent gas. Comparison with an authentic sample of 2,4,6-triphenoxy-1,3,5-triazine showed the peak at a relative retention volume of 12·1 to be caused by this compound. The compound, causing the peak at a relative retention volume of 2·2, was isolated by condensation from the eluent gas and confirmed by mass spectroscopic examination to be 2-*methyl*-4,6-*diphenoxy*-1,3,5-*triazine*.

(*b*) 2-*Ethyl*-4,6-*di*-o-*tolyloxy*-1,3,5-*triazine*. To a solution of *o*-cresol (5·7 g.) in dioxan (60 ml.) sodium (4·5 g.) was added. The suspension which formed was left overnight and to it, with stirring, was added a solution of 2,4-dichloro-6-ethyl-1,3,5-triazine (3·05 g.) in dioxan (40 ml.)

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[4] Dudley, Thurston, Schaeffer, Holm-Hansen, Hull, and Adams, *J. Amer. Chem. Soc.*, 1951, **73**, 2986.
[5] U.S.P. 2,911,337.
[6] Pearlman and Banks, *J. Amer. Chem. Soc.*, 1948, **70**, 3726.
[7] Koopman, Uhlenbroek, Hoech, Daams, and Koopmans, *Rec. Trav. chim.*, 1959, **78**, 967—980.
[8] Schaeffer, Thurston, and Dudley, *J. Amer. Chem. Soc.*, 1951, **73**, 2991.
[9] U.S.P. 2,741,606.

at 25°. After the reaction mixture had been heated under reflux, with stirring, for 3·5 hr., it was cooled to 40° and poured into water; a viscous yellow oil separated. Evaporation of an ether extract of this oil left a residue (4·4 g., 73%) of 2-*ethyl*-4,6-*di*-o-*tolyloxy*-1,3,5-*triazine*. 2-*Ethyl*-4,6-*diphenoxy*-1,3,5-*triazine*, 2-*ethyl*-4,6-*di*-o-*t*-*butylphenoxy*-1,3,5-*triazine*, and 2-*t*-*butyl*-4,6-*diphenoxy*-1,3,5-*triazine*, were similarly prepared.

(*c*) 2-*Ethoxy*-4,6-*diphenoxy*-1,3,5-*triazine*. To a stirred solution of 2,4-dichloro-6-ethoxy-1,3,5-triazine (5·9 g.) in acetone (40 ml.) was added a solution of phenol (6·0 g.) and sodium hydroxide (2·6 g.) in water. The reaction mixture was stirred for 4 hr. at 15—25°. The solid that separated was filtered off, washed with water, and crystallised from heptane, to give 2-*ethoxy*-4,6-*diphenoxy*-1,3,5-*triazine* (8·1 g.).

1,3,5-*Triazines Containing Hetero-groups*.—(*a*) 2-*Dimethylamino*-4,6-*di*-o-*tolyloxy*-1,3,5-*triazine*. A solution of 2,4-dichloro-6-dimethylamino-1,3,5-triazine (1·0 g.) in dioxan (10 ml.) was added, with stirring at 25°, to a solution of the sodium salt (3·05 g.) of *o*-cresol in dioxan (50 ml.). After 2 hr. the mixture was poured into benzene (100 ml.) and washed with aqueous sodium hydroxide and then with water. The organic layer was separated and dried. Evaporation of the solvents left a heterogeneous residue which on crystallisation from heptane gave the *compound*.

(*b*) 2-*Dimethylamino*-4,6-*di*-(1H,1H,7H-*dodecafluoroheptyloxy*)-1,3,5-*triazine*. The sodium salt of technical grade 1*H*,1*H*,7*H*-dodecafluoroheptanol was prepared by stirring a mixture of sodium methoxide in methanol with the fluoroalcohol (11 g.) in dioxan (15 ml.) at 20° for 4 hr. Distillation at 20°/20 mm. Hg left a syrupy residue (9·0 g.). The mixture, obtained by adding to this residue a suspension of 2,4-dichloro-6-dimethylamino-1,3,5-triazine (2·0 g.) in dioxan (30 ml.), was heated under reflux for 4·5 hr. After this time the reaction mixture was evaporated to small bulk and the residue (4·7 g.), was crystallised from cyclohexane to give 2-*dimethylamino*-4,6-*di*-(1H,1H,7H-*dodecafluoroheptyloxy*)-1,3,5-*triazine* as needles.

(*c*) 2-(2,2,3,3-*Tetrafluoropropoxy*)-4,6-*di*-o-*tolyloxy*-1,3,5-*triazine*. To the sodium salt of *o*-cresol, obtained by removal of methanol and excess of *o*-cresol from a mixture of *o*-cresol (1·9 g.) and 2N-sodium methoxide (7·65 ml.) in methanol, was added, at 25°, a solution of 2,4-dichloro-6-(2,2,3,3-tetrafluoropropoxy)-1,3,5-triazine (2·0 g.) in dioxan (30 ml.). After 2·5 hr., part of the reaction mixture was poured into water and the solution was extracted with ether. Evaporation of the ether left the *product* (2·4 g.), which was recrystallised from light petroleum (b. p. 60—80°) as needles.

(*d*) *Attempted preparation of* 2-*phenylthio*-4,6-*di*-o-*tolyloxy*-1,3,5-*triazine*. To a solution of the sodium salt of *o*-cresol (0·56 g.) in dioxan (10 ml.) was added, with stirring at 20°, a solution of 2,4-dichloro-6-phenylthio-1,3,5-triazine (0·5 g.) in dioxan (5 ml.). After 3 hr., the mixture was evaporated (20°/20 mm. Hg) to small bulk and the residue dissolved in ether. The ethereal solution was washed successively with 5% aqueous sodium hydroxide, dilute hydrochloric acid, and water, and then evaporated (20°/20 mm. Hg) to give a paste (0·76 g.). Extraction of the paste with heptane left an undissolved solid, m. p. 153—156° (ex dibutyl ether) which was filtered off. Evaporation of the filtrate left a viscous oil. Mass spectroscopic examination was consistent with the solid being 2,4,6-tri-*o*-tolyloxy-1,3,5-triazine and the oil being a mixture of 2-phenylthio-4,6-di-*o*-tolyloxy- and 2,4-diphenylthio-6-*o*-tolyloxy-1,3,5-triazine. It was impossible to obtain sufficient separation of the peaks caused by the two compounds on g.l.c. examination of the oil to allow samples of sufficient purity for elemental analysis to be trapped out.

Trialkoxy- and Triaryloxy-1,3,5-*triazines*.—(*a*) 2,4,6-*Tri*-(2,2,4-*trimethylpentyloxy*)-1,3,5-*triazine*. To a suspension of sodium 2,2,4-trimethylpentyloxide (33·0 g.) in dioxan (150 ml.) was added, with stirring at 30°, a solution of cyanuric chloride (12·0 g.) in dioxan (50 ml.). The suspension was heated under reflux for 2 hr., cooled to 0° and poured into an ice–water mixture. A solid which separated was crystallised from pentane to give the *compound*.

(*b*) 2,4,6-*Tri*-o-*tolyloxy*-1,3,5-*triazine*. Needles of 2,4,6-tri-*o*-tolyloxy-1,3,5-triazine, from dibutyl ether, were obtained after part of the reaction mixture used for the preparation of 2-(2,2,3,3-tetrafluoropropoxy)-4,6-di-*o*-tolyloxy-1,3,5-triazine had been stirred under reflux for an additional 2 hr. A peak at an *m*/*e* value of 399 in the mass spectrum of the compound was consistent with the assignment.

Reaction of Magnesium Bromide Dietherate with Cyanuric Chloride.—To a solution of magnesium bromide dietherate in ether, prepared by the method of Rowley,[10] from magnesium (0·5 g.), was added a solution of cyanuric chloride (8·0 g.) in benzene (80 ml.). The solution was stirred for 4 hr. at 10° after which the solvents were removed by evaporation (21°/20 mm.

[10] Rowley, *J. Amer. Chem. Soc.*, 1936, **58**, 1337.

Hg). Evaporation (21°/20 mm. Hg) of a pentane extract of the residue left a solid (5·5 g.) which was shown by mass spectroscopic techniques to contain 2-bromo-4,6-dichloro-1,3,5-triazine.

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