

Department of Chemistry, University of Pittsburgh

## The Chemistry of Triazine Derivatives. I.

### The Alkylation of 2,4,6-Trimethyl-*s*-triazine. (I)

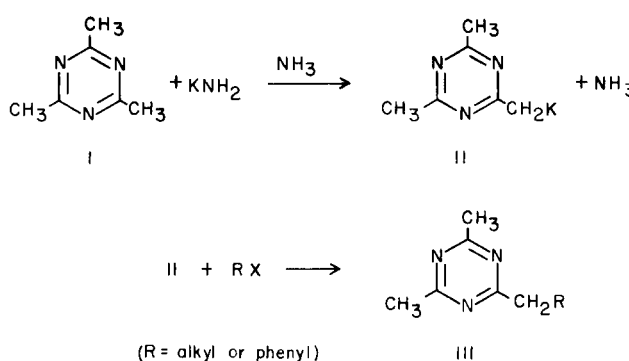
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The direct alkylation of 2,4,6-trimethyl-*s*-triazine (I) has been effected by treating (I) with a series of alkyl halides using potassium amide in liquid ammonia as the condensing agent. The present method gives a simple, direct route to the preparation of unsymmetrically substituted trialkyl-*s*-triazines.

The alkali metal amide-effected alkylations of methyl substituted heterocyclic nitrogen compounds such as the isomeric picolines (3, 4), methylpyrazine (5) and 2,6-dimethylpyrazine (6) have been extensively studied in recent years in our laboratory. We now report the synthesis of some new unsymmetrically substituted trialkyl-*s*-triazines of the type (III) which have been prepared by reacting 2,4,6-trimethyl-*s*-triazine (I) with alkyl halides in the presence of potassium amide in liquid ammonia as the condensing agent. The overall reactions are shown in the following scheme.

The results are found in Table I. It may be seen that fair yields (39-61%) of monoalkylated products were obtained in all cases. In order to minimize the formation of dialkylated materials, an excess of 2,4-dimethyl-6-triazylmethyl potassium over alkyl halide was employed. In spite of these conditions small amounts of higher boiling materials, presumably dialkylated products, were produced in all the reactions. Only in the alkylation of 2,4-dimethyl-6-triazylmethylpotassium with benzyl chloride was enough higher boiling material obtained in a sufficiently high state of purity so that it could be subjected to elemental analysis and its structure elucidated. Previously dialkylated products have been observed in alkylation reactions carried out on other methyl substituted heterocyclic nitrogen compounds, such as methylpyrazine (5), the isomeric picolines (7) and 2,6-lutidine (8).

Unsymmetrically substituted trialkyl-*s*-triazines are fairly rare compounds and have only recently been prepared in small numbers by (a) the condensation of two different aliphatic amidines (9), (b) the condensation of two different aliphatic imidates (10, 11), and (c) the condensation of aliphatic amidine salts with lower aliphatic imidates (12), to produce in all cases mixtures of unsymmetrically substituted trialkyl-*s*-triazines. Apparently only one of the compounds listed in Table I, *viz.*, 2,4-dimethyl-6-(*n*-propyl)-*s*-triazine (11), was isolated previously and the present method therefore seems to offer an attractive new method for the synthesis of certain unsymmetrically substituted trialkyl-*s*-triazines.



#### EXPERIMENTAL

In this section the synthesis of a typical 2,4-dimethyl-6-alkyl-*s*-triazine is described.

Preparation of 2,4-dimethyl-6-(*n*-butyl)-*s*-triazine.

2,4,6-Trimethyl-*s*-triazine (13) (0.1 mole, 12.3 g.) dissolved in 20 ml. of anhydrous ether was added to potassium amide (0.1 mole) in 100 ml. of anhydrous liquid ammonia and the resulting solution stirred for one hr. *n*-Propyl bromide (0.05 mole, 6.15 g.) diluted with an equal volume of anhydrous ether was added, the reaction mixture stirred for an additional hr. and the ammonia replaced by anhydrous ether. The reaction mixture was poured onto a mixture of 100 g. of crushed ice and concentrated hydrochloric acid (0.1 mole) and any excess acid was neutralized by the addition of solid sodium bicarbonate. After separating the ether phase, the residual aqueous phase was extracted with several portions of chloroform. Distillation of the combined ether-chloroform extracts gave in addition to recovered 2,4,6-trimethyl-*s*-triazine, 4.1 g. (49.6%) of 2,4-dimethyl-6-(*n*-butyl)-*s*-triazine, b.p. 108-110° at 29 mm.

#### REFERENCES

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TABLE I

Unsymmetrically Substituted Trialkyl-*s*-triazines of Type III,  
Prepared by Alkylating 2,4,6-Trimethyl-*s*-triazine with Alkyl Halides, RBr

R	Yield %	B. P.	mm.	Formula	% Carbon		% Hydrogen	
					Calcd.	Found	Calcd.	Found
C <sub>2</sub> H <sub>5</sub> (a, b)	39.0	100-102	43	C <sub>8</sub> H <sub>13</sub> N <sub>3</sub>	63.54	63.10	8.66	8.23
<i>n</i> -C <sub>3</sub> H <sub>7</sub>	49.6	108-110	29	C <sub>9</sub> H <sub>15</sub> N <sub>3</sub>	65.40	65.20	9.17	9.23
<i>n</i> -C <sub>4</sub> H <sub>9</sub>	59.2	118-119	23.5	C <sub>10</sub> H <sub>17</sub> N <sub>3</sub>	66.98	66.67	9.58	9.68
<i>iso</i> -C <sub>4</sub> H <sub>9</sub>	61.5	115-116	28	C <sub>10</sub> H <sub>17</sub> N <sub>3</sub>	66.98	66.64	9.58	9.52
<i>n</i> -C <sub>6</sub> H <sub>13</sub>	61.4	132-133	9	C <sub>12</sub> H <sub>21</sub> N <sub>3</sub>	69.51	69.32	10.23	10.16
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> (c)	41.4 (d)	100-101	0.4	C <sub>13</sub> H <sub>15</sub> N <sub>3</sub>	73.19	73.19	7.10	6.54

(a)  $n_D^{25}$  1.4680. (b)  $n_D^{20}$  1.4685, b.p. 98.5-99 at 44 mm (11). (C) The alkyl halide was a chloride. In all other cases bromides were used. (d) In addition 37% of a dialkylated product was isolated b.p. 163-170° at 1.0 mm and m.p. 61.5-62.5° (from petroleum ether b.p. 30-60°). *Anal.* Calcd. for C<sub>20</sub>H<sub>21</sub>N<sub>3</sub>: C, 79.16; H, 6.99. Found: C, 78.78; H, 7.07. The proton N.M.R. spectrum of this compound and also its acidic hydrolysis to dibenzylacetic acid indicated the compound to be 2,4-dimethyl-6-dibenzylmethyl-*s*-triazine.

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