TABLE I

β-ARYLAMINOPROPIOPHENONES

$C_6H_5COCH_2CH_2NHR$

| R | M.P. | Yield, % | | Formula | Carbon, % | | Hydrogen, % | | Nitrogen, % | | Chlorine, % | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Calcd. | Found | Calcd. | Found | Calcd. | Found | Calcd. | Found |
| $C_6H_5$ | 111–112[a] | 55[b] | 66[c] | $C_{15}H_{15}ON$ | 80.00 | 80.01 | 6.66 | 6.70 | 6.22 | 6.20 | | |
| $C_6H_5$ | 150–151[d] | | | $C_{15}H_{16}ONCl$ | | | | | 5.35 | 5.62 | 13.57 | 13.74 |
| p-$ClC_6H_4$ | 136–138 | 39 | 58 | $C_{15}H_{14}ONCl$ | 69.36 | 69.41 | 5.40 | 6.03 | 5.40 | 5.11 | | |
| p-$ClC_6H_4$ | 160[d] | | | $C_{15}H_{15}ONCl_2$ | | | | | 4.73 | 5.07 | 23.98 | 24.39 |
| p-$CH_3C_6H_4$ | 113–114 | 62 | 66 | $C_{16}H_{17}ON$ | 80.34 | 79.73 | 7.11 | 6.73 | 5.85 | 5.50 | | |
| p-$CH_3C_6H_4$ | 137–138[d] | | | $C_{16}H_{18}ONCl$ | | | | | 5.08 | 5.45 | 12.90 | 13.65 |
| p-$CH_3OC_6H_4$ | 114–115 | 40 | 53 | $C_{16}H_{17}O_2N$ | 75.29 | 74.86 | 6.66 | 6.38 | 5.49 | 5.91 | | |
| p-$CH_3OC_6H_4$ | 149–150[d] | | | $C_{16}H_{18}O_2NCl$ | | | | | 4.80 | 5.05 | 12.18 | 12.43 |
| p-$C_2H_5OC_6H_4$ | 105–106 | 37 | 52 | $C_{17}H_{19}O_2N$ | 75.70 | 75.46 | 7.06 | 7.29 | 5.40 | 5.23 | | |
| p-$C_2H_5OC_6H_4$ | 154–155[d] | | | $C_{17}H_{20}O_2NCl$ | | | | | 4.58 | 4.83 | 11.62 | 11.91 |

[a] Reported m.p. 111–112°, J. Kenner and F. S. Statham, *J. Chem. Soc.*, 299 (1935). [b] The yield reported in this column is that obtained by the use of β-dimethylaminopropiophenone. [c] The yield reported in this column was obtained when β-piperidinopropiophenone was employed. [d] Hydrochloride.

1.4 g. of p-toluidine for 30 min. The solvent was removed, and the residue was recrystallized from ethanol; m.p. and mixed m.p. 113–115°.

## Silicon-Containing s-Triazine Derivatives

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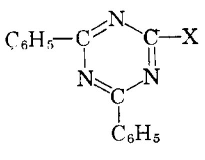
Most reactions involving organic substituent in silanes, particularly those in which the functional group is separated from the silicon atom by only one methylene group, are only slightly affected by the presence of silicon and are not very different from those of analogous purely organic compounds.[2] Since many derivatives of s-triazine can be obtained by nucleophilic displacement reactions with chloro-s-triazines,[3] it seemed to us that one route to the preparation of s-triazines having silicon-containing substituents would lie in the treatment of chloro-s-triazines with various nucleophilic carbon-functional silanes. In this paper we wish to report the success of this approach, which has led to the preparation of the s-triazine derivatives I–III by the reaction of the appropriate silicon-containing amine, alcohol, or thiol with 2,4-diphenyl-6-chloro-s-triazine (IV).



I. $X = NHCH_2Si(CH_3)_3$
II. $X = OCH_2Si(CH_3)_3$
III. $X = SCH_2Si(CH_3)_3$

The reaction with the silicon-containing amine was extended to other chloro-s-triazines to form 2,4-diamino-6-trimethylsilylmethylamino-s-triazine (V) and 2,4,6-tris(trimethylsilylmethylamino)-s-triazine (VI). It seems likely that a large number of silicon-containing derivatives of s-triazine are accessible through reactions of chloro-s-triazines with carbon-functional silanes.

Because of the extremely low water solubility of the silanes their reactions with chloro-s-triazines were carried out in nonaqueous solvents. The amino-s-triazines I, V, and VI were prepared in benzene from the chloro-s-triazines and trimethylsilylmethylamine in the presence of triethylamine. Attempts to obtain II and III using triethylamine as the hydrogen chloride acceptor were not successful, and these compounds were synthesized through the interaction of the chloro-s-triazines and the sodium alcoholate or thiolate. It is probably that the slight electron-releasing effect of silicon, which makes trimethylsilylmethylamine a strong base,[4,5] favors the reaction with chloro-s-triazines; however, the low reactivity of alcohols and thiols toward chloro-s-triazines[6] does not seem to be greatly affected by the presence of silicon.

### Experimental

**2,4-Diphenyl-6-trimethylsilylmethylamino-s-triazine (I).**—A solution of 0.10 mole of trimethylsilylmethylamine[5] (b.p. 94–95°/756 mm.) and 0.13 mole of freshly distilled triethylamine in 200 ml. of dry benzene was placed in a 500-ml., three-necked flask equipped with a mechanical stirrer, reflux condenser, and dropping funnel. Provision was made for keeping the entire system under an atmosphere of dry nitrogen. Stirring was begun and 0.10 mole of 2,4-diphenyl-6-chloro-s-triazine[7] (IV) in 100 ml. of benzene was added over a period of 1 hr. The mixture was then heated to reflux and stirring continued for 6 hr. After cooling, the precipitate of triethylamine hydrochloride (0.074 mole, 74%) was filtered off and the filtrate was evaporated to dryness under reduced pressure. Upon recrystallization of

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[1] Present address: Melpar, Inc., Falls Church, Va.

[2] P. D. George, M. Prober, and J. R. Elliott, *Chem. Rev.*, **56**, 1065 (1956).

[3] E. M. Smolin and L. Rapoport, "s-Triazines and Derivatives," Interscience Publishers, Inc., New York, N. Y., 1959, pp. 53–62.

[4] J. E. Noll, B. F. Daubert, and J. L. Speier, *J. Am. Chem. Soc.*, **73**, 3781 (1951).

[5] L. H. Sommer and J. Rockett, *ibid.*, **73**, 5130 (1951).

[6] H. Schroeder, *ibid.*, **81**, 5659 (1959).

[7] R. Ostrogovich, *Chem. Ztg.*, **36**, 738 (1912).

TABLE I

| Reactants | Product | Yield | M.p.[a] | Analysis for[b] | | C | H | N |
|---|---|---|---|---|---|---|---|---|
| IV + trimethylsilylmethylamine (TMSMA) | I | 48% | 126–127 | $C_{19}H_{22}N_4Si$ | Calcd. | 68.22 | 6.64 | 16.75 |
| | | | | | Found | 67.82 | 6.47 | 16.89 |
| IV + Na alcoholate of trimethylsilylmethanol[c] | II | 43 | 94–95 | $C_{19}H_{21}N_3OSi$ | Calcd. | 68.02 | 6.32 | 12.53 |
| | | | | | Found | 68.14 | 6.51 | 12.10 |
| IV + Na thiolate of trimethylsilylmethylthiol[d] | III | 50 | 103–104 | $C_{19}H_{21}N_3SSi$ | Calcd. | 64.91 | 6.04 | 11.95 |
| | | | | | Found | 65.07 | 6.35 | 11.19 |
| 2,4-Diamino-6-chloro-*s*-triazine[e] + TMSMA | V | 34 | 153–155 | $C_7H_{16}N_6Si$ | Calcd. | 39.60 | 7.60 | 39.58 |
| | | | | | Found | 39.40 | 7.30 | 39.39 |
| 2,4,6-Trichloro-*s*-triazine[f] + TMSMA | VI | 48 | 136–137 | $C_{15}H_{36}N_6Si_3$ | Calcd. | 46.85 | 9.43 | 21.83 |
| | | | | | Found | 47.20 | 9.92 | 21.59 |

[a] Fisher-Johns—uncorrected. [b] Analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., and by Dr. Mary Aldridge, American University, Washington, D. C. [c] J. L. Speier, B. F. Daubert, and R. R. McGregor, *J. Am. Chem. Soc.*, **70**, 1119 (1948). [d] D. C. Noller and H. W. Post, *J. Org. Chem.*, **17**, 1395 (1952). [e] J. T. Thurston, J. R. Dudley, D. W. Kaiser, I. Hechenbleikner, F. C. Schaefer, and D. Holm-Hansen, *J. Am. Chem. Soc.*, **73**, 2981 (1951). [f] Eastman Practical grade cyanuric chloride.

the residue from 95% ethanol, I was obtained in 48% yield.

In general, all preparations were conducted in a manner similar to that used for compound I. Compounds II and III were prepared directly from the products of the reaction of sodium and the alcohol or thiol without isolating the intermediate. All products were white needles except I and III; these were light yellow. Ethanol (95%) was the recrystallization solvent except for compound III which was recrystallized from methanol, and VI, for which 60:40 mixture of benzene and *n*-hexane was employed. Table I shows the reactants, yields, analysis, etc.

Each of the compounds reported here shows strong infrared absorption at 860 cm.$^{-1}$ and 1243 cm.$^{-1}$, frequencies considered characteristic of the $(CH_3)_3$ Si—$CH_2$ — group.[8]

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(8) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, New York, N. Y., 1954, pp. 274–281.

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## Polyphosphoric Acid in the Bernthsen Reaction[1]

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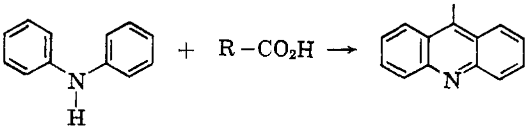
The Bernthsen reaction, one of the earliest used for the synthesis of acridines, (II) consists in heating a mixture of an aromatic or aliphatic carboxylic acid with a diphenylamine (I) and zinc chloride at 200–270° for about twenty hours.[2]



I II

The wide use of polyphosphoric acid[3] as a reagent in organic chemistry has led to this study of the use of polyphosphoric acid as a catalyst in the Bernthsen reaction. In a previous study of this type Elston[4] has reported that the reaction of diphenylamine and an excess of benzoic or *p*-toluic acid, in the presence of polyphosphoric acid at 160° for fifteen minutes, led to the formation of a diacyldiphenylamine (probably bis-*p*-) in a 12–15% yield, rather than a 9-substituted acridine.

It was felt that perhaps by changing the reaction conditions, particularly the ratio of amine and acid, one could successfully apply polyphosphoric acid to the Bernthsen reaction.

From the results of the reaction of benzoic acid and diphenylamine in polyphosphoric acid under a variety of conditions it appears that a ratio of one mole of acid to two moles of amine and a temperature of about 200° for fifteen minutes are the best conditions. Use of benzoic anhydride and ethyl benzoate gave results similar to benzoic acid. It is of interest to note that in one run the reaction was scaled up from 0.03 to 0.1 mole and the yield increased from 18 to 48%.

Table I lists the results obtained. No attempts were made to find the ideal reaction conditions in these cases. The use of *p*-nitro- and *p*-aminobenzoic acids did not lead to acridines by the use of zinc chloride.[5] With polyphosphoric acid the latter gave 9-(*p*-aminophenyl)acridine while *p*-nitrobenzoic acid did not lead to any acridine.

The use of polyphosphoric acid, rather than zinc chloride, is more convenient, particularly in regard to reaction times, and in view of the ready availability of starting materials this may be a worthwhile procedure in many cases, despite the poorer yields.

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(1) Presented in part at the Combined Southeastern-Southwestern Regional American Chemical Society Meeting, New Orleans, Louisiana, December, 1961.

(2) For references see: (a) R. M. Acheson, "Acridines," A. Weissberger, ed., Interscience Publishers, New York, N. Y., 1956, pp. 19–25; (b) A. Albert, "Heterocyclic Compounds," Vol. 4, R. C. Elderfield, ed., J. Wiley and Sons, Inc., New York, N. Y., 1952, pp. 502–503.

(3) (a) F. D. Popp and W. E. McEwen, *Chem. Rev.*, **58**, 321 (1958); (b) F. D. Popp and W. E. McEwen, *Proc. Kansas Acad. Sci.*, **63**, 169 (1960).

(4) C. T. Elston, Ph.D. thesis, University of Illinois, 1954; quoted in ref. 3a.

(5) W. Hess and A. Bernthsen *Ber.*, **18**, 689 (1885).