ture at 0.05 mm. afforded 79% of the excess isocyanate, b.p. 71–72°. To the residue was added 50 ml. of carbon tetrachloride and the insoluble solid, m.p. 284°, 3.7 g., was filtered from the mixture. To the filtrate was added 100 ml. of petroleum ether (b.p. 30–60°) and after chilling, the crude product II, 14.0 g., was obtained. The filtrate was reduced in volume and 4.4 g. (total crude yield 63%) of solid, m.p. 150–160°, was obtained. Recrystallization of the two crops of crystals from acetone allowed the isolation of II, m.p. 160–161° (lit.,[2] m.p. 162–163°). The total weight of the acetone-insoluble solid (probably *N,N'*-bis(1-naphthyl)urea or the isocyanate dimer) was 6.0 g. An analytical sample of II was recrystallized from aqueous acetone and yielded small, colorless needles, m.p. 159–160°.

Anal. Calcd. for $C_{29}H_{28}N_2O_5$: C, 71.88; H, 5.82; N, 5.78; OCH_3, 6.40. Found: C, 72.54; H, 5.88; N, 5.94; OCH_3, 6.02.

The product II gave a positive test for a methyl ketone using the alkaline sodium nitroprusside reagent.[5] The infrared spectrum of II had bands at 3322 and 3413 cm.$^{-1}$ (free and bonded NH, respectively[10]) and at 1701, 1725, and 1734 cm.$^{-1}$. The near infrared spectrum of a solution of II in benzene showed a strong band at 4826 cm.$^{-1}$ but no band in the range 6667–7042 cm.$^{-1}$. A 2-g. sample of II was heated at 170° below 1 mm. pressure and a small amount of liquid was distilled from the melt by heating to 195° at 0.1 mm. Reaction of this liquid with ethanol gave ethyl 1-naphthylurethane, identified by melting point and mixture melting point with an authentic sample.

(2-Methoxymethyl-2-methyl-3-oximino)butyl 2,4-bis(1-naphthyl)allophanate (III) was prepared by refluxing for 2 hr. a solution of II, hydroxylamine hydrochloride, and pyridine in absolute ethanol. The oxime (80% yield), after three recrystallizations from aqueous ethanol, had m.p. 168–169°.

Anal. Calcd. for $C_{29}H_{29}N_3O_5$: C, 69.72; H, 5.85; N, 8.41. Found: C, 69.76; H, 5.78; N, 8.34.

The infrared spectrum of III showed a broad band at about 3268 cm.$^{-1}$ (free and bonded NH and OH[10]) and three well resolved bands at 1690, 1727, and 1733 cm.$^{-1}$.

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Mannich Bases and Aromatic Amines in Amine Exchange Reactions

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It was of interest to determine if Schiff bases could be obtained by reaction of hydrochlorides of Mannich bases with primary arylamines in the presence of a condensation agent.

After a mixture of β-dimethylamino- (I) or β-piperidinopropiophenone hydrochloride (II), aniline, zinc chloride-aniline complex,[1] and ethanol had been refluxed, the reaction product isolated in each instance proved to be β-phenylaminopropiophenone. It was evident, therefore, that amine exchange reactions, instead of Schiff base formation, had taken place; these reactions are similar to those which have been reported[2–6] for Mannich bases or their salts and aliphatic amines.

When I or II was allowed to react with other aromatic amines such as *p*-chloroaniline, *p*-toluidine, *p*-anisidine, or *p*-phenetidine, the products, β-arylaminopropiophenones, obtained from interaction of either I or II with a specific amine were identical.

In order to establish identity, the β-arylaminopropiophenones were synthesized from β-chloropropiophenone and the required arylamine. β-*p*-Toluidinopropiophenone was also obtained when I was heated under reduced pressure and the phenyl vinyl ketone formed was allowed to react with *p*-toluidine.

In an attempt to obtain a Schiff base of the desired type in a different manner, a mixture of equimolar amounts of acetophenoneanisil, dimethylamine hydrochloride, paraformaldehyde, and ethanol was heated for two hours on a water bath; only oily intractable material was obtained.

Experimental

β-Arylaminopropiophenones (Table I).—A. A mixture of the hydrochloride of the Mannich base (I or II) (0.02 mole) the required amine (0.02 mole), and 25 ml. of absolute ethanol was refluxed for 6 hr. After 12 hr. at room temperature, the precipitate was recrystallized from absolute ethanol.

B. A mixture of β-chloropropiophenone[7] (0.0065 mole), the required amine (0.015 mole), and water was heated for 30 min. at 100°, cooled, and the precipitate was recrystallized from ethanol.

The melting points and mixed melting points of corresponding products prepared by methods A and B were identical.

The products are insoluble in water, slightly soluble in benzene and ether, and soluble in chloroform.

The hydrochlorides, which are insoluble in water, were prepared by mixing a solution of β-arylaminopropiophenone in dry acetone with dry acetone made acid to congo red by passing in dry hydrogen chloride, and recrystallizing the precipitate from alcohol.

β-Anilinopropiophenone hydrochloride and β-*p*-phenetidinopropiophenone hydrochloride separated only on trituration after addition of ether. The former was recrystallized from alcohol–acetone mixture. The hydrochloride of β-*p*-toluidinopropiophenone was recrystallized from alcohol–ether mixture.

β-*p*-Toluidinopropiophenone.—Compound I (4.0 g.) was heated in an oil bath at 160–170° under 18 mm. pressure. The phenyl vinyl ketone which distilled (1.8 g.), b.p. 114–116°/18 mm., was dissolved in chloroform and refluxed with

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TABLE I

β-ARYLAMINOPROPIOPHENONES

$C_6H_5COCH_2CH_2NHR$

R	M.P.	Yield, %		Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found	Chlorine, % Calcd.	Chlorine, % 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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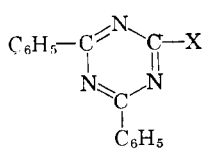
Most reactions involving organic substituent in silanes, particularly those in which the functional group is separated from the silicon atom by only one methylene group, are only slightly affected by the presence of silicon and are not very different from those of analogous purely organic compounds.[2] 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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