Anal. Calcd. for $C_{15}H_{21}O_6Rh$: Rh, 25.75; C, 45.01; H, 5.29; mol. wt., 400. Found: Rh, 25.5; C, 45.2; H, 5.35; mol. wt. (Rast in camphor), 390.

Tris-acetylacetone-iridium(III).—Freshly precipitated iridium dioxide, from potassium hexachloriridate(IV) (1.0 g.) was dissolved by heating with sulfuric acid (1 *N*, 25 ml.) and a few crystals of sodium sulfate, and evaporated until the acid started to fume. The cooled solution was diluted to the original volume, and the undissolved iridium dioxide removed by centrifuging. The light green solution was treated with 10% caustic soda solution until the green iridium(III) hydroxide precipitate was just redissolved. The substance was reprecipitated quickly in order to avoid oxidation, the solution adjusted to *p*H 6, and the mixture heated at 60° with acetylacetone (2 ml.) for an hour. The solution became red, depositing a yellow crystalline precipitate, which crystallized from aqueous methanol in orthorhombic plates, m.p. 269° (yield 0.1 g., 10%). The substance sublimed at 260° under 1 mm. pressure and decomposed at 290° depositing an iridium mirror. The solubility in solvents was similar to the rhodium compound.

Anal. Calcd. for $C_{15}H_{21}O_6Ir$: Ir, 39.37; C, 36.73; H, 4.32; mol. wt., 490. Found: Ir, 39.3; C, 36.9; H, 4.4; mol. wt. (Rast in camphor), 400.

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Extension of the Leuckart Synthesis of Tertiary Amines, Including its Application to α,β-Unsaturated Carbonyl Compounds[1]

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In 1949, we reported[3] the preparation of a number of tertiary amines by the reaction of ketones with dialkylformamides in the presence of formic acid and magnesium chloride; conversions[4] in the range 20 to 55% and adjusted yields[4] in the range 40 to 60% were obtained. We now report the application of an improved variation of this technique to a number of additional carbonyl compounds; our results are summarized in Table I.

TABLE I

TERTIARY AMINES SYNTHESIZED BY THE LEUCKART REACTION

Tertiary amine product[a]	Conversion,[4] %	Adjusted yield,[4] %	B.p. °C.	B.p. Mm.	Picrate m.p., °C.	Hydrochloride m.p., °C.	Refractive index n_D^t	Refractive index t, °C.
N,N-Dimethyl-α-ethylbenzylamine (I)	30	79	105–106	25	165.5–166.6		1.5002	25
α-Ethylbenzylpiperidine (II)	65	77	155–157	25		187–188	1.5210	25
N,N,1-Trimethyl-3-phenylpropylamine (III)	43	60	118–121	14	113.5–114		1.4985	23
1-Methyl-3-phenylpropylpiperidine (IV)	57	57	176–177	25		164.5–165.5	1.5140	25
N,N,1-Trimethyl-3-(*p*-methoxyphenyl)-propylamine (V)	30	55	152–154	14	129.5–130.5	169–170	1.5060	24
N,N-Dimethyl-3-phenylallylamine (VI)	55	55	125–132	25	123.5–124.5	187.5–188.5		
N,N,1-Trimethyl-3-phenylallylamine (VII)	23	44	139–140	25	138–139		1.5350	25
1-Methyl-3-phenylallylpiperidine (VIII)	15	15	180–187	25	142.5–143.5			

[a] Experimental details and data supporting structures are given in the Experimental section.

It will be noted that in general the yields reported here range higher than those reported previously. This improvement is due in part to the use of a longer reaction time (eight hours instead of three or four hours) and in part to a modified technique for removing the low-boiling constituents (principally water and formic acid) of the original reaction mixture. This technique involves distilling the reaction mixture rapidly until the pot temperature approximates the boiling point of the formamide being used, and then allowing the system to reflux. Efforts to improve the yield by the use of excess formic acid or by the use of nickel catalyst[5] (from pyrolysis of nickel formate) were not fruitful. It is of parenthetical interest that when the magnesium chloride and formic acid of a typical reaction mixture were replaced by phosphoric acid (making the molar ratio phosphoric acid:propiophenone:formpiperidide = 1:1:4), the conversion[4] to α-ethylbenzylpiperidine was 30% compared to 65% by our best procedure.

Shortly after the appearance of our earlier paper,[3] Staple and Wagner[6] published a careful study of factors influencing the rate of formation of tertiary amines from piperidine formate or formpiperidide and benzaldehyde or cyclohexanone. Using these particularly reactive carbonyl compounds, they found that a faster reaction and better yields were obtained when the amine formate was used rather than formpiperidide. On the basis of this experience, they suggested that the amine formate would in general prove to be the better reagent for tertiary amine synthesis. We attempted to prepare amines from 4-(*p*-methoxyphenyl)-butanone-2 and dimethylamine formate, and from propiophenone and piperidine formate by their recommended procedure, but in neither case were we able to obtain any measurable amount of the expected tertiary amine. Since the successful preparation of both these tertiary amines is recorded in Table I, we believe that our procedure is more suitable for the preparation of tertiary amines from carbonyl compounds in general.

Our success in obtaining unsaturated tertiary amines (the last three amines in Table I) from α,β-unsaturated carbonyl compounds contrasts with the

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[1] Based in part on the B.A. Thesis of Henry Moe, June, 1952. Presented at The Northwest Regional Meeting of The American Chemical Society, Corvallis, Oregon, June 20, 1952.

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[3] J. F. Bunnett and J. L. Marks, THIS JOURNAL, **71**, 1587 (1949).

[4] In this paper, "conversion" means yield based on the amount of ketone introduced, and "adjusted yield" means yield based on the amount of ketone consumed, that is, on the amount introduced less the amount recovered.

[5] A. N. Kost, A. P. Terent'ev and G. A. Shvekhgeimer, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 150 (1951) [*C. A.*, **45**, 10194 (1951)], reported catalysis of the Leuckart synthesis of primary and secondary amines by nickel metal and other hydrogenation catalysts.

[6] E. Staple and E. C. Wagner, *J. Org. Chem.*, **14**, 559 (1949).

failure of others[7–9] to obtain unsaturated primary amines by the Leuckart reaction. From carvone and ammonium formate, Wallach[9] obtained dihydrocarvylamine in which the double bond α,β- to the carbonyl group has been reduced. Irwin[8] allowed formamide to act upon a number of α,β-unsaturated ketones; in general, mixtures were formed from which, in two cases, the saturated primary amines were isolated and identified. However, he adduced no evidence that any unsaturated amines were formed.

With these considerations in mind, we made special efforts to confirm the identity of our unsaturated amine products. The structure assigned to VII (obtained from benzalacetone and dimethylformamide) is confirmed by analyses on the amine and its picrate, by the fact that it differs from the saturated amine (III), by the fact that it absorbs bromine rapidly, and by its conversion by catalytic hydrogenation (palladium-on-carbon catalyst, ethanol solution) into III. In the case of VI, the physical constants we obtained agree with those reported by King and Holmes[10] for VI prepared by another method. The structure assigned to VIII is supported by analyses and by the fact that it differs from the saturated amine IV.

Whereas the saturated amines I–V were obtained in a condition of high purity from the initial vacuum distillation, the unsaturated amines VI–VIII were obviously contaminated by impurities at this stage of purification. The nature of the impurities is perhaps indicated by the fact that the saturated amine III was isolated, as its picrate, from the liquors from recrystallization of crude VII picrate. It is suspected that crude VI and VIII were also contaminated with the corresponding saturated amines, but in these cases efforts to isolate the saturated amines as by-products were not successful.

Several efforts to prepare the *p*-methoxy derivative of VII by the reaction of *p*-methoxybenzalacetone with dimethylformamide were rewarded very meagerly. In each run a very small amount of amine was obtained; the substance was not investigated further.

The action of hydrobromic acid on V produced N,N,1-trimethyl-3-(*p*-hydroxyphenyl)-propylamine; our melting points for this product and its hydrochloride were in each case nine degrees higher than those reported elsewhere.[11]

Experimental[12]

Materials.—Dimethylformamide was generously donated by the Grasselli Chemicals Department, E. I. du Pont de Nemours and Co. Other starting materials were commercial products repurified, or were synthesized by standard methods. Our 4-phenyl-2-butanone, prepared both from ethyl α-benzylacetoacetate and by hydrogenation of benzalacetone, followed by purification through its bisulfite addition product, had $n^{25}\mathrm{D}$ 1.5100, a value different from that reported by Briggs, De Ath and Ellis,[13] but in approximate agreement with the value given by Klages.[14] The melting point of the semicarbazone of our product, 142°, agrees with the generally accepted value. The melting point of its 2,4-dinitrophenylhydrazone was 125–126.3°, in comparison to 131–132° reported by Briggs, De Ath and Ellis.[13]

Preparations Summarized in Table I.—In most cases, 0.13 mole of carbonyl compound was used, though the preparations of III, V and VII were run on a scale approximating 0.5 mole. The ketone or aldehyde, the formamide (dimethylformamide or formpiperidide, 4 moles per mole of carbonyl compound), magnesium chloride hexahydrate ($^1/_6$ mole per mole of carbonyl compound) and 85% formic acid (one mole per mole of carbonyl compound) were mixed in a three-neck flask equipped with a stirrer, thermometer and condenser set for downward distillation. The mixture was heated and volatile constituents were removed until the pot temperature approximated the boiling point of the formamide being used. A reflux condenser was then installed in place of the condenser set for downward distillation, and the mixture was refluxed with stirring for eight hours. After the mixture had been poured into dilute mineral acid, unreacted ketone was removed by steam distillation and purified by standard procedures. The mixture was then made basic and the amine was distilled off with steam. The steam distillate was saturated with sodium chloride and extracted with ether. The ether extract, after drying over solid sodium hydroxide, was distilled, the amine finally being distilled at reduced pressure. Saturated amines were obtained from this distillation in a state of considerable purity, but unsaturated amines were, to judge from the refractive indices and boiling points of distillation fractions, not pure, and were further purified by recrystallization of their picrate or hydrochloride salts. Picrates were recrystallized from ethanol and hydrochlorides from acetone.

The following data support the structures assigned to the products:

I.—Dunn and Stevens[15] reported for I b.p. 100–105° (22 mm.), picrate m.p. 161–164°.

II.—Calcd. for $C_{14}H_{21}N$ (amine): C, 82.70; H, 10.41. Found: C, 83.02; H, 10.43. Calcd. for $C_{14}H_{22}ClN$ (hydrochloride): C, 70.12; H, 9.25; Cl, 14.79. Found: C, 70.26; H, 9.00; Cl, 14.68.

III.—Calcd. for $C_{12}H_{19}N$: C, 81.29; H, 10.80; N, 7.93. Found: C, 81.38; H, 10.38; N, 8.21.

IV.—Calcd. for $C_{15}H_{24}ClN$ (hydrochloride): C, 70.98; H, 9.53; Cl, 13.97. Found: C, 71.40; H, 9.59; Cl, 13.92.

V.—Davies, Haworth, Jones and Lamberton[11] reported for V b.p. 155° (14 mm.), picrate m.p. 129°, hydrochloride m.p. 166°.

VI.—King and Holmes[10] reported for VI: picrate m.p. 124–125°, hydrochloride m.p. 190.5–191°.

VII.—Calcd. for $C_{12}H_{17}N$ (amine): C, 82.22; H, 9.78. Found: C, 82.24; H, 9.84. Calcd. for $C_{18}H_{20}N_4O_7$ (picrate): C, 53.46; H, 4.98. Found: C, 54.05; H, 4.77. From the liquors from recrystallization of the picrate, a small amount of yellow material, m.p. 113–113.5°, was recovered. It did not depress the m.p. of III picrate.

VIII.—Calcd. for $C_{21}H_{24}N_4O_7$ (picrate): C, 56.75; H, 5.44. Found: C, 56.55; H, 5.62.

N,N,1-Trimethyl-3-(*p*-hydroxyphenyl)-propylamine.—A solution of 30 g. of V in 150 cc. of 48% hydrobromic acid was refluxed five hours. The mixture was made alkaline by adding sodium carbonate and extracted with ether. The ether extracts were dried and evaporated, and the residue distilled at reduced pressure, furnishing 13.2 g. (47.3%) of the phenolic amine, b.p. 192–195° (14 mm.), m.p. 73.5–76°.

Anal. Calcd. for $C_{12}H_{19}NO$: C, 74.56; H, 9.91. Found: C, 74.96; H, 9.58.

The hydrochloride was recrystallized from absolute ethanol, m.p. 161–162°; a mixed melting point with V hydrochloride was depressed (154–157°).

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[7] A. W. Ingersoll, J. H. Brown, C. K. Kim, W. D. Beauchamp and G. Jennings, THIS JOURNAL, **58**, 1808 (1936).

[8] O. R. Irwin, Ph.D. Thesis, University of Missouri, 1950; Univ. Microfilms, pub. No. 1785; *C. A.*, **45**, 6204 (1951).

[9] O. Wallach, *Ber.*, **24**, 3984 (1891).

[10] F. E. King and D. Holmes, *J. Chem. Soc.*, 168 (1947).

[11] R. E. Davies, R. D. Haworth, B. Jones and A. H. Lamberton, *ibid.*, 191 (1947).

[12] Melting points are uncorrected. Analyses for carbon and hydrogen by Clark Microanalytical Laboratories, Urbana, Ill.; Dr. Adalbert Elek, Los Angeles, Calif.; and Dr. Carl Tiedcke, New York, N. Y.

[13] L. H. Briggs, G. C. De Ath and S. R. Ellis, *J. Chem. Soc.*, 61 (1942), reported for 4-phenyl-2-butanone: $n^{25}\mathrm{D}$ 1.5140.

[14] A. Klages, *Ber.*, **37**, 2313 (1904), reported for 4-phenyl-2-butanone: $n^{21.7}\mathrm{D}$ 1.511.

[15] J. L. Dunn and T. S. Stevens, *J. Chem. Soc.*, 281 (1934).

Anal. Calcd. for $C_{12}H_{20}ClNO$: Cl, 15.43. Found: Cl, 15.50.

Davies, Haworth, Jones and Lamberton[11] have reported melting points for this phenolic amine and its hydrochloride in each case about nine degrees lower than our values.

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t-Alkyl-*n*-alkyl Orthosilicates

BY PHILIP D. GEORGE AND JOHN R. LADD

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Mixed alkyl orthosilicates are produced by the interaction of ethyl orthosilicate and an alcohol in the presence of a basic catalyst, provided that the ethanol formed is continuously removed.

$$(EtO)_4Si + x\,ROH \xrightarrow{NaOR} (RO)_xSi(OEt)_{4-x} + x\,EtOH$$

Furthermore, this reaction is applicable to the synthesis of mixed alkyl orthosilicates containing tertiary alkoxy groups.[1,2] We have applied this method of synthesis to the preparation of six mixed alkyl orthosilicates. The pertinent data on synthesis and properties are summarized in Table I.

In general, the experimental procedure was as follows. The reaction mixture, consisting of several small pieces of sodium and equimolar amounts of ethyl orthosilicate and the appropriate alcohol, was heated, and the resulting reflux was rectified through an efficient column. Distillate was removed slowly at the boiling point of ethyl alcohol until the refluxing slowed and the weight of distillate approximately equalled the theoretical amount of ethyl alcohol. The reaction mixture was allowed to cool, washed thoroughly with water, dried and fractionally distilled. The mixed-alkyl silicates thus obtained were water-white mobile liquids having an odor similar to the alcohol from which they were prepared. Yields ranged from 10% to 50%. Table I summarizes physical properties and analyses.

Experimental

Intermediates.—The ethyl orthosilicate was purchased from Carbide and Carbon Chemicals Company and used as received. Distillation of other samples had indicated that this material is of high quality. The *n*-butyl alcohol, *t*-butyl alcohol and *t*-amyl alcohol were the ordinary materials of commerce used without further purification.

Synthesis of *t*-Alkyl-*n*-alkyl Orthosilicates.—All six compounds were prepared in essentially the same manner. The following detailed description of the synthesis of *t*-amyltriethyl silicate (V) and di-*t*-amyldiethyl silicate (VI) is illustrative of the method used. Yields, properties and analyses of the six compounds prepared may be found in Table I.

In a round-bottom flask was placed 1040 g., 5.0 moles, of ethyl orthosilicate and 440 g., 5.0 moles, of *t*-amyl alcohol. Several pea-sized chunks of sodium were added and the reaction flask was attached to a glass helix-packed rectification column having an estimated efficiency of twenty theoretical plates. As heat was applied to the reaction vessel, the sodium went into solution and reflux appeared at the head of the column. The reaction was stopped after 233 g. of distillate had been taken off at 78° over a period of six hours; the theoretical yield of ethanol was 230 g.

TABLE I

		Unreacted $(EtO)_4$-Si, %	Yield,[a] %	B.p., uncorr.[b] °C.	B.p., uncorr.[b] Mm.	n^{20}_D[b]	d^{20}[b]	R_D[c] Calcd.	R_D[c] Obsd.	Analyses, % Carbon Calcd.	Carbon Obsd.	Hydrogen Calcd.	Hydrogen Obsd.	Mol. wt.[d] Calcd.	Mol. wt.[d] Obsd.
I	*n*-BuOSi(OEt)$_3$[e]		49	128	77	1.3939	0.919	0.2585	0.2602	50.8	50.7	10.2	11.1	...	...
II	(*n*-BuO)$_2$Si(OEt)$_2$[e]	27	24	155	78	1.4019	.912	.2661	.2669	54.5	54.4	10.7	10.9	...	...
III	*t*-BuOSi(OEt)$_3$		54	95	40	1.3872	.905	.2585	.2602	50.8	51.3	10.2	10.4	236	231
IV	(*t*-BuO)$_2$Si(OEt)$_2$	32	11	101	34	1.3899	.887	.2661	.2675	54.5	55.7	10.7	11.1	264	266
V	*t*-AmOSi(OEt)$_3$[f]		53	116	55	1.3859	.910	.2625	.2640	52.8	53.3	10.5	10.8	250	242
VI	(*t*-AmO)$_2$Si(OEt)$_2$	24	19	141	59	1.4052	.900	.2722	.2724	57.5	57.7	11.0	11.1	278	290

[a] Based on unrecovered ethyl orthosilicate and calculated from distillation curves. [b] These physical properties are those of a center fraction of the particular distillation flat. [c] The calculated values were obtained by use of bond refractions given by K. G. Denbigh, *Trans. Faraday Soc.*, **36**, 936 (1940), and by E. L. Warrick, THIS JOURNAL, **68**, 2455 (1946). Similar results may be obtained by use of the method of R. O. Sauer, *ibid.*, **68**, 954 (1946). [d] Determined cryoscopically in cyclohexane. [e] H. W. Post and C. H. Hofrichter, *J. Org. Chem.*, **5**, 576 (1940), reported the synthesis of these two compounds in 22 and 30% yields, respectively, by prolonged heating of ethyl orthosilicate with *n*-butyl orthosilicate. These workers found that the *n*-butylethyl orthosilicates disproportionate on heating at their atmospheric boiling points. [f] G. W. Pedlow and C. S. Miner, Jr., U. S. Patent 2,566,365 (September 4, 1951), reported the synthesis of this compound by the reaction of *t*-amoxytrichlorosilane with ethanol in the presence of pyridine.

The crude reaction product was washed thoroughly with four 300-ml. portions of distilled water and dried for several days over Drierite. Fractional distillation was carried out at reduced pressure in a glass helix-packed column having an estimated efficiency of thirty theoretical plates. Graphical analysis of the distillation data revealed three plateaus identified as ethyl orthosilicate (physical properties and molecular weight), *t*-amyltriethyl silicate (V) and di-*t*-amyldiethyl silicate (VI).

Other compounds prepared by this method were: *n*-butyltriethyl silicate (I), di-*n*-butyldiethyl silicate (II), *t*-butyltriethyl silicate (III) and di-*t*-butyldiethyl silicate (IV).

In the case of the *t*-butyl compounds the proximity of the boiling points of ethanol and *t*-butyl alcohol necessitated a slightly modified procedure. The distillate consisted of a mixture of the two alcohols whose composition was determined by refractive index. More *t*-butyl alcohol was added to the reaction mixture and distillation was continued until one mole of ethanol had been removed for each mole of ethyl orthosilicate used.

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(1) We learned of this reaction through a private communication from Dr. C. S. Miner, Jr., and co-workers of the Miner Laboratories of Chicago, Illinois.

(2) (a) D. F. Peppard, W. G. Brown and W. C. Johnson, THIS JOURNAL, **68**, 73 (1946), reported that acid-catalyzed alcoholysis of ethyl orthosilicate did not occur with *t*-butyl alcohol; while *t*-amyl alcohol did react to give ethyl alcohol, these workers did not report any *t* amyl silicate. (b) D. Ridge and M. Todd, *J. Chem. Soc.*, 2637 (1949), reported that uncatalyzed alcoholysis of ethyl orthosilicate occurred to a slight extent with *n*-butyl alcohol but not at all with *t*-butyl alcohol or with *t*-amyl alcohol.