helices-packed column, leaving a red oil. Addition of some pentane yielded an amorphous yellow solid and a solution which was chromatographed through neutral alumina. The major fraction (0.46 g.) was eluted with 10% methanol–diethyl ether but appeared to be a mixture containing no 1,2-dihydropyridine on the basis of its infrared spectrum.

n-**Butylimine of Acetone** (**8**).—The procedure of Norton, *et al.*,[17] was followed. The imine was obtained in 34% yield as a colorless liquid, b.p. 129–131°/740 mm., n^{25}D 1.4191. A sample distilled from sodium was analyzed.

Anal. Calcd. for $C_7H_{15}N$: C, 74.27; H, 13.43. Found: C, 73.87; H, 13.84.

An infrared maximum for the liquid film was found at 1670 cm.$^{-1}$.

Reaction of 8 with Crotonaldehyde.—*p*-Toluenesulfonic acid monohydrate (5.0 g., 0.026 mole) in ethyl ether (2 l.) was stirred for 3 hr. with molecular sieve 4A (650 g.). To this solution was added **8** (205 g., 1.81 moles), freshly distilled crotonaldehyde (127 g., 1.81 moles), and molecular sieve 4A (450 g.). The mixture was allowed to stand for 18 hr. at room temperature. Initial heat evolution was not sufficient to cause the ether to reflux. The mixture was filtered from the molecular sieve, washed with dilute sodium bicarbonate and water, then dried over potassium carbonate. Removal of the ether and distillation of the residual oil at 0.1 mm. gave two fractions b.p. under 31° (95 g.) and b.p. 31–44° (57 g.). Redistillation of the first fraction gave the *n*-butylimine of crotonaldehyde (**9**), b.p. 77–80°/40 mm., n^{26}D 1.4580. The colorless liquid darkens rapidly on exposure to oxygen (reported[7] b.p. 162–164°, n^{23}D 1.4595).

Fractionation of the second cut yielded about 10 g. of the *n*-butylimine of crotonylideneacetone (**10**), b.p. 49–50°/0.1 mm., n^{25}D 1.5120. The colorless liquid darkens rapidly in air.

Anal. Calcd. for $C_{11}H_{19}N$: C 79.94; H, 11.59. Found: C, 79.62; H, 11.47.

The yield of crude material which contains mostly **10** is *ca.* 20%, but only 4% of pure material was isolated.

Hydrolysis of 10.—The imine (**10**) (0.5 g.) was dissolved in 95% ethanol (75 ml.) to which was added a buffer, pH 9.80, prepared from sodium bicarbonate (5 g.), sodium carbonate (5 g.), and water (150 ml.). The mixture was stirred and allowed to stand 30 min., extracted twice with ethyl ether, and treated with excess acidic 2,4-dinitrophenylhydrazine solution after removal of most of the ether. An immediate red precipitate formed, 0.50 g. (59%), m.p. 193–197°. After three recrystallizations from ethy acetate, the bright red needles had m.p. 205–206° (in bath at 180°); reported[11] 205–206°.

Hydrogenation of 10.—The imine (**10**) (6.81 g.) was hydrogenated in 95% ethanol over 1 g. of 10% palladium on charcoal. After 24 hr., 2.2 moles of hydrogen/mole of **10** had been absorbed, the solution filtered, the solvent removed, and the residue distilled. Only 2.64 g. (37%) *N*-*n*-butyl-1-methylhexylamine, b.p. 42°/0.4 mm., n^{25}D 1.4308, was isolated, along with several grams of an oil, b.p. 125°/0.4 mm.

Anal. Calcd. for $C_{11}H_{25}N$: C, 77.11; H, 14.71. Found: C, 77.53; H, 14.63.

A perchlorate salt of the amine had m.p. 159–160°. In a number of other hydrogenations in methanol or 95% ethanol, from 1.66 to 2.16 moles of hydrogen/mole of imine were absorbed.

n-**Butylimine of Sorbaldehyde** (**11**).—Redistilled sorbaldehyde (28.8 g.) (Aldrich Chemical Co., Milwaukee), b.p. 47–47.5°/7 mm., $n^{20.5}$D 1.5391, in ethyl ether (100 ml.) was mixed with *n*-butylamine (21.9 g.). After refluxing of the ether had ceased, potassium carbonate (60 g.) was added and the mixture allowed to stand several hours. After removal of the ether, distillation gave 23.1 g. of **11**, b.p. 35–40°/0.1 mm. Redistillation gave the pure imine, b.p. 37°/0.1 mm., n^{27}D 1.5175.

Anal. Calcd. for $C_{10}H_{17}N$: C, 79.41; H, 11.33. Found: C, 79.70; H, 11.62. The imine is colorless but darkens rapidly in air; it solidifies when stored in the refrigerator.

Ultraviolet Spectra.—These were measured with a Cary Model 11 recording spectrophotometer.

The ultraviolet absorption of the aldehydes (data in Table I) in various solvents are correlated by the relations,

$$E_T(1) = -0.214\ Z + 116.81$$

and

$$E_T(2) = -0.208\ Z + 122.06$$

Nuclear Magnetic Resonance Spectrum.—Carried out at 60 Mc. with a Varian instrument in carbon tetrachloride solution (*ca.* 20% of alcohol **3**) with a benzene capillary reference.

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[17] D. C. Norton, *et al.*, *J. Org. Chem.*, **19**, 1054 (1954).

The Preparation of Aldimines through the Stephen Reaction[1]

T. L. TOLBERT[2] AND BRUCE HOUSTON

Department of Chemistry, University of Oklahoma, Norman, Oklahoma

Received September 7, 1962

A general method for the preparation of aldimines of the type RCH=NH is described. The procedure, a modification of the Stephen aldehyde synthesis, involves the anhydrous decomposition of an aldimine hydrochloride–stannic chloride complex formed by reaction of a nitrile, hydrogen chloride, and stannous chloride. A comparison of steric and electronic effects is made and twelve aldimines are reported.

Primary imines, aldimines, of the type RCH=NH are considered to be intermediates in many well known organic reactions, yet in only a few instances[3–5] have any been isolated and identified. In the cases where aldimines have been reported, there has been serious disagreement on properties; for example, benzaldimine has been described both as a high boiling liquid[3] and as a solid[4] unstable at room temperature. This confusion and general lack of information led P. L. Pickard, at that time a member of this department, to suggest and initiate the work discussed here. The research was designed to establish the chemical properties of aldimines as a class, to resolve the differences in reported properties, and to develop a general method of aldimine synthesis.

Twelve aldimines were prepared and characterized; they are shown in Table I. These compounds proved to be reactive, water-sensitive bases chemically similar to the ketimines. They were characterized by hydrolysis to the corresponding aldehyde, by the formation of salts, and by the replacement of hydrogen to form N-substituted derivatives. More recent studies on the reduction of the carbon–nitrogen double bond to form amines and infrared characterization of aldimines will be discussed in a forthcoming publication.

The method of preparation was a modification of the Stephen aldehyde synthesis. Stephen's method[6] con-

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[1] Based on the dissertation submitted by T. L. Tolbert to the Graduate School, University of Oklahoma, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] Chemstrand Research Center, Inc., Durham, N. C.

[3] V. Grignard and R. Escourrou, *Compt. rend.*, **180**, 1883 (1925); R. Escourrou, *Bull. soc. chim. France*, **45**, 735 (1929).

[4] H. H. Strain, *J. Am. Chem. Soc.*, **49**, 1558 (1927); **54**, 1221 (1932).

[5] E. P. Kohler and N. L. Drake, *ibid.*, **45**, 1281 (1923).

[6] H. Stephen, *J. Chem. Soc.*, 1874 (1925).

TABLE I

ALDIMINES RCH═NH

No.	R	M.p.,[a] °C.	B.p.,[a] °C./mm.	n^{20}_D	d^{20}_4	Yield, %		Nitrogen, %		Equiv. wt.[b]	
						Complex[c]	Imine[d]	Calcd.	Found	Calcd.	Found
1	C_6H_5		58/4	1.5259	0.9799	90	94	13.33	13.48	105	105
2	$C_6H_5CH_2$		212/731	1.5251[e]		80	[f]				
3	$(C_6H_5)_2CH$	129[g]									
4	o-$CH_3C_6H_4$		192/734	1.5212	0.9586	30	11[h]	11.76	11.84	119	120
5	m-$CH_3C_6H_4$					98	[i]				
6	p-$CH_3C_6H_4$		35/1	1.5358	1.002	70	25[j]	11.76	11.88		
7	o-ClC_6H_4		177/733	1.5589	1.1912	72	22	10.03	10.07	139.5	139
8	p-ClC_6H_4	48				99	72[k]	10.03	10.00	139.5	140
9	p-$HO_2CC_6H_4$		182/733	1.4927	1.0505	95	27	9.39	9.40		
10	o-$Cl_3CC_6H_4$	112	208/728				44[l]	5.84	5.87	222.5	220
11	p-$Cl_3CC_6H_4$	135					1				
12	α-$C_{10}H_7$	37	267/734			15	49	9.03	9.01	155	153
13	α-$C_{10}H_7CH_2$	85	115/728			1	23[l]	8.28	8.33		

[a] Uncorrected. [b] Non-aqueous titration method of P. L. Pickard and F. A. Iddings, *Anal. Chem.*, **31,** 1228 (1959). [c] As the dry solid. Previous workers have shown that complex precipitation can not be taken as a criterion of the extent of reaction. [d] Highest yields obtained, based on nitrile used in the complex formation. [e] Immediately after distillation. V Grignard and R. Escourrou, *Compt. rend.*, **180,** 1833 (1925), report 212–213°/750 mm. and n^{20}_D 1.5402. [f] 70%, if calculated on weight of polymer obtained. [g] Ref. 5. [h] Plus 10.1% polymer. [i] 50%, if calculated on weight of polymer obtained. [j] Isolated as the hydrochloride. Distillation yielded 8.4% imine and 65% polymer. [k] Isolated as the hydrochloride, regenerated with liquid ammonia, and purified by sublimation. [l] Isolated as the hydrochloride and regenerated with liquid ammonia.

sists of two steps: the formation of a stable intermediate, $(RCH{=}NH \cdot HCl)_2SnCl_4$, by reduction of a nitrile with a stannous chloride–hydrogen chloride complex, followed by hydrolysis of the intermediate to the aldehyde. We found that decomposition of the intermediate under anhydrous conditions results in the liberation of the aldimine, RCH═NH, which then can be separated by distillation or salt formation. The use of a large molar excess of triethylamine proved to be the most satisfactory of the fourteen methods of nonaqueous decomposition evaluated. In general, yields were moderate to good.

The tendency of the aldimines to polymerize was a major problem, the extent of which is readily seen by comparing the yields of monomer and polymer shown in Table I. In nearly every case at least some polymer was formed during distillation and in some instances aldimines at room temperature polymerized. Aldimines distilled directly from the decomposition filtrates appeared to polymerize more readily than those which were isolated as a salt and regenerated. It seems likely, therefore, that codistillation of traces of volatile impurities enhanced polymer formation. The polymers were usually highly colored, gummy resins which on long refluxing in acidic media were completely hydrolyzed to the aldehyde corresponding to the monomeric imine.

No clear picture of the degree to which ring substitution affected the yields of aromatic aldimines was obtained. Several generalizations can be made, however. If the combined yields of imine and polymer are taken as a measure of reaction, there seems to have been a definite steric influence on the reduction of chloro- and methyl-substituted benzonitriles. Electronic effects appear to have influenced yields less than steric ones, but the electronic character of substituents does seem to have strongly influenced polymerization of the aldimines. For example, the tolualdimines, the only compounds prepared which have electron-donating substituents on the ring, polymerized much more readily than either benzaldimine or the benzaldimines having electron-withdrawing substituents.

Experimental

p-Cyanobenzoic Acid.—The synthesis of this compound reported by Valby and Lucas,[7] involving the reaction of a cuprous chloride–sodium cyanide mixture with diazotized p-aminobenzoic acid, was modified to include 0.1 mole of cupric sulfate in the cyanide mixture. A 75% yield of nitrile after recrystallization (m.p. 219°) was obtained; a yield of 45% (m.p. 216°) is reported for the unmodified method.

Anal. Calcd. for $C_8H_5NO_2$: N, 9.52. Found: N, 9.65.

o- and p-Trichloromethylbenzonitrile.—The *ortho* isomer was obtained in 85% yield by bubbling dry gaseous chlorine into a mixture of 1 mole of o-tolunitrile and 5 g. of phosphorus pentachloride at 180° until the theoretical weight of chlorine had been taken up (70 hr.). The mixture was vacuum distilled and the nitrile (b.p. 146°/0.15 mm., m.p. 96.5°) was recrystallized from hot absolute ethanol. Similar results were obtained under quartz lamp illumination by Yagupol'skii and Man'ko.[8]

Anal. Calcd. for $C_8H_4Cl_3N$: N, 6.34. Found: N, 6.32.

The *para* isomer was prepared in 11% yield by bubbling dry gaseous chlorine into p-tolunitrile at 180° under strong light. The light source was a 200-w. unfrosted, incandescent light bulb. After 40 hr., the mixture was distilled; the nitrile was recrystallized (m.p. 209°) from hot absolute ethanol.

Anal. Calcd. for $C_8H_4Cl_3N$: N, 6.34. Found: N, 6.39; neut. equiv. of terephthalic acid; 166; neut. equiv. of the hydrolyzed nitrile: 167.

3-Cyanopyridine.—A 60% yield of nitrile was obtained by dehydration of nicotinamide with a 30% molar excess of phosphorous pentachloride. Final purification was by distillation (m.p. 50°).

Preparation of the Stannic Halide Complexes.—The method of preparing the intermediate complexes was similar to that of Stephen.[6] A mixture of diethyl ether and anhydrous stannous halide was saturated with the corresponding hydrogen halide giving two liquid layers, a clear, colorless ethereal layer over a clear, pale yellow layer of stannous halide–hydrogen halide–ether complex. Nitrile was added to the mixture with stirring, giving immediate though not vigorous reaction. Precipitation of the stannic complex usually occurred within 12 hr., although in some cases several days was required; once begun, it was usually complete within 12 hr. In order to push the reaction as near completion as possible, the mixtures were resaturated with hydrogen halide every 12 hr. until precipitation seemed complete. In a typical reaction, 500 ml. of anhydrous ether, 1.5 moles of stannous halide, and 0.5–0.6 mole of nitrile were used.

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(7) E. P. Valby and H. J. Lucas, *J. Am. Chem. Soc.*, **51,** 2718 (1929).

(8) L. M. Yagupol'skii and N. I. Man'ko, *Zh. Obshch. Khim.*, **23,** 988 (1953); *Chem. Abstr.*, **48,** 8194 (1954).

TABLE II

DERIVATIVES OF ALDIMINES AND THEIR HYDROLYSIS PRODUCTS

	RCH=NH derivative m.p. (lit.), °C.[a]				RCH=O derivative m.p. (lit.), °C.[a]		
R	Hydrochloride	Oximide[b]	Phenylthiourea[c]	Benzenesulfonamide[d]	2,4-Dinitrophenylhydrazone	Oxime	Semicarbazone
C_6H_5	203 (203–204)[e]				235–236	35	222
$C_6H_5CH_2$	173 (180)[e]			84–86	110		153–154
$(C_6H_5)_2CH$						120 (120)[f]	
o-$CH_3C_6H_4$	239		225 dec.		193		212
m-$CH_3C_6H_4$		200		200	194 (193–195)[g]		203–205
p-$CH_3C_6H_4$		212 dec.			234		233
o-ClC_6H_4	111				206		226
p-ClC_6H_4	226	149			264 dec. (270)[h]		230
p-$HO_2CC_6H_4$	237				287 dec. (260)[h]	209	199
o-$Cl_3CC_6H_4$	194		212		111[i]		
p-$Cl_3CC_6H_4$	172				112[i]	209[i]	
p-$OCHC_6H_4$					278 dec.[i]	155	
α-$C_{10}H_7$	195		292			98	221
α-$C_{10}H_7CH_2$	65		223			118–119	208

[a] Experimental values are uncorrected. Literature values are cited only for those derivatives not found in common reference works such as Heilbron's "Dictionary of Organic Compounds," Oxford University Press, New York, N. Y. [b] Prepared by boiling a 2:1 mixture of ethyl oxalate and imine for two minutes and recrystallizing the product from ethanol. [c] Prepared by boiling a 1:1 mixture of phenylthiourea and imine for two minutes, and then cooling the mixture to 0° and filtering. The product was washed with ligroin and was recrystallized from ethanol. [d] Prepared by warming a mixture of equal parts of benzenesulfonyl chloride and a 1:1 solution of absolute ethanol and imine for five minutes, followed by slowly adding 10% sodium hydroxide solution until reaction ceased. The product was recrystallized from ethanol. [e] Ref. 3. [f] Ref. 5. [g] F. Sorm, M. Suchy, and V. Herout, *Chem. Listy*, **46**, 55 (1952). [h] J. J. Blanksma and M. L. Wackers, *Rec. trav. chim.*, **55**, 655 (1935). [i] No literature reference found.

All of the complexes were stable, crystalline solids. There was no difficulty in filtering, washing, and drying the precipitates, and no change was apparent when they were stored for long periods in the dark. Some discoloration and decomposition did occur in samples which were stored in the light or which were inadequately dried.

The choice of halide used in a complex was based, whenever possible, on reported yields of that complex in the Stephen reaction. Stannous chloride was used in preparing the complexes of aldimines 1–3, 5, and 6 in Table I, while the bromide was used for the complexes of aldimines 4 and 7–13. Complexes from each halide were prepared only in the cases of benzaldimine and p-tolualdimine; in each case yields of both the complex and the imine were equivalent. Anhydrous stannous chloride was prepared by the dehydration of the dihydrate with a two-fold molar excess of acetic anhydride.[6] Anhydrous stannous bromide was obtained by gradually distilling water from the solution resulting from reaction of metallic tin and aqueous hydrogen bromide until only molten salt remained (at about 450°). No advantage was found in distilling the salt (620°), so in most cases the melt was simply poured into a porcelain dish and allowed to cool in dry air. The resulting cake was powdered and stored in the dark.

Decomposition of the Intermediate Complexes.—Diethyl ether, pyridine, acetone, dimethylformamide, ethyl formate, and 1,4-dioxane were tested as solvents for the decomposition reaction; due primarily to the ease of handling, diethyl ether proved to be the most satisfactory and was used throughout the study.

The stannic complexes of benzaldimine, phenylacetaldimine, diphenylacetaldimine, and p-tolualdimine were used in evaluating agents for the decomposition step. The compounds found to be most effective were triethylamine, tributylamine, silver acetate and sodium acetate. Each reagent gave about the same yields, but triethylamine proved to be the most generally satisfactory. Tributylamine is difficult to separate from the imine, sodium acetate seems to enhance polymerization, and silver acetate is too expensive in the quantities required. Incomplete decomposition with the release of at least some imine was achieved with ammonia, pyridine, dimethylformamide, sodium methoxide, sodium ethoxide, diethylamine, ethylenediamine, hydrogen sulfide, and heat under vacuum. Treatment of the complexes with sodium iodide failed to release any imine.

The amount of solid complex which precipitated was not a good criterion of the extent of reaction. For this reason yields are based on the amount of nitrile used initially and on the amount of monomeric imine actually isolated. It was often possible to obtain higher yields by treating the complex-containing mixture directly rather than by isolating the complex before decomposition; for example, treatment of the isolated complex gave a 70% overall yield of benzaldimine, while treatment of the reaction mixture gave a 94% yield. As a matter of economy ammonia was bubbled into the reaction mixture to remove excess hydrogen halide before the triethylamine (five times the molar quantity of nitrile) was added. In cases where unchanged nitrile and imine were difficult to separate by distillation, it was often more convenient to isolate the complex and wash it free of nitrile before the aldimine was liberated. In these cases ammonia was bubbled into a slurry of the complex in ether until reaction ceased; triethylamine was then added. Usually 5–6 moles of amine for each mole of nitrile were required.

Aldimines.—Following the decomposition step, the reaction mixtures were composed of a clear, colorless liquid containing the imine and a heavy, sometimes gummy solid. The aldimines were isolated by either distillation or precipitation as the hydrochloride, from which the imine was regenerated with liquid ammonia. Imines were purified by fractional distillation when possible; footnotes in Table I indicate the compounds purified by recrystallization or sublimation. Derivatives of the aldimines and their hydrolysis products are shown in Table II.

Yields of aldimines by this method are not always reproducible; the tendency for the yields to fluctuate seems greatest with benzaldimine. No explanation for the variation has been found.

The preparation of six aldimines not shown in Table I was attempted without success. No imine was liberated when the reaction mixtures of 2- and 3-cyanopyridine and 4-cyanobenzaldehyde were treated with triethylamine, but treatment with cold water did give the corresponding aldehydes, indicating that reduction had occurred. A trace of imine was obtained by reduction of p-nitrobenzonitrile, but attempts to further reduce the major product, p-aminobenzonitrile, and its N-acetyl derivative failed.

Molecular refractivities were calculated and computed for the five aldimines on which refractive index and density measurements were made. The value 7.154 was used for the structural unit, $>C=NH$, in the calculation; this value was obtained by comparing calculated and computed refractivities for twelve alkyl aryl ketimines reported by Pickard.[9] The refractivities found are: calcd. for $C_6H_5CH=NH$, 33.542, comp., 32.886; calcd. for o-$H_3CC_6H_4CH=NH$, 38.189, comp., 37.813; calcd. for p-$H_3CC_6H_4CH=NH$, 38.189, comp., 37.020; calcd. for o-$ClC_6H_4CH=NH$, 38.354, comp., 37.806; calcd. for p-$HO_2CC_6H_4CH=NH$, 39.744, comp., 41.198.

Acknowledgment.—The authors wish to thank the Phillips Petroleum Company whose grants supported this work.

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(9) P. L. Pickard and D. J. Vaughan, *J. Am. Chem. Soc.*, **72**, 876 (1950); P. L. Pickard and S. H. Jenkins, Jr., *ibid.*, **75**, 5899 (1953).