Anal. Calcd. for $C_{15}H_{18}N_4O_5$: C, 53.88; H, 5.43. Found: C, 53.99; H, 5.44.

The analysis corresponds to the 2,4-dinitrophenylhydrazone of the ethoxyallenal; λ_{max} 3720 (ϵ 33,100).

Reactions of Cumulenal (3).—The aldehyde (0.12 g.) and maleic anhydride (0.11 g.) were allowed to stand in ethyl ether (10 ml.) for 60 hr. at room temperature. After removal of the solvent, the residual oil had an infrared spectrum characteristic of the two reactants.

The aldehyde was refluxed with a trace of *p*-toluenesulfonic acid in 90% tetrahydrofuran–water for 24 hr. After work-up, the residual oil had an infrared spectrum identical to that of the dihydropyrone (4).

A mixture of tetracyanoethylene and cumulenal in ether shows no apparent color change. Heating at 100° after removal of the solvent produces a black solid with neither cumulene nor allene absorption in the infrared.

A mixture of cumulenal and methylamine hydrochloride in acetonitrile at room temperature for 3 days in concentrations of *ca.* 0.05 *M* yielded an oil with an infrared spectrum almost identical to that of starting material.

Ultraviolet and Infrared Spectra.—Spectra were measured using 1-cm. cells and a Cary Model 11 spectrophotometer. Infrared spectra were obtained with an Infracord or, in the case of pure compounds, a Baird double beam instrument (Model B or Model 4-55).

Nuclear Magnetic Resonance Spectra.—Measurements were made on a Varian Associates HR-60 instrument at 60 Mc. Spectra were run on dilute carbon tetrachloride solutions (15–20%) and with a benzene capillary for reference except for the dihydropyrone (4) which was measured with a Varian Associates A-60 instrument with tetramethylsilane as reference. Approximate conversion to τ-values was made by the addition of 3.52.

Acknowledgment.—The authors are grateful to Dr. James W. Patton for obtaining many of the n.m.r. spectra and to Dr. S. Seltzer of Brookhaven National Laboratory for the A-60 spectrum. We are indebted to Professor J. D. Roberts, Dr. F. C. Nachod, and Dr. Paul C. Lauterbur for helpful criticism and advice.

Some Unsaturated Imines

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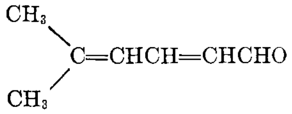
The synthesis of the unsaturated imines derived from *n*-butylamine and 5-methyl-2,4-hexadienal and 2,4-hexadienal is reported. The former could not be cyclized to a 1,2-dihydropyridine. The *n*-butylimine of crotonylideneacetone is formed in the reaction of crotonaldehyde and the *n*-butylimine of acetone. A large and striking shift of the ultraviolet maximum of the unsaturated imines to longer wave lengths occurs on protonation. The synthesis of 5-methyl-2,4-hexadienal and its formation from 2,2-dimethyl-3,4-dihydro-4*H*-pyran-4-ol as well as another acid-catalyzed reaction of the latter are described. The ultraviolet spectra of the aldehyde and 2,4-hexadienal in solvents of a wide range of **Z**-value are reported.

In connection with some attempted syntheses of 1,2-dihydropyridines, a number of unsaturated imines were prepared. Certain of their properties were investigated and are here reported.

Results

Dienals.—The unsaturated aldehyde, 5-methyl-2,4-hexadienal (1), was synthesized in 71% yield by the lithium aluminum hydride reduction of 5-methyl-5-hydroxy-1-methoxy-3-hexyn-1-ene[2] followed by acid hydrolysis according to the general procedure of Inhoffen and co-workers.[3]



$(CH_3)_2C{=}CHCH{=}CHCHO$

1

The aldehyde was also prepared by the reaction of 1-methoxy-5-methyl-5-hydroxy-1-*trans*,3-*cis*-hexadiene with boron trifluoride. The ultraviolet spectrum of the aldehyde was measured in solvents of different polarity (as measured by **Z**-value).[4,5] Data for the aldehyde (1) and the closely related sorbaldehyde (2) are listed in Table I.

TABLE I

ULTRAVIOLET ABSORPTION DATA FOR ALDEHYDES

	Aldehyde	
Solvent (Z)[a]	5-Methyl-2,4-hexadienal[d] (**1**) λ_{max}, Å. (ϵ_{max})	2,4-Hexadienal[c] (**2**) λ_{max}, Å. (ϵ_{max})
Isoöctane (60.1)	2742 (31,000)	2604 (28,600)
Acetonitrile (71.3)	2838 (30,900)	2690 (31,800)
2-Propanol (76.3)	2858 (29,200)	.. ...
Methanol (83.6)	2866 (29,000)	2712 (30,100)
Water (94.6)	2964 (27,800)	2797 (29,700)
TFP[b] (96.3)[e]	2958 (30,300)	2779 (29,600)
10 *M* LiCl (106.8)[e]	3058 (21,000)	2882 ...

[a] Ref. 4. [b] 2,2,3,3-Tetrafluoropropanol. [c] Sorbaldehyde. [d] $n \rightarrow \pi^*$ transition in isoöctane at 3330 Å. [e] Ref. 5.

The 5-methyl-2,4-hexadienal was formed by heating 2,2-dimethyl-3,4-dihydro-4*H*-pyran-4-ol (3) in tetrahydrofuran saturated with hydrogen chloride, as shown by the infrared spectrum of the product and the isolation of the 2,4-dinitrophenylhydrazone. It was of some interest that the pyranol, which is readily available from the lithium aluminum hydride reduction of the corresponding ketone,[2] did not form the dienal with aqueous hydrochloric acid. Instead, a rapid reaction led to a solution thought to contain 5-hydroxy-5-methyl-*cis*-2-hexenal (4) with λ_{max} 2325 Å. (ϵ 7300). Crotonaldehyde had λ_{max} 2235 Å. (ϵ 16,000) in the same medium. Attempted isolation of the *cis*-aldehyde by extraction with ether led to a material with a camphoraceous odor and negligible ultraviolet absorption past 2100 Å. This material was probably the 2-isomer (5) of the 4-pyranol. The n.m.r. data for the 4-pyranol are tabulated in Table II and the n.m.r. spectrum shown in Fig. 1. The reactions of the pyran-4-ol are shown in equa-

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[2] E. M. Kosower and T. S. Sorensen, *J. Org. Chem.*, **28**, 687 (1963).

[3] H. H. Inhoffen, F. Bohlmann, and G. Rummert, *Ann.*, **569**, 226 (1950).

[4] E. M. Kosower, *J. Am. Chem. Soc.*, **80**, 3253 (1958).

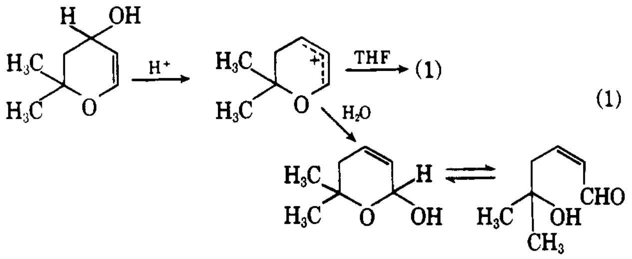
[5] E. M. Kosower and G.-S. Wu, *ibid.*, **83**, 3142 (1961).

Table II

N.m.r. Spectrum of Dihydropyranol (**3**)

Band centered at *ca.*[a]	Interpretation
3.91 τ	6-H; split by 5-H, $J_{56} = 7$ c.p.s.
5.41 τ	5-H; split by 6-H, $J_{56} = 7$ c.p.s. and split by 4-H, $J_{45} = 4$ c.p.s.
5.92 τ	4-H; split by 3-CH_2 triplet apparent but unresolved.
6.82 τ	4-OH
8.13 τ 8.23 τ	3-CH_2 group, axial and equatorial H each split by 4-H, $J = 6$ c.p.s.[b]
8.82 τ 8.91 τ	Two methyl groups, equatorial and axial

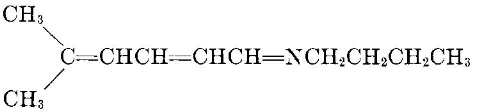
[a] Band positions measured against benzene capillary reference and converted to τ-values by addition of 3.52. [b] Geometric relationship of pseudoequatorial (or pseudoaxial) hydrogen to methylene hydrogens implies similar coupling constants for the non-equivalent methylene hydrogens.



(1)

tion 1. Previous attempts to prepare aliphatic *cis*-alkenals have failed.[6]

Imines.—Reaction of methylamine and **1** in ether over potassium carbonate produced the *N*-methylimine of **1**, a compound **6** with an odor reminiscent of raw mushrooms. The similarity in the boiling points of the *N*-methylimine and the aldehyde prompted the preparation of the corresponding *N*-butylimine **7**. Attempts to cyclize these compounds to 1,2-dihydropyridines using acid, peroxide, or light led either to polymer or mixtures which did not apparently contain the desired product.



$(CH_3)_2C{=}CHCH{=}CHCH{=}NCH_2CH_2CH_2CH_3$

7

A reported synthesis[7] of 1,2-dihydropyridines induced us to carry out the reaction of the *n*-butylimine of acetone (**8**) with crotonaldehyde in ethyl ether with *p*-toluenesulfonic acid as catalyst and molecular sieve 4A as drying agent. In our hands, the products were 27–35% of the *n*-butylimine of crotonaldehyde (**9**)[8] and 10–20% of a new compound which proved to be the *n*-butylimine of crotonylideneacetone (**10**). The latter had an equivalent weight of 162, an ultraviolet spectrum indicating at least three double bonds in conjugation, and neither carbonyl nor hydroxyl and/or amino group absorption in the infrared. Hydrogenation data confused the issue, since only two moles were absorbed per mole of compound but it was found that dimeric material accounted for a substantial proportion of the product, as has been reported in other cases of imine hydrogenation.[9] Hydrolysis of **7** with aqueous sodium carbonate–bicarbonate solution yielded a material with the same ultraviolet absorption maximum [2791 Å. (ϵ 22,000)] as crotonylidene acetone [λ_{max} 2791 Å. (ϵ 24,000)].[10] A 2,4-dinitrophenylhydrazone prepared from the hydrolysis product had the same melting point, 205–206°, as that reported for the derivative of crotonylidene acetone.[11]

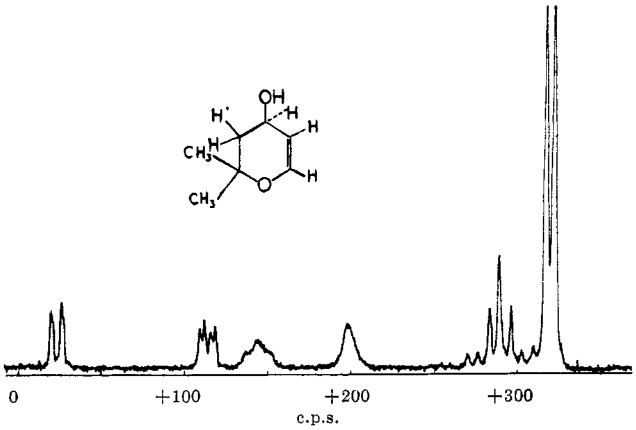


Fig. 1.—The n.m.r. spectrum of 2,2-dimethyl-3,4-dihydro-4*H*-pyran-4-ol (**3**).

The *n*-butylimine of sorbaldehyde (**11**) was prepared for comparison with **10** by reaction in ether over potassium carbonate.

Ultraviolet spectroscopic data for the unsaturated imines and the salts derived by the addition of perchloric acid to the acetonitrile solutions are listed in Table III.

Table III

Ultraviolet Absorption Data for Imines

Imine	Solvent	λ_{max}, Å. (ϵ_{max})	Protonated form[a] λ_{max} (ϵ_{max})
$CH_3CH{=}CHCH{=}N$-n-Bu[b] (**9**)	CH_3CN	2200 (23,300)	2475 (23,900)
$CH_3CH{=}CHCH{=}CHCH{=}N$-n-Bu (**11**)	CH_3CN	2617 (38,500)	3100 (39,900)
$(CH_3)_2C{=}CHCH{=}CHCH{=}N$-$n$-Bu (**7**)	CH_3CN	2735 (40,000)	3300 (40,000)
	Isoöctane	2708 (39,100)	
	CH_3OH	2810 (37,700)	
$CH_3CH{=}CHCH{=}CH\overset{CH_3}{\overset{\vert}{C}}{=}N$-$n$-Bu (**10**)	CH_3CN	2615 (29,200)	3076 (30,500)

[a] Formed by the addition of a two- to threefold excess of 0.5 *N* perchloric acid in dioxane to an acetonitrile solution of the imine. [b] *n*-Butyl.

Discussion

All of the imines are sensitive to oxygen and must be stored under nitrogen. The α,β-unsaturated imines have a characteristic infrared absorption band between 1653 and 1667 cm.$^{-1}$, while the $\alpha,\beta,\gamma,\delta$-unsaturated imines have absorption between 1613 and 1630 cm.$^{-1}$.

The unsaturated imines were more resistant to acid hydrolysis or nucleophilic attack than the *n*-butylimine

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[6] G. Gamboni and H. Schinz, *Helv. Chim. Acta*, **41**, 1603 (1958).

[7] (a) *Chem. Abstr.*, **50**, 1926c (1956); (b) *Cf.*, however, footnote 19 of E. M. Kosower and T. S. Sorensen, *J. Org. Chem.*, **27**, 3764 (1962).

[8] H. C. Barany, E. A. Braude, and M. Pianka, *J. Chem. Soc.*, 1898 (1949).

[9] A. Skita and G. Pfeil, *Ann.*, **485**, 152 (1931).

[10] G.-S. Wu, unpublished results.

[11] R. Ahmad and B. C. L. Weedon, *J. Chem. Soc.*, 3815 (1953).

of acetone, as judged by the rate of formation of 2,4-dinitrophenylhydrazone derivatives. The imines of sorbaldehyde (**8**) and crotonaldehyde (**6**) were basic, with pK_a values of 8.5 and 8.6, respectively, as measured by the method of Hall[12] in acetonitrile solution.[13]

Ultraviolet Spectra.—Both aldehydes (**1**) and (**2**) have solvent-sensitive $\pi - \pi^*$ transitions. The magnitude of the sensitivity, *m*, calculated from the relationship of transition energy (E_T) and solvent polarity (**Z**) is comparable to that observed for $\pi \rightarrow \pi^*$ transitions of α,β-unsaturated ketones,[14] utilizing the equation, $E_T = m\,\mathbf{Z} + b$. However, the linearity of the relationship between E_T and **Z** is not so good as that found for cyclic unsaturated ketones, presumably because the open chain system has more conformational possibilities. It is noteworthy that the solvent sensitivity of the ultraviolet maximum of the *n*-butylimine of **1**, **7**, is almost the same as that of the aldehyde.

The most striking property possessed by the unsaturated imines is the large shift to longer wave length found for the ultraviolet maximum upon conversion to the protonated species. These data are listed in Table II along with the ultraviolet absorption data for the imines.

Experimental

5-Methyl-2,4-hexadienal (**1**).—An ethyl ether solution (100 ml.) of 5-methyl-5-hydroxy-1-methoxy-3-hexyn-1-ene[2] (8.0 g., 0.057 mole) was added over 1 hr. to a solution of lithium aluminum hydride (2.17 g., 0.057 mole) in ethyl ether (200 ml.). The reaction mixture was stirred for 4 hr. after addition and then treated cautiously with 4 *N* hydrochloric acid (100 ml.). The resulting two phases were stirred for 90 min., the ether layer separated and washed with saturated sodium bicarbonate solution and water. After drying over magnesium sulfate, the ether was removed and the residue distilled to yield 4.5 g. of **1**. Pure aldehyde has a b.p. 72–73°/8 mm., n^{25}D 1.5550, d^{27}_4 0.887. Infrared absorption bands for **1** are found at 2994, 2933, 2833, 2747, 1678, and 1631 cm.$^{-1}$.

Anal. Calcd. for $C_7H_{10}O$: C, 76.32; H, 9.15. Found: C, 76.25; H, 9.34.

The 2,4-dinitrophenylhydrazone was prepared in the usual way and recrystallized many times from acetonitrile, m.p. 210–212°, λ_{max} 3965 Å. (ϵ 38,000) in acetonitrile.

Anal. Calcd. for $C_{13}H_{14}N_4O_4$: C, 53.79; H, 4.86. Found: C, 54.43; H, 5.00.

The semicarbazide of the dienal (**1**) was recrystallized from 95% ethanol, m.p. 211.5–212.5°.

Anal. Calcd. for $C_8H_{13}N_3O$: C, 57.46; H, 7.84. Found: C, 57.44, H, 7.90.

1-Methoxy-5-methyl-5-hydroxy-1-*trans*,3-*cis*-hexadiene.—5-Methyl-5-hydroxy-1-methoxy-3-hexyn-1-ene (25.0 g.) was hydrogenated at room temperature and atmospheric pressure over 4.0 g. of Lindlar catalyst.[15] The reaction was interrupted after 1 mole of hydrogen per mole of starting material had been taken up. Distillation of the residue after removal of the catalyst gave 17.1 g. of material b.p. 95–103°/18 mm., n^{25}D 1.4920. Redistillation gave 13.9 g. liquid, b.p. 50.3–53°/0.7 mm., n^{25}D 1.4919, which contained some dienal ($\bar{\nu}_{C=O}$ 1680 cm.$^{-1}$) but was used in subsequent reactions. A solution of 1.0 g. of product in ethyl ether was treated with 10 mg. of boron trifluoride ethereate. A light green color developed immediately. After 8 hr. stirring, the boron trifluoride was neutralized with *t*-butylamine (6 mg.). Evaporation of the ether left a residue with an infrared spectrum identical to that of the dienal (**1**).

2,2-Dimethyl-3,4-dihydro-4*H*-pyran-4-ol (**3**).—A solution of lithium aluminum hydride (2 g., 0.053 mole) was prepared by refluxing the solid with ethyl ether (200 ml.) for 9 hr. under nitrogen. A solution of 2,2-dimethyl-3,4-dihydro-4*H*-pyran-4-one[2] (12.6 g., 0.1 mole) in ethyl ether (100 ml.) was added to the hydride solution over a 25-min. period. The mixture was stirred for 1 hr. after addition, water (100 ml.) was added, the ether phase separated and combined with an ether extract of the aqueous phase and dried over sodium sulfate. After removal of the ether, the colorless residue was distilled, b.p. 35–38°/0.2 mm., to yield 11.5 g. (90%) of the alcohol. Redistillation removed a small amount of carbonyl compound in the early fractions and provided pure **3**, b.p. 35–37°/0.2 mm., n^{30}D 1.4651.

Anal. Calcd. for $C_7H_{12}O_2$: C, 65.59; H, 9.40. Found: C, 65.42; H, 9.54.

Infrared: 3290 cm.$^{-1}$ (hydroxyl), 1642 cm.$^{-1}$ (double bond). Ultraviolet: λ_{max} 1980–1990 Å. (ϵ 6400) [dihydropyran: λ_{max} 1950 Å. (ϵ 3800)].[16]

The n.m.r. spectrum is shown in Fig. 1 and described in Table I. The relative areas of the peaks (by weight) are (from lower to higher field) 1:1:1:1:2:6:7

Acid Rearrangement of Dihydropyranol (**3**).—A solution of the alcohol (0.1 g.) in ethanol (3 ml.) was diluted with water to 15 ml. and treated with 2 drops of 60% perchloric acid. Acidic 2,4-dinitrophenylhydrazine was added; the orange needles which separated were filtered off and recrystallized from aqueous ethanol to give 5-methyl-5-hydroxy-*cis*-2-hexenal 2,4-dinitrophenylhydrazone, m.p. 160–161° (in bath at 150°). In some instances, a yellow isomer formed, m.p. 161–162° (turned red at about 100°). The red isomer was observed to turn yellow when the crystals were allowed to stand in contact with a small amount of solvent. The ultraviolet spectrum of both red and yellow forms in methanol was the same, λ_{max} 3728 Å. (ϵ 29,200).

Anal. Calcd. for $C_{13}H_{16}N_4O_5$: C, 50.64; H, 5.23. Found (red isomer): C, 50.81; H, 5.32. Found (yellow isomer): C, 50.75; H, 5.41.

In another experiment, 2.6 g. of dihydropyranol (**3**) was added to 0.5 *N* perchloric acid in 30% methanol-water and allowed to stand, 3 min. After ether extraction and removal of the ether, a colorless oil was distilled into a trap at −78°, b.p. <25°/0.1 mm. The ultraviolet spectrum in ethanol had only end absorption and the infrared spectrum had no carbonyl band, very weak hydroxyl band, and a medium intensity band at 1639 cm.$^{-1}$. The yield was 40%, assuming the structure, 6,6-dimethyl-2-methoxy-5,6-dihydro-2*H*-pyran.

Conversion to 1.—A solution of dihydropyranol (**3**) (26.6 mg.) in dry, pure tetrahydrofuran was saturated with hydrogen chloride and refluxed for 30 min. The ultraviolet absorption of an aliquot occurred at 2822 Å. (ϵ 27,000). Evaporation of the solvent gave a yellow oil with an infrared spectrum similar to that of the dienal. Acidic 2,4-dinitrophenylhydrazine yielded 35 mg. (73%) of a brick red precipitate, m.p. 197–205°.

***N*-Methylimine of 1** (**6**).—The dienal (**1**) (10.0 g.) in ethyl ether (150 ml.) was mixed with dry potassium carbonate (20 g.) and methylamine bubbled into the solution for 2 hr. After 2 hr. additional stirring, the reaction mixture was allowed to stand overnight. The ether was removed and the residue distilled under nitrogen, b.p. 35–37°/0.15 mm. The distillate crystallized below room temperature. The infrared spectrum had a strong band at 1634 cm.$^{-1}$, but absorption at 1681 cm.$^{-1}$ indicated contamination by starting aldehyde, which had about the same boiling point.

Treatment with 0.5 *N* perchloric acid in dioxane formed black tars. A solution of the imine in ether gave a precipitate of the salt with *p*-toluenesulfonic acid. Attempted distillation of the imine from small amounts of benzoyl peroxide resulted in polymerization, no distillable product being formed.

***n*-Butylimine of 1** (**7**).—*n*-Butylamine (7.3 g.) reacted with the dienal (**1**) in the manner described for the methylimine except that 10 hr. stirring was used. The product distilled at 49.5–52.5°/0.15 mm., n^{25}D 1.5279 as a colorless liquid. Yield 10.6 g. (85%).

Anal. Calcd. for $C_{11}H_{19}N$: C, 79.94; H, 11.59. Found: C, 80.16; H, 11.67.

Photolysis of 7.—The *n*-butylimine (**7**) (1.18 g.) in 4.5 l. of redistilled pentane was irradiated with a Hanovia mercury vapor lamp (cat. no. 679 A-36) in an immersion well fitted with a Corex sleeve. Optical density at 2710 Å. of an aliquot decreased from 3.2 to 0.62 in 102 hr. The pentane was removed through a

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[12] H. K. Hall, Jr., *J. Phys. Chem.*, **60**, 63 (1956).

[13] Data have been reported in ref. 7b.

[14] E. M. Kosower, G. S. Wu, and T. S. Sorensen, *J. Am. Chem. Soc.*, **83** (1961).

[15] H. Lindlar, U. S. Patent 2,681,938; *Chem. Abstr.*, **49**, 10375h (1955).

[16] J. R. Platt, H. B. Klevens, and W. C. Price, *J. Chem. Phys.*, **17**, 466 (1949).

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]

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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).