This compound was homogeneous by thin layer chromatography, using ethyl acetate as developer. It gave a negative ninhydrin test. It was unstable at room temperature but could be stored, under dry conditions, for several weeks.

Phenyl 2-Acetamido-3,5,6-tri-*O*-acetyl-2-deoxy-β-D-glucofuranoside (III).—Crude II (7.2 g) and phenol (8.2 g) were gently fused and *p*-toluenesulfonic acid (100 mg) was added to the melt. The melt was heated, with stirring, for 1 hr at 110–115°. After cooling, the residue was extracted with chloroform and the extract was washed repeatedly with 1 *N* sodium hydroxide and water. The dried (magnesium sulfate) chloroform solution was evaporated to dryness and the residue was dissolved in methanol. This solution was decolorized with activated carbon and the solvent was evaporated. The colorless syrup remaining was crystallized from ether: yield 1.60 g (17%); mp 72–85° (several recrystallizations from methanol–ether failed to improve the melting point); $[\alpha]^{18}\text{D}$ $-80 \pm 2°$ (*c* 2.37, chloroform); $\lambda_{\text{max}}^{\text{KBr}}$ 3.1 (NH), 5.74 (OAc), 6.03, 6.42 (NHAc), 6.25, 6.71 (aryl C=C), and 14.47 μ (substituted benzene); nmr data (deuteriochloroform), δ 1.95, 2.00, 2.04 (12 protons, OAc, NAc), 3.82–4.82 (four protons, sugar ring), 5.12–5.57 (two protons, sugar ring), 5.68 (one-proton doublet, $J_{1,2}$ = 1 cps, H1′), 6.82–7.67 (seven protons, phenyl and NH) ppm; X-ray powder diffraction data, 16.06 w, 12.27 m, 9.21 s (3), 6.10 m, 5.30 s (1), 4.90 w, 4.59 vw, 4.27 m, and 4.00 s (2).

Anal. Calcd for $C_{20}H_{25}NO_9$: C, 56.71; H, 5.95; N, 3.31. Found: C, 56.44; H, 6.25; N, 3.51.

This compound was homogeneous by thin layer chromatography using ethyl acetate as developer.

Phenyl 2-Acetamido-2-deoxy-β-D-glucofuranoside (IV).—To the fully acetylated phenyl glycoside (III, 1.49 g) in anhydrous methanol (50 ml) was added sodium (0.1 g) and the solution was maintained for 2 hr at room temperature. The solution was neutralized to pH 7 by the addition of Amberlite IR-120 (H^+) resin. The resin was removed by filtration and washed with methanol. The filtrate and washings were evaporated to dryness. The residue was dissolved in ethanol and the solution was decolorized with activated carbon. The syrup obtained on solvent removal was crystallized from ethyl acetate, yield 0.78 g (79%), mp 136–138°. Recrystallization from methanol–ethyl acetate yielded pure material: mp 137–138°; $[\alpha]^{21}\text{D}$ $-104 \pm 2°$ (*c* 1.46, acetone); $\lambda_{\text{max}}^{\text{KBr}}$ 2.9–3.1 (OH,NH), 6.05, 6.48 (NHAc), 6.15, 6.35, 6.71 (aryl C=C), and 14.47 μ (substituted benzene); X-ray powder diffraction data, 14.48 w, 10.04 m, 9.40 m, 8.58 vw, 7.43 w, 7.02 m, 6.46 vw, 6.06 m, 5.15 s (3), 4.92 vw, 4.64 s, 4.43 s(1), 4.21 vw, 4.07 s (2), 4.05 m, 3.67 m, 3.56 m, 3.37 vw, and 3.29 w.

Anal. Calcd for $C_{14}H_{19}NO_6$: C, 56.70; H, 6.44; N, 4.71. Found: C, 56.63; H, 6.48; N, 4.75.

This compound was homogeneous by thin layer chromatography using ethyl acetate–methanol (4:1) as developer.

9-(2-Acetamido-3,5,6-tri-*O*-acetyl-2-deoxy-D-glucofuranosyl)-2,6-dichloropurine (V).—Finely ground II (4.73 g) and 2,6-dichloropurine (2.30 g) were mixed and fused at 110–120°. *p*-Toluenesulfonic acid (60 mg) was added and the melt was well stirred and heated for 10 min at 110–120°. The cooled melt was extracted with chloroform and the extract was filtered. The filtrate was washed successively with cold, saturated, aqueous sodium bicarbonate solution and water and dried (magnesium sulfate). The residue obtained on solvent removal at 40° was dissolved in methanol and the solution was decolorized with activated carbon. The solution was evaporated to a syrup, which was crystallzed from methanol–ether, yield 0.75 g (10%), mp 148–150°. Further recrystallizations produced pure material: mp 152–153°; $[\alpha]^{25}\text{D}$ $+7 \pm 1°$ (*c* 1.56, methanol); $\lambda_{\text{max}}^{\text{KBr}}$ 3.1 (NH), 5.68 (OAc), 6.05, 6.25, 6.42, and 6.75 μ (NHAc, purine); $\lambda_{\text{max}}^{\text{MeOH}}$ 253 mμ (sh, ε 4960), 274 mμ (ε 9410); nmr data (deuterioacetone), δ 2.03, 2.06, 2.08, 2.17 (12 protons, NAc, OAc), 4.00–5.05 (four protons, sugar ring), 5.37–5.83 (two protons, sugar ring), 6.40 (one-proton doublet, $J_{1,2}$ = 4 cps, H1′), 8.09 (one-proton broad doublet, NH at 2′), 8.86 (one-proton singlet, H-8) ppm; X-ray powder diffraction data, 13.39 m, 11.48 s (3), 9.61 m, 8.50 s (2), 7.76 w, 6.91 w, 6.41 s (2), 5.86 w, 5.43 w, 5.21 vw, 4.71 w, 4.69 s (1), 4.25 vw, 4.17 vw, 4.00 vw, and 3.90 m.

Anal. Calcd for $C_{19}H_{21}Cl_2N_5O_8$: C, 44.02; H, 4.08; Cl, 13.68; N, 13.51. Found: C, 43.55; H, 4.29; Cl, 13.89; N, 13.75.

This compound was homogeneous by thin layer chromatography using ethyl acetate as developer.

Attempts to remove the *O*-acetyl groups and to replace the chlorine atoms in this nucleoside derivative did not lead to crystalline products.

Acknowledgment.—We are pleased to acknowledge the counsel of D. Horton in interpreting the nmr data.

The Synthesis of Aldehydes from the Reaction of Amines with Butadiene

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The interaction of butadiene and amines in the presence of alkali metal compounds, such as hydrides and amides, has been found to give aldimine products. Upon acid hydrolysis, the major component was a novel C_{12} aldehyde (I) containing a quaternary carbon system. A structural assignment has been made from infrared and nmr spectroscopy and by the independent synthesis of an amine derivative. The formation of this aldehyde can be directed to high yields by the utilization of *t*-butylamine and certain aldimine reactants.

The alkali metal initiated addition of ammonia and amines to conjugated diolefins was first described in 1929.[1] Since then a number of related investigations have been reported.[2] For the most part, the reactions of secondary amines with 1,3-butadiene afforded good yields of simple butenyl compounds, whereas the major products from primary amines were of a higher molecular weight; *i.e.*, they contained more than 2 moles of butadiene per mole of amine.

Upon infrared examination of the products obtained from the reaction of butadiene and some primary amines, we observed absorption bands characteristic of aldimine compounds, and were able to isolate aldehydes after hydrolysis. The preparation, isolation, and structural proof of these compounds will be described herein, along with related reactions.

The interaction of methylamine, butadiene (1:1 molar ratio), and a catalytic quantity of an alkali metal compound, such as sodium hydride, was found to give a mixture of amines and aldimine materials. Separation of these materials was obtained by steam distillation from a dilute acid solution (Scheme I).

Scheme I

$$CH_2{=}CH{-}CH{=}CH_2 + CH_3NH_2 \xrightarrow{NaH} \xrightarrow[\text{steam distillation}]{H+} \begin{array}{c}\text{steam volatiles}\\ C_8\text{ aldehyde,}\\ C_{12}\text{ aldehyde I}\end{array} + \begin{array}{c}\text{acid solubles}\\ CH_3NHC_4H_7,\ CH_3N(C_4H_7)_2,\\ \text{high-boiling amines}\end{array}$$

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[1] O. Schmidt, F. A. Fries, and L. Kollek, German Patent 528,466 (1931); British Patent 313,934 (1929).

[2] (a) I. D. Danforth, U. S. Patents 2,495,890 and 2,518,528 (1950); (b) W. F. Gresham, R. E. Brooks, and W. M. Bruner, U. S. Patent 2,501,509 (1950); (c) L. D. Goodhue and C. E. Tissol, U. S. Patent 2,726,980 (1955); (d) I. E. Hyre and A. R. Bader, *J. Am. Chem. Soc.*, **80**, 437 (1958).

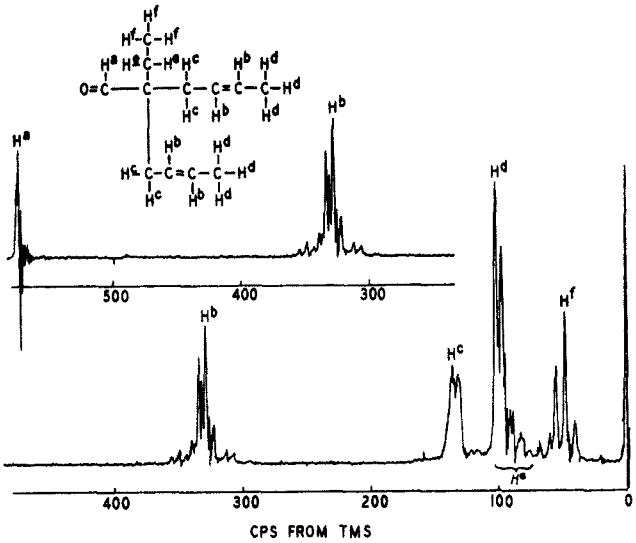


Figure 1.—Nmr spectrum of C_{12} aldehyde I.

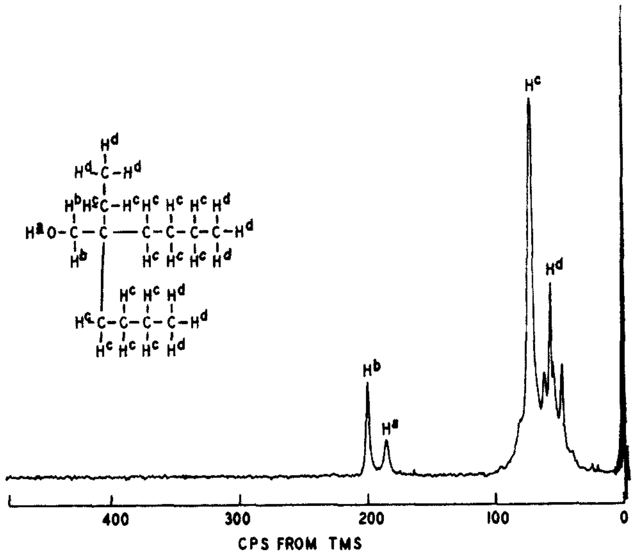
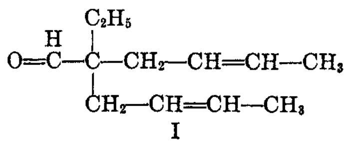


Figure 2.—Nmr spectrum of C_{12} alcohol II, 25 vol. % in carbon tetrachloride.

Neutralization of the residual solution gave low yields of butenyl- and dibutenylmethylamines, together with some higher boiling amines. Work-up and distillation of the steam distillate gave aldehydes which appeared to be C_8 and C_{12} compounds in yields of 4 and 14%, respectively.

A comparison of physical properties showed the C_8 aldehyde portion to be a mixture of approximately one part of 2-ethyl-2-hexenal[3] and four parts of 2-ethyl-4-hexenal. Hydrogenation of a sample over 10% palladium on charcoal gave only one compound, 2-ethylhexanal, which was identified by comparison of the infrared spectra and by the melting point of the 2,4-dinitrophenylhydrazone derivative.[4]

The nuclear magnetic resonance spectrum of the C_{12} aldehyde is shown in Figure 1. The assignment for each resonance was made as follows: H^a, aldehydic hydrogen, splitting (2 cps) probably due to long-range coupling or rotational isomerism; H^b, nonterminal olefinic hydrogens; H^c, methylene α to double bond with doublet caused by adjacent CH; H^d, methyl α to double bond with doublet due to splitting by adjacent CH; H^e, methylene β to CHO; and H^f, methyl γ to CHO, with triplet produced by adjacent methylene. The structure assignment was then made to be 2-(2-butenyl)-2-ethyl-4-hexenal (I). The absence of any

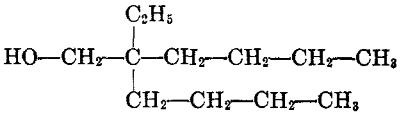


$$\mathrm{O{=}\overset{H}{C}-\underset{CH_2-CH{=}CH-CH_3}{\overset{C_2H_5}{C}}-CH_2-CH{=}CH-CH_3}$$

I

resonance for protons α to the carbonyl and the simple doublet, H^c, for the methylene groups α to the double bond were consistent only with compound I. In addition, the integral of the relative number of protons in each resonance was in excellent agreement with this structure.

Subsequently, a sample of I was hydrogenated over Raney nickel to give the saturated alcohol. The nmr spectrum is shown in Figure 2 with the resonance assignments being H^a, alcoholic hydrogen (shifted to 275 cps in undiluted sample); H^b, methylene α to OH, single peak; H^c, other methylene groups; and H^d, methyl groups. From these data the structure proposed for the alcohol was 2-*n*-butyl-2-ethylhexanol-1 (II). Therefore, compound II further confirmed the quaternary carbon structure for the aldehyde I in that H^b, the resonance for the methylene group α to the OH, was a single peak, whereas a CH β to the OH would have split this resonance.



$$\mathrm{HO-CH_2-\underset{CH_2-CH_2-CH_2-CH_3}{\overset{C_2H_5}{C}}-CH_2-CH_2-CH_2-CH_3}$$

II

The double bonds in aldehyde I are predominantly of the *trans* configuration. As is the usual case with addition reactions to butadiene, the infrared spectrum shows the presence of weak absorption bands which are characteristic of *cis* and terminal olefins. In addition, I appears to be composed of three components by gas chromatography having the form of a large peak with two small shoulders. However, the single carbon skeleton was demonstrated by the fact the alcohol II exhibited only one gas chromatographic peak.

In a reaction of butadiene and methylamine conducted at a 2:1 molar ratio, hydrolysis of a portion of this product afforded a 37% yield of I. Another portion was then hydrogenated over palladium on charcoal to give an 18% yield of di-*n*-butylmethylamine and a 33% yield of N-methyl-2-*n*-butyl-2-ethylhexylamine. This branched amino compound would be expected from the reduction of the methyl aldimine of I and its structure was confirmed by nmr analysis. In an effort to directly interrelate these compounds, the monomethylamine was reductively methylated to the dimethyl derivative with formaldehyde, and the aldehyde I was subjected to reductive amination in the presence of dimethylamine. The same dimethyl compound, N,N-dimethyl-2-*n*-butyl-2-ethylhexylamine (III), was obtained in both reactions.

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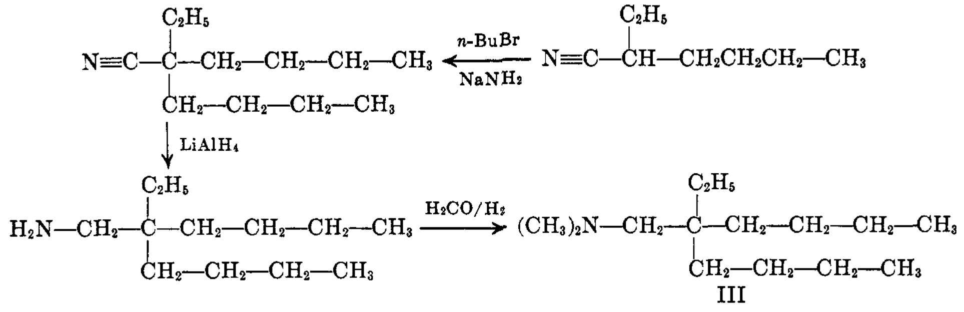
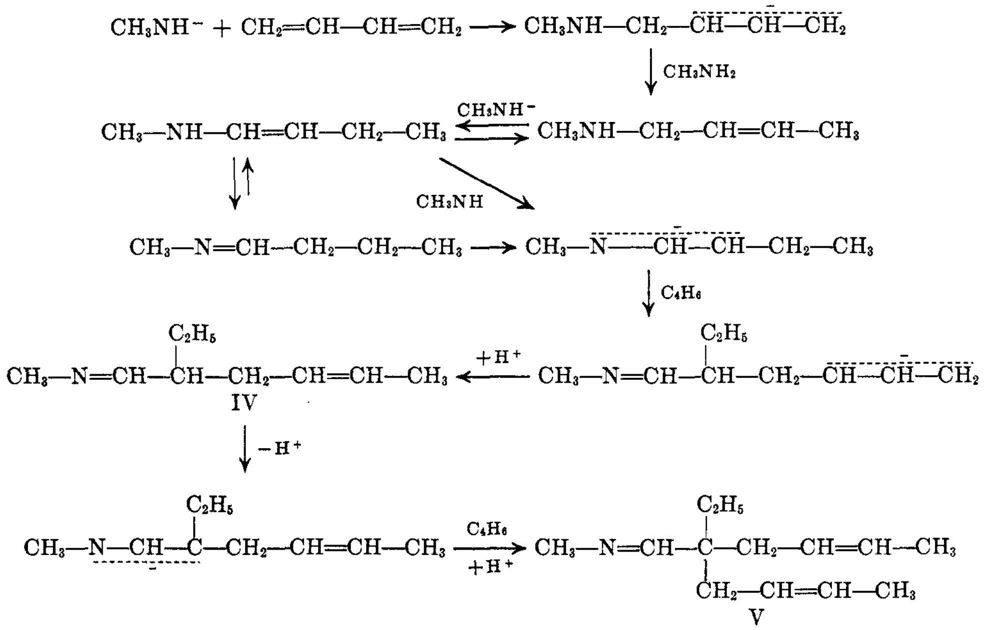
[3] T. M. Patrick, Jr., *J. Am. Chem. Soc.*, **74**, 2984 (1952); S. G. Powell and W. J. Wasserman, *ibid.*, **79**, 1934 (1957).

[4] C. Weizmann, E. Bergmann, and L. Haschelberg, *Chem. Ind.* (London), 587 (1937).

SCHEME II



SCHEME III



To prove unambiguously the carbon skeletal structures of these compounds, the dimethylamine III was synthesized by an independent method (Scheme II). 2-Ethylhexanal was converted to the oxime[5] and then dehydrated with acetic anhydride to give the known 2-ethylhexanonitrile.[6] Alkylation of the nitrile was accomplished by treatment with *n*-butyl bromide and sodium amide in refluxing toluene. This α-disubstituted nitrile was subsequently reduced to the amine with lithium aluminum hydride, and finally dimethylated with formaldehyde and hydrogen over platinum. The physical properties of this material proved to be identical with those of the previously described dimethyl compound III. The infrared spectra were superimposable and an admixture of hydrochlorides melted without depression.

One plausible explanation for the formation of aldimine intermediates is given in Scheme III. In the initial step, the methylamide anion adds to butadiene to give the amino-substituted butenyl anion. Since methylamine is present, this anion should readily abstract a proton to give butenylmethylamine thereby regenerating the methylamide base. In contact with this strong base, the 2-butenyl derivative undergoes isomerization to the 1-butenyl, which is the tautomer of the aldimine. The methylamide then effects a metalation of an acidic α hydrogen of the aldimine or of the hydrogen on the nitrogen of the 1-butenyl compound to give what may be regarded as an enolate or allyl-type resonance stabilized anion. Upon addition to butadiene and abstraction of a proton, the aldimine of 2-ethyl-4-hexenal is obtained. Since one α hydrogen remains, this final sequence can be repeated to give aldimine of I. Hydrolysis of compounds IV and V would, of course, give 2-ethyl-4-hexenal and I, respectively. 2-Ethyl-2-hexenal could then be formed by either isomerization of the 4-hexenal compound or by an aldol-type condensation of the butylidene aldimine. Undoubtedly, several variations can be readily embodied in the sequential order of proton abstractions or additions without departing from the over-all scheme.

Some precedence for the above reaction pathway can be found in the recent literature. Price and Snyder[7] have demonstrated that propenylamines are highly favored over allylamines in base catalyzed equilibria. A dimethyl sulfoxide solution of allyl dimethylamine in the presence of potassium *t*-butoxide soon reached an equilibrium containing 64% of the propenyl compound. Wittig and co-workers[8] found that aldimines could be metalated by lithium dialkyl amides and that these derivatives could then be condensed with certain aldehydes to give good yields of the addition products. In somewhat of a similar process, Stork and Dowd[9] reported that certain aldimines could

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(5) J. von Braun and G. Manz, *Ber.*, **67**, 1696 (1934).

(6) J. A. Krynitsky and H. W. Carbart, *Org. Syn.*, **32**, 65 (1952).

(7) C. C. Price and W. H. Snyder, *Tetrahedron Letters*, 69 (1962).

(8) G. Wittig, H. D. Frommeld, and P. Suchanek, *Angew. Chem.*, **75**, 978 (1963).

(9) G. Stork and S. R. Dowd, *J. Am. Chem. Soc.*, **85**, 2178 (1963).

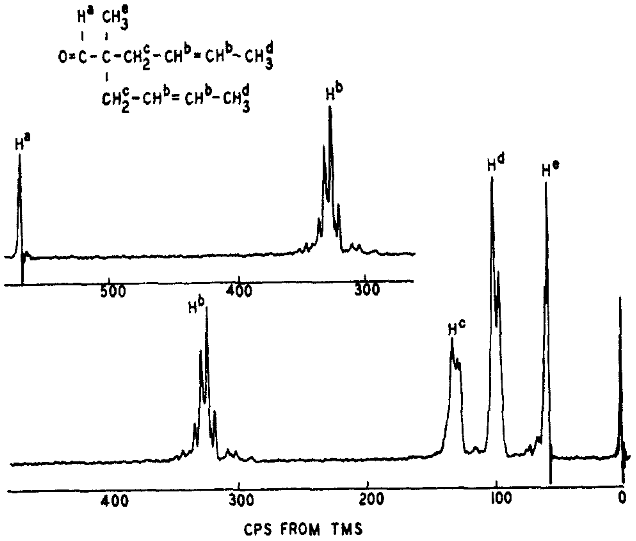

Figure 3.—Nmr spectrum of C_{11} aldehyde VI.

be metalated with Grignard reagents. These magnesium salts were found to react readily with halides to afford, after hydrolysis, good yields of substituted aldehydes.

In substantiation of the proposed reaction scheme, we found that N-butylidene-*n*-propylamine would react with butadiene in the presence of sodium amide. Hydrolysis of the product gave a 72% yield of the aldehyde I. Similarly, upon treating a mixture of N-butylidene-*t*-butylamine and butadiene with sodium amide, it was possible to distil from the reaction mixture aldimines containing the addition of 1 and 2 moles of butadiene in yields of 16 and 70%, respectively. The first compound, upon hydrolysis, gave again a mixture of 2-ethyl-2-hexenal and 2-ethyl-4-hexenal, while the latter gave the C_{12} aldehyde I.

Diallylamine, butadiene, and sodium hydride interact to give after hydrolysis a C_{11} aldehyde in 28% yield. In view of the structure of aldehyde I and the analytical and spectral data, this compound is 2-(2-butenyl)-2-methyl-4-hexenal (VI). The nmr spectrum is shown in Figure 3. The presence of a strong infrared absorption band at 10.35 μ indicates the double bonds to be predominantly of the *trans* configuration.

As summarized in Table I, the maximum yields of C_{12} aldehyde I from reactions involving methylamine were obtained in runs 2 and 4 in which a 2:1 molar ratio of butadiene to amine was used. With lithium hydride (run 3), no evidence of aldimine formation could be detected, and as indicated a good yield of the isomeric dibutenylmethylamines was obtained. This seems to be in accord with the proposed mechanism for the formation of aldehyde I, since lithium compounds are less prone to effect the isomerization of double bonds than the corresponding sodium or potassium compounds.

Upon interacting butadiene and sodium hydride with *n*-butylamine or with *n*-dodecylamine, the aldehyde I was obtained in low yield. However, considerable quantities of the mono- and dibutenylamines could be readily isolated from the acid layers. In the reaction of *n*-dodecylamine, butadiene, and lithium hydride (run 6), only a trace of aldimine material was detected but none of the aldehyde could be isolated, which is similar to the methylamine reaction (run 3).

TABLE I

REACTIONS OF AMINES AND BUTADIENE

No.	Amine	Molar ratio, C_4H_6 to amine	Catalyst	% yield Aldehyde I	% yield RN-$(C_4H_7)_2$	% yield RNH-(C_4H_7)
1	CH_3NH_2	1:1	NaH	14	15	6
2	CH_3NH_2	2:1	NaH	37	...	...
3	CH_3NH_2[a]	2:1	LiH	None	80	Trace
4	CH_3NH_2[b]	2:1	$KNHCH_3$	38	...	...
5	*n*-$C_4H_9NH_2$[c]	2:1	NaH	11	69	5
6	*n*-$C_{12}H_{25}NH_2$[d]	3:1	LiH	Trace	67[e]	21[f]
7	*n*-$C_{12}H_{25}NH_2$[g]	3:1	NaH	17	62	10
8	*t*-$C_4H_9NH_2$[h]	2:1	LiH	18	...	50[i]
9	*t*-$C_4H_9NH_2$[j]	3:1	NaH	56	...	...
10	*t*-$C_4H_9NH_2$[j]	2:1	NaH	71	...	7
11	*t*-$C_4H_9NH_2$[k]	2:1	NaH	78	...	...

[a] Exothermic reaction at 75°. [b] Exothermic at 25°. [c] Exothermic at 80°. [d] Heated at 120° for 5 hr. [e] Bp 136–138° (0.3 mm). *Anal.* Calcd for $C_{20}H_{39}N$: C, 81.8; H, 13.4. Found: C, 81.9, 81.7; H, 13.1, 13.4. [f] Bp 116–119° (0.3 mm). *Anal.* Calcd for $C_{16}H_{33}N$: C, 80.2; H, 13.9. Found: C, 80.1, 80.3; H, 13.8, 14.0. [g] Exothermic at 115°. [h] Heated at 120° for 2 hr. [i] Bp 78–80° (100 mm). *Anal.* Calcd for $C_8H_{17}N$: C, 75.5; H, 13.5; N, 11.0. Found: C, 75.3, 75.3; H, 13.4, 13.3; N, 11.2. [j] Exothermic at 110°. [k] Catalyst and amine were heated to 120° for 1 hr, the reactor was cooled, and butadiene was charged; exothermic at 80°.

The highest yields of aldehyde I were obtained in reactions employing *t*-butylamine (reactions 9, 10, and 11). In reaction 11, for example, the yield of I was 78% employing the procedure of preheating this amine and sodium hydride prior to the introduction of butadiene. These results further substantiate the above aldimine pathway, in that *t*-butylamine is known to form very stable aldimines[10] and that aldimine anions, such as *t*-$BuNCHCHC_2H_5$ and *t*-$BuNCHC(C_2H_5)CH_2CH{=}CHCH_3$, should have greater tendency to react at carbon rather than at nitrogen owing to the bulky *t*-butyl group. Corresponding to the above lithium hydride reactions, the yield of aldehyde I from the reaction of butadiene, *t*-butylamine, and lithium hydride (reaction 8) was reduced, while butenyl-*t*-butylamine was obtained in moderate yield.

Experimental Section

All melting and boiling points are uncorrected. Reactions involving alkali metals, or moisture- and air-sensitive derivatives thereof, were conducted in previously dried equipment under nitrogen. Phillips special purity butadiene was used without further purification. For the high-pressure work, a 1-l. stainless steel Magne-Dash autoclave, Autoclave Engineers, Inc., was used. Infrared spectra were obtained on a Perkin-Elmer Infracord spectrophotometer and nmr spectra were determined on a Varian A-60 spectrometer. The chemical shifts are in cycles per second from the resonance of tetramethylsilane.

Reaction of Butadiene and Methylamine (1:1).—A mixture of 10 g of sodium hydride, 192 g (3.56 moles) of butadiene, and 110 g (3.55 moles) of methylamine was slowly heated in the autoclave. At 72° (150 psi), an exothermic reaction occurred in which the reaction temperature increased to 223° with the pressure being above 600 psi. The autoclave heaters were turned off, and, after 1 hr, the reactor was cooled in an ice bath. The unreacted materials were vented, and methanol and then water were added. The reaction mixture was extracted with a mixture of pentane and ether, and the organic layer was separated and dried over calcium sulfate. Stripping of the solvent to a pot temperature of 100° gave 218 g of red-brown liquid residue.

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(10) M. D. Hurwitz, U. S. Patent 2,582,128 (1952).

The above product was treated with 1500 ml of water and 300 ml of concentrated hydrochloric acid and subjected to steam distillation. After 3 hr, approximately 2 l. of distillate was collected. The resultant acid layer was made strongly basic with 35% sodium hydroxide solution and extracted with several portions of ether. The combined ether solution was then dried and the ether was removed to give 125.6 g of dark red liquid. Subsequent distillation of this gave 16.8 g (6%) of butenylmethylamines,[1,2a] bp 83–84°, and 35.8 g (15%) of dibutenylmethylamines,[1,2a] bp 75–83° (30 mm). There was 64.4 g of dark residue.

The steam distillate was treated with a mixture of *n*-pentane and ether and the organic layer was separated. After drying over calcium sulfate, the solvent was stripped and the resultant 62.9 g of yellow liquid was distilled to give 8.9 g of colorless liquid, boiling mostly at 73–78° (30 mm), $n^{20}\mathrm{D}$ 1.4507–1.417. Analysis of this material by gas–liquid partition chromatography (glpc) on a 10-ft silicone oil column indicated the presence of two major components in a ratio of 1:4. The infrared spectrum was found to be nearly identical with that of 2-ethyl-2-hexenal,[11] except that strong bands were present at 5.77 and 10.35 μ. The first band is characteristic of saturated aliphatic aldehydes and was considerably stronger than the band at 5.90 μ for the α,β-unsaturated aldehyde. The band at 10.35 μ is characteristic of *trans* double bonds.

A small quantity of this aldehyde mixture in methanol was hydrogenated over prereduced 10% palladium on charcoal. At room temperature and atmospheric pressure, 0.97 equiv of hydrogen was quickly absorbed. Upon glpc analysis only one compound was detected and it possessed the same retention time as 2-ethylhexanal. In addition, the infrared spectra[12] were nearly superimposable and the melting points of the 2,4-dinitrophenylhydrazone derivatives were identical.[4] It is therefore concluded that the above mixture of aldehydes was one part of 2-ethyl-2-hexenal and four parts of 2-ethyl-4-hexenal and was formed in 4% yield.

Continued distillation of the above steam volatile fraction then gave 30.4 g of colorless liquid, bp 78–82° (4 mm). The center cut, bp 82° (4 mm), $n^{20}\mathrm{D}$ 1.4646, showed strong infrared bands at 5.8 (unconjugated aldehyde) and 10.35 μ (*trans* double bond) and several very weak absorption bands which may be associated with terminal and *cis* double bonds. From the nmr analysis (see Figure 3) and the information to be presented below, this material was found to be mainly 2-(*trans*-2-butenyl)-2-ethyl-*trans*-4-hexenal (I). The yield was 14%. A portion of the same aldehyde prepared in another experiment was distilled to obtain an analytical sample, bp 80–82° (3.5 mm), $n^{20}\mathrm{D}$ 1.4640.

Anal. Calcd for $C_{12}H_{20}O$: C, 79.9; H, 11.2. Found: C, 79.8, 79.8; H, 11.3, 11.2.

A 2,4-dinitrophenylhydrazone[13] was prepared and recrystallized from 1:1 ethanol–benzene, mp 155–157°.

Anal. Calcd for $C_{18}H_{24}N_4O_4$: C, 60.0; H, 6.7. Found: C, 59.9, 59.8; H, 6.9, 6.9.

Analysis of the aldehyde I by glpc on a 10-ft silicone oil column showed the presence of three components having the form of a large peak with two small unresolvable shoulders. On a 20-ft column containing 1,2,3-tris(cyanoethoxy)propane, this and other samples of I were resolved slightly into three peaks with an approximate area ratio of 5:65:30, in the same order of increasing retention times. Because this polar column will separate olefins in the order of terminal, *trans* and then *cis*, and of the presence of small absorption bands in the infrared spectrum for terminal and *cis* double bonds, these materials appear to be a mixture of the terminal and *trans,trans* and *trans*, and *cis* and *trans* isomers of the unsaturated aldehyde of the general structure I.

Hydrogenation of Aldehyde I.—A mixture of 100 ml of absolute ethanol, 12.1 g (0.067 mole) of aldehyde I, and 2 ml of commercial Raney nickel suspension was treated with hydrogen at 400 psi. Upon heating to 150°, the hydrogen pressure was raised to 1000 psi and maintained at that value for 4 hr. The reaction mixture was filtered, the ethanol was removed, and the product was distilled to give 10.1 g (81%) of colorless liquid, bp 66–68° (0.3 mm), $n^{20}\mathrm{D}$ 1.4508. This material showed the presence of only one component by glpc and was identified as 2-*n*-butyl-2-ethylhexanol-1 (II) by nmr (see Figure 2) and infrared analyses.

Anal. Calcd for $C_{12}H_{26}O$: C, 77.4; H, 14.1. Found: C, 77.3, 77.3; H, 14.0, 14.1.

Reaction of Butadiene and Methylamine (2:1) Followed by Hydrogenation.—Butadiene (178 g, 3.3 moles), 50 g (1.6 moles) of methylamine and 10 g of sodium hydride were reacted as described above. Work-up in the usual manner gave 222 g of red liquid. Fifty grams of this was treated with 500 ml of 5% hydrochloric acid and subjected to steam distillation. The distillate was worked up to give 17.7 g (37%) of the aldehyde I.

Seventy grams of the above reaction product, 2 g of 10% palladium on charcoal, and 100 ml of cyclohexane were charged to the reactor and hydrogen was introduced to a pressure of 410 psi. The reactor was then heated to 150° and the hydrogen pressure was adjusted to and maintained at 800 psi for 4 hr and 10 min. The resultant material was filtered and stripped of cyclohexane to give 61 g of pale yellow liquid. This was combined with the product from the hydrogenation of a 42-g sample and distilled to give 22.7 g (18%) of colorless liquid, bp 62–69° (25 mm), $n^{20}\mathrm{D}$ 1.4192. By comparisons of the infrared spectra and of the retention times upon glpc, this was identified as di-*n*-butylmethylamine.[14] Continued distillation gave 38.7 g of colorless liquid, bp 86–95° (5 mm). The analytical sample boiled at 91.5–92° (5 mm), $n^{20}\mathrm{D}$ 1.4464. Analysis by glpc showed the presence of only one component and the nmr and infrared spectra were consistent with the structure being N-methyl-2-*n*-butyl-2-ethylhexylamine.

Anal. Calcd for $C_{13}H_{29}N$: C, 78.3; H, 14.7; N, 7.0. Found: C, 78.3, 78.2; H, 14.6, 14.5; N, 7.4.

N,N-Dimethyl-2-*n*-butyl-2-ethylhexylamine (III). A. From N-Methyl-2-*n*-butyl-2-ethylhexylamine.—A suspension of 0.25 g of PtO_2 in 25 ml of absolute ethanol was prereduced at 50 psi of hydrogen pressure. A mixture of 12.6 g (0.063 mole) of the above amine, 15 ml of 40% formaldehyde and 50 ml of ethanol was added and the hydrogen pressure was adjusted to 54 psi. Over a period of 2 hr, a drop of approximately 2 psi was noted. An additional 5 ml of formaldehyde solution was then added and the reaction was continued for 1 hr. The catalyst was filtered and most of the ethanol was removed at reduced pressure. Attempts to distil the resultant product were spoiled owing to contamination by formaldehyde residues. It was therefore necessary to treat the product with ether and 10% hydrochloric acid. The acid layer was then made basic and extracted with ether. Work-up and distillation of the ethereal solution gave 7.4 g (55%) of the amine III, boiling mostly at 86–88° (3 mm), $n^{20}\mathrm{D}$ 1.4455. Glpc analysis indicated the presence of a small amount of starting material.

Anal. Calcd for $C_{14}H_{31}N$: C, 78.8; H, 14.6; N, 6.6. Found: C, 78.4; H, 14.4; N, 7.2.

B. From Aldehyde I.—The reactor was charged with 15 g of 10% palladium on charcoal, 226 g (1.25 moles) of aldehyde I, 250 ml of anhydrous methanol, and 119 g of dimethylamine, and pressured to 400 psi with hydrogen. It was then heated to 150° and the hydrogen pressure was adjusted to and maintained at 1000 psi for 4 hr and 45 min. The resultant product was freed of catalyst by filtration and stripped of methanol. It was then treated with a mixture of 800 ml of water and 200 ml of concentrated hydrochloric acid and extracted with several portions of ether. From the ether extract, there was obtained 8.8 g of the alcohol II. The aqueous layer was made basic and again extracted with ether. After drying and removal the ether, the product was distilled to give 230.6 g (86%) of the dimethylamine III, bp 88–90° (3 mm), $n^{20}\mathrm{D}$ 1.4450. Upon glpc analysis, only one compound was indicated and it had the same retention time as that above.

Anal. Calcd for $C_{14}H_{31}N$: C, 78.8; H, 14.6. Found: C, 78.5, 78.8; H, 14.6, 14.9.

The hydrochloride was prepared by treating an ethereal solution of a small sample of the above compound with dry hydrogen chloride and recrystallized from ethyl acetate to give colorless needles, mp 127.5–129°.

Anal. Calcd for $C_{14}H_{32}ClN$: C, 67.3; H, 12.9. Found: C, 67.5, 67.4; H, 12.9, 13.0.

2-Ethylhexanonitrile.—Employing the procedure for heptaldoxime,[15] 2-ethylhexanal was converted to the oxime[5] in 92%

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[11] Sadtler Research Laboratories, Philadelphia, Pa., Infrared Spectrum No. 5723.

[12] Sadtler Research Laboratories, Philadelphia, Pa., Infrared Spectrum No. 5720.

[13] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1940, p 143.

[14] O. Westphal and D. Jerchel, *Ber.*, **73B**, 1002 (1940); W. D. Emmons, K. S. McCallum, and J. P. Freeman, *J. Org. Chem.*, **19**, 1472 (1954).

[15] E. W. Bousquet, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p 313.

yield, bp 100–101° (10 mm), $n^{20}\mathrm{D}$ 1.4472. Acetic anhydride (210 g, 2 moles) was heated to slight reflux and treated with 197 g (1.38 moles) of the oxime by dropwise addition over a period of 1 hr and 15 min. Refluxing was continued for 45 min, and the reaction mixture was then fractionally distilled to give 130.4 g (76%) of 2-ethylhexanonitrile,[6] bp 121–123° (100 mm), $n^{20}\mathrm{D}$ 1.4163–1.4170.

2-*n*-Butyl-2-ethylhexanonitrile.—A suspension of 20 g (0.51 mole) of sodium amide powder in 100 ml of toluene was treated with a mixture of 64.2 g (0.51 mole) of 2-ethylhexanonitrile and 70.5 g (0.51 mole) of *n*-butyl bromide. Upon warming, a sudden evolution of ammonia and rapid refluxing of the toluene were noted. When this subsided, the mixture was heated to reflux for 3 hr. After cooling, isopropyl alcohol and then water were added carefully. The organic layer was worked up and distilled to give 11.3 g (18%) of recovered starting nitrile, bp 60–63° (5 mm), and 40.8 g (44%) of colorless liquid, bp 90–95° (2.8 mm). The analytical sample boiled at 93° (2.8 mm), $n^{20}\mathrm{D}$ 1.4359.

Anal. Calcd for $C_{12}H_{23}N$: C, 79.5; H, 12.8; N, 7.7. Found: C, 79.7, 79.6; H, 12.9, 12.8; N, 7.6.

2-*n*-Butyl-2-ethylhexylamine.—A suspension of 5.7 g (0.15 mole) of lithium aluminum hydride in 250 ml of ether, cooled in an ice bath, was treated with 27.2 g (0.15 mole) of 2-*n*-butyl-2-ethylhexanonitrile in 100 ml of ether. The mixture was then heated to reflux for 1.5 hr. After again cooling in an ice bath, 6 ml of water, 4.5 ml of 20% sodium hydroxide, and finally 21 ml of water were added in succession.[16] The resultant white solid was filtered and washed with ether. After combining, drying, and distilling the ethereal solution, the product was distilled to give 16.8 g (60%) of colorless liquid, bp 71–72° (1 mm), $n^{20}\mathrm{D}$ 1.4465–1.4485. The analytical sample boiled at 72° (1 mm), $n^{20}\mathrm{D}$ 1.4472.

Anal. Calcd for $C_{12}H_{27}N$: C, 77.8; H, 14.7; N, 7.6. Found: C, 77.8, 77.9; H, 14.3, 14.5; N, 7.2, 7.5.

N,N-Dimethyl-2-*n*-butyl-2-ethylhexylamine (III).—A suspension of 0.5 g of PtO_2 in 100 ml of absolute ethanol was reduced at 40 psi of hydrogen. After the pressure was constant, 15.9 g (0.086 mole) of 2-*n*-butyl-2-ethylhexylamine, 50 ml of ethanol, and 20 ml of 40% formaldehyde were added and the hydrogen was pressured to 50 psi. After 5 hr, an additional 10 ml of formaldehyde solution was added and the reaction was continued for 3 hr. The catalyst was then filtered and most of the ethanol was evaporated under reduced pressure. Infrared and gas chromatographic analyses indicated the material to be a mixture of mono- and dimethyl compounds. Accordingly, this material was again treated with 20 ml of 40% formaldehyde and 0.5 g of reduced PtO_2 in 50 ml of absolute ethanol under approximately 50 psi of hydrogen for 5 hr and 45 min. As before the catalyst and most of the ethanol were removed, and then the resultant material was treated with a mixture of 30 ml of concentrated hydrochloric acid and 70 ml of water. After extracting with ether, the aqueous layer was made basic with 35% sodium hydroxide solution and extracted with ether again. This ethereal solution was dried and stripped of ether, and the product was distilled to give 12.2 g (67%) of colorless liquid, bp 83–87° (2 mm), $n^{20}\mathrm{D}$ 1.4430–1.4452, with the main fraction boiling at 87° (2 mm), $n^{20}\mathrm{D}$ 1.4450.

The infrared spectra of this material and those described above were superimposable, as were the glpc retention times. The hydrochloride, recrystallized from ethyl acetate, had a melting range of 128–130°, and an admixture with the above hydrochloride melted without depression.

N-Butylidene-*n*-propylamine and Butadiene.—A mixture of 53.9 g (0.48 mole) of N-butylidene-*n*-propylamine,[17] 5 g of sodium hydride, 138 g (2.5 moles) of butadiene, and 5 g of ammonia was heated at 75–80° for 105 min. After cooling and venting, methanol was added and the reaction product was worked up to give 107 g of red liquid. It was then treated with 5% hydrochloric acid and subjected to steam distillation. Work-up of the steam volatile material gave 61.9 g (72%) of aldehyde I, bp 74–76° (2.5 mm), $n^{20}\mathrm{D}$ 1.4645.

N-Butylidene-*t*-butylamine and Butadiene.—N-Butylidene-*t*-butylamine[10] (61 g, 0.48 mole), 5 g of sodium hydride, 137 g (2.5 moles) of butadiene, and 5 g of ammonia were heated at 80° for 3 hr. After cooling, the excess reactants were vented and methanol was added. The resultant material was subsequently treated with water and ether and worked up to give 108.6 g of pale yellow liquid. Twenty-five grams of this was distilled to give as a first fraction 3.2 g (16%) of colorless liquid, bp 38–40° (0.5 mm), $n^{20}\mathrm{D}$ 1.4408. The infrared spectrum showed strong bands at 6.05 (C=N) and 10.35 μ (*trans* double bond) indicating the material to be predominantly N-(2-ethyl-*trans*-4-hexenylidene)-*t*-butylamine. The analytical sample boiled at 90–93° (25 mm), $n^{20}\mathrm{D}$ 1.4405.

Anal. Calcd for $C_{12}H_{23}N$: C, 79.5; H, 12.8; N, 7.7. Found: C, 78.9, 79.2; H, 12.8, 13.0; N, 7.8.

Continued distillation of the above gave 18.3 g of colorless liquid, bp 68–70° (0.5 mm), $n^{20}\mathrm{D}$ 1.4592. As described above, the infrared spectrum exhibited strong bands at 6.05 and 10.35 μ indicating the material to be mainly N-(*trans*-2-butenyl-2-ethyl-*trans*-4-hexenylidene)-*t*-butylamine.

Anal. Calcd for $C_{16}H_{29}N$: C, 81.6; H, 12.4; N, 6.0. Found: C, 81.5, 81.5; H, 12.4, 12.5; N, 6.4.

Steam distillations from dilute acid mixtures of portions of the above materials gave a mixture of 2-ethyl-4-hexenal and 2-ethyl-2-hexenal, as described previously, and the C_{12} aldehyde I.

Diallylamine, Butadiene and Sodium Hydride.—A mixture of 68 g (0.7 mole) of diallylamine, 5 g of sodium hydride, and 142 g (2.6 mole) of butadiene was heated at 80° for 2.5 hr and then at 100° for 1.5 hr. After cooling and venting, methanol was added followed by water. The mixture was treated with ether and worked up to give 130 g of orange-red liquid. The infrared spectrum showed a strong C=N band at 6.05 μ. The liquid was subsequently treated with 5% hydrochloric acid and steam distilled. Work-up of the distillate gave 33 g (28%) of colorless liquid, bp 73–76° (5 mm), $n^{20}\mathrm{D}$ 1.4596. The infrared spectrum exhibited strong absorption bands at 5.8 (unconjugated aldehyde) and at 10.35 μ (*trans* double bond). When coupled with the nmr analysis (see Figure 3) the material was concluded to be 2-(*trans*-2-butenyl)-2-methyl-*trans*-4-hexenal (VI).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.5; H, 10.9. Found: C, 79.5, 79.2; H, 10.7, 10.7.

The 2,4-dinitrophenylhydrazone,[13] recrystallized from 95% ethanol, melted at 113.5–116°.

Anal. Calcd for $C_{17}H_{22}N_4O_4$: C, 58.9; H, 6.4. Found: C, 58.7, 58.9; H, 6.6, 6.6.

Reactions of Table I.—Runs numbered 1 and 2 are described in the first part of the Experimental Section. The other reactions were conducted employing similar procedures. The amine, butadiene, and the catalyst were charged to the reactor and it was slowly heated. After the resultant exothermic reaction or heating period as described in the table, the reactor was cooled and vented. Methanol was usually added to destroy the catalyst residues followed by water. The reaction mixture was then treated with ether and/or *n*-pentane and the organic layer separated. It was subsequently dried and stripped of solvent. The resultant liquid was treated with sufficient dilute acid to afford a slight excess over that necessary to react with all the amine present and subjected to steam distillation. The usual techniques were then used to isolate the aldehydes from the steam distillate and the amines from the aqueous layer.

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(16) L. H. Amundsen and L. S. Nelson, *J. Am. Chem. Soc.*, **73**, 242 (1961).

(17) K. N. Campbell, A. H. Sommers, and B. K. Campbell, *ibid.*, **66**, 82 (1944).