

117°), with lithium aluminum hydride using the procedure described above for the preparation of Xb gave 7.6 g. of crude product which on redistillation yielded 5.73 g. (71%) of 1,4-dihydro-1-methyl-1-naphthylmethanol, b.p. 102–104° (0.15 mm.). Gas chromatographic analysis<sup>16a</sup> of the first fraction (3.43 g.) showed the presence of 3% of an impurity while the second fraction (2.3 g.) had 7% of the same impurity.

The reaction of 3.4 g. of 1,4-dihydro-1-methyl-1-naphthylmethanol and 3.8 g. of *p*-toluenesulfonyl chloride, using the procedure described above for the preparation of Ia, gave 6.0 g. (94%) of crude 1,4-dihydro-1-methyl-1-naphthylmethyl *p*-toluenesulfonate, m.p. 49–54°. Several recrystallizations of the crude product from ethanol gave an analytical sample of XIIIc, m.p. 58–59°,  $\nu_{\text{max}}^{\text{CCI}_4}$  1370 (s) and a doublet at 1190–1180 (s, sulfonate group)  $\text{cm}^{-1}$ .

*Anal.* Calcd. for  $\text{C}_{19}\text{H}_{20}\text{O}_2\text{S}$ : C, 69.50; H, 6.14; S, 9.74. Found: C, 69.46; H, 6.14; S, 9.91.

Solvolysis of 1,4-Dihydro-1-methyl-1-naphthylmethyl *p*-Toluenesulfonate (XIIIc).—The solvolysis was carried out as described above for Ic using 6.0 g. of 1,4-dihydro-1-methyl-1-naphthylmethyl *p*-toluenesulfonate and 4.6 g. of sodium dihydrogen phosphate monohydrate in 70 ml. of purified acetic acid. The usual work-up procedure gave 2.0 g. (70%) of a hydrocarbon fraction, b.p. 136° (25 mm.), and 0.19 g. (6%) of an ester fraction.

Purification of the hydrocarbon fraction by gas chromatography<sup>16f</sup> showed the presence of two materials. The first fraction eluted accounted for 97% of the crude product, and was presumably a mixture of 2-benzo-3-methylcycloheptatriene (XV) and 1,2-benzo-4-methylcycloheptatriene (XVIII) (or double bond isomers of these compounds),  $\lambda_{\text{max}}^{\text{EtOH}}$  274  $\text{m}\mu$  ( $\epsilon$  6790). The infrared spectrum ( $\text{CCl}_4$  solution) of the product shows a weak band at 1385  $\text{cm}^{-1}$  (C-CH<sub>3</sub>).

*Anal.* Calcd. for  $\text{C}_{12}\text{H}_{12}$ : C, 92.26; H, 7.74. Found: C, 92.05; H, 7.92.

The second material to be eluted from the column consisted of 3% of an unidentified material.

Attempted purification of the ester fraction by gas chromatography<sup>16e</sup> failed to effect complete separation of the three components which appeared to be present in the mixture.

Hydrogenation of the Hydrocarbon Mixture from the Solvolysis of 1,4-Dihydro-1-methyl-1-naphthylmethyl *p*-Toluenesulfonate.—A solution of 0.50 g. of the distilled

hydrocarbon mixture and 5 ml. of glacial acetic acid was hydrogenated at atmospheric pressure in the presence of 75 mg. of 10% palladium-on-carbon catalyst. The hydrogenation stopped when 100% of two molecular equivalents of hydrogen had been absorbed. The catalyst was removed by filtration and the filtrate was cooled and neutralized with sodium hydroxide solution. The product was extracted with ether and the ether extract was dried and concentrated giving 0.48 g. (96%) of product which, when purified by gas chromatography,<sup>16e</sup> showed the presence of two materials. The first fraction eluted amounted to 15% of an unidentified hydrocarbon, presumably 1,2-benzo-4-methylcycloheptene (XIX), and the second fraction was 85% of 1,2-benzo-3-methylcycloheptene (XVI),  $\lambda_{\text{max}}^{\text{EtOH}}$  257 ( $\epsilon$  230), 261 (shoulder), 264 ( $\epsilon$  300), 267 ( $\epsilon$  230) and 271  $\text{m}\mu$  ( $\epsilon$  270), whose retention time and infrared spectrum are essentially identical to those of an authentic sample (see below).

*Anal.* Calcd. for  $\text{C}_{12}\text{H}_{14}$ : C, 89.94; H, 10.06. Found: C, 89.81; H, 10.15.

1,2-Benzo-3-methylcycloheptene (XVI).—To the Grignard reagent prepared from 5.2 g. of methyl iodide and 0.86 g. of magnesium in 40 ml. of ether was added, with stirring, 5 g. of benzosuberone<sup>25</sup> in 20 ml. of ether at such a rate as to maintain gentle refluxing of the ether. When the addition was complete, the mixture was allowed to stand overnight, and then poured into dilute sulfuric acid and ice. The product was extracted with ether, dried over magnesium sulfate and filtered. The ether was removed, and the product heated on the steam-bath for 1 hour in the presence of a 50% (by volume) aqueous sulfuric acid solution. The product was then extracted with ether, and the ether extract was dried. Removal of the solvent gave 5 g. (95%) of crude olefin which was distilled to give 3.1 g. of material in two fractions, b.p. 128° (30 mm.). The first fraction contained a red-colored impurity which came over in the early stages of the distillation. The structure of this red material has not been investigated. A portion of fraction 2 (0.5 g.) was hydrogenated as in the previous experiment to give 0.5 g. of crude 1,2-benzo-3-methylcycloheptene which on gas chromatographic purification<sup>16e</sup> showed only one material to be present, whose retention time and infrared spectrum were essentially identical to those of the XVI obtained from the hydrogenated solvolysis product above.

(25) We are indebted to Roger L. Thorton for supplying a sample of this compound.

[CONTRIBUTION FROM THE PHILLIPS PETROLEUM CO., BARTLESVILLE, OKLA.]

## Ethylidenimines by the Reaction of Acetylene with Primary Aliphatic Amines

BY CARL W. KRUSE AND ROGER F. KLEINSCHMIDT

RECEIVED JULY 8, 1960

The reaction of acetylene with primary aliphatic amines in the presence of zinc and cadmium acetates has been shown to yield ethylidenimines,  $\text{CH}_2\text{CH}=\text{NR}$ , instead of the *N*-vinylamines,  $\text{CH}_2=\text{CH}-\text{NHR}$ , as reported by Reppe and co-workers. Infrared, ultraviolet and mass spectral data indicated the presence of higher boiling vinyllogs,  $\text{CH}_2(\text{CH}=\text{CH})_n\text{CH}=\text{NR}$  (*R* = ethyl or cyclohexyl) in the distillation residues and in heat-treated samples of the ethylidenimines. *N*-Cyclohexyl-2-butenylideneimine was isolated, and its structure was established by reduction to *N*-*n*-butylcyclohexylamine.

Although vinylamines are postulated to be intermediates in several reactions, including the synthesis of 2-methyl-5-ethylpyridine, they have seldom been isolated and have been considered to be very unstable. However, Reppe recently reported the preparation of *N*-vinylamines in low or unspecified yields by the reaction of acetylene with certain primary and secondary amines over cadmium and zinc acetates.<sup>1</sup> *N*-Vinylethylamine (24% theoretical yield) and *N*-vinylcyclohexylamine were two of the products claimed to have been isolated, but the only supporting data were elemental analyses and boiling points. In addition,

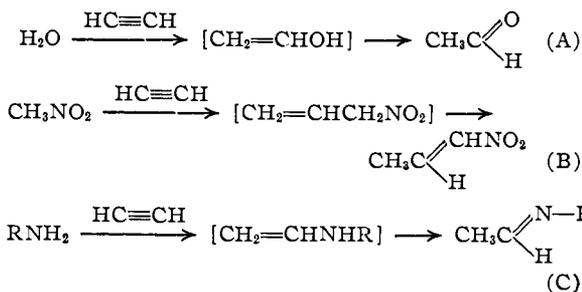
the formation of *N,N*-divinylcyclohexylamine was reported.

It is well known that water adds to acetylenic bonds to produce aldehydes and ketones, not vinyl alcohols (eq. A). Similarly, as shown in eq. B, nitromethane adds to acetylene to produce 1-nitropropene, not 3-nitropropene.<sup>2</sup>

By analogy, the addition of ammonia or a primary amine to acetylene would be expected to produce an ethylidenimine,  $\text{CH}_2\text{CH}=\text{NR}$ , not a vinylamine  $\text{CH}_2=\text{CHNHR}$  (eq. C). In the light of these reactions it is surprising that the earlier work did

(1) W. Reppe, *et al.*, *Liebig's Ann. Chem.*, **601**, 81 (1956).

(2) B. M. Vanderbilt and H. B. Hass, *Ind. Eng. Chem.*, **32**, 34 (1940).

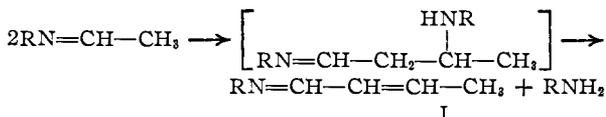


not present a proof of structure, and it appeared worthwhile to investigate these claims for the preparation of vinylamines.

The procedure described was followed as closely as the experimental details would permit. The boiling points of the products obtained by the reaction of acetylene with ethylamine and with cyclohexylamine corresponded to those reported for N-vinylethylamine, N-vinylcyclohexylamine and N,N-divinylcyclohexylamine. Chemical and physical methods were then employed to establish the structures of these compounds.

N-Ethylethylideneimine,  $\text{CH}_3\text{CH}=\text{N}-\text{C}_2\text{H}_5$ , was prepared from acetaldehyde and ethylamine<sup>3</sup> for a comparison of its physical and chemical properties with those of the product obtained from acetylene and ethylamine by Reppe's procedure. N-Ethylethylideneimine was heat-sensitive; slow distillation at atmospheric pressure was accompanied by a continuous evolution of ethylamine, which condensed with the distillate. The product prepared from acetylene showed the same behavior as N-ethylethylideneimine in every detail. Although samples completely free of ethylamine were never obtained, a comparison of the boiling points, refractive indices, mass spectra and infrared spectra of the purest samples left no doubt that the Reppe product was N-ethylethylideneimine.

Alkylideneimines have been shown to undergo condensation-elimination reactions to produce unsaturated alkenylideneimines (I) in the following manner.<sup>4</sup> Compound I.



being a vinylog of the alkylideneimine, can react in an analogous manner with the alkylideneimine to produce even higher vinylogs. This type of reaction not only accounts for the continuous liberation of ethylamine during distillation of N-ethylethylideneimine, but it also provides an explanation for the other compounds that were formed during the distillation of the N-ethyl- and N-cyclohexylethylideneimines.

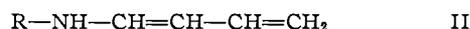
The mass spectrogram of a heat-treated sample of N-ethylethylideneimine had peaks at 97, 123 and 149 mass units corresponding to compounds of structures  $\text{C}_2\text{H}_5\text{N}=\text{CH}(\text{CH}=\text{CH})_n\text{CH}_3$ , where  $n = 1, 2, 3$ . Furthermore, mass spectra of samples of N-ethylethylideneimine taken before and after a period of more than 10 days in the refrigerator

(3) R. Toillais, *Bull. soc. chim. France*, 708 (1947).

(4) R. Toillais and H. Guillermin, *Compt. rend.*, 236, 1798 (1953).

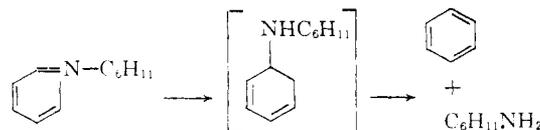
showed that the intensity of the peak at 45, attributed to dissolved ethylamine, and the intensity of the one at 97, attributed to N-ethylbutenylideneimine (compound I,  $\text{R} = \text{C}_2\text{H}_5$ ), increased at the expense of the N-ethylethylideneimine peak at 71 mass units. This change was accompanied by an increase in the refractive index and by increased ultraviolet absorption at 2150 Å., indicating an increase in the concentration of molecules possessing conjugated unsaturation.

The ultraviolet spectrum of the compound reported to be N,N-divinylcyclohexylamine also had a peak at 2150 Å. indicative of a conjugated system. Reduction of the compound with hydrogen produced only N-*n*-butylcyclohexylamine, which was identified by a mixed melting point of its thiourea derivative with an authentic sample. The absence of N,N-diethylcyclohexylamine in the reduction mixture was established by infrared spectral comparison; diethylcyclohexylamine has infrared bands at 1067, 1192 and 1205  $\text{cm}^{-1}$  which were absent in the reduction product. Only two structures, I and II, were



possible for a conjugated, unsaturated system with a straight-chain  $\text{C}_4$ -unit. The enamine structure II, where  $\text{R} = \text{C}_6\text{H}_{11}$ , was not consistent with the infrared spectrum, which indicated the presence of  $-\text{CH}_3$  and  $-\text{N}=\text{CHCH}=\text{CH}-$  groupings by bands at 1378, 1630 and 1660  $\text{cm}^{-1}$ . The spectrum possessed no bands at 3095–3075 and 915–905  $\text{cm}^{-1}$  which are characteristic of  $=\text{CH}_2$  groups. The correct structure,  $\text{C}_6\text{H}_{11}\text{N}=\text{CHCH}=\text{CHCH}_3$ , is the one expected from a condensation of two molecules of N-cyclohexylethylideneimine followed by an elimination of cyclohexylamine.

Although unsaturated imines containing more than two double bonds were not isolated and characterized, the mass and ultraviolet data indicated that higher vinylogs were present in heat-treated samples of N-ethylethylideneimine. There was no corresponding spectral evidence, however, for these products from the acetylene-cyclohexylamine reaction. It is possible that the low volatility of compounds in the molecular weight range of 177 and above may have excluded the detection of the higher vinylogs of N-cyclohexylethylideneimine by mass spectroscopy. The absence of N-cyclohexyl-2,4-hexadienylideneimine can also be explained by a cyclization-elimination reaction which resulted in the formation of benzene.

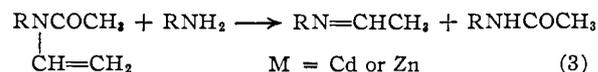
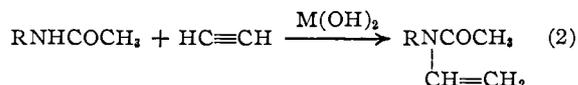


Although the amount of benzene found was small, it was definitely detected by ultraviolet spectroscopy.

A very small amount of an unknown amine was isolated at the end of the distillation of N-*n*-butylcyclohexylamine from the reduction of N-cyclohexyl-2-butenylideneimine. It distilled with bicyclohexyl, which was used as a chaser in the frac-

tionation. The thiourea derivative, m.p. 107–109°, of this unknown amine was shown not to be the thiourea derivative of N-*n*-hexylcyclohexylamine.

A white solid, which was obtained before and also after reduction of cyclohexylamine-acetylene reaction products, was shown to be N-cyclohexylacetamide. There is no experimental evidence to show that this amide was other than a by-product. However, in postulating a reaction mechanism for the "ethylidenation" of primary, aliphatic amines with acetylene, the possibility should be considered that the amide was vinylated and the ethylenimine was produced *via* a transamidation reaction.



It was shown that the acetates do not catalyze reaction 2; N-vinyl-N-methylacetamide was not obtained by treatment of N-methylacetamide with acetylene over cadmium and zinc acetates. Hydroxides of alkali metals are known to be catalysts for reaction 2, but it remains to be shown that Group IIa metal hydroxides are also catalysts for this reaction. Further experiments will be necessary to reach a conclusion regarding the mechanism.

### Experimental<sup>5</sup>

**Instrumentation.**—A standard one-liter, high pressure, stainless steel, stirred autoclave (rated at 5000 p.s.i. working pressure) manufactured by Autoclave Engineers, Inc., was used. The autoclave was equipped with a blowout disk rated at 520 p.s.i. for the cyclohexylamine experiments. A 1500 p.s.i.g. gage and 1500 p.s.i. blowout disk were used for the ethylamine experiments.

Infrared spectra were obtained from a Perkin-Elmer model 21 double beam recording spectrophotometer equipped with sodium chloride optics.

Ultraviolet spectra were obtained from a Cary model 11 recording spectrophotometer.

Mass spectra were obtained from a Consolidated Electrodynamics Mass Spectrometer type 21-103B.

**Catalyst Preparation.**—Fresh catalyst was prepared for each reaction from 2.5 g. each of cadmium acetate dihydrate and zinc acetate dihydrate. The acetates were mixed in a casserole and heated on a hot-plate to remove the water of hydration. The pasty mixture was stirred with a spatula during the early part of the desiccation. A pestle was used to reduce the hot cake to a free flowing powder, which was used immediately before it cooled.

**Chemicals.**—Commercial grade acetylene (Linde Air Products Co.) was used after removing the entrained acetone by a trap cooled in ice or ice-salt water to 0 to -10°.

The amines were obtained from Distillation Products Industries or Matheson Coleman and Bell, and were for the most part used without further purification. N,N-Diethylcyclohexylamine was fractionally distilled to obtain a pure sample, b.p. 87–89° (9 mm.), *n*<sub>D</sub><sup>20</sup> 1.4530, for an infrared reference spectrum.

**N-Ethylethylidenimine from Acetylene and Ethylamine.**—The autoclave containing the catalyst was evacuated, chilled in Dry Ice-acetone and charged with 188.5 g. (4.18 moles) of ethylamine. Acetylene at 200 p.s.i.g. readily dissolved in the stirred amine at 0°; the absorption time was arbitrarily limited to about 5 minutes. The sealed autoclave was then heated at 120° for 17 hours and at 140° for 12 hours. More acetylene was added after cooling to 20° before a final heating period of 6 hours at 140°. The maximum pressure was 785 p.s.i.g. When cool, the gases

were vented slowly through traps at Dry Ice temperature. Fifty grams of colorless liquid, assumed to be mostly ethylamine, was trapped. The liquid remaining in the reactor weighed 28 g. more than the weight of the ethylamine charged. Thus, the minimum amount of acetylene absorbed was calculated to be 78 g. (3 moles).

The product was distilled in a 24-inch column of 23 mm. diameter, which was packed with Podbielniak, stainless steel, 0.094 inch × 0.175 inch × 0.175 inch, Heli-pak packing. The boiling point and refractive index of the distillate varied with the rate of distillation. Approximately 100 g. of ethylamine was recovered. The yield of N-ethylethylidenimine, b.p. 38–47° (*n*<sub>D</sub><sup>20</sup> 1.3873–1.3990), was 77 g. or 55% theoretical based upon the ethylamine consumed. Redistillation of this colorless liquid over a 2.5-hour period resulted in 13.4 g. of pot residue, b.p. above 205°.

The infrared spectrum of a cut, b.p. 46°, *n*<sub>D</sub><sup>20</sup> 1.3860, was compared with that of a sample of N-ethylethylidenimine, b.p. 45.5°, *n*<sub>D</sub><sup>20</sup> 1.3872, prepared from acetaldehyde and ethylamine (see preparation below). The spectra were essentially identical. The mass spectra of the same samples taken after standing for 11 to 18 days in the refrigerator showed an increase in the intensity of mass peaks at 45 and 97, but a decrease in the intensity of the mass 71 peak.

Three cuts of N-ethylethylidenimine totaling 19 g., which originally had a b.p. 45.8–46.4° and *n*<sub>D</sub><sup>20</sup> 1.3880–1.3911 (from the redistillation above), were combined after standing for 2 weeks at room temperature. The refractive index of the composite sample was *n*<sub>D</sub><sup>20</sup> 1.4275. By warming to 69°, 3.5 g. of gas, assumed to be ethylamine, escaped through the distillation column, and the residue had a refractive index of *n*<sub>D</sub><sup>20</sup> 1.4475. N-Ethylethylidenimine, 6.5 g., was then removed by distillation until the pot temperature reached 127°. The mass spectrogram of the residue, *n*<sub>D</sub><sup>20</sup> 1.4745, had peaks at 71, 97, 123 and 149 which corresponded to the parent peaks for a series of compounds, C<sub>2</sub>H<sub>5</sub>N=CH(CH=CH)*n*CH<sub>3</sub>, where *n* = 0, 1, 2, 3.

**N-Ethylethylidenimine from Acetaldehyde and Ethylamine.**—N-Ethylethylidenimine was prepared according to the procedure described in the literature.<sup>3</sup> By rapid distillation in an 18-inch Vigreux column, 15.5 g., b.p. 45.5°, *n*<sub>D</sub><sup>20</sup> 1.3872–90, was obtained. The refractive index of the distillate changed upon standing at room temperature. The following changes took place in a cut that had an initial index of refraction of *n*<sub>D</sub><sup>20</sup> 1.3872: 1 day, 1.3925; 3 days, 1.3965; 6 days, 1.4040. A comparison of the mass spectra taken 11 days apart on a fraction stored in a refrigerator at near 0° showed that the concentration of components having mass numbers of 45 and 97 had doubled while the intensity of the 71 peak had decreased by about 3%. The infrared spectrum of this same fraction soon after distillation had bands at 1373 and 1675 cm.<sup>-1</sup> associated with —CH<sub>2</sub> and —C=N— groups, respectively.

**N-Cyclohexylethylidenimine and N-Cyclohexyl-2-butenylidenimine from Acetylene and Cyclohexylamine.**—The autoclave was charged with catalyst and 200 g. (2.02 moles) of freshly distilled cyclohexylamine and flushed with nitrogen and propane. The temperature of the stirred slurry was raised to 120° and the pressure was brought to 70 p.s.i.g. with propane. Acetylene was then added to 220 p.s.i.g. There was no detectable pressure drop at this temperature over a period of 1.5 hours. The temperature was raised to 140° for 74 hours during which time the autoclave was re-pressured periodically to a pressure of 250 p.s.i.g. The acetylene absorbed amounted to 40 g. (1.55 moles) or 77% of the theoretical quantity calculated for a 1:1 reaction with cyclohexylamine.

The product was fractionally distilled in an 18-inch × 5/8-inch column packed with 1/4-inch Penn State packing. The yield of N-cyclohexylethylidenimine, b.p. 31–41° (3.5 to 10 mm.), *n*<sub>D</sub><sup>20</sup> 1.459, was 140 ml. (estd. 115 g.) or a 60% theoretical yield based upon the acetylene consumed. The yield of N-cyclohexyl-2-butenylidenimine, b.p. 64–77° (3.5–4 mm.), *n*<sub>D</sub><sup>20</sup> 1.4855, was 33 g. or 29% of the theoretical quantity based on acetylene. The boiling points reported by Reppe for these products, which he assumed to be N-vinyl- and N,N-divinylcyclohexylamines, were 21° (2 mm.) and 60° (2 mm.), respectively.

The mass spectrum of the N-cyclohexyl-2-butenylidenimine had peaks at 110, 125, 136 and 151. The first two indicate that the sample probably contained some N-cyclohexylethylidenimine, mol. wt. 125. The ultraviolet spectrum

(5) All melting and boiling points are uncorrected.

had a peak at 2150 Å. with an intensity of absorption of  $E = 1.34$  at a dilution of  $1 \times 10^{-6}$  in cyclohexane.

A 31-g. portion of *N*-cyclohexyl-2-butenylideneimine was reduced in a Parr hydrogenation apparatus at 50 p.s.i.g. at room temperature in ethanol with platinum as catalyst. The mass and infrared spectra of the crude reduction product were compared to the corresponding spectrum of an authentic sample of *N,N*-diethylcyclohexylamine. No diethylcyclohexylamine,  $b.p. 98^\circ$  (31 mm.),  $n_D^{20} 1.4532$ , was obtained. The phenylthiourea derivative, m.p. 102–103°, was prepared and its melting point was not depressed when mixed with an authentic sample of the phenylthiourea derivative of *N-n*-butylcyclohexylamine (see below).

Bicyclohexyl was used as a chaser in the distillation. A small amount of an unknown amine distilled at the end of the bicyclohexyl cuts. Its thiourea derivative, m.p. 107–109°, was prepared.

*Anal.* C, 68.6; H, 8.8; N, 8.5.

A portion of a reaction product, prepared as before from cyclohexylamine and acetylene over cadmium and zinc acetates at 140°, was flash distilled, and all material which distilled below 78° (0.3 mm.) was hydrogenated over platinum in ethanol as solvent. *n*-Heptane and octane were added before distillation to facilitate a separation of products. By ultraviolet analysis, 0.14 ml. (1.6 mmoles) of benzene was found to be present in the cuts boiling below 45° (8 mm.). A portion of the highest boiling material taken overhead, b.p. 73–99° (0.7 mm.), crystallized. The crystals, m.p. 105–106°, were shown by infrared analysis to be an amide and were positively identified as *N*-cyclohexylacetamide by a mixed m.p. with an authentic sample. The yield, 2.6 g.,

corresponded to 50% of theory based upon the moles of acetate catalyst used.

*N-n*-Butylcyclohexylamine was prepared by a modification of the procedure described by Campbell, *et al.*,<sup>6</sup> for its preparation from butyraldehyde and cyclohexylamine. The modified procedure employed *n*-butylamine and cyclohexanone. The phenylthiourea derivative, m.p. 103–104°, was prepared from a portion of the amine, b.p. 113° (29 mm.),  $n_D^{20} 1.4530$  (lit.<sup>6</sup> b.p. 87–90° [12 mm.],  $n_D^{20} 1.4533$ ).

*Anal.* Calcd. for  $C_{17}H_{26}N_2S$ : C, 70.3; H, 8.97. Found: C, 70.2; H, 8.8.

*N-n*-Hexylcyclohexylamine was also prepared by the procedure referred to above; cyclohexanone and *n*-hexylamine were used in this case.

*Anal.* Calcd. for  $C_{12}H_{25}N$ : C, 78.7; H, 13.6. Found: C, 78.7; H, 13.6.

The phenylthiourea derivative, m.p. 91–91.5°, was prepared from a fractionally distilled portion of the amine, b.p. 66° (0.6 mm.),  $n_D^{20} 1.4560$ .

*Anal.* Calcd. for  $C_{19}H_{30}N_2S$ : C, 71.7; H, 9.52. Found: C, 71.6; H, 9.3.

**Acknowledgment.**—The authors are indebted to H. W. Rollmann for interpretation of mass spectral data, and to R. S. Silas and M. E. Smith for analyses of infrared spectra.

(6) K. N. Campbell, A. H. Sommers and B. K. Campbell, *This Journal*, **66**, 82–84 (1944).

[CONTRIBUTION FROM RESEARCH DIVISION, PHILLIPS PETROLEUM CO., BARTLESVILLE, OKLA.]

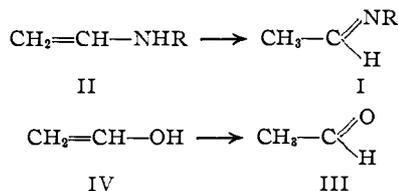
## *N,N*-Dialkyl-1,1-dimethyl-2-butynylamines by the Reaction of Propyne with Secondary Aliphatic Amines

BY C. W. KRUSE AND R. F. KLEINSCHMIDT

RECEIVED JULY 8, 1960

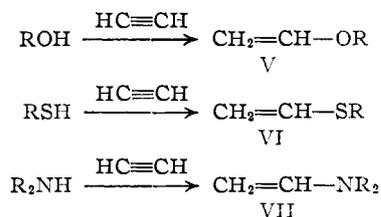
Propyne was allowed to react in a 2:1 molar ratio with secondary aliphatic amines in the presence of cadmium and zinc acetates to produce *N,N*-dialkyl-1,1-dimethyl-2-butynylamines (XI) in excellent yields. The structure was proved by an independent synthesis. 2-Methyl-1-penten-3-yne was obtained by pyrolysis of the amine oxide of XI. The normal hydrogenation of the triple bond was accompanied by hydrogenolysis of the tertiary carbon-nitrogen bond when ethanol was used as a solvent. Mesityl oxide was obtained by acid hydrolysis of XI.

Recent studies in our laboratories<sup>1</sup> have shown that *N*-alkylethylideneimines (I), not *N*-vinylamines (II), are produced by the cadmium acetate-zinc acetate-catalyzed reaction of acetylene with primary amines. An analogous reaction is observed when acetylene reacts with water in the presence of mercuric ion; acetaldehyde (III), not vinyl alcohol (IV), is obtained. It is reasonable, but not necessary, to assume that vinyl derivatives II and IV are intermediate products, and that tautomerization favors the imino form in the nitrogen system as it does the keto form in the oxygen compounds.



Tautomerization is possible, however, only when there is a hydrogen atom attached to the hetero atom. Vinyl ethers (V) and vinyl sulfides (VI)

can be prepared readily from alcohols or mercaptans by Reppe's vinylation techniques.<sup>2</sup> By analogy, one would expect to obtain *N*-vinylalkylamines (VII) in the same manner.



Reppe reported that although secondary amines absorbed acetylene in the presence of basic compounds (sodium or potassium hydroxides) or in the presence of cadmium salts and zinc salts, in most cases only unidentified, resin-like products were formed.<sup>2</sup> Although conditions were not found for a simple vinylation of secondary amines with acetylene, cuprous acetylide catalyzed a reaction in a 2:1 molar ratio to produce *N,N*-dialkyl-1-methyl-2-propynylamines (VIII) in 50 to 67% theoretical yields.<sup>3</sup>

(1) C. W. Kruse and R. F. Kleinschmidt, *This Journal*, **83**, 213 (1961).

(2) W. Reppe and co-workers, *Liebig's Ann. Chem.*, **601**, 81 (1956).