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The Zeolite-Catalyzed Amination of Acetylenes

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N-Isopropylidenemethylamine, $(CH_3)_2C{=}NCH_3$, has been synthesized in 80% yield (based on conversion) by the continuous condensation of methylamine with propyne at 1 atm pressure under catalysis by a zinc (II) ion-exchanged Y zeolite. This is the first synthesis of a heteroatomfunctional organic compound possessing broad synthetic utility that is not equally or better catalyzed by a nonzeolitic material. Condensations involving other amines and acetylenes are also described.

INTRODUCTION

Organic imines $R_1R_2C{=}NR_3$, the nitrogen analogs of aldehydes and ketones, are highly versatile synthetic intermediates which participate in reactions similar to those of the corresponding carbonyl compounds as well as in those unique to imines, including transimination (*1*); aldol condensation (*2*); addition of organometallic reagents (*3*), hypophosphorous acid or diethyl hypophosphite (*4*); condensation with mercaptoacetic acid (*5*), acid chlorides (*6*), chloramines (*7*), or carbon disulfide (*8*); oxidation to oxaziranes (*9*); and addition of 1,3-dipolar reagents (*10*). We now report a novel technique for the synthesis of simple ketimines which utilizes the continuous, direct condensation of amines and acetylenes at atmospheric pressure under catalysis by a zinc (II) ion-exchanged Y zeolite.

The synthesis of *N*-isopropylidenemethylamine from methylamine and methylacetylene is described below. Also reported are some reactions involving other amines and acetylenes which illustrate the potential scope of this new synthetic technique. Critical to the success of the general reaction is the use of certain metal ion-exchanged Y zeolites as heterogeneous catalysts. Zeolites were selected as potential catalysts because they contain the exchanged metal ions in an environment wherein they remain stable and isolated from one another and, following dehydration, are strongly associated with the zeolite surface through only three of their available coordination sites. Coordination of one or of two different molecules at the remaining, unfilled sites of the metal ions was considered probable and a potential means of facilitating addition reactions of organic molecules.

Previous attempts to prepare imines directly by amination of acetylenes under mild conditions have failed. Although the addition of amines to acetylenes activated by adjacent carbonyl groups is efficient and facile (*11*), the reaction of acetylene itself with primary aliphatic amines yields isolable 1:1 adducts only upon heating the reactants under several atmospheres of pressure (*12*). Krause and Kleinschmidt (*13*) showed that the resulting adducts were not the vinylamines earlier claimed by Reppe (*12*) but were actually the tautomeric imines (Eq. 1) expected by analogy to the hydration of acetylenes, which gives ketones rather than vinyl alcohols.

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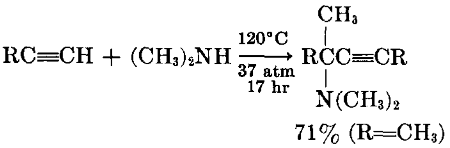
$$HC{\equiv}CH + C_2H_5NH_2 \xrightarrow[53\text{ atm, }140°\text{C, }35\text{ hr}]{Zn(OAc)_2\text{–}Cd(OAc)_2} \underset{58\%}{C_2H_5N{=}CHCH_3} \quad (1)$$



$$RC{\equiv}CH + (CH_3)_2NH \xrightarrow[37\text{ atm},\ 17\text{ hr}]{120°\text{C}} R\overset{CH_3}{\underset{N(CH_3)_2}{C}}C{\equiv}CR \quad (2)$$

71% (R=CH$_3$)

Reactions with secondary amines and the same catalyst gave 2:1 adducts with alkylacetylenes (Eq. 2) (*14*), but polymers resulted when acetylene itself was used. However, with a copper acetylide catalyst in tetrahydrofuran solvent, adducts of acetylene have been isolated in good yield (Eq. 2, R=H) (*15*).

Most amination reactions of acetylenes, however, do not yield the simple 1:1 adducts but instead give products derived from them. Thus ammonia and acetylene have yielded piperidine (*16*) or acetonitrile (*17*), depending upon the conditions, and ring substituted anilines react with acetylenes to give quinolines (*18*). Several other, related reactions have been described (*19*).

EXPERIMENTAL

Catalysts and Apparatus

The catalysts were prepared by two exhaustive exchanges of powdered Linde Y zeolite with hot, aqueous solutions of the appropriate nitrate salts of transition metals. About 70% exchange of sodium was realized in most cases after extensive washing of the exchanged zeolites with distilled water, as determined by elemental analysis. The washed zeolites were dried on a Büchner funnel under aspirator pressure at 25°C for 15 hr to give unactivated materials whose x-ray powder patterns showed a high degree of crystallinity in the samples.

Analysis of the ZnY material disclosed a Si/Al ratio about 5:1 and a cation deficiency of 5% in the 69% Zn (II)-exchanged Y zeolite. The average molar composition was found to be (anhydrous basis): 1.00 Al_2O_3, 4.87 SiO_2, 0.26 Na_2O, and 0.69 ZnO.

The catalytic properties of the Zn (II) ion-exchanged Y zeolite (ZnY) samples were found to be highly dependent upon the manner in which the materials were finally activated prior to use. The most effective activation, in terms of catalyst productivity, consisted of "flash vacuum activation" (FVA), wherein a flask was half loaded with the air-dried zeolite, evacuated to less than 0.1 mm pressure, and then surrounded with glass wool maintained at 300–400°C with a heating mantle. The temperature of the air bath was brought to 475°C within 5 min and vacuum dehydration was continued for 2 hr. Other methods of activation were less effective than the flash vacuum activation technique just described, as judged by the observations recorded in Table 1.

Flash vacuum activated seasand was used as a diluent of the zeolite and, alone, as a preheater. The catalyst column was prepared in a dry box under nitrogen in a Pyrex glass tube 30 × 1.5 cm. Introduced in order were a glass wool plug, sand for a length of 8 cm, a mixture of 5 g of catalyst powder with 20 g of sand, and finally another 8 cm sand. The tube was then installed in the reactor apparatus under a flow of dry air.

At the top of the catalyst tube was a glass head with three seals to Tovar metal ¼ in. tubing. Each metal tube was fitted with a tapered Teflon plug within a compression nut through which was passed a ⅛ in. stainless steel line. The amine and acetylene were mixed in a tee and passed through one of the head inlets; each reactant supply line was fitted with a heated flow meter and micrometer needle valve as a flow regulator. The second head fitting contained an annular thermocouple probe which reached to the center of the catalyst bed and was connected to an automatic temperature controlling apparatus. Through the third head inlet was passed air or nitrogen as desired. At the lower end of the reactor tube was attached a Graham

TABLE 1

Synthesis of Isopropylidenemethylamine $(CH_3)_2C{=}NCH_3$ (**1**) from Methylamine (0.18 mol/hr) and Methylacetylene (0.09 mol/hr) at 300°K with ZnY Zeolite as Catalyst[a]

Entry	Conditions	Time on stream (hr)	Liquid effluent (g/hr av)	Weight % yield		Weight % 1 in liquid effluent
				Ketimine **1**	Nonvolatiles	
1	5 g ZnY in 20 g sand, activated 450°C/2 hr under high vacuum, reactor brought to 300°C in dry air	0–15.5	2.7	25	4.6	77
		15.5–39.5	2.4	23	3.5	81
		39.5–71.5	2.2	21	2.6	82
2	2.5 g ZnY/10 g sand, activated 450°C/2 hr/vac, to 300°C rapidly in amine	0–21.5	3.3	—	—	—
		21.5–46.5[b]	2.1	19.5	2.8	79
3	Catalyst from entry 2 "reactivated" in reactor at 500°C/20 hr/ dry air	18.5	1.9	—	—	—
4	1 g ZnY/3 g sand[c] activated 475°C/2 hr/vac, to 300°C in amine	22	1.2	—	—	—
5	5 g 25% exchanged ZnY/20 g sand, activated 475°C/2 hr/vac, to 300°C amine	0–22	2.8	26	11	66
		22–45.5	2.0	—	—	—
		45.5–61[b]	1.6	—	—	—
6	As in entry 1, except amine flow decreased to afford amine/ propyne = 1.2	25.5	2.2	20.5	4	76
7	As in entry 1, except catalyst activated at 650°C	0–28	2.0	17	4.8	71
		28–72	1.3	—	—	—
8	5 g ZnY/20 g sand, 450°C/N_2 in reactor, 16 hr, no vacuum activation	21.5	3.0[d]	28	7.3	73
9	5 g ZnY/20 g sand, 300°C/1 hr in amine in reactor, no other activation	29	1.5	<8	10	<45

[a] The nominal contact time was 15 sec for a single pass of the reactants through the catalyst zone if the space occupied by the solids (5 g zeolite in 20 g sand) is neglected.

[b] Reaction arbitrarily terminated.

[c] Same result with 1 g ZnY in 10 g sand.

[d] Rate had decreased to 0.8 g/hr at the end of the stated reaction period.

condenser, vacuum adaptor with a line to a bubbler, and a receiver for liquid products. The reactor tube was heated by a cylindrical, heavy duty, heating mantle.

N-Isopropylidenemethylamine (1)

The best preparation of **1** (entry 1, Table 1) was carried out as follows. The reactor was heated to 300°C in dry air at 75 ml/min and methylamine was then introduced at 0.18 mol/hr as the air flow was terminated. The methylacetylene (0.09 mol/hr) was added to the input stream when the amine first emerged from the reactor (~5 min). Other prereaction conditions and the results of additional experiments are recorded in Table 1. The flow of reactants was continued at a steady rate over 71 hr; the yellow, effluent liquid was analyzed by glpc (15 ft × $\frac{1}{4}$ in. SF96, 20% on Chromosorb W, 25°C) at the intervals and with the results shown in the table. There did not appear to be a significant difference in rate when half the catalyst was used at the same reactant flow rate (half the contact time) after being brought to temperature in the amine rather than in air (entry 2, Table 1). The catalyst mixtures recovered following these reactions or those recorded in Table 2 were not examined in any detail, nor was the effluent mixture of volatile, unreacted amine and acetylene analyzed. The yields of any aldimine products were not determined except where indicated.

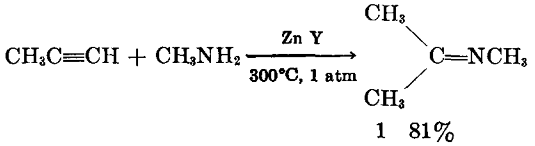
Results

N-Isopropylidenemethylamine (Table 1)

In the best of the reactions studied (entry 1), the yield of the ketimine **1** was about 23% based on the reactants fed into the reactor and about 81% based on reactants consumed (Eq. 3); unconverted amine and acetylene should be readily recyclable. After 71 hr of continuous operation and a catalyst turnover >1000, the reaction was terminated. In this and the other reactions in Table 1, the first 2–3 ml of liquid produced had a high refractive index (>1.50) which fell in the next 10–20 ml of condensate collected until a constant value typical of the main product mixture, n_D^{25} ~ 1.410, was reached. The initially formed side products and other impurities could be removed by distilling the more volatile product imine **1** from the mixtures. In the case of reaction 1, Table 1 distillation separated a volatile product fraction of bp 58–64°C (*20*). The composition of the distilled material was determined by glpc analysis as >90% *N*-isopropylidenemethylamine; the only other significant product was the isomeric aldimine, *N*-*n*-propylidenemethylamine (~6%). The distillation residue was composed of several compounds, as determined by glpc analysis, and contained both NH and C=N bands in its infrared spectrum.

N-Isopropylidenemethylamine was characterized by its physical properties, bp 65–66°C, n_D^{25} 1.4010 to 1.4030 (variable depending on purity; *lit*[21] bp 65–66°C, n_D^{25} 1.4069); the formation of acetone 2,4-dinitrophenylhydrazone, mp 122–123°C, mixture mp with authentic material 122–123°C; and spectral data. The infrared spectrum of the ketimine contained no N–H bands but exhibited strong C=N absorption (*22*) at 1670 cm^{-1}, and the NMR spectrum consisted of two (*23*) C=C—CH$_3$ peaks at δ 1.85 and 1.72, which were split into quartets (J = 1.2, 0.75 Hz) by the *N*-methyl group (δ 2.93).

The isomeric aldimine was partially purified by preparative glpc and identified from its 2,4-dinitrophenyhydrazone, mp 152–153°C (mixture mp with propionaldehyde 2,4-dinitrophenylhydrazone 151.5–152.5°C), and NMR spectrum, which contained absorption (*24*) due to the RCH=N- hydrogen at δ 7.66 and a doublet N–CH$_3$ peak at δ 3.20 (*syn–anti* isomers). Also present in very small amount was the saturated secondary amine, isopropylmethylamine, which was identified from its NMR spectrum (N–CH$_3$ singlet at δ 2.30, isopropyl doublet at δ 0.97).



$$\mathrm{CH_3C{\equiv}CH + CH_3NH_2 \xrightarrow[300^\circ C,\ 1\ atm]{Zn\ Y} \overset{CH_3}{\underset{CH_3}{>}}C{=}NCH_3} \qquad (3)$$

1 81%

In order to show that an equilibrium established in the first part of the reactor did not determine the extent of product formation, a sample of isopropylidenemethylamine was passed through a fresh bed of catalyst at 300°C and 15 sec contact time. Over 80% of the ketimine was recovered, although none of the aldimine survived and more isopropylmethylamine and high-boiling compounds were now present in the recovered product.

Many different metal-exchanged zeolites, as well as Linde Y zeolite itself, were found not to produce any liquid products from methylamine and methylacetylene under the conditions of Table 1. These included samples of Y zeolite exchanged with the univalent cations of Ag and Cu, the divalent cations of Ca, Co, Ni, Cu, Pd, Pt, and Hg, and the trivalent cations of Rh, Os, Ir, and Au. Also tested was Co (II) ion-exchanged X zeolite, which proved ineffective, and Cu (II) ion-exchanged X zeolite, which gave 2.9 g/hr of condensate over 2.5 hr before the reaction was arbitrarily terminated; however, the high-boiling products formed in greater quantity than with ZnY and did not decrease in favor of the desired imine. A Pb (II) ion-exchanged Y zeolite gave pure **1** for a brief period before becoming inactive, and Cd (II) ion-exchanged Y zeolite (CdY) gave results roughly comparable to those with ZnY, except that more high-boiling products were formed.

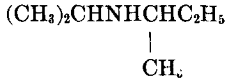
Some additional experiments related to the synthesis of *N*-isopropylidenemethylamine, but not included in Table 1, were also carried out. Use of 5 g ZnY activated at 450°C/15 hr in air gave products similar to those from a vacuum activated catalyst but for only 22 hr. When 5 g ZnY, activated at 475°C/2 hr in vacuum was employed with the reactants diluted with an equal flow of N_2, only 0.7 g/hr condensate was observed over 24 hr. Under similar conditions, except with pentane added as solvent such that pentane/$HC\equiv CCH_3$/amine = 1:1:2, only 46% of the products were distillable and volatiles contained much more isopropylmethylamine than usual. A ZnY catalyst treated with excess $Zn(NO_3)_2$, dried without washing, and flash vacuum activated failed to give liquid products. Reactions run as in entry 1, Table 1, except at a reactor temperature of 250 or 350°C produced only half the liquid condensate noted in entry 1. A reaction gave ~2.6 g/hr of liquid condensate, not analyzed, when the amine (0.17 mol/hr) and a 1:1 mixture of allene and propyne (0.18 mol/hr) were allowed to react over 6.5 hr under the conditions of entry 1. When allene alone was used, the reaction ceased spontaneously after producing 28 g of condensate in 23 hr. A 25% Zn (II) ion-exchanged X zeolite (ZnX, 5 g), activated 475°C/2 hr/vacuum, gave 0.6 g condensate per hr over 5 hr, and high boilers comprised an increasing percentage of products with time. Nonzeolite Zn catalysts performed poorly, e.g., 16 g $ZnWO_4$ activated 150°C/16 hr in N_2 (0.1 g hr condensate after 8 hr); 11 g $Zn(OAc)_2\cdot 2H_2O$ activated 300°C/1 hr in a stream of methylamine (0.2 g/hr condensate after 4 hr at 400°C); and 12 g $ZnMoO_4\cdot H_2O$ activated 300°C/0.5 hr in methylamine (no product in 2 hr at 300°C, then 1.5 g/hr for 2 hr at 400°C).

Condensations Involving Other Amines or Acetylenes (Table 2)

None of these reactions was repeated more than twice. The conditions chosen were near those described for entry 1, Table 1, but the optimum conditions for each new reaction remain undefined.

Propyne and ethylamine (entry 2). Distillation of a portion of the reactor effluent gave fractions of bp 52–76°C, n_D^{25} 1.3923–1.4043, that contained five products, of which two predominated. Strong absorption at 1655 cm^{-1} in the infrared spectrum of the last fraction, which was 90% pure in a compound believed to be *N*-isopropylideneethylamine, was typical of the imine C=N stretch; the strong band at 1235 cm^{-1}, also present, may be characteristic of *N*-isopropylidineimines, since it was present in the ketimines obtained from propyne with methylamine or isopropylamine and was part of a doublet characteristic of the imine from aniline (1220,

TABLE 2
KETIMINE SYNTHESES FROM AMINES AND ACETYLENES AT 300°C IN THE PRESENCE OF Zn Y ZEOLITE[a]

Entry	Amine (mol/hr)	Acetylene (mol/hr)	Reaction time (hr)	% Yield[b] 1:1 adduct	Weight % ketimine in liquid effluent	Product
1	$(CH_3)_3CNH_2$ (0.18)	$CH_3C{\equiv}CH$ (0.09)	4.5	0	0	—
2	$C_2H_5NH_2$ (excess)	$CH_3C{\equiv}CH$ (0.09)	6.0	[c]	—	—
3	$(CH_3)_2CHNH_2$ (0.24)	$CH_3C{\equiv}CH$ (0.09)	4.7	32	50	$(CH_3)_2CHN{=}C(CH_3)_2$
4	$C_6H_5NH_2$ (0.20)	$CH_3C{\equiv}CH$ (0.09)	4.0	16	54	$C_6H_5N{=}C(CH_3)_2$
5[d]	CH_3NH_2 (0.15)	$CH_3C{\equiv}CCH_3$ (0.15)	3.3	16	32	$CH_3N{=}C(CH_3)CH_2CH_3$
6	$(CH_3)_2CHNH_2$ (0.18)	$CH_3C{\equiv}CCH_3$ (0.09)	9.8	2[e]	11[e]	 $(CH_3)_2CHNH\underset{CH_3}{\underset{\vert}{CH}}C_2H_5$
7	$(CH_3)_2NH$ (0.14)	$CH_3C{\equiv}CH$ (0.18)	3.5[f]	—	—	—
8	NH_3 (0.14)	$CH_3C{\equiv}CH$ (0.18)	3.0[f]	—	—	—
9	CH_3NH_2 (0.14)	$HC{\equiv}CH$ (0.14)	2.3[f]	—	—	—
10	CH_3NH_2 (0.18)	$n\text{-}C_4H_9C{\equiv}CH$ (0.09)	4.5	57	66	$n\text{-}C_4H_9C(CH_3){=}NCH_3$

[a] Five grams of zeolite in 20 g sand, activated at 475°C/2 hr under vacuum.
[b] Relative to theoretical weight of 1:1 adduct from the limiting reagent fed into the reactor.
[c] Two major plus three minor products.
[d] Two and one-half grams ZnY used.
[e] Yield of saturated amine shown.
[f] Reaction ceased spontaneously.
[g] Purified by passage through activated carbon and 3A sieves.

1235 cm^{-1}). The other principal product, concentrated in an earlier fraction, also showed the 1640 cm^{-1} imine band but less of the 1235 cm^{-1} band; this compound may have been the aldimine *N*-*n*-propylidene-ethylamine.

Propyne and isopropylamine (entry 3). The amine was introduced as a liquid from a Teflon syringe driven by a Model 255-2 Variable Speed Sage pump and cooled by a demountable condenser made of brass pipe and sealed with O-rings. The reactor effluent was distilled twice and then analyzed by glpc for the imine. The third distillation afforded 97% pure *N*-isopropylideneisopropylamine, bp 89–91°C, n_D^{24} 1.4085 (glpc collected sample, *lit*[25] bp 93.5°C, n_D^{20} 1.4088), which could never be obtained completely free of isopropylamine by simple distillation. The pure ketimine had strong ir bands at 1655 and 1230 cm^{-1} and NMR peaks at δ 3.5 (seven-line pattern with 6 Hz splitting, 1 H), δ 1.83, 1.72 (strong singlets, $RN{=}C(CH_3)_2$, 6 H) and δ 0.98 (doublet, isopropyl methyls, 6 H).

Propyne and aniline (entry 4). Aniline was introduced as a liquid and the reactor effluent was distilled after the indicated reaction time, bp 67–81°C (13 mm); the distillation fractions contained 1.5–79% of the anil, *N*-isopropylideneaniline, mixed with aniline. No other product was detected on glpc analysis (SE52 at 130°C). The 79% sample compared favorably by ir and glpc with an authentic 80/20 mixture of the anil with aniline. The pure anil has bp 80–81°C (13 mm) (*26*) or 85–87°C (13 mm) (*27*) and n_D^{20} 1.5398 (*28*).

2-Butyne and methylamine (entry 5). The acetylene was pumped into the reactor head as a liquid. Distillation of 24 g of reactor effluent gave 2 g of forerun, bp 25–80°C, and 9.7 g of distillate, bp 80–87°C, n_D^{24} 1.4115. Glpc analysis showed the latter material to contain 78% of *N*-2-butylidenemethylamine, 9% of 2-butylmethylamine, 5% of various low boilers, and 13% of reactants. The distillate afforded a 2,4-dinitrophenylhydrazone, mp 112–113°C after one recrystallization, mixture mp with authentic 2-butanone 2,4-DNP 112–113°C (*lit* [29]mp 117°C).

The ketimine was also obtained by distillation in 95% purity from another run, bp 87°C, n_D^{24} 1.4134. The ir spectrum of this material contained the characteristic C=N band at 1670 cm^{-1}, no N–H bands, and only medium intensity absorption at 1220, 1235 cm^{-1} (doublet). The NMR spectrum, consistent with the given structure, contained 3 H at δ 3.00 ($N–CH_3$, seven lines within 5 Hz); 4.9 H at δ 2.35–1.80 ($=C–CH_2$, five groups of five lines each) and δ 1.73 ($=C–CH_3$, four lines within 3 Hz); and 3.00 H at δ 1.00 ($C–CH_3$, triplet, each with four narrowly spaced lines).

The major impurity in the distillate was indicated to be 2-butylmethylamine by the ir spectrum of a glpc-collected sample, which was typical of a secondary aliphatic amine, and the NMR spectrum which contained an unsplit $N–CH_3$ peak at δ 2.36 overlapping a one-hydrogen multiplet ($N–CHR_2$) at δ 2.6–2.1, with the remainder of the absorption (9 H) at δ 1.6–0.7.

2-Butyne and isopropylamine (entry 6). Both reactants were introduced to the reactor as liquids. Little volatile product was produced. The major component of the distillate (38%) was isolated by glpc, n_D^{24} 1.4006, and identified by ir and NMR analysis as the *saturated* 1:1 adduct, isopropyl-2-butylamine.

Discussion

We have observed a novel condensation reaction whereby an acetylene and a primary amine yield a ketimine as the major product in the presence of zinc(II) ion-exchanged Y zeolite. Although a Zn ion-exchanged X zeolite has been used previously for the conversion of alkylaromatic compounds to nitriles (*30*), the use of related catalysts in reactions of acetylenes with amines has not been noted previously. Our reaction is unique in that it affords unsaturated 1:1 adducts under conditions which permit operation at 1 atm pressure, in contrast to the prior work noted above, and is the first reaction of preparative value in the organic synthesis of polar materials to be catalyzed much better by a zeolite than by other means. Many reactions have been achieved with a zeolite catalyst that also proceed well in other systems, however (*31*).

In addition to suggesting that further studies with ion-exchanged zeolite catalysts may reveal other, unique condensation reactions involving heteroatom molecules and hydrocarbons, our results offer a practical alternative for the synthesis of simple ketimines to the ketone–amine condensation method commonly used (*6*), since no water is formed that requires continuous removal to drive the equilibrium (*32*) forward (Eq. 4). In the case of highly volatile reactants,

$$R_2C{=}O + R'NH_2 \overset{H^+}{\rightleftarrows} R_2C{=}NR' + H_2O \qquad (4)$$

azeotropic removal of water (*25*) with benzene or toluene is not feasible, and excessive amount of inorganic drying agents (*6*) must be used.

The most studied reaction was the preparation of *N*-isopropylidenemethylamine (**1**, acetone *N*-methylimine) from methylacetylene and methylamine. Only ZnY and CdY were highly effective in producing imines; under the optimum of the conditions studied, the yield of ketimine **1** was about 80% over 71.5 hr based on starting materials reacted, and a turnover of >1000 moles of product formed per mole of Zn ion present confirmed the efficiency of the heterogeneous catalyst following the proper mode of activation. Some methods of activating the zeolite catalysts greatly reduced their activity (see Table 1), which no doubt reflects differences in the environment at the catalytic centers resulting from the various methods of dehydration. The superior FVA technique is probably capable of further refinement.

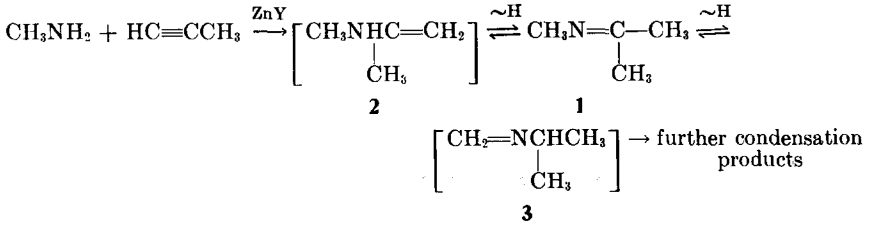
It will be recalled that attempts to catalyze reaction 3 with zinc catalysts other than ZnY failed with $ZnWO_4$, $Zn(OAc)_2$, $ZnMoO_4$, and a ZnY containing excess $Zn(NO_3)_2$. This contrasts with the $Zn(OAc)_2$–$Cd(OAc)_2$ catalyzed additions of Krause and Kleinschmidt (*13*) (Eq. 1). When ZnX was used, the rate of product formation was only ¼ that with ZnY, and high boilers comprised an increasing percentage of the products with time. This could reflect an increasing residence time of the product imine in the pores, due to slow plugging, which one would expect to enhance still further condensation reactions.

We assume that the unique catalytic activity of ZnY involves active participation of the dehydrated zeolitic zinc(II) ions via the partially unoccupied coordination positions characteristic of the activated material. Among the various zeolites, those exchanged with metals bearing a completely filled *d*-subshell seem to be best suited to catalyzing the reaction, as judged by the superior performance of ZnY and CdY. The third member of the IIB subgroup, the mercury (II) ion-exchanged Y zeolite, yielded metallic mercury under the conditions of the reaction. The isoelectronic copper (I) ion-exchanged Y zeolite was apparently also reduced once it had been exposed to the reactants. The specific advantage of the 4-coordinate over the higher coordinate transition metal ions more commonly encountered in catalysis is noteworthy but presently without clear-cut explanation.

Modifications of the conditions, such as dilution of the reactants with an equal flow of N_2 to reduce the contact time, dilution with pentane, or operating at 50°C above or below the preferred temperature of 300°C, were all deleterious to the rate of product formation and the selectivity for the imine. The temperature dependence probably reflects a balance of that needed for reaction and that required to expell products from the zeolite pores, and may well prove to be different for each pair of reactants.

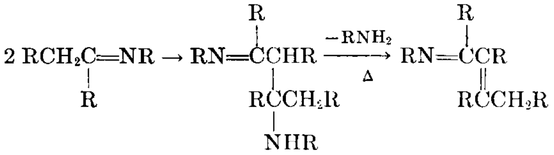
Two reactions run using allene in place of the isomeric propyne did produce the imine **1**, but the extent of product formation was less than that when propyne was used. Whether a common intermediate was involved in both cases is unknown. Several other condensations involving other amines or acetylenes were also attempted (Table 2). This survey was carried out in an attempt to roughly characterize the scope of the imine direct synthesis. In general, the reaction appears most suited to the use of monoalkylacetylenes and primary amines, at least under the conditions examined. The potential remains for improving upon these reactions by judicious adjustment of the reaction conditions and improvements in the catalyst.

Although the data do not permit mechanistic conclusions to be drawn, it is probable that the initial products were vinylamines (enamines, **2**) and that the ketimine tautomers were formed subsequently by a hydrogen shift (Eq. 5). No attempt has been made to trap or isolate such enamines, if indeed this were possible. Further tautomerizations can give aldimines **3**, which may well be the principal precursors to the high boiling side products observed in varying amounts, as noted below.



$$CH_3NH_2 + HC{\equiv}CCH_3 \xrightarrow{ZnY} \underset{\mathbf{2}}{\left[CH_3NH\underset{CH_3}{C}{=}CH_2\right]} \overset{\sim H}{\rightleftharpoons} \underset{\mathbf{1}}{CH_3N{=}\underset{CH_3}{C}{-}CH_3} \overset{\sim H}{\rightleftharpoons} \underset{\mathbf{3}}{\left[CH_2{=}N\underset{CH_3}{C}HCH_3\right]} \rightarrow \text{further condensation products} \quad (5)$$

Another means of generating reactive aldimines is via terminal amination of acetylenes $RC{\equiv}CH$, such as the aldimine $CH_3CH_2CH{=}NCH_3$ isolated from propyne and methylamine in very low yield. Amination of the substituted acetylenic carbon would not be expected to the total exclusion of terminal amination in any of the reactions, although preferential nonterminal addition would be anticipated by analogy to other nucleophilic additions to acetylenes (*13*). We presently feel that reactive (*6*) aldimines $RCH_2CH{=}NR$ were produced in all the experiments but mainly decomposed to high boiling products via aldol reactions (*6*). The decomposition of aldol products thus formed (Eq. 6) may account for the continued presence (<1%) of starting amines in all the fractions obtained on distilling the crude imines. It is also probable that the reaction of methylamine with acetylene itself failed due to rapid clogging of the zeolite pores with aldol polymers, since the expected product is $CH_3CH{=}NCH_3$, one of the most reactive of the simple aldimines.



$$2\,RCH_2\underset{\substack{|\\R}}{C}{=}NR \rightarrow RN{=}\overset{\substack{R\\|}}{C}\underset{\substack{|\\RCCH_2R\\|\\NHR}}{}CHR \xrightarrow[\Delta]{-RNH_2} RN{=}\overset{\substack{R\\|}}{C}\underset{\substack{\|\\RCCH_2R}}{}CR \qquad (6)$$

The formation of the saturated amine from isopropylamine and 2-butyne in low yield (entry 6, Table 2) may reflect a failure of the relatively bulky imine to survive an unduly long residence within the zeolite, but we cannot account for its origin in a definitive way at present. It might be noted that the reduction of enamines by amines has been observed in certain instances (*33*) and could possibly be involved in this case. In the absence of steric effects, the ketimine expected in this experiment, $(CH_3)_2CHN{=}C(CH_3)CH_2CH_3$ or $(CH_3)_2C{=}NCH(CH_3)CH_2CH_3$, might have formed more cleanly than usual, since no aldimine $RCH{=}NR$ could have been formed by hydrogen shifts alone. Quite possibly, the use of substrates of increasingly larger critical diameter, as in this example, may introduce undesirable steric factors into the reaction; a limitation due to the zeolite pore size on the access to and proper type and extent of complexing of the reactants at a catalytic site would be anticipated, and steric inhibition of diffusion of product molecules out of the pores should be even more limiting.

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