The Mechanism of Base-Catalyzed Ethynylation in Donor Solvents

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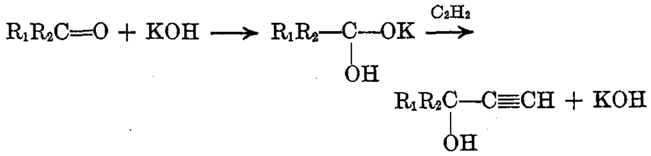
The catalytic ethynylation of aldehydes and ketones in donor solvents exhibiting high solubilities for acetylene has been shown to involve the intermediate formation of acetylene–base and ethynylcarbinol–base complexes. Solvent–acetylene complexes functioning as cocatalysts are also strongly indicated. The highly specific process of catalytic ethynylation is compared with stoichiometric acetylenic diol formation, and a mechanism for the latter, independent of carbinol formation, is suggested.

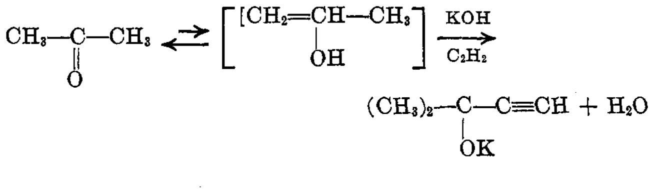
The base-catalyzed ethynylation of aldehydes and ketones to yield secondary and tertiary acetylenic carbinols or glycols has had various mechanistic interpretations since the discovery of this reaction. Favorskii,[1] its discoverer, regarded the initial step of the reaction as involving addition of potassium hydroxide to the carbonyl component followed by subsequent reaction with acetylene and liberation of free base.



$$R_1R_2C{=}O + KOH \longrightarrow R_1R_2{-}\underset{OH}{\underset{|}{C}}{-}OK \xrightarrow{C_2H_2} R_1R_2\underset{OH}{\underset{|}{C}}{-}C{\equiv}CH + KOH$$

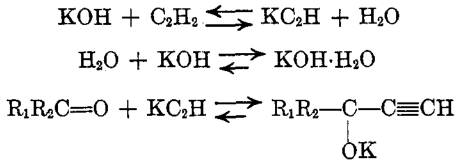
This mechanism is invalid owing to the fact that alkali hydroxide–carbonyl-type adducts have never been isolated from this reaction.[2,3] For example, the reaction of ketones such as acetone or methyl ethyl ketone with a stoichiometric amount of powdered, 98–99% potassium hydroxide in methylal or diisopropyl ether at 0–40° (standard ethynylation conditions) fails to yield ketone–base adducts. Also it has been shown[4] that tertiary acetylenic carbinols and glycols react rapidly and essentially quantitatively with potassium and rubidium hydroxides to form 1:1 mole adducts, proving that the existence of free potassium hydroxide in this reaction is not possible.

Ethynylation through an enolic intermediate was also discredited when it was observed[5] that ketones such as benzophenone, incapable of enolization, still underwent ethynylation. Also the exceedingly small concentration of enolate derived from ketones is not in line with the observed rapidity of base-catalyzed ethynylation.[6,7]



$$CH_3{-}\underset{O}{\underset{\|}{C}}{-}CH_3 \rightleftarrows \left[CH_2{=}\underset{OH}{\underset{|}{C}}H{-}CH_3\right] \xrightarrow[C_2H_2]{KOH} (CH_3)_2{-}\underset{OK}{\underset{|}{C}}{-}C{\equiv}CH + H_2O$$

Bergman[8] has favored an ethynylation route which involved the intermediate formation of potassium acetylide *via* reaction of free base with acetylene in methylal and the subsequent reaction of the postulated acetylide with the carbonyl component. However, no explanation was advanced for the failure of sodium hydroxide to catalyze the reaction, although sodium acetylide was known to react with carbonyl compounds. Bergman considered at least twice the stoichiometric amount of base to be necessary to absorb water and prevent the reverse hydrolytic reaction. He also postulated the formation of molecular compounds (of inner complex nature) between potassium hydroxide and the solvents (acetals and glycol dialkyl ethers) used to activate the ethynylation reaction. The large amount of synthetic work carried out in recent years in liquid ammonia[2,9] using alkali metal acetylides has given further indirect support to Bergman's views.



$$KOH + C_2H_2 \rightleftarrows KC_2H + H_2O$$

$$H_2O + KOH \rightleftarrows KOH\cdot H_2O$$

$$R_1R_2C{=}O + KC_2H \rightleftarrows R_1R_2{-}\underset{OK}{\underset{|}{C}}{-}C{\equiv}CH$$

However, recent work[7] at this laboratory concerned with the catalytic ethynylation of aldehydes and ketones (using sodium or potassium hydroxides) in liquid ammonia under pressure has led to new conclusions regarding the mechanism of this reaction. The reaction is no longer considered to involve the intermediate formation of alkali metal acetylide and water. Instead both stoichiometric and catalytic ethynylation are believed to proceed *via* alkali hydroxide adducts of acetylene and the resulting acetylenic carbinol. Further, the formation of these intermediate species is significantly aided by donor solvents which solvate acetylene.

The activating effects due to certain solvents possessing donor centers which are capable of hydrogen bonding strongly with acetylene[10] have been recognized in recent years, particularly in catalytic and stoichiometric ethynylation.[6–8] It was also previously noted[7] that potassium acetylide formed *in situ* in liquid ammonia was surprisingly inferior to potassium hydroxide as an ethynylation catalyst under identical conditions. The above results and those described below further strengthen the belief that, in catalytic or

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[1] A. E. Favorskii, *J. Russ. Phys. Chem. Soc.*, **37**, 643 (1905); *Chem. Zentr.*, II, 1018 (1905).

[2] A. W. Johnson, "Acetylenic Compounds," Vol. I., Edward Arnold Co., London, 1946, pp. 11, 12, 136–147, and references cited therein.

[3] R. J. Tedeschi, J. P. Russell, and R. K. Frantz, unpublished work.

[4] R. J. Tedeschi, M. F. Wilson, J. Scanlon, M. Pawlak, and V. Cunicella, *J. Org. Chem.*, **28**, 2480 (1963).

[5] A. T. Babayan, *J. Gen. Chem. USSR*, **10**, 1177 (1940); *Chem. Abstr.*, **35**, 2858 (1941).

[6] N. Schachat and J. J. Bagnell, Jr., *J. Org. Chem.*, **27**, 1498 (1962).

[7] R. J. Tedeschi, A. W. Casey, G. S. Clark, Jr., R. W. Huckel, L. M. Kindley, and J. P. Russell, *ibid.*, **28**, 1740 (1963); U. S. Patent 3,082,260 (March 19, 1963).

[8] E. D. Bergmann, "The Chemistry of Acetylene and Related Compounds," Interscience Publishers, Inc., New York, N. Y., 1948, pp. 50, 51, and references cited therein.

[9] R. A. Raphael, "Acetylenic Compounds in Organic Synthesis," Academic Press Inc., New York, N. Y., 1955, pp. 10–12, 194, and references cited therein.

[10] A. C. McKinnis, *Ind. Eng. Chem.*, **47**, 850 (1955).

stoichiometric ethynylation with alkali hydroxides, the intermediate formation of alkali metal acetylide is not involved or plays a very minor part.

Complexes of acetylene and alkali hydroxides (NaOH and KOH) can be readily formed either at atmospheric pressure or under acetylene pressure. A potassium hydroxide–acetylene complex formed at atmospheric pressure in methylal at 20–25° during 24 hr. by slowly bubbling acetylene into the base–solvent slurry gave a 15% conversion (based on 1 mole of base per 500 ml. of methylal) to a KOH–C_2H_2 complex. When potassium or sodium hydroxides (1.5 moles) are slurried in liquid ammonia (50 ml.) under pressure and allowed to react with excess (6.0 moles) acetylene at 30–35° for 4 hr., conversions calculated as 1:1 mole complexes with KOH or NaOH were 12 and 7%, respectively. All the above products were isolated under anhydrous conditions and vacuum dried at room temperature below 1 mm.

A KOH–C_2H_2 complex formed by treating 0.15 mole of potassium hydroxide with 0.60 mole of acetylene in 20 ml. of liquid ammonia at 15–21° for 2 hr., followed by isolation and drying of the resulting finely divided, cream-colored solid in an atmosphere of dry acetylene, gave a 44% conversion to the 1:1 complex. It is likely that in an excess of liquid ammonia and in the presence of excess solvated acetylene prior to isolation the conversion to the complex is substantially higher. The dry complexes when heated at 1 mm. and 110° lost all their acetylene during a 4-hr. period. In contrast, a sample of sodium acetylide prepared[11] by treating sodium dispersion with acetylene in dioxane at atmospheric pressure and 65–75° was unchanged on identical treatment. This marked difference in thermal stability compared with a true alkali metal acetylide clearly shows that these acetylene–alkali hydroxide products are complexes rather than acetylides.

Infrared examination of a freshly prepared KOH–C_2H_2 adduct (in Nujol and KBr disk) failed to show the presence of $C{\equiv}C$ or $\equiv CH$ stretches at 4.68–4.76 and 2.96–3.08 μ, respectively, indicating acetylene has interacted with base *via* its π cylinder and acidic hydrogens. The resulting complex also has a strong tendency to associate strongly with solvents such as ammonia, methylal, or diisopropyl ether, and even prolonged vacuum drying fails to remove them completely. A complex dried under an acetylene atmosphere at room temperature initially contained 14% acetylene. After standing for 116 hr. at ambient room temperature under anhydrous conditions, the acetylene content was 11.5%, indicating fair stability for the complex.

The rapid, stoichiometric reaction of 3-methyl-1-butyn-3-ol (MB) and potassium hydroxide has been shown[4] to yield a solid reaction product in high conversion (98–100%) in solvents such as toluene, isopropyl ether, or liquid ammonia. The product is a white, crystalline solid of higher stability than the KOH–C_2H_2 complex and its composition corresponds to a 1:1 mole adduct. Present results indicate that the product is a complex in which both the tertiary hydroxyl group and ethynyl group are bound to the base, rather than a tertiary alkoxide containing a water of hydration. The adduct can also be prepared by the *in situ* reaction of acetone–acetylene and potassium hydroxide. Either adduct, freshly prepared or after several months storage at 0–5°, can be substituted for potassium hydroxide in catalytic ethynylation. When a sample of MB–KOH adduct prepared in isopropyl ether was employed in the catalytic ethynylation of acetone in liquid ammonia under pressure (1.2 moles acetone, 1.6 moles of acetylene, 0.10 mole of MB–KOH adduct, 200 ml. ammonia) a 97% conversion to methylbutynol was obtained, while the catalytic conversion based on the complex (moles of MB/mole of adduct) was 1170%. These results are somewhat superior to those realized with KOH (conversion based on acetone and KOH, 75 and 902%, respectively). However, a sixfold greater volume of ammonia was used in the former run (to facilitate stirring) although the mole ratio of other reactants was the same. The superior results are probably due to the greater concentration of ammonia, and its ability to exert a stronger cocatalyst effect.

The dry methylbutynol–potassium hydroxide adduct has been observed[4] to undergo a gradual, solid-phase transformation into the corresponding acetylenic diol (2,5-dimethyl-3-hexyn-2,5-diol)–potassium hydroxide adduct. This adduct can also be readily formed[4] in essentially quantitative conversion by simply treating the diol with powdered potassium hydroxide in toluene or isopropyl ether at 30–35°. The 2,5-dimethyl-3-hexyn-2,5-diol–KOH adduct is not formed to any significant extent during catalytic ethynylation as evidenced by the very low conversions[6,7] to diol obtained in liquid ammonia or dimethyl sulfoxide. However, if isolated diol adduct is substituted for the MB–KOH catalyst, comparable results are still obtained. A sample of diol–KOH adduct prepared 6 months earlier and used as an ethynylation catalyst employing 0.07 mole of diol adduct, 1.2 moles of acetone, 1.1 moles of acetylene, and 200 ml. of liquid ammonia under the above conditions was found also to be an efficient catalyst. The total conversion to MB was 81% and the catalytic conversion based on adduct was 1370%. This observation is of importance in the continuous ethynylation of acetone since the intermediate MB–KOH catalyst will eventually be converted into the diol–KOH complex[4] at 30–35° (optimum ethynylation temperature). However, since the latter adduct is essentially as active as the MB–KOH complex, catalytic efficiency remains unimpaired. It was also shown[4] that the MB–KOH complex does not react with acetone in ether solvents to yield the expected 2,5-dimethyl-3-hexyn-2,5-diol (*via* its base adduct) in spite of claims[12] that this is a good method of preparing acetylenic diols. The above results further emphasize the difficulty of preparing acetylenic diols in liquid ammonia and the specificity of the ethynyl carbinol–base adduct as a catalyst for carbinol formation.

Sodium hydroxide, in contrast to potassium hydroxide does not form adducts to any significant extent with acetylenic carbinols and glycols[4] in inert organic solvents at atmospheric pressure. This observation also explains the failure of sodium hydroxide in catalytic or excess amounts to function effectively in ethynylations at atmospheric pressure[2,3] in organic solvents.

However, if excess (0.48 mole) methylbutynol is allowed to react with 0.30 mole of finely ground 97% so-

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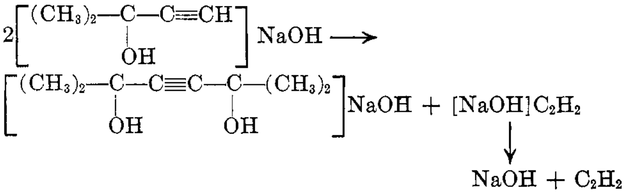
(11) T. F. Rutledge, *J. Org. Chem.*, **22**, 649 (1957).

(12) A. T. Babayan, *J. Gen. Chem. USSR*, **10**, 480 (1940); *Chem. Abstr.* **34**, 7851 (1940).

diium hydroxide in 320 ml. of liquid ammonia at 14–20° under ammonia pressure during 3.5 hr., an 83% conversion to a fluffy, white, crystalline 1:1 complex results. This adduct, like the previously reported[4] MB–KOH complex, readily disproportionates into the 2,5-dimethyl-3-hexyn-2,5-diol–NaOH complex by the following route.



$$2\left[(CH_3)_2-\underset{\mathrm{OH}}{\underset{|}{C}}-C\equiv CH\right]NaOH \longrightarrow \left[(CH_3)_2-\underset{\mathrm{OH}}{\underset{|}{C}}-C\equiv C-\underset{\mathrm{OH}}{\underset{|}{C}}-(CH_3)_2\right]NaOH + [NaOH]C_2H_2 \downarrow NaOH + C_2H_2$$

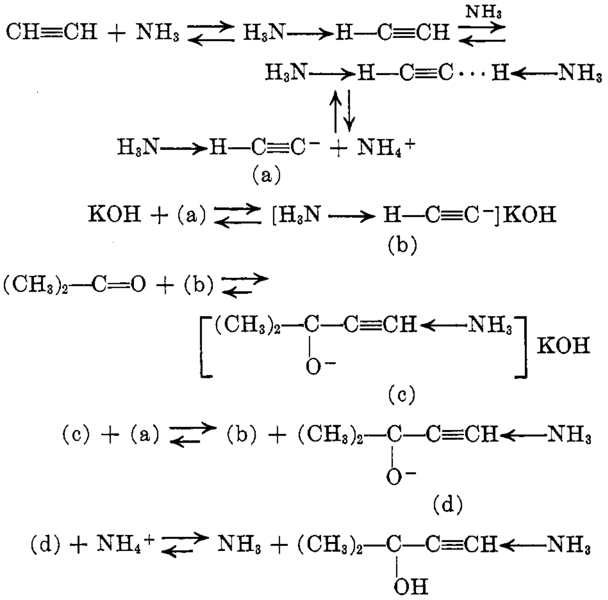
A sample of isolated adduct, after standing for 23 days at 3° under anhydrous conditions, lost 74% of its methylbutynol content in the formation of acetylenic diol. The above transformation takes place readily in the solid phase with no change in physical appearance. Either freshly prepared or transformed complex is surprisingly inert (over several weeks) to atmospheric water vapor, with no gain in weight noted. This behavior indicates chelate- or clathrate-type bonding since the unreacted sodium hydroxide (17%) in the sample does not absorb water. The infrared spectrum is similar to the KOH adduct. The absence of the characteristic C≡C and ≡CH stretches at 4.68–4.76 and 2.96–3.08 μ, respectively, and the presence of a broad, weak -OH absorption at 3.5–4.0 in place of the -OH absorption of MB at 3.00–3.07 μ indicates bonding involving both ethynyl and hydroxyl functions.

A sample of dry, isolated MB–NaOH complex used in place of sodium or potassium hydroxides in the liquid ammonia system (0.05 mole of MB–NaOH, 200 ml. of liquid NH_3, 1.2 moles of acetone, and 1.6 moles of C_2H_2) at 30–32° for 3 hr. gave a 79% conversion to MB (based on acetone) and a catalytic conversion of 1864% based on the complex. A MB–RbOH adduct[4] formed *in situ* and used under identical conditions gave an 84% conversion to MB and a catalytic effect of 1970%. The somewhat superior results realized with the RbOH–MB and KOH–MB complexes are in line with the quantitative conversion[4] realized with these adducts at atmospheric pressure and in weakly polar solvents.

Lithium hydroxide, however, in the ammonia system gave essentially no MB (1.2% conversion). These results are in complete accord with its failure to form a MB–LiOH complex even in liquid ammonia. The small amount of MB formed is probably due to the cocatalyst properties of liquid ammonia itself as reported previously[7] when a 4% conversion to MB was realized in the absence of KOH. However, lithium acetylide in liquid ammonia has been used successfully in stoichiometric ethynylations.

The above data, together with earlier results[7] which show that both catalytic and carbonyl conversions markedly decrease in solvents less active than ammonia, support the cocatalyst role of ammonia in this catalytic system. This behavior is strongly indicative of the intermediate formation of hydrogen-bonded solvent–acetylene complexes. Further, a diacetylene–N-methylpyrrolidone complex has recently been isolated and studied,[13] which further supports hydrogen bonding between acetylene and the donor electrons of ammonia to form an intermediate ammonia–acetylene complex.

Based on the above experimental evidence, the following cyclic exchange mechanism appears plausible and also illustrates the cocatalyst role of ammonia in the catalytic cycle. The ammonia system even at 35–40° is highly selective with essentially no acetylenic diol being formed using either an excess or stoichiometric amount of acetylene with respect to ketone.



$$CH\equiv CH + NH_3 \rightleftarrows H_3N\rightarrow H-C\equiv CH \overset{NH_3}{\rightleftarrows} H_3N\rightarrow H-C\equiv C\cdots H\leftarrow NH_3 \rightleftarrows \underset{(a)}{H_3N\rightarrow H-C\equiv C^-} + NH_4^+ \tag{1}$$

$$KOH + (a) \rightleftarrows \underset{(b)}{[H_3N\rightarrow H-C\equiv C^-]KOH} \tag{2}$$

$$(CH_3)_2-C{=}O + (b) \rightleftarrows \underset{(c)}{\left[(CH_3)_2-\underset{O^-}{\underset{|}{C}}-C\equiv CH\leftarrow NH_3\right]KOH} \tag{3}$$

$$(c) + (a) \rightleftarrows (b) + \underset{(d)}{(CH_3)_2-\underset{O^-}{\underset{|}{C}}-C\equiv CH\leftarrow NH_3} \tag{4}$$

$$(d) + NH_4^+ \rightleftarrows NH_3 + (CH_3)_2-\underset{\mathrm{OH}}{\underset{|}{C}}-C\equiv CH\leftarrow NH_3 \tag{5}$$

Step 3 is essentially nonreversible at 25° and only above 60° is the carbinol–KOH adduct gradually decomposed to acetylene, ketone, and hydroxide. The decomposition can also proceed competitively through the formation of the 2,5-dimethyl-3-hexyn-2,5-diol–potassium hydroxide complex,[4] which, however, is still an efficient ethynylation catalyst.

The ability of the diol–KOH complex to function as an effective catalyst can be explained by a modification of the above cycle which involves exchange of the diol complex with solvated acetylene to generate the KOH–C_2H_2 complex and free diol.

$$H_3N\rightarrow H-C\equiv C^- + \text{diol-KOH} \rightleftarrows [NH_3\rightarrow H-C\equiv C^-]KOH + \text{diol} \tag{6}$$

Steps 3, 4, and 5 would then describe the usual catalytic cycle, and the diol would constitute inert material. A competitive method for forming the necessary carbinol–base adduct might be exchanged with free methylbutynol formed as the reaction proceeds. This

$$\text{diol-KOH} + MB \leftrightarrows \text{diol} + \text{MB-KOH} \tag{7}$$

route, however, should only become significant in the later stages of ethynylation after a significant amount of MB has formed.

All attempts to date at this laboratory to prepare acetylenic diols catalytically by base catalysis (alkali hydroxides, or basic ion-exchange resins) have been negative.[3] It was previously assumed that the intermediate formation of ethynyl carbinol and its potassium hydroxide adduct were necessary precursors to diol formation. However, the failure[4] of the carbinol adduct to react with acetone in diisopropyl ether or liquid ammonia to yield the dimethylhexyndiol–potassium

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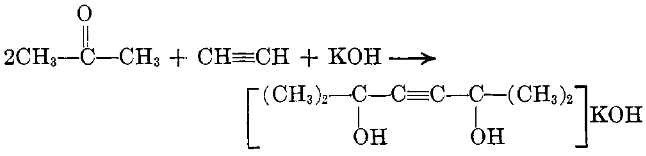
[13] N. Shachat, *J. Org. Chem.*, **27**, 2928 (1962).

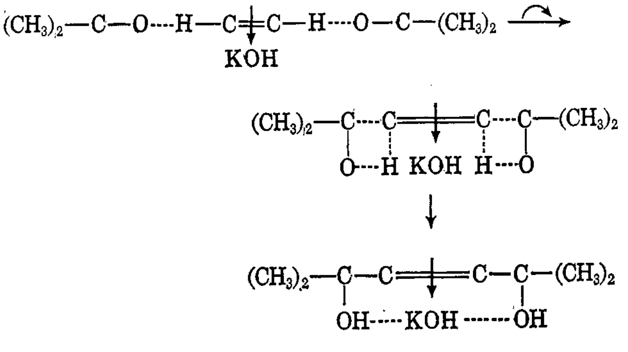
hydroxide adduct disproves this view. Also in the exchange reaction (6), the KOH–C_2H_2 complex formed reacts almost exclusively with acetone to form the MB–KOH complex.

Both the literature[2] and work at this laboratory[3] confirm the fact that tertiary acetylenic diols are best prepared at 30–40° using a slight excess (10–20%) of potassium hydroxide according to the following equation. The amount of water in the base dictates the excess over theory required. This reaction proceeds best in acetal or ether solvents and with the more reactive ketones gives 85–95% conversions to the diol with the remainder being ethynyl carbinol. The mode of addition of reactants is not critical although the usual method is first to saturate the solvent–KOH slurry with acetylene at 30–35° and then simultaneously to add ketone and acetylene. At least 1 mole of potassium hydroxide per mole of acetylene is required and the reaction has never been observed to be catalytic with respect to base, nor has sodium hydroxide ever been effective at atmospheric pressure.



$$2CH_3-\overset{\overset{O}{\|}}{C}-CH_3 + CH\equiv CH + KOH \longrightarrow \left[(CH_3)_2-\underset{OH}{\underset{|}{C}}-C\equiv C-\underset{OH}{\underset{|}{C}}-(CH_3)_2\right]KOH$$

Based on the data cited earlier, it is certain that diol formation is not dependent upon the intermediate formation of carbinol. A simultaneous bimolecular attack of ketone upon the acetylene–KOH complex appears to be the most reasonable route. This heterogeneous reaction initially may involve chemisorption *via* hydrogen bonding on the surface of the complex. The initially formed hydrogen bonded complex then rearranges to the stable diol–base adduct. Both the diol and carbinol complexes derived from acetone are stabilized by hydrogen and π bonding.[4] The MB–KOH complex as a result of the bimolecular attack does not form to any significant extent at 30–35° as verified experimentally by carbinol conversions with the more active ketones (acetone, methyl ethyl ketone), seldom being higher than 5–10% of theory. However, with less active ketones (methyl *n*-butyl and hexyl ketones) formation of the ethynylcarbinol adduct begins to compete successfully with the diol intermediate and ethynylcarbinol conversions are often 30–50% of theory. The high specificity for diol formation in the broad range of 30–50° appears to involve simultaneous activation of both hydrogen atoms of acetylene in the base complex, aided both by temperature and by solvent activation (dioxane, diisopropyl ether).



diol–KOH adduct

Experimental

Reactions with Acetylene under Pressure.—All pressure runs were carried out in 1.0- or 3.8-l.-capacity stainless steel autoclaves (Autoclave Engineers, Inc., Erie, Pa.) equipped with inner coil and jacket cooling and a turbo-type stirrer. The measurement and introduction of acetylene and ammonia have been described previously together with a description of the equipment and the general technique of operation.[7]

Alkali Hydroxide–Acetylene Complex Formation.—Into a cylindrical, stainless steel liner equipped with an airtight cover was weighed 1.5 moles (100% basis) of 98–99% powdered sodium or potassium hydroxides. The entire operation was carried out in a drybox at 0% relative humidity. The preparation of finely divided base was readily effected by use of a Waring Blendor. The base can be either ground dry in a screw-cap stainless steel blender or an inert dry solvent (toluene, xylene) can be used followed by filtration of the slurry, washing with low-boiling petroleum ether (b.p. 30–50°), and vacuum drying over calcium carbide pellets. The solvent-grinding method gives a base of finer and more uniform particle size.

The following reaction charge was employed: 1.5 moles of potassium or sodium hydroxide, 6.0 moles of acetylene, 500 ml. (~24 moles) of liquid ammonia. The liner was introduced to the dry autoclave in the presence of a positive stream of dry nitrogen, and the autoclave was quickly sealed. Liquid ammonia was added next[7] at room temperature and the base–ammonia slurry was stirred for several minutes before the introduction of acetylene.[7] The resulting reaction was not exothermic and the reaction temperature was maintained at 30–35° for 4 hr. at a total pressure of 160–180 p.s.i.g.

Isolation was effected by venting off ammonia at an initial temperature of −30° followed by the gradual addition of 300 ml. of dry isopropyl ether as replacement solvent. When all the ammonia and acetylene had been vented off and the system was purged several times with nitrogen, the liner was quickly removed, sealed, and transferred to the drybox. After filtration and vacuum drying to constant weight for 6 hr. at 10–20° and below 1 mm., aliquots of the resulting light yellow solids added to water quickly liberated acetylene. The following conversions to 1:1 adduct were obtained based on ethynyl group analysis (see Table I).[14]

TABLE I

	Acetylene, %		Conversion to adduct,
	Calcd.	Found	%
KOH–C_2H_2	31.7	3.65	11.5
NaOH–C_2H_2	39.4	2.72	6.9

Both samples on heating to 110° for 4 hr. lost all their acetylene. An authentic sample of dry, powdered sodium acetylide (90% pure) prepared by the reaction of sodium dispersion in dioxane at 65–75° and atmospheric pressure[11] was unchanged by identical treatment.

A KOH–C_2H_2 complex formed by treating 0.15 mole of KOH with 0.60 mole of C_2H_2 in 20 ml. of liquid ammonia at 15–21° followed by drying the product at atmospheric pressure in an atmosphere of dry acetylene yielded 9.3 g. of an almost white, powdered complex in 44% conversion.

Anal. Calcd. (1:1 complex): KOH, 68.3; C_2H_2, 31.7. Found: KOH, 77.0; C_2H_2, 14.0.

Methylbutynol–Potassium Hydroxide Adduct.—This white, microcrystalline material was readily formed in solvents such as liquid ammonia, diisopropyl ether, or toluene using stoichiometric amounts of reactants, and the previously described procedure.[4] If the complex was not used within several hours after being prepared, it was preferably stored in an ice chest desiccator at 0° to avoid disproportionation.

Methylbutynol–Sodium Hydroxide Adduct.—Into a 1-l. stainless steel autoclave liner, under anhydrous conditions, was

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[14] L. Barnes, Jr., and L. J. Molinini, *Anal. Chem.*, **27**, 1025, (1955).

weighed 12.4 g. of 97% finely ground sodium hydroxide (0.30 mole). The tightly sealed liner was quickly transferred to a standard, 1-l., stirred autoclave under a positive flow of dry nitrogen. To the sealed autoclave then was added 320 ml. of liquid ammonia in the usual manner,[7] followed by 40 g. (0.48 mole) of methylbutynol at a temperature of 14–20°. The reaction mixture was stirred for 3.5 hr. and isolated in the usual manner using hexane as inert diluent.

The isolated adduct, vacuum dried to constant weight (26.0 g.), was a fluffy, white solid showing no tendency to absorb water. The excess (0.18 mole) methylbutynol used solubilized some of the complex in the hexane layer. This was determined by decomposing the adduct to sodium bicarbonate and free acetylenic carbinol by carbonation (Dry Ice) of the hexane layer, followed by filtration of the solid sodium bicarbonate. A total of 4.5 g. of white, air-dried solid was obtained which contained 73.7% $NaHCO_3$ by acid titration, and was equivalent to 4.9 g. (0.040 mole) of MB–NaOH complex (total conversion of purity to MB–NaOH complex, 83.1%).

Anal. Calcd. for $C_5H_9NaO_2$: C, 48.4; H, 7.26. Found: C, 39.0. H, 9.11; per cent purity based on carbon analysis, 80.6.

Isolation of Dimethylhexynediol (DMH) from MB–NaOH Adduct.—An aliquot (16.6 g.) of the powdered adduct which had been standing for 23 days at 3° in a refrigerator desiccator under anhydrous conditions, was slurried in 150 ml. of cold diethyl ether and carbonated with small pieces of Dry Ice, and filtered from $NaHCO_3$. The diol was freed from ether by evaporation. The yield of unrecrystallized, dry DMH was 5.2 g. (m.p. 92–94°, lit. 95°).

The MB–NaOH adduct from an initial MB content of 67.6% contained only 17.5% MB 6 days before isolation. Loss of MB during this time due to disproportionation was 74.2%. This adduct was considerably less stable than the KOH adduct. The theoretical yield of DMH from 16.6 g. (0.134 mole) of MB–NaOH was 4.96 g. (0.067 mole). The slightly higher (105%) than theory yield of unrecrystallized DMH was probably due to occluded solvent, water, and sodium bicarbonate.

Catalytic Formation of 3-Methyl-1-butyn-3-ol Using the Methylbutynol–KOH Adduct as Catalyst.—A 1-l. stirred autoclave was used for the reaction. This scaled-down run corresponded to a high-concentration (loading) ethynylation of acetone (18 moles of acetone, 24 moles of acetylene, and 1.5 moles of KOH) with the exception that 200 ml. of ammonia was used instead of the calculated 33 ml.[15] The larger volume of ammonia was used to stir the batch more efficiently and to ensure good thermal contact between the reaction mixture and the thermocouple well.

The following reaction charge was employed: 0.10 mole of methylbutynol–KOH adduct,[16] 1.2 moles of acetone, 1.6 moles of acetylene, and 200 ml. of liquid ammonia. The total reaction time was 1.5 hr. at 30–32 using 0.5-hr. addition time for introducing acetone into the NH_3–KOH–C_2H_2 reaction mixture. The total pressure in the autoclave averaged 160–185 p.s.i.g.

Isolation of product was effected in the usual manner,[7] employing dry CO_2 gas to neutralize the catalyst complex to $KHCO_3$ and methylbutynol after venting off ammonia. The total conversion to methylbutynol before distillation was 97%, and the catalytic conversion of (moles of MB per mole of KOH) was 1170%. The conversion to pure methylbutynol was 88% (88 g.), b.p. 103–104° (lit. 104°).

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[15] High-concentration (loading) runs described earlier[7] would have used 33 ml. of ammonia instead of 200 ml. of ammonia in an exact, scaled-down run.

[16] Adduct prepared in isopropyl ether according to method is described in ref. 7; dry, isolated adduct was used.

Properties of Triphenyltin Nitrate

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The properties of triphenyltin nitrate are described. The thermal decomposition of this compound was investigated by heating in both the presence and absence of solvent. Two independent modes of decomposition, decomposition by a distribution reaction and by heterolytic dissociation of the β-oxygen–nitrogen bond, were found.

According to a recent report in the literature,[1] triphenyltin nitrate is a relatively unstable material decomposing readily to a mixture of products. However, we have found, during the course of an investigation of a variety of organotin compounds, that this material is in fact quite stable at ordinary temperatures and can easily be prepared, purified, and studied. Trimethyltin nitrate[2] and dimethyltin dinitrate[3] have also recently been reported and found to be thermally stable at ordinary temperatures. It is the purpose of this paper to report the results of this investigation.

We have found that triphenyltin nitrate can be obtained either from the reaction of hexaphenylditin with silver nitrate in acetone or from the method of Shapiro and Becker[1] as a white crystalline solid which melts at 182–184° with some decomposition to a reddish brown liquid. It will sublime slowly under a high vacuum. It is very soluble in polar solvents but not in water and less soluble in benzene, chloroform, and many others from which it readily crystallizes. When it was taken up in commercialan hydrous methanol, no solvolysis could be observed as indicated by the infrared spectrum of the solid collected after removal of the methanol in air at room temperatures. However, a mixed solvent of methanol and water hydrolyzed it partially to a mixture of triphenyltin nitrate and triphenyltin hydroxide. The absence of any brown nitrogen oxide fumes and a negative test for nitrite ions was taken to indicate that no homolytic dissociation[4] had occurred during the hydrolysis reaction. Titration of the nitric acid produced by the hydrolysis of the triphenyltin nitrate was found to be an effective and satisfactory method for determining the quality of the material. Although wet triphenyltin nitrate turns yellow in a few days, a well-dried sample, in analogy to trimethyltin nitrate,[2] is not affected by exposure to air.

The infrared spectrum of triphenyltin nitrate in Nujol consists of absorption bands arising from the phenyltin groups and nitrate group. The bands from the phenyltin group[5] were the same as those of other phenyltin compounds. Bands from the nitrate are listed in Table I along with those found for covalently

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[1] P. J. Shapiro and E. I. Becker, *J. Org. Chem.*, **27**, 4668 (1962).

[2] H. C. Clark and R. J. O'Brien, *Inorg. Chem.*, **2**, 740 (1963).

[3] C. C. Addison, W. B. Simpson, and A. Walker, *J. Chem. Soc.*, 2360 (1964).

[4] C. C. Addison, Advances in Chemistry Series, No. 36, American Chemical Society, Washington, D. C., 1962, p. 131.

[5] V. S. Griffiths and G. A. W. Derwish, *J. Mol. Spectry.*, **5**, 148 (1960).