during the subsequent increase in temperature to room temperature. At this time the color test was negative. The double Schlenk tube was resealed *in vacuo* and part of the tetrahydrofuran was distilled into the other branch in the hope of isolating a crystalline product. Since none was found hydrolysis was performed and the reaction products isolated as described in a previous section. Chromatography yielded 266 mg. of biphenyl in addition to several fractions of intractable oils which on addition of trinitrofluorenone gave 21 mg. of the triphenylene complex, m.p. 230–232°. Since the solution of *o*-dilithiobenzene had been allowed to stand for 16 hr. at room temperature the reaction was repeated without storing the solution before reaction. The same color changes were noticed and there was found no octaphenylene. Chromatography yielded biphenyl, 256 mg., m.p. 64–65° (18%), and a triphenylene complex with trinitrofluorenone, m.p. 230–231°. Particular care was taken to dissolve the metal to search for octaphenylene but none was found.

**Attempted Preparation of *o*-Dilithiobenzene in Ethylene Glycol Dimethyl Ether.**—Ethylene glycol dimethyl ether was purified by a standard procedure, b.p. 85°, $n^{20}\mathrm{D}$ −1.37965. A slurry of 2.5 g of *o*-phenylenemercury and 1 g. of lithium in 50 ml. of ethylene glycol dimethyl ether was shaken for 7 days. A gray-black suspension resulted. Neither the precipitate nor the solution gave a positive color test. Filtration of the slurry yielded no crystalline product on concentration of the filtrates. A small amount of lithium carbonate was found, 71 mg.

**Reaction of *p*-Bromoanisole with *o*-Dilithiobenzene.**—Distillation of *p*-bromoanisole under reduced pressures yielded a pure sample, $n^{20}\mathrm{D}$ −1.509 (lit. 1.5605), b.p. 132–134° (20 mm.).

A solution containing 18 mmoles of *o*-dilithiobenzene in 100 ml. of ether was added to 3.35 g. (18 mmoles) of *p*-bromoanisole and the reaction mixture was left at room temperature for 15 min. before 6.6 g. (36 mmoles) of benzophenone was added. The color test was negative after 10 min. and hydrolysis with water was performed. The aqueous extracts of the organic phase contained 9.6 mmoles of lithium bromide (on Volhard analysis). The *p*-bromoanisole remaining was recovered by distillation, 2.3 g. (35%), and partly also by later chromatograms. Biphenyl was contained in the higher boiling fractions (estimated 150 mg.). The oils remaining from the distillation were combined and chromatographed. A fraction containing 34% biphenyl and 66% *p*-bromoanisole was obtained in addition to several oily and solid fractions. These fractions were recombined and chromatographed anew. From the second chromatogram was obtained *o*-xylyleneglycol-tetraphenyl, 776 mg. (1.75 mmoles); this sample showed no depression with an authentic sample, m.p. 196–197°; 2-methoxy-5-bromotritanol, 1.13 g. (3 mmoles); *p*-methoxytritanol, 1.40 g. (3.8 mmoles). Several other fractions were obtained but none corresponding to *p*-methoxybiphenyl, bis(*p*-methoxyphenyl). A fraction, m.p. 121–122°, was assigned the structure 2-*p*-methoxyphenyltritanol on basis of spectral data and analysis. In addition there was obtained a compound, 0.5 g., m.p. 246–247°, after several recrystallizations. This compound gave no melting point depression with bis(-2-diphenyloxymethyl)diphenyl, m.p. 246–247°.

**Attempted Metalation of Diphenylmethane with *o*-Dilithiobenzene.**—Diphenylmethane was purified by distillation. A solution containing 18 mmoles of *o*-dilithiobenzene was added to 36 mmoles of diphenylmethane in ether (5.7 g.). The reaction mixture was left standing for 16 hr. before 6.6 g. of benzophenone was added. The color test was negative almost immediately after addition and the reaction mixture was worked up by removing 5.185 g. (91%) of diphenylmethane by distillation. From the residue left after the removal of the diphenylmethane there was obtained 2.876 g. (22%) of tetraphenyl-*o*-xylylene glycol, m.p. 196–197° (lit. reports a 15% yield). The mother liquors yielded 1.807 g. of benzophenone (27% recovery), m.p. 48–49°, on distillation and the oils now remaining were chromatographed to yield triphenylmethane, 33 mg. (probably present in the diphenylmethane as an impurity). There was found no tetraphenyl-*o*-xylylene glycol from this chromatogram, 18 mg. of tritanol, and a total of 130 mg. of tetraphenylphthalan after the various oily fractions were dehydrated with glacial acetic acid.

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# Base-Catalyzed Reaction of Acetylene and Vinylacetylenes with Carbonyl Compounds in Liquid Ammonia under Pressure

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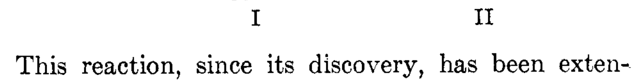
A high productivity, catalytic method for the ethynylation of aldehydes and ketones to the corresponding secondary and tertiary acetylenic carbinols is described. The method uses catalytic amounts of potassium or sodium hydroxide in liquid ammonia with acetylene, vinylacetylene, or isopropenylacetylene under pressure.

The condensation of aldehydes and ketones with acetylene at atmospheric pressure in the presence of excess, finely divided potassium hydroxide is known as the Favorskiĭ[1,2] reaction. At temperatures below 5° ethynylcarbinol (I) is formed almost exclusively, while acetylenic glycol formation predominates at higher temperatures (25–35°).



$$3R_1R_2C{=}O + 2CH{\equiv}CH \underset{\longleftarrow}{\xrightarrow{\text{KOH}}} \underset{\text{OH}}{R_1R_2C}{-}C{\equiv}CH + R_1R_2{-}\underset{\text{OH}}{C}{-}C{\equiv}C{-}\underset{\text{OH}}{C}R_1R_2$$

I II

This reaction, since its discovery, has been extensively studied[3–6] and modified.[7–10] Results of these investigations have shown that ether, acetal, or amine solvents used with stoichiometric to excess amounts of finely ground potassium hydroxide give optimum results at atmospheric pressure (Favorskiĭ conditions).

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(1) A. E. Favorskii and M. Skossarewsky, *Russ. J. Phys. Chem. Soc.*, **32**, 652 (1900); *Bull. Soc. Chim.*, **26**, 284 (1901).

(2) A. E. Favorskii, *J. Gen. Chem. USSR*, **32**, 356, 652 (1902).

(3) A. W. Johnson, "Acetylenic Compounds," Vol. I, "The Acetylenic Alcohols," Edw. Arnold Co., London, 1946, pp. 6–16, 28, 122, 137–143.

(4) J. Zeltner and M. Genas, British Patent 544,221 (April 2, 1942); U. S. Patent 2,345,170 (March 28, 1944); *Chem. Abstr.*, **38**, 4273 (1944).

(5) C. Weizmann, British Patents 573,527 (November 26, 1945); 580,921, (September 25, 1946); 580,922 (September 25, 1946). *Chem. Abstr.*, **41**, 2066, 2429 (1947).

(6) E. D. Bergmann, "The Chemistry of Acetylene and Related Compounds," Interscience Publishers, Inc., New York, N. Y., 1948, pp. 49–53.

(7) E. F. Smith, U. S. Patent 2,385,546 (September 25, 1945); 2,385,548, (September 25, 1945). D. F. Herman, U. S. Patent 2,455,058 (December 30, 1948). C. Weizmann, U. S. Patent 2,474,175 (June 21, 1949). A. Brotman, U. S. Patent 2,536,028 (January 2, 1951).

(8) R. J. Tedeschi, T. F. Rutledge, R. K. Frantz, and J. P. Russell, unpublished work, Air Reduction Co., Murray Hill, N. J. (September, 1953).

(9) Air Reduction Chemical Co., Bound Brook, N. J., and Calvert City, Ky. Supplier of secondary and tertiary ethynyl carbinols and tertiary acetylenic glycols.

(10) I. N. Nazarov, *et al.*, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 960 (1956); *Chem. Abstr.*, **49**, 927 (1955).

To avoid the use of excess base, a number of catalytic processes have been reported through the years utilizing the mass action effect of excess acetylene under pressure, polar solvents, or various catalysts. Prominent among these methods are those of Reppe[11] (heavy metal acetylides), Whitfield[12] (basic ion exchange resins), Schachat and Bagnell,[13] Blumenthal[14] (polar solvents either at atmospheric or higher pressures), and Nedwick and Watanabe[15] (continuous high pressure liquid phase technique). Recent work[8,13,14] has emphasized the fact that the ethynylation reaction gives maximum catalytic results in highly polar organic solvents (dimethylsulfoxide, N-methylpyrrolidone, and hexamethylphosphoramide, etc.). These results are in agreement with data[16] on the high solubility of acetylene in donor solvents.

However, preceding catalytic methods for general use with aldehydes and ketones are limited, due to either low conversions,[11,12,15] failure to react successfully with aldehydes and sensitive ketones,[12,13,15] or isolation problems.[13,14] Polar solvents boiling in the broad range of 80–200° have a characteristic tendency to form stable hydrogen-bonded complexes with the resulting polar ethynylcarbinols. Consequently, either inseparable azeotropes result with the more volatile solvents (acetonitrile, ethylenediamine, and dioxane) or else the higher boiling carbinols cannot be readily distilled pure from the tenacious solvent. To eliminate this problem, isolation is generally effected by dilution with water, followed by ether extraction, and subsequent fractional distillation. This method, besides being tedious, is still somewhat unsatisfactory since some of the polar solvent is also extracted into the ether layer.

In contrast, liquid ammonia, well known as a solvent for noncatalytic acetylene reactions,[17] should be free of isolation problems with the majority of ethynylcarbinols, due to its low boiling point (−33°). Furthermore, the use of catalytic amounts of alkali hydroxides in liquid ammonia with excess acetylene under pressure might lead to a more efficient ethynylation system. Solubility studies of acetylene in liquid ammonia under pressure at temperatures from −40° to +30° showed a large and fairly constant solubility of approximately 1 mole of acetylene per mole of ammonia. This small change in acetylene concentration in the liquid phase over a wide temperature range strongly indicated the formation of a hydrogen-bonded complex ($H—C\equiv C—H\cdots NH_3$), and strengthened the belief that liquid ammonia should be a superior reaction medium. Subsequent work verified the above assumptions.

The ammonia–alkali hydroxide–acetylene system is so specific for ethynylation that even a base-sensitive aldehyde such as acetaldehyde gives conversions of 30–50% depending on the initial aldehyde concentration. Higher aliphatic aldehydes (propionaldehyde, isobutyraldehyde, and 2-ethylhexaldehyde) give minor to insignificant amounts of expected side products such as aldols, aldehyde–ammonia adducts, and Schiff bases. Formaldehyde, however, either as 30% formalin, or paraformaldehyde was the only aldehyde observed not to yield any acetylenic carbinol (1-propyn-3-ol).

The liquid ammonia system is characterized by a much higher productivity of ethynylcarbinol per unit solvent volume than that realized by earlier methods. When 18 moles of acetone reacted in a system composed of 24 moles of acetylene, 1.5 moles of potassium hydroxide, and 500 cc. of liquid ammonia, a minimum yield or conversion of 75% (1138 g.) to pure, distilled 3-methyl-1-butyn-3-ol is realized with a catalytic conversion based on potassium hydroxide of 900% (*cf.* Table I). In contrast, the highly polar dimethyl sulfoxide when used under identical conditions gives a conversion to methylbutynol of only 42% based on ethynyl group analysis.[21] In practice pure methylbutynol can be isolated only in 15% conversion by direct distillation; therefore, actual results are considerably inferior to those in ammonia.

TABLE I

3-METHYL-1-BUTYN-3-OL. VARIATION OF CONVERSION[a] (YIELD) AND PRODUCTIVITY[b] WITH ACETONE LOADING[c] AND SOLVENT

| Acetone loading, moles | Solvent, 500 cc. | Per cent distilled conversion based on | | Productivity MB (2), g. |
|---|---|---|---|---|
| | | (—C═O) | KOH | |
| 1 | $NH_3$ | 95 | 95 | 80 |
| 6 | $NH_3$ | 95 | 381 | 478 |
| 12 | $NH_3$ | 82 | 660 | 830 |
| 12 | $NH_3$[d] | 81 | 647 | 815 |
| 18 | $NH_3$ | 75 | 902 | 1138 |
| 24 | $NH_3$ | 52 | 835 | 1050 |
| 1 | Methylal | 90 | 60 | 76 |
| 18 | Methylal | 32 | 388 | 487 |
| 18 | Acetone | 23 | 276 | 347 |
| 1 | Diisopropyl ether | 80 | 53 | 67 |
| 10 | Diisopropyl ether | 16 | 107 | 135 |
| 18 | Dimethyl sulfoxide[e] | 42 | 497 | 635 |

[a] Conversion is defined as the moles of ethynylcarbinol formed divided by the moles of ketone or base used times 100. Where the conversion is in the 75–90% range excess acetone is usually not recoverable and yield and conversion are identical. For example, at low conversions (16–32%) excess acetone is recoverable but yields are seldom higher than 70–80% due to the formation of ketone self condensation products such as mesityl oxide, phorone, and losses due to entrainment. [b] Productivity is the total weight (g.) of ethynylcarbinol obtained from 500 cc. of solvent. MB is 3-methyl-1-butyn-3-ol. [c] Loading is the concentration in moles, of carbonyl compound used in 500 cc. of solvent. In all catalytic runs described in Table I, 1.5 moles of NaOH or KOH are used with 24 moles of acetylene to ethynylate 6–24 moles of carbonyl compound at 30–35° under ambient (190–200-p.s.i.g.) pressure. One-mole acetone runs were carried out at atmospheric pressure and 0–5° using 1.5 moles of acetylene and 1.5 moles of KOH, except in the case of liquid ammonia where a stoichiometric amount of KOH and acetylene can be successfully employed at −40 to −45°. [d] Powdered NaOH (96%) was used as catalyst in place of KOH. [e] Methylbutynol could not be isolated pure by simple distillation. Data are based on solution analysis (ref. 21).

When vinylacetylene and isopropenylacetylene (3-methyl-3-butene-1-yne) are substituted for acetylene under previous conditions (*cf.* Table III) using methyl ethyl ketone and acetone concentrations (loadings) of 18 moles and 6 moles, respectively, conversions of 46% and 69% based on ketone of the corresponding ene-yn-ols are obtained. The corresponding catalytic con-

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(11) W. Reppe, *et al.*, *Ann.*, **596**, 1 (1955); **601**, 81 (1956).

(12) G. H. Whitfield, British Patent, 735,118 (August 17, 1955); U. S. Patent 2,826,614 (March 11, 1958).

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

(14) J. H. Blumenthal, U. S. Patent 2,996,522 (August 15, 1961).

(15) J. J. Nedwick and W. H. Watanabe, U. S. Patent 2,973,390 (February 28, 1961).

(16) A. C. McKinnis, *Ind. Eng. Chem.*, **47**, 850 (1955).

(17) (a) K. N. Campbell, B. K. Campbell, and L. T. Eby, *J. Am. Chem. Soc.*, **60**, 2882 (1938); (b) J. F. Froning and G. F. Hennion, *ibid.*, **62**, 653 (1940); (c) J. A. Nieuwland, *Ind. Eng. Chem.*, **27**, 850 (1935); (d) T. H. Vaughn, R. R. Vogt, and J. A. Nieuwland, *J. Am. Chem. Soc.*, **56**, 2120 (1934).

Table II

CATALYTIC ETHYNYLATION OF KETONES AND ALDEHYDES IN LIQUID AMMONIA[a]

| Carbonyl compound | 2° or 3° ethynyl carbinol | Loading, moles | Reaction conditions | | | Per cent distilled conversion based on | | B.p., °C. | Press., mm. | Purity[b] |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | Time, hr. | Temp., °C. | Pressure, $C_2H_2$ | (>C=O) | KOH | | | |
| $(CH_3)_2CO$ | 3-Methyl-1-butyn-3-ol | 18 | 4 | 20–27 | 154–184 | 75 | 900 | 104–105 | 760 | 99–100 |
| $C_2H_5COCH_3$ | 3-Methyl-1-pentyn-3-ol | 18 | 2 | 28–35 | 176–239 | 67 | 800 | 121–122 | 760 | 99–100 |
| $C_2H_5COC_2H_5$ | 3-Ethyl-1-pentyn-3-ol | 6 | 4 | 0–6 | 110–180 | 66 | 264 | 138–140 | 760 | 97–99 |
| $(CH_3)_2CHCH_2COCH_3$ | 3,5-Dimethyl-1-hexyn-3-ol | 17 | 5 | 30–35 | 151–174 | 47 | 524 | 150–151 | 760 | 97–99 |
| $C_6H_{10}O$ | 1-Ethynylcyclohexanol | 18 | 2 | 30–42 | 290–309 | 71 | 846 | 102–103 | 50 | 99–100 |
| $C_6H_5COCH_3$ | 3-Phenyl-1-butyn-3-ol | 12 | 4.5 | 35–40 | 324–376 | 58 | 463 | 110–112 | 10 | 95–98 |
| $CH_3CHO$ | 1-Butyn-3-ol | 6 | 3 | 0–5 | 75–135 | 31 | 178 | 106–107 | 760 | 92–97 |
| $C_2H_5CHO$ | 1-Pentyn-3-ol | 5 | 3 | 19–27 | 195–220 | 46 | 587 | 72–74 | 100 | 93–99 |
| $C_3H_7CHO$ | 1-Hexyn-3-ol | 6 | 4 | 18–20 | 190–230 | 53 | 206 | 88–89 | 100 | 98–100 |
| $(CH_3)_2CHCHO$ | 4-Methyl-1-pentyn-3-ol | 12 | 4 | 25–30 | 190–205 | 72 | 615 | 79–81 | 100 | 97–99 |
| $C_4H_9CH(C_2H_5)CHO$ | 4-Ethyl-1-octyn-3-ol | 7.3 | 4 | 18–20 | 340–350 | 75 | 650 | 106–126 | 50 | 96–99 |

[a] A standard charge of 500 cc. of liquid ammonia, 1.5 moles of powdered (90%) KOH, and 24 moles of acetylene (dry) was used in all runs. [b] Purity is based on solution analysis (ref. 21).

TABLE III

CATALYTIC[a] FORMATION OF SECONDARY AND TERTIARY ENE-YN-OLS[b] AT 30–40°

| Moles | Ene-yne | Moles | Carbonyl compound | Distilled[c] conversion based on | | B.p., °C. | Press., mm. | Purity by (C, H, O) |
|---|---|---|---|---|---|---|---|---|
| | | | | >C=O | KOH | | | |
| 6 | $CH_2{=}CH{-}C{\equiv}CH$ | 6 | $(CH_3)_2CO$ | 62 | 249 | 68 | 24 | 96.5 |
| 12 | $CH_2{=}CH{-}C{\equiv}CH$ | 6 | $(CH_3)_2CO$ | 54 | 217 | 68 | 24 | ... |
| 18 | $CH_2{=}CH{-}C{\equiv}CH$ | 18 | $CH_3{-}COC_2H_5$ | 46 | 554 | 75 | 20 | 98.0 |
| 6 | $CH_2{=}CH{-}C{\equiv}CH$ | 6 | $(CH_3)_2CHCHO$ | 52 | 209 | 173–175 | 760 | 97.5 |
| 6 | $CH_2{=}CH{-}C{\equiv}CH$ | 6 | $C_4H_9CH(C_2H_5)CHO$ | 61 | 242 | 228–230 | 760 | 99.0 |
| 6 | $CH_2{\equiv}C(CH_3)C{\equiv}CH$ | 6 | $(CH_3)_2CO$ | 69 | 274 | 70 | 14 | 99.4 |
| 12 | (3)$CH_2{=}C(CH_3)C{\equiv}CH$ | | | 21 | | | | |
| | | 18 | $(CH_3)_2CO$ | | 982 | [d] | | [d] |
| 12 | $CH{\equiv}CH$ | | | 60 | | | | |
| | | | | Total 81% | | | | |

[a] Ethynylation charge was 500 cc. of ammonia and 1.5 moles of KOH used with carbonyl and ene-yne loadings specified in table. [b] The following ene-yn-ols are obtained from the above reactants: VA = vinylacetylene, IPA = 3-methyl-3-butene-1-yne; VA + acetone, 2-methyl-5-hexene-3-yn-2-ol; VA + methyl ethyl ketone, 3-methyl-6-hexene-4-yn-3-ol; VA + isobutyraldehyde, 2-methyl-6-heptene-4-yn-3-ol; VA + 2-ethylhexaldehyde, 6-ethyl-1-decene-3-yn-5-ol; IPA + acetone, 2,5-dimethyl-5-hexene-3-yn-2-ol. [c] Conversions are defined in footnote *a*, Table I. No attempt was made to recover the low boiling VA, hence yields cannot be given, although they are probably higher. For example, the mixed acetylene–IPA run (12 moles each) gave a total conversion of 81% and a total yield of 95% based on careful recovery of starting materials. (Total catalytic yield based on KOH is 1134%.) [d] The products were readily separable by distillation to give typical (*cf.* table) purity values, which are the average of C, H, O combustion analyses.

versions based on potassium hydroxide are 554% and 274%. The competitive reaction of 12 moles each of isopropenylacetylene and acetylene with 18 moles of acetone results in a 60% conversion to methylbutynol and a 21% conversion to the ene-yn-ol, 2,5-dimethyl-5-hexene-3-yn-2-ol, with a total catalytic conversion of 982%. The results of Tables II and III show that vinyl- and isopropenylacetylenes are comparable in ethynylation reactivity, but noticeably inferior to acetylene.

The results in Table I show the variation in ketone and potassium hydroxide conversions together with grams of methylbutynol produced at different acetone concentrations (loadings) in 500 cc. of solvent. The superiority of the catalytic ammonia system over stoichiometric ethynylation in typical Favorskiĭ solvents is clearly evident. Further, a marked drop in conversion is noted at atmospheric pressure in methylal, if the acetone loading is increased substantially beyond one mole.[8] Total yields and conversions are generally 5–10% higher than the distilled values. As shown in the formation of methylbutynol, the liquid ammonia system can produce eight to ten times more ethynylcarbinol per unit of solvent than typical ether or acetal solvents using the noncatalytic method at atmospheric pressure. The point of diminishing returns is reached beyond 18 moles of ketone. A 23% drop in conversion (75%–52%) results at a 24 moles loading of acetone.

A further, interesting property of this solvent system is the high specificity for ethynylcarbinol formation. No significant amount of 1,4-acetylenic glycol is obtained at temperatures of 20–40° even when a stoichiometric amount of acetylene is used. When acetal or ether type solvents are used at atmospheric pressure with excess base only by operating at temperatures below 5° are good conversions to the ethynylcarbinol realized. At higher temperatures (20–40°) the acetylenic glycol is the principal product.

While sodium hydroxide (powdered) cannot be employed successfully using Favorskiĭ conditions, it gives results comparable to potassium hydroxide in liquid ammonia particularly at high ketone loadings as shown in Table I. The results in Table II show that the average productivity (grams) of ethynylcarbinol in 500 cc. of ammonia even for less reactive ketones is quite high (900–1200 g).

Potassium acetylide prepared *in situ* in liquid ammonia was found to be a good ethynylation catalyst, but surprisingly inferior to sodium or potassium hydroxides in the critical loading (concentration) range of 18–24 moles of ketone. Using standard reaction charge of 18 moles of acetone, 24 moles of acetylene, and 1.5 moles of potassium acetylide in 500 cc. of ammonia, conversions based on acetone and potassium acetylide were 45% and 545%. These results show that potassium acetylide is approximately half as effective a catalyst as either potassium or sodium hydroxide, and indicates that base-catalyzed ethynylation may not proceed through the intermediate formation of alkali metal acetylide[18] from the corresponding hydroxide. An attempt to ethynylate acetone (18 moles) in the absence of base gave a 4% total conversion to methylbutynol, showing that solvated acetylene is not present in any degree as the hypothetical ammonium acetylide. This species would presumably react with acetone in a manner analogous to sodium acetylide.

## Experimental

**General Ethynylation Procedure.**—All catalytic runs were carried out in a 1-gallon stainless steel autoclave,[19] equipped with an inner coil, jacket cooling, and a turbotype stirrer. The total free volume of the autocalve was 3800 cc. when the head (includes coil, stirrer, and thermocouple well) piece was in place. The autoclave had a 1000-p.s.i.g. blowout disk which was substantially below its maximum rated operating pressure (7500 p.s.i.g.). Efficient cooling to as low as −40° could be realized by the use of a 3-gallon, Dry-Ice cooled, refrigeration system using an equal volume mixture of methanol and ethylene glycol as the circulatory coolant.

Ammonia was introduced as liquid under its own vapor pressure to a graduated glass pressure buret,[20] or weighed directly into the autoclave. Acetylene could be conveniently measured and introduced by the use of a 1-l. to 1-gallon high pressure cylindrical buret. The buret was calibrated in terms of pressure drop (p.s.i.g.) *vs.* liters of acetylene. Moles of acetylene introduced at a given temperature were calculated from the Ideal Gas Law. Vinyl- or isopropenyl acetylenes were conveniently introduced *via* the pressure buret.

The ethynylation was started by quickly adding 92 g., 91.4%, of powdered potassium hydroxide (84 g., 100%, 1.5 moles) to the dry autoclave under a nitrogen atmosphere, and immediately sealing the autoclave. The reactor was purged several times with 50–100-p.s.i.g. portions of nitrogen followed by venting to zero-gage pressure. The reaction temperature was lowered to 0 to 5° and liquid ammonia (500 cc.) and acetylene (24 moles) were consecutively added. The liquid ammonia–potassium hydroxide mixture was stirred during acetylene addition. Ammonia and acetylene can be introduced at 25–30° if desired, but the addition is much faster if prior cooling is used. The initial pressure of the potassium hydroxide–ammonia mixture at 0–5° is 60–75 p.s.i.g. After the introduction of 24 moles of acetylene the total pressure is 190–200 p.s.i.g.

The reaction temperature was raised to the 25–40° range and optimum reaction temperature determined (*cf.* Tables I, II, and III). The carbonyl compound (6–18 moles) was added uniformly during a period of 15 min. to 1 hr. For more reactive aldehydes such as acetaldehyde and propionaldehyde an addition time of 1–2 hr. is preferable. A slight reaction exotherm was noted during a 1-2-hr. reaction time, and intermittent cooling was applied to maintain the desired reaction temperature. For the more reactive carbonyl compounds reaction is complete in about 30 min. or less.

Isolation was effected by venting the ammonia and acetylene either into a cooled (−30 to −50°) pressure vessel or directly to the atmosphere. During the venting about 500 cc. of a replacement solvent (diethyl or diisopropyl ether, hexane, etc.) was gradually added over a period of 15–30 min. It was preferable to allow the venting of ammonia to proceed overnight to avoid loss of product by entrainment. When the autoclave temperature again reached 25–35° (cooling effect due to ammonia evaporation), the vapor space was purged with two 100-p.s.i.g. nitrogen chasers, and the reactor then cooled to 0–5°.

Dry carbon dioxide gas was then added to the autoclave to a pressure of 200 p.s.i.g. and this pressure maintained for 10 min. with good stirring. The excess carbon dioxide was then vented and the autoclave contents removed. The resulting mixture of ethynylcarbinol, solvent, a minor amount of unchanged carbonyl compound, and ammonium (small) and potassium bicarbonates was filtered to remove inorganic salts which were washed with solvent. An alternate method of isolation involved the usual addition of water instead of carbon dioxide, followed by layer separation, neutralization of the organic layer with carbon dioxide, azeotropic removal of water, and finally distillation. The combined organic phase was fractionally distilled through a column of about 15–20 theoretical plates. The choice of replacement solvent was dictated primarily by the boiling point distribution of the carbonyl compound and the resulting ethynylcarbinol. If the boiling point difference between an ether solvent and an ethynylcarbinol was less than 20°, difficulty was often experienced due to azeotrope formation. A one-pass careful fractionation was sufficient in most cases to yield purities of 96–99.5%.

The simplest and most direct method[21] of analyzing the ethynylcarbinols is to treat the compound with 50% silver nitrate followed by titration of the liberated nitric acid with standard alkali using methyl purple indicator. Vapor phase chromatographic analysis using pure starting carbonyl compound and ethynylcarbinol as references has also been used successfully, but offers no advantages over the volumetric method.

**Acknowledgment.**—The authors wish to thank Mr. Joseph Improta for his valuable assistance in setting up and operating the reaction system.

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(18) R. J. Tedeschi, work to be published in connection with the mechanism of base-catalyzed ethynylations.

(19) High pressure stainless steel autoclave, designed and fabricated by Autoclave Engineers, Inc., serial no. 10943, working pressure, 5000 p.s.i.g.; test pressure, 7500, p.s.i.g.

(20) Strahman glass pressure buret (100 cc.), type 100 c, size 7, working pressure, 2000 p.s.i.g.

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