Anal. Calcd. for $C_{13}H_{14}O$: C, 83.83; H, 7.58. Found: C, 83.7; H, 7.59.

Alkylation of 2-chlorophenol with isobutylene. The catalyst was prepared in the autoclave by heating 644 g. (5 moles) of 2-chlorophenol with 4.5 g. ($^1/_6$ formula wt.) of aluminum turnings. Alkylation with isobutylene was effected at 80–90° and the product worked up to give 550 g. (60%) of 2-*tert*-butyl-6-chlorophenol (b.p. 123° at 30 mm.; n^{20}_D 1.5265).

Anal. Calcd. for $C_{10}H_{13}ClO$: Cl, 19.2. Found: Cl, 19.3.

Proof of structure of 2-tert-butyl-6-chlorophenol. A portion of the product of the above experiment was chlorinated with sulfuryl chloride to yield 2,4-dichloro-6-*tert*-butylphenol (for chlorination method see under structure proof of 2,6-diisopropylphenol). The 2,4-dichloro-6-*tert*-butylphenol was obtained in 54% yield (b.p. 134° at 15 mm., n^{20}_D 1.5421).

Anal. Calcd. for $C_{10}H_{12}Cl_2O$: Cl, 32.3. Found: Cl, 32.4.

This material had physical properties and infrared spectrum identical with those of material obtained by the pyridine-catalyzed sulfuryl chloride chlorination of 2-*tert*-butylphenol.

Alkylation of 2-ethylphenol with 1-butene. The catalyst was prepared in the autoclave in the usual manner by heating 357.4 g. (2.88 moles) of 2-ethylphenol (prepared as above) with 4 g. (0.15 formula wt.) of aluminum turnings. At a temperature of 215° the reaction mixture was alkylated with 1-butene at 200–500 p.s.i. over a 3-hr. period. Working up the product in the usual manner gave 300 g. (58%) of 2-ethyl-6-*sec*-butylphenol (b.p. 140–141° at 30 mm.; n^{20}_D 1.5153).

Anal. Calcd. for $C_{12}H_{18}O$: C, 80.9; H, 10.2. Found: C, 81.1; H, 9.98.

The phenylurethan of the 2-ethyl-6-*sec*-butylphenol was prepared and found to melt at 132.5–134°.

Anal. Calcd. for $C_{19}H_{23}NO_2$: C, 76.9; H, 7.8. Found: C, 76.5; H, 7.5.

Dealkylation of isobutylene-phenol alkylation products. A sample of phenyl *tert*-butyl ether was refluxed in a system connected to a gas bubbler. Upon boiling at atmospheric pressure for 1 hr. (liquid temperature 182°) only trace amounts of gas were evolved. Similar treatment of 2-*tert*-butylphenol (at 221–222°) and of 4-*tert*-butylphenol (at 237°) gave no evidence of gas evolution.

In order to repeat the above experiments in the presence of aluminum phenoxide, each tube was first charged with 0.01 g. of aluminum turnings and 0.5 g. of phenol. The mixture was briefly heated to effect formation of the phenoxide. To each of the three tubes was then added 5 g. of the desired compound. The tubes were then heated in an oil bath. The ether began to evolve gas at 95° and dealkylated readily at 100°. The 2-*tert*-butylphenol evolved gas rapidly at 190°. The 4-*tert*-butylphenol failed to dealkylate even when refluxed with the catalyst.

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE ETHYL CORPORATION]

Base-Catalyzed Alkylation with Olefins

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The base catalyzed addition of very weak acids to simple olefins has been studied using the preformed sodium salts of the very weak acids as catalysts. A variety of reactants were employed, and the data are examined in regard to the mechanism of the process.

The base catalyzed addition of very weak acids to activated olefinic systems is a relatively familiar reaction as typified by the addition of alcohols, amines, and acidic hydrocarbons to acrylonitrile,[2a] butadiene,[2b] and styrene.[2c] Although the addition of very weak acids to simple olefins is a somewhat more recent development, four papers[3] and numerous patents[4] have appeared on the subject.

In several of these papers the investigators have relied upon the *in situ* formation of the sodium salt of the very weak acids, which is in reality a reaction intermediate rather than a catalyst in the process.[3b] In the present investigation the sodium salt was preformed before the alkylation step in order to assure somewhat more uniform reaction conditions. The ethylation was applied to a series of compounds including both acidic hydrocarbons and primary and secondary amines. An attempt has been made to correlate the pK_a with the reactivity of the very weak acid.

In general, the greater the pK_a of the very weak acid,[5] the lower the reaction temperature that was required to effect ethylation at a reasonable rate.

Thus cumene (relative pK_a 37)[5] and toluene are readily ethylated at temperatures of 120–140° whereas aniline (relative pK_a 27),[5] methylaniline, and *ortho*-toluidine require temperatures of 240–275°. The aliphatic amines are known to be less acidic than the aromatic amines, as evidenced by their low reactivity with sodamide, and it is found that the temperature required for their ethylation (135–160°) is lower than that required for aniline but higher than that required for toluene.

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[2] (a) Bruson, *Org. Reactions*, **5**, 79 (1949). (b) Wegler and Pieper, *Ber.*, **83**, 6 (1950). (c) Wegler and Pieper, *Ber.*, **83**, 1 (1950).

[3] (a) Howk, Little, Scott, and Whitman, *J. Am. Chem. Soc.*, **76**, 1899 (1954). (b) Pines, Vesely, and Ipatieff, *J. Am. Chem. Soc.*, **77**, 554 (1955). (c) Hart, *J. Am. Chem. Soc.*, **78**, 2619 (1956). (d) Pines and Mark, *J. Am. Chem. Soc.*, **78**, 4316 (1956).

[4] Whitman, U. S. Patent **2,448,641** (Sept. 7, 1948) and U. S. Patent **2,501,556** (March 21, 1950); Gresham, Brooks, and Bruner, U. S. Patent **2,501,509** (March 21, 1950); Little, U. S. Patent **2,548,803** (Apr. 10, 1951): Pines and Ipatieff, U. S. Patent **2,670,390** (Feb. 23, 1954) and U. S. Patents **2,721,885–2,721,887** (Oct. 25, 1955); Closson, Kolka, and Ligett, U. S. Patent **2,728,802** (Dec. 27, 1955), U. S. Patents **2,750,384** and **2,750,417** (June 12, 1956), and U. S. Patent **2,751,426** (June 19, 1956).

[5] McEwen, *J Am. Chem. Soc.*, **58**, 1124 (1936).

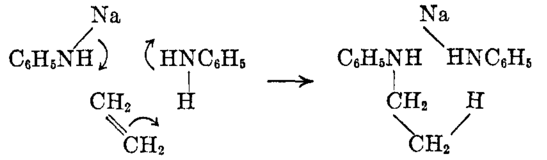
Since the strongest conjugate bases arise from the weakest acids, it is convenient to discuss this temperature correlation in terms of the base strengths of the anions participating in the first step of the ethylation. Thus anilide ion adds to ethylene (Equation 1) to yield an aliphatic carbanion, one of the strongest bases known. The greater the difference in the basicities of the two anions, the higher the temperature that will usually be required to effect ethylation.

$$(1)\ C_6H_5NH^- + CH_2{=}CH_2 \rightleftharpoons C_6H_5NHCH_2CH_2^-$$

The carbanion produced in (Equation 1) might be expected to have a short life at the temperature employed in the alkylations. It may loose a hydrogen to produce sodium hydride, it may undergo fission to the parent anion and olefin, it occasionally will add to a second molecule of ethylene, or more commonly it may acquire a proton from a molecule of the very weak acid being alkylated (Equation 2). The possibility of a concerted process should

$$(2)\ C_6H_5NHCH_2CH_2^- + C_6H_5NH_2 \longrightarrow C_6H_5NHC_2H_5 + C_6H_5NH^-$$

possibly be considered (Equation 3).



The failure of aniline to undergo dialkylation to a major extent is probably to be associated both with the fact that anilide ion is a weaker base than *N*-ethylanilide ion, and to the fact that the ethylation is a reversible process. An attempt to ethylate *N*-ethylaniline resulted both in partial fission to ethylene and aniline, and also yielded a small amount of *N*-*n*-butylaniline. The abstraction of a proton from the ethyl group to yield the β-*N*-ethylaniline carbanion would appear requisite to the production of such compounds.

Steric factors can play an appreciable role in the base-catalyzed alkylation reaction. Thus cumene required a somewhat higher temperature for alkylation than did toluene, whereas tetralin was readily ethylated twenty degrees lower than toluene. Similarly piperidine was ethylated some thirty degrees lower than dibutylamine. Although 2-methyl-6-ethylaniline readily formed the *N*-sodio catalyst, attempts at ethylation were unsuccessful, and this behavior is likely the result of steric hindrance.

An amide ion displacement reaction was observed to occur between certain amines and *N*-sodio amines. Sodium anilide reacted with hexylamine to yield *N*-hexylaniline:

$$C_6H_5NH^- + C_6H_{13}NH_2 \longrightarrow C_6H_5NHC_6H_{13} + NH_2^-$$
$$C_6H_5NH_2 + NH_2^- \longrightarrow C_6H_5NH^- + NH_3$$

Since sodamide reacts with aniline to form sodium anilide, the process should be a catalytic one and require only a catalytic amount of sodium anilide. A second type of this reaction represented by the reaction of hexylamine with *N*-sodiohexylamine to yield dihexylamine and amide ion, might be expected to be stoichiometric with the amount of *N*-sodiohexylamine used.

The use of higher olefins in the base catalyzed alkylation reaction does not appear promising in view of their sluggish behavior.

EXPERIMENTAL

All liquid reagents were dried by azeotropic distillation before use. Reactive intermediates were protected from moisture and air by handling under a nitrogen atmosphere. Melting and boiling points are uncorrected except where otherwise stated.

Ethylation of aniline. The catalyst was prepared by adding 19.5 g. (0.5 mole) of sodamide to 300 ml. of aniline and slowly heating to 180° to insure complete ammonia evolution. The mixture was charged to a 2-l. steel autoclave along with an additional 300 ml. of aniline (600 g., 6.45 moles total). The solution was heated to 150° at which point the autoclave was pressured to 400 p.s.i. with ethylene. Heating was then continued and a drop in pressure noted when 270° was reached. The reaction mixture was maintained at 275° and under ethylene pressures of 600–800 p.s.i. for a 6-hr. period.

After cooling, the catalyst was destroyed by the addition of 200 ml. of water. The product was washed with water, dried by azeotropic distillation with toluene, and fractionally distilled. The following products were obtained: aniline (106 g., 18%), *N*-ethylaniline (588 g., 75%), *N*,*N*-diethylaniline (24 g., 2%), and a higher boiling residue (23 g.). The structures of the products were determined by their physical properties and by comparison of their infrared spectra with those of authentic samples.

Ethylation of o-toluidine. The reaction was carried out in the same manner as the above experiment, except that ethylene absorption occurred at 240°. The product consisted of unreacted 2-methylaniline and *N*-ethyl-2-methylaniline (206 g., 27%; b.p. 212–212.5°; n_D^{20} 1.5469).

Attempted ethylation of 2-methyl-6-ethylaniline. This experiment was carried out in the manner of the above reactions; however, the use of reaction temperatures of up to 322° failed to produce any evidence of ethylene absorption. The product consisted solely of recovered 2-methyl-6-ethylaniline.

Ethylation of N-methylaniline. The catalyst was prepared by the reaction of 18 g. (0.5 mole) of sodamide with 585 g. (5.48 moles) of *N*-methylaniline. Ethylation was effected over a 4.5-hr. period at 250–255° and 600–800 p.s.i. The product was worked up to yield 171 g. (29%) of *N*-methylaniline and 389 g. (53%) of *N*-methyl-*N*-ethylaniline. The *N*-methyl-*N*-ethylaniline (b.p. 202.5°; n_D^{20} 1.5476) yielded a picrate melting at 128–129° (lit. 128–131°[6]).

Attempted ethylation of N-ethylaniline. The catalyst was prepared from 19.5 g. (0.5 mole) of sodamide and 575 g. (4.75 moles) of *N*-ethylaniline. The mixture was heated in the autoclave to 150° and ethylene added to 400 p.s.i. pressure. Upon further heating to 290°, the pressure increased to 640 p.s.i. with no evidence of ethylene absorption. The product was worked up in the usual manner to yield 63 g. (14%) of aniline, 410 g. (71%) of *N*-ethylaniline, 8 g. (1%) of *N*-butylaniline, and 18 g. of residue. The *N*-butylaniline was identified by its physical properties (b.p. 127–128° at 20 mm.; n_D^{20} 1.5379) and by the preparation of its

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(6) Wittig and Merkle, *Ber.*, **76B**, 109 (1943).

meta-nitrobenzene sulfonyl derivative (m.p. and mixed m.p. 92–93°). No evidence of *N*,*N*-diethylaniline was found.

In order to demonstrate that no decomposition had occurred during the preparation of the catalyst, *N*-sodio-*N*-ethylaniline was prepared as above. Upon hydrolysis and fractionation only *N*-ethylaniline was obtained.

Alkylation of aniline with propylene. The autoclave charge was identical to that used in the ethylation of aniline. The mixture was heated to 200° and the autoclave pressured to 360 p.s.i. with propylene. Alkylation was effected at 330° and 700 p.s.i. over a 30-min. period after which no further pressure drop was evident. The product was worked up to yield 470 g. (78%) of aniline, 56 g. (6%) of *N*-isopropylaniline, and a 17 g. residue. The *N*-isopropylaniline (b.p. 201.5–203°; n_D^{20} 1.5394) yielded an acetyl derivative melting at 41–42° (lit.[7] m.p. 42°).

Ethylation of dibutylamine. The *N*-sodio-dibutylamine catalyst was prepared using the method employed by Danforth.[8] Butadiene (10 g., 0.18 mole) was bubbled into a stirred dispersion of 11 g. (0.48 mole) of sodium in 400 ml. of dibutylamine at 10°. This mixture along with an additional 200 ml. of dibutylamine (456 g., 3.52 moles total) was charged to the autoclave. Ethylation was carried out at 132–135° over a 5-hr. period using ethylene pressures of 300–800 p.s.i. The catalyst was hydrolyzed and the product fractionated to yield 35 g. (8%) of dibutylamine and 354 g. (63%) of *N*-ethyldibutylamine (b.p. 177.5–178°; n_D^{20} 1.4221).

Ethylation of piperidine. In the case of piperidine it was found that the presence of a few percent of pyridine (which could not be removed from the piperidine) rendered the use of butadiene unnecessary in the preparation of the catalyst. The autoclave was charged with a dispersion of 3.5 g. (0.15 mole) of sodium in 425 g. (5 moles) of piperidine. Ethylation was effected over a 3-hr. period at 97–100° and 600–750 p.s.i. The product was found to consist of 43 g. (10%) of piperidine, 446 g. (80%) of *N*-ethylpiperidine, and 28 g. of residue. The *N*-ethylpiperidine boiled at 129°; n_D^{20} 1.4431. The picrate was prepared and found to melt at 168° (lit. 165–166°[9]).

Ethylation of hexylamine. The autoclave charge was prepared from 500 g. (4.93 moles) of hexylamine and 11 g. (0.48 mole) of sodium using the butadiene technique as in the dibutylamine alkylation. Ethylation was effected over a 1-hr. period at 150–160° and 400–600 p.s.i. There were obtained 140 g. (28%) of hexylamine, 190 g. (38%) of *N*-ethylhexylamine, 76 g. (10%) of *N*-hexyldiethylamine, and 58 g. (13%) of dihexylamine. The *N*-ethylhexylamine boiled at 159°; n_D^{20} 1.4206, and the *N*-hexyldiethylamine boiled at 179.5°. The dihexylamine (b.p. 75° at 1 mm.; n_D^{20} 1.4339) had the physical properties and infrared spectrum identical with those of an authentic sample prepared by the reaction of hexylamine and hexyl chloride.

Reaction of hexylamine with N-sodiohexylamine. Using the butadiene method described in the dibutylamine ethylation, 7 g. (0.3 mole) of sodium was reacted with 422 g. (4.15 moles) of hexylamine. The mixture was heated in the autoclave under a nitrogen atmosphere at 165° for 2 hr. The product was hydrolyzed and fractionated to yield 310 g. (73%) of hexylamine and 39 g. (10%) of dihexylamine (b.p. 63–68° at 0.5–1 mm.; n_D^{20} 1.4333).

Reaction of hexylamine and sodium anilide. A solution of sodium anilide in aniline was prepared by heating 18 g. (0.5 mole) of sodamide and 400 ml. of aniline to 180°. This solution together with an additional 150 ml. of aniline (5.9 moles total) was charged to the autoclave and 152 g. (1.5 moles) of hexylamine added. The mixture was heated at 330° for 2 hr. and a 200 p.s.i. increase in pressure noted. The product was worked up to yield 478 g. (88%) of aniline, 46 g. (30%) of hexylamine, 50 g. (19%) of *N*-hexylaniline, and 28 g. of residue. The *N*-hexylaniline boiled at 156–168° at 20 mm.; n_D^{20} 1.5218.

Anal. Calcd. for $C_{12}H_{19}N$: N, 7.9. Found: N, 8.1.

The physical properties and infrared spectrum of this material were identical with those of an authentic sample prepared from the reaction of aniline with hexyl bromide.

Ethylation of toluene. The preparation of the benzylsodium catalyst was effected using 11.5 g. (0.5 mole) of sodium, 28.2 g. (0.25 mole) of chlorobenzene, and 300 ml. of toluene.[10] The mixture was charged to the autoclave together with an additional 300 ml. of toluene. Ethylation was carried out at 125–130° at pressures of 300–800 p.s.i. over a 4-hr. period. The reaction was highly exothermic, and relatively low ethylene pressures were used in the early stages of the reaction. The catalyst was hydrolyzed by the addition of ethanol, and the product was washed and fractionated. There were obtained 7 g. (1%) of toluene, 179 g. (27%) of *n*-propylbenzene, 549 g. (66%) of 3-phenylpentane, and 15 g. of residue. The *n*-propylbenzene (b.p. 158.5°; n_D^{20} 1.4914) and the 3-phenylpentane (b.p. 187.5; n_D^{20} 1.4882) had been previously reported from the ethylation of toluene.[3b]

Ethylation of cumene. Amyl sodium was prepared by a method similar to that described in the literature.[11] To a dispersion of 23 g. (1 mole) of sodium in 200 ml. of heptane and 100 ml. of octane was added 53 g. (0.5 mole) of 1-chloropentane. High speed stirring was used and the mixture was maintained at −5 to 5° during the 40-min. addition period. To the amyl sodium prepared in this manner was added 300 ml. of cumene at 10°, and the mixture let stand at room temperature overnight. The catalyst mixture together with an additional 650 ml. (6.85 moles total) of cumene was charged to the autoclave and reacted with ethylene at 140°. The ethylation was effected using ethylene pressures of 450–600 p.s.i. over a 90-min. period. The product yielded 346 g. (34%) of *tert*-amylbenzene (b.p. 188.5°; n_D^{20} 1.4970), which was identified by comparison of its infrared spectrum with that of an authentic sample of *tert*-amylbenzene.[12]

The compound was previously reported by the ethylation of cumene with ethylene using sodium promoted with anthracene as a catalyst.[3b]

Alkylation of toluene with propylene.[3d] The autoclave charge, consisting of benzylsodium and toluene, was identical with that used in the ethylation of toluene. Reaction with propylene occurred slowly at 185–188° and 700–800 p.s.i. The product was hydrolyzed and fractionated to yield 425 g. (76%) of toluene and 47 g. (6%) of isobutylbenzene. The isobutylbenzene (b.p. 170.5–171°; d_4^{20} 0.853; n_D^{20} 1.4863) was identified by its physical properties and by comparison of its infrared spectrum with that of an authentic sample.

Ethylation of tetralin. The α-sodio tetralin catalyst was prepared in the same manner as benzylsodium using tetralin in place of toluene. Interchange of the phenylsodium and tetralin was effected by heating at 60–80° for 3 hr. The ethylation was carried out at 140° and 600–700 p.s.i. over a 6-hr. period. There were obtained 4% of recovered tetralin, 21% of 1-ethyltetralin, 41% of 1,4-diethyltetralin, and 8% of a compound believed to be 1,1,4-triethyltetralin. The 1-ethyltetralin boiled at 239.9° (corr.); n_D^{20} 1.5320 (lit.[13] b.p. 239.4°; n_D^{20} 1.5316). The 1,4-diethyltetralin boiled at 261°; n_D^{20} 1.5262.

Anal. Calcd. for $C_{14}H_{20}$: C, 89.29; H, 10.71. Found: C, 89.3; H, 10.7.

The structure of the 1,4-diethyltetralin was established by dehydrogenation. A 1.0 g. sample was heated with 0.34 g. of sulfur at 250° for 10 min. The product was distilled at 90–

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(7) Hickinbottom, *J. Chem. Soc.*, 994 (1930).

(8) Danforth, U. S. Patent **2,527,709** (Oct. 31, 1950); *Chem. Abstr.*, **45**, 3870 (1951).

(9) Winans and Adkins, *J. Am. Chem. Soc.*, **54**, 310 (1932).

(10) Gilman, Pacevitz, and Baine, *J. Am. Chem. Soc.*, **62**, 1517 (1940).

(11) Morton, Massengale, and Brown, *J. Am. Chem. Soc.*, **67**, 1620 (1945).

(12) The authors are indebted to Dr. John Derfer of API Project 45 for this authentic spectrum.

(13) Hipsher and Wise, *J. Am. Chem. Soc.*, **76**, 1747 (1954).

100° at 1 mm. A picrate melting at 90.5–92.5° was prepared from the distillate. The literature[14] reports the picrate of 1,4-diethylnaphthalene to melt at 91–93°.

The material believed to be 1,1,4-triethyltetralin boiled at 174° at 50 mm; n_D^{20} 1.5236.

Anal. Calcd. for $C_{16}H_{24}$: C, 88.89; H, 11.11. Found: C, 88.9; H, 11.2.

Acknowledgment. The authors wish to express their appreciation to Dr. Waldo B. Ligett for his helpful suggestions and continued interest during the course of this work.

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[14] Arnold and Barnes, *J. Am. Chem. Soc.*, **66**, 960 (1944).

[CONTRIBUTION FROM THE RESEARCH LABORATORIES, AIR REDUCTION CO., INC.]

Sodium Acetylide. I. Preparation of Sodium Acetylide by Reaction of Acetylene with Sodium in Organic Media

T. F. RUTLEDGE

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A procedure for preparing sodium acetylide in organic diluents is described. Sodium metal, as a dispersion, is reacted with acetylene at atmospheric pressure and at a critical temperature. Acetylene purity is extremely important. Dry, stable, finely divided sodium acetylide is described.

The preparation of sodium acetylide in liquid ammonia is a well-known reaction.[1] Liquid ammonia is relatively difficult to handle, and accordingly it has not been used extensively for large scale work. Although a fairly pure sodium acetylide can be prepared in liquid ammonia, attempts to isolate dry sodium acetylide from this reaction medium have been reported to be somewhat hazardous.[2] Experience in this laboratory confirmed a literature report[3] that sodium acetylide prepared in liquid ammonia could not be placed in inert organic diluents to form a finely divided suspension. A coarse, dark, and somewhat hard solid resulted in most cases.

Sodio derivatives of monosubstituted acetylenes are prepared readily in organic diluents such as benzene and ether.[4,5] Acetylene reacts with sodium metal in organic diluents with great difficulty. One of the few references found is a German patent[6] which describes preparation of sodium acetylide by passing acetylene into a stirred mixture of sodium and xylene at reflux temperature (about 135–140°). The product was stated to be a yellowish-white powder, the sodium acetylide content of which corresponded to 83% yield. Although no reaction time was mentioned, a time of more than 60 hours was apparently required. This is inferred from a statement contained in a later German patent,[7] which claims faster production of sodium acetylide by reaction of acetylene with sodium deposited on sand. It is interesting to note that in 1897 Matignon[8] described a process for preparing sodium acetylide which is almost identical to that described in the patent.[7]

Since sodium acetylide is an important intermediate in the practice of acetylene chemistry, it appeared desirable to find a method for fast and easy preparation of this material in organic diluents. A stable, dry powder of good purity should be valuable as a reagent.

DISCUSSION OF RESULTS

When sodium metal of 10–25 micron particle size was suspended in xylene and subsequently treated with pure acetylene at various temperatures, optimum reaction was obtained at 100–110°. The course of the reaction was followed by means of a hydrogen analyzer attached to the exit end of the reactor.[9] Complete reaction of 0.25 mole of sodium in 300 ml. of xylene required 1.5 to 2.5 hours. Yield of sodium acetylide based on sodium was virtually quantitative. Yield based on acetylene was 75–85%.

The data in Table I summarize experiments which demonstrate the effect of reaction tempera-

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[1] T. H. Vaughn, U. S. Patent **2,198,236**, April 23, 1940. E. A. Bried and G. F. Hennion, *J. Am. Chem. Soc.*, **59**, 1310 (1937). T. H. Vaughn, G. F. Hennion, R. R. Vogt, and J. A. Nieuwland, *J. Org. Chem.*, **2**, 1 (1937). P. Pomerantz, A. Fookson, T. W. Mears, S. Rothberg, and F. L. Howard, *J. Res. Nat'l Bur. Standards*, **52**, 51 (1954).

[2] Private communications from J. H. Wotiz and M. S. Newman.

[3] G. F. Hennion and E. P. Bell, *J. Am. Chem. Soc.*, **65**, 1847 (1943).

[4] J. R. Johnson, A. M. Schwartz, and T. L. Jacobs, *J. Am. Chem. Soc.*, **60**, 1882 (1938). H. Gilman and R. V. Young, *J. Org. Chem.*, **1**, 315 (1936).

[5] P. Ivitsky, *Bull. soc. chim. France*, **35**, 357 (1924).

[6] O. Ernst and O. Nicodemus, German Patent **494,575**, Nov. 21, 1926.

[7] W. Schulenberg, German Patent **535,071**, Feb. 8, 1929.

[8] C. Matignon, *Compt. rend.*, **124**, 775 (1897).

[9] Use of a hydrogen analyzer for this purpose was suggested by Dr. A. J. Buselli of this laboratory. This proved to be the best method of following the course of the reaction. Dr. Buselli contributed other valuable suggestions prior to and during the conduct of the work.