the decline in rate constant would not be nearly so great as that often observed. The decline in slope may have been caused by admission of air to the reaction flask when opening it to the sample. In addition, and at times which varied with each experiment, lithium chloride precipitated from the supersaturated solutions, and no more samples could be utilized. We were never able to withdraw more than seven samples without observing the decrease and in several cases the decrease occurred earlier. We therefore have used the first 40–60% of the reaction to determine the rate constants and Table II thus reports initial values of k_2.

The method of following rates in these experiments led to somewhat larger errors in individual points than are generally observed, as the bromide titration involved a difference between two values. For this reason, we have analyzed the data statistically for the two runs that ap-

peared to have the largest deviations and have shown that the data and the correlations derived from them are statistically satisfactory. The slopes derived in these runs were placed by the method of least squares. Calculations from the least squares equations for these two runs indicate that the probable errors in rate constant were 7.3 and 8.8%. These values may be compared with values of average deviation from the mean rate constants for the cis isomer of 4.9% and for the trans isomer of 8.7% listed in Table II. Approximate values for k_3, based upon the third-order rate law (9) which were obtained by dividing k_2 by initial phenyl-

$$\frac{d(Br^-)}{dt} = k_3(PhLi)^2(\text{halide}) \qquad (9)$$

lithium concentrations, also are given in Table II.

BOULDER, COLORADO

Vinylation: Kinetics and Mechanism of the Methoxide-catalyzed Addition of Methanol to Phenylacetylene[1]

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As a model of the vinylation reaction we have studied the kinetics of the methoxide-catalyzed addition of methanol to phenylacetylene in the solvents methanol and dioxane. The reaction appears to be first order in phenylacetylene, first order in methoxide and zero order in methanol, with $\Delta H^* = 28.5$ kcal. mole^{-1} and $\Delta S^* = -8$ e.u. at 126°. Our data are consistent with the following general mechanism: the rate-determining step is the addition of alkoxide ion to the acetylene; this is followed by the rapid abstraction of a proton from the alcohol by the carbanion intermediate. This mechanism predicts correctly that increased electron-withdrawing power of substituents of the acetylene increases the rate of vinylation; it is also consistent with our hypothesis that increased nucleophilic power of the species attacking the acetylene increases the rate of vinylation.

The base-catalyzed addition of compounds with an acidic hydrogen to any acetylenic compound, vinylation

$$RQH + R'C{\equiv}CR'' \xrightarrow{\text{base}} R'CH{=}CR''QR \qquad (1)$$
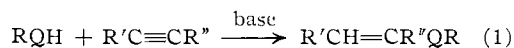
has been widely applied in syntheses.[2,3] Some sixty years ago, in his studies of the ethoxide-catalyzed isomerization of 1-alkynes to 2-alkynes and allenes, Favorsky isolated an ethoxyalkene.[4] Later Moureu and Nef prepared β-alkoxystyrenes from phenylacetylene and alkoxide–alcohol solutions.[5,6] Related addition reactions of water, phenols, malonic ester, mercaptans, amines and possibly acetic acid to various acetylenes are scattered throughout the literature.[7–9]

Perhaps the most systematic exploitation of the vinylation reaction is found in the recent work of Reppe and co-workers at I. G. Farben.[10] Their high pressure reactions of acetylene led to whole families of vinyl compounds. Similar work has

been reported in the Russian and Japanese literature.[11,12] The scope, diversity and ramifications of all of these base-catalyzed additions and their products have been ably reviewed.[7,10,13–15]

Except for the preliminary work of some Russian workers, very little was done to clarify the mechanism of these reactions.[16] As a model of the vinylation reaction we have studied the kinetics of the methoxide-catalyzed addition of methanol to phenylacetylene in the solvents methanol and dioxane

$$C_6H_5C{\equiv}CH + CH_3OH \xrightarrow{NaOCH_3} C_6H_5CH{=}CHOCH_3 \qquad (2)$$
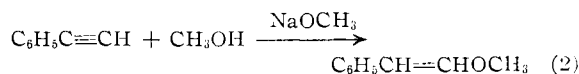
That β-methoxystyrene is the chief product has been amply demonstrated.[5,6,17] Reaction (2) was found to be second order, first order in phenylacetylene, first order in sodium methoxide and zero order in methanol. These results allow us to

(1) Work supported by the Office of Ordance Research.

(2) In this paper the term "vinylation" will be used only in the sense indicated by equation (1).

(3) It does not include the large group of acid-catalyzed vinylations.

(4) A. Favorsky, J. prakt. Chem., 44, 208 (1891).

(5) C. Moureu, Bull. soc. chim., [3] 31, 526 (1904).

(6) J. U. Nef, Ann., 308, 264 (1899).

(7) A. W. Johnson, "The Chemistry of the Acetylenic Compounds," Vol. II, Edward Arnold and Co., London, 1950, pp. 69–73, 106–119, 218–221.

(8) K. Bowden, E. A. Braude and E. R. H. Jones, J. Chem. Soc., 945 (1946).

(9) A. L. Henne, J. V. Schmitz and W. G. Finnegan, THIS JOURNAL, 72, 4195 (1950).

(10) J. W. Copenhaver and M. H. Bigelow, "Acetylene and Carbon Monoxide Chemistry," Reinhold Publ. Corp., New York, N. Y., 1949, Ch. 11.

(11) M. F. Shostakovskii and M. S. Burmistrova, Akad. Nauk. S. S. S. R., Inst. Org. Khim., Sintezy Org. Soldinenii, Sbornik, 2, 48 (1952); C. A., 48, 627 (1954) (one of a long series of papers by Shostakovskii, et al.).

(12) J. Furukawa, T. Ando and M. Yokoyama, Bull. Inst. Chem. Res., Kyoto University, 31, 220 (1953); J. Furukawa, et al., ibid., Commemoration Volume, 110 (1951).

(13) J. A. Nieuwland and R. R. Vogt, "The Chemistry of Acetylene," Reinhold Publ. Corp., New York, N. Y., 1945, Ch. IV.

(14) C. E. Schildknecht, "Vinyl and Related Polymers," John Wiley and Sons, Inc., New York, N. Y., 1952, Ch. XI.

(15) P. Piganiol, "Acetylene Homologues and Derives," Dunod, Paris, 1945.

(16) E. S. Wassermann and A. B. Bedrintzeva, Compt. rend. acad. sci. U. S. S. R., 33, 34 (1941); C. A., 37, 6539 (1943).

(17) (a) C. Dufraisse and R. Chaux, Bull. soc. chim., [4] 39, 905 (1926); (b) we have recently shown that small quantities of α-methoxystyrene also are produced, unpublished work.

describe the probable mechanism for the formation of β-methoxystyrene which can presumably be applied to vinylations generally.

Experimental

Materials and Analysis.—Anhydrous methanol and dioxane were used as solvents. The methanol was prepared from Baker and Adams "absolute methanol" by the method of Lund and Bjerrum.[18] Technical grade dioxane was purified by a method described by Fieser.[19]

Solutions of ca. 1 N hydrochloric acid, 0.1 N sodium hydroxide and 0.05 N sulfuric acid were prepared and standardized according to conventional procedures. Concentrated stock solutions of sodium methoxide were prepared from anhydrous methanol and freshly-cut reagent grade sodium which had first partially reacted with three portions of anhydrous methanol. The concentration of this methoxide was determined by titration with standard acid.

Phenylacetylene was prepared from β-bromostyrene and potassium hydroxide at 210–220°.[20] In one typical procedure the product was separated, dried over potassium hydroxide pellets, and distilled. Since even the middle cut boiling at 141–142° was yellow, it was redistilled. An almost colorless middle fraction boiling 36–40° at ca. 15 mm. was collected and then stored in the refrigerator for use in the kinetic studies. During the course of our work the phenylacetylene was redistilled, again at reduced pressure.

Analyses for phenylacetylene were based on the method of Hanna and Siggia.[21] The reaction involved is

$$2C_6H_5C\equiv CH + Na_2HgI_4 + 2NaOH \longrightarrow$$
$$(C_6H_5C\equiv C)_2Hg + 4NaI + 2H_2O \quad (3)$$
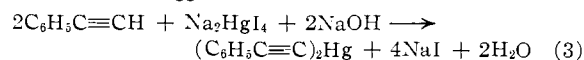
in which one equivalent of sodium hydroxide is consumed for each equivalent of insoluble acetylide formed. Stock sodium mercuric iodide reagent was prepared from reagent grade sodium iodide and mercuric iodide. The samples of phenylacetylene were shaken with sodium mercuric iodide reagent and a known volume of standard sodium hydroxide, both in stoichiometric excess. The excess sodium hydroxide was titrated with standard sulfuric acid to the phenolphthalein end-point (if for any reason titration was delayed, the flasks were capped). Freshly distilled phenylacetylene, ca. 1 mmole, could be estimated to within 1–2% or about as accurately as has been claimed for 10 mmoles.[21]

After several weeks in the refrigerator our phenylacetylene took on a yellow cast. Analyses of "old" phenylacetylene, or its methanol or dioxane solutions which had been exposed to the conditions of our kinetic runs, ran low. The losses in solution could be reduced by using freshly distilled solvents and by displacing the air above the solution with dry nitrogen just before the containing ampules were sealed. In any case, both in the blanks and in the kinetic runs it appeared that there was a constant value for the initial phenylacetylene concentration under a given set of reaction conditions. We shall return to this point shortly.[22]

Solutions of sodium methoxide in dioxane, in methanol, or in methanol–phenylacetylene solutions retained their titer under conditions of our kinetic runs. The dioxane solutions yellowed somewhat with heating.

Kinetic Studies.—The sealed ampule technique was used in this work. Weighed portions of phenylacetylene and known volumes of stock sodium methoxide were diluted, usually to 250 ml., with the appropriate solvent. When dioxane was the solvent the methanol concentration could be varied by the addition of known volumes of methanol beyond that already introduced with the sodium methoxide. Glass ampules were filled with 10-ml. aliquots of this solution, capped and then cooled in Dry Ice; the vapor space

(18) H. Lund and J. Bjerrum, *Ber.*, **64**, 210 (1931).

(19) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., New York, N. Y., 1941, p. 369.

(20) A. H. Blatt, editor, "Organic Syntheses," Coll. Vol. 1, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 438.

(21) J. G. Hanna and S. Siggia, *Anal. Chem.*, **21**, 1469 (1949).

(22) Though the effects of oxygen, solvent, impurities, handling operations and possibly methoxystyrene may all bear on the stability of phenylacetylene they were not investigated in detail. It is relevant to point out that T. L. Jacobs (private communication) has found that phenylacetylene in bulk polymerizes in the temperature range of our kinetic study and that it undergoes autoxidation when exposed to air.

of the ampule was blown out with dry nitrogen (in later runs only), and the ampule was sealed. These ampules were left in oil thermostats for desired periods, the uncertainty in the time being less than 3 minutes. When not in the thermostats the ampules were stored in a refrigerator.

For analysis the contents of an ampule were rinsed with several portions of methanol and carbon dioxide free water into a 250-ml. flask containing sodium mercuric iodide; standard sodium hydroxide was added only in those runs in which the phenylacetylene concentration exceeded that of sodium methoxide. For these analyses a titration blank of 0.005 mmole was added to the acid readings.

Reaction (2) was apparently first order in each of phenylacetylene and methoxide. Since the methoxide concentration remained constant in any given run we fitted the raw data with the equation

$$kt = \frac{2.303}{b} \log \frac{a}{a - x} \quad (4)$$

where k = rate constant defined by (4), a = initial concentration of phenylacetylene, b = concentration of sodium methoxide, $a - x$ = concentration of phenylacetylene at time t.

According to the experimental procedure $a - x$ was determined by analysis. Since b and t were known, k could be determined without a; indeed, a could be calculated from the kinetic data. For runs at a given temperature, plots of $2.303/b \log (a - x)$ against t would (ideally) give rise to a set of parallel straight lines from whose slope k could be obtained. If, however, a were known and kt were plotted against t, a single straight line passing through the origin and representing all runs should result.

In our case kt was plotted against t for each run at a given temperature, and the best straight line was drawn through the experimental points. This procedure gave a set of straight lines with very nearly the same slope k (see Fig. 1).
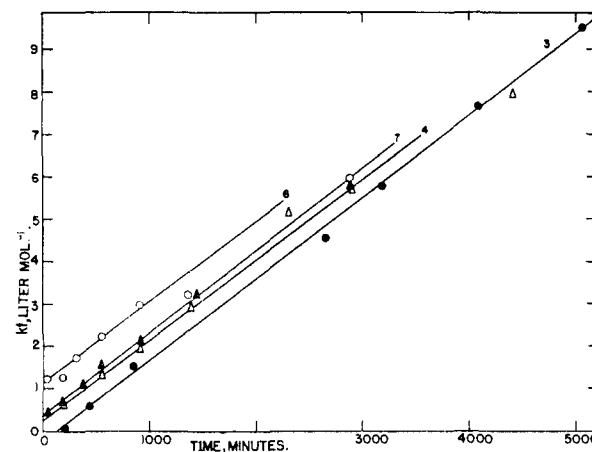

Fig. 1.—Methoxide-catalyzed addition of methanol to phenylacetylene at 125.78°.

The intercepts on these plots suggest that our estimates of a required an adjustment. Since this adjustment was relatively small, usually less than 6%, and since the rate constants would not have been affected, the approximate value of a was used in the calculations. It should perhaps be emphasized that this approximate value of a for the phenylacetylene concentration, which is also listed in Table I, was determined by analysis of several unheated ampules of each run.

The kinetic data for the runs in methanol, in part illustrated in Fig. 1, are summarized in Table I. These runs were carried to high conversions, usually greater than 80%. The experimental points that were obviously erratic fell into no clear pattern although they apparently derived more often from long term ampules. From the mean slope of the kt versus t plots at a given temperature rate constants were obtained. These constants were corrected for the expansion of methanol[23] and are listed in Table I.

(23) Landolt-Börnstein, "Tabellen," Vol. I, Julius Springer, Berlin, 1923, p. 278.

TABLE I

RATES OF ADDITION OF METHANOL TO PHENYLACETYLENE IN THE SOLVENT METHANOL

Run	Temp., °C.	$C_6H_5C\equiv$ CH, mole/l.	NaOCH$_3$, mole/l.	k, l. mole^{-1} min.$^{-1}$
11	149.35 ± 0.10	0.1037	0.1995	1.75 × 10^{-2}
12		.0948	.3990	1.87 × 10^{-2}
14		.2538	.0599	2.05 × 10^{-2}
3		.0895	.1123	1.79 × 10^{-2}
4		.0796	.2242	1.78 × 10^{-2}
7		.2804	.4486	1.87 × 10^{-2}
6		.4116	.3364	1.89 × 10^{-2}
		Mean		(1.86 ± 0.07) × 10^{-2}
11	126.05 ± 0.10	0.1037	0.1995	2.35 × 10^{-3}
12		.0948	.3990	2.42 × 10^{-3}
14		.2538	.0599	2.64 × 10^{-3}
		Mean		(2.47 ± 0.11) × 10^{-3}
3	125.78 ± 0.10	0.0895	0.1123	2.22 × 10^{-3}
4		.0796	.2242	2.19 × 10^{-3}
7		.2804	.4486	2.24 × 10^{-3}
6		.4116	.3364	2.19 × 10^{-3}
		Mean		(2.21 ± 0.02) × 10^{-3}
11	108.97 ± 0.20	0.1037	0.1995	4.64 × 10^{-4}
3	108.60 ± .20	.0895	.1123	4.38 × 10^{-4}
4	108.29 ± .20	.0796	.2242	4.58 × 10^{-4}
7	108.29 ± .20	.2804	.4486	4.67 × 10^{-4}
6	108.29 ± .20	.4116	.3364	4.29 × 10^{-4}
Mean	108.5		Mean	(4.51 ± 0.14) × 10^{-4}

Using the standard expression[24]

$$k = \frac{KT}{h} e^{\Delta S^*/R} e^{-\Delta H^*/RT} \qquad (5)$$

where k is the corrected rate constant converted to the units liter mole^{-1} sec.$^{-1}$ and K is the Boltzman constant, we plotted (log k − log T) versus $1/T$ to obtain $\Delta H^* = 28.5 ± 0.7$ kcal. mole^{-1}, and from this $\Delta S^* = -8 ± 2$ e.u. at 126°.

Three kinetic runs in dioxane at 149.35 ± 0.10° are shown in Fig. 2. The initial concentrations of phenylacetylene and sodium methoxide were 0.1372 and 0.0998 mole liter^{-1},
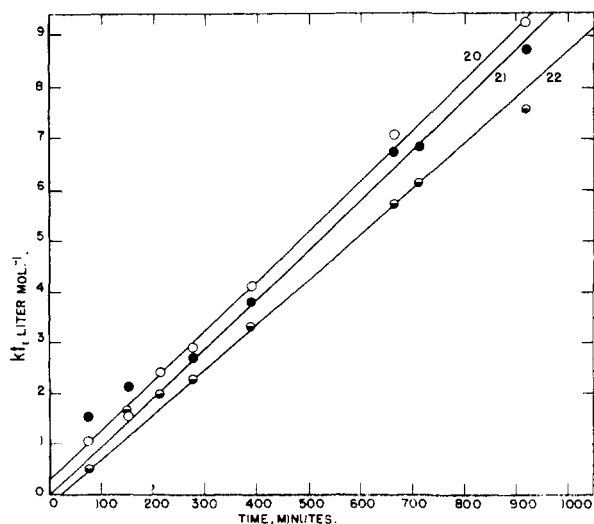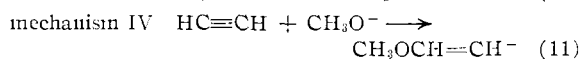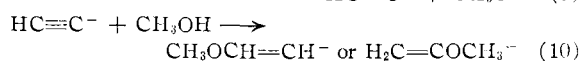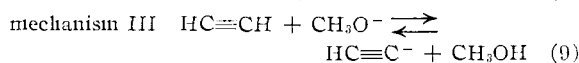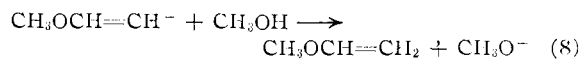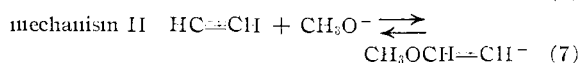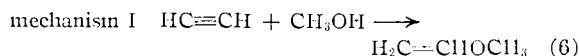

Fig. 2.—Methoxide-catalyzed addition of methanol to phenylacetylene at 149.35° in dioxane.

(24) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 196.

respectively, while the initial methanol concentrations were varied 2.4, 4.9 and 7.3 mole liter^{-1}. The corresponding rate constants were 0.983, 0.971, 0.889 × 10^{-2} liter mole^{-1} min.$^{-1}$. (Since the density of dioxane was not available at 149°, these constants were not corrected for solvent expansion; we estimate that such a correction would increase them by about 12%).[25] Essentially zero-order dependence of reaction (2) on methanol is indicated.[26]

Discussion

Taking the synthesis of vinyl methyl ether in methanol as representative, we may summarize some of the possible vinylation mechanisms[27]

mechanism I $HC\equiv CH + CH_3OH \longrightarrow$
$$H_2C=CHOCH_3 \quad (6)$$

mechanism II $HC\equiv CH + CH_3O^- \rightleftarrows$
$$CH_3OCH=CH^- \quad (7)$$

$CH_3OCH=CH^- + CH_3OH \longrightarrow$
$$CH_3OCH=CH_2 + CH_3O^- \quad (8)$$

mechanism III $HC\equiv CH + CH_3O^- \rightleftarrows$
$$HC\equiv C^- + CH_3OH \quad (9)$$

$HC\equiv C^- + CH_3OH \longrightarrow$
$$CH_3OCH=CH^- \text{ or } H_2C=COCH_3^- \quad (10)$$

mechanism IV $HC\equiv CH + CH_3O^- \longrightarrow$
$$CH_3OCH=CH^- \quad (11)$$

In the preceding scheme equilibrium arrows refer to rapid processes while the single arrows refer to rate-determining steps. In mechanisms III and IV, however, equations (10) and (11) are followed by a rapid step of the type (8).

In one of the few kinetic studies in this field, Wassermann and Bedrintzeva report a vinylation mechanism similar to I.[16] Working in the temperature range 140–170° with 96.5% ethanol, potassium hydroxide and 30–33 atm. of acetylene, they followed the progress of the vinylation up to 10% conversion of the alcohol. Assuming the acetylene concentration in the liquid phase to be approximately constant during a run, they obtained pseudo first-order rate constants. From an Arrhenius plot they found the energy of activation to be 36 kcal. mole^{-1}. They suggest a mechanism involving the activation of acetylene promoted by heat and alkali, followed by its reaction with ethanol. It would appear from their kinetic analysis that their mechanism is equivalent to I.

Since Wassermann and Bedrintzeva did not vary the initial concentrations of their reactants, the kinetic order of their reaction remains in doubt. Moreover, under their reaction conditions the concentration of ethanol is roughly proportional to that of ethoxide through the equilibrium and mechanism

$$C_2H_5OH + OH^- \rightleftarrows C_2H_5O^- + HOH \quad (12)$$
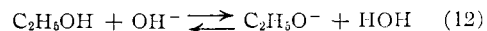
IV becomes equally applicable. Finally, our finding that reaction (2) is zero order in methanol argues against mechanism I.

Our kinetics are also inconsistent with mechanism II as proposed by Hanford, since II would require dependence on the methanol concentration.[10]

(25) W. Herz and E. Lorentz, Z. physik. Chem., **A140**, 406 (1929).

(26) It is interesting to note that the rate of vinylation appears to have a minimum at some intermediate dioxane-methanol composition

(27) Furukawa, et al., propose still other general vinylation mechanisms.[12]

Elsewhere Hanford and Fuller have written the intermediate carbanion, $HC\equiv CHOCH_3^-$.[28]

Because of equilibrium (9) it is clear that the rate-determining steps of mechanisms III and IV are indistinguishable. Both are consistent with the kinetics reported in this paper. Shildknecht has suggested that the "alkali acetylide is the active catalyst in the vinylation process" and presumably favored mechanism III.[29] However, the facile base-catalyzed additions of alcohols to $RC\equiv CCO-OH$ and their esters (R = alkyl, aryl and carboxyl),[7,30,31] and to dichloroacetylene[32] suggest that mechanisms involving acetylide cannot be general and are probably unimportant.

Mechanism IV, the slow addition of methoxide to acetylene followed by the rapid abstraction of a proton from the solvent by the carbanion intermediate, is consistent with the available data.[33]

It is interesting to note that the kinetics of reaction (2) are closely similar to those found by Hagglund and Ringbom[34] for the reaction

$$CH_3C\equiv CCOO^- + NaHSO_3 \longrightarrow$$
$$CH_3C(SO_3Na)=CHCOO^- \quad (13)$$
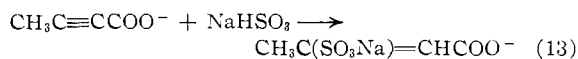
Indeed, mechanism IV has also been written as a matter of course.[35]

Mechanism IV predicts, not uniquely however, that electron-withdrawing substituents of acetylene such as trifluoromethyl, carboxyl and phenyl

should encourage nucleophilic attack and thus increase the rate of vinylation. Available examples indicate that this is the case[30]; for example, ethanol in the presence of ethoxide adds to trifluoromethylacetylene merely upon mixing,[36] and the activation energy for the vinylation of phenylacetylene is *ca.* 6 kcal. lower than that of acetylene.[16]

From the available evidence it would also appear that the nucleophilicity of the species attacking the acetylene is more important than its base strength in increasing the rate of vinylation. From the relative rates of displacement of halide ion at an aromatic carbon, Bunnett and Zahler find nucleophilic power decreasing in the order mercaptide > alkoxide > phenoxide.[37] Mercaptides apparently react more readily with acetylenes than do alkoxides,[38,39] and phenols are more difficult to vinylate than alcohols.[10,12] Assuming that the order of nucleophilicity given above can be carried over to vinylation,[40] it would appear that the order of decreasing nucleophilic power is also the order of decreasing vinylation rate. This conclusion is certainly consistent with predictions one might make on the basis of mechanism IV.

An interesting analog to the vinylation reaction is found in base-catalyzed additions to substituted alkenes. A mechanism similar to IV has been postulated for the base-catalyzed addition to fluorinated alkenes[41]

$$CCl_2=CF_2 + ROH \xrightarrow{\ \ RONa\ \ } CHCl_2-CF_2OR \quad (14)$$

Similar additions to alkenes substituted by RSO_2-, $CN-$ and NO_2- presumably have the same mechanism.[42]

CHICAGO, ILLINOIS

(28) W. E. Hanford and D. L. Fuller, *Ind. Eng. Chem.*, **40**, 1171 (1948).

(29) E. R. Blout, W. P. Hohenstein and H. Mark, "Monomers," Interscience Publishers, Inc., New York, N. Y., 1951, Chapter on "Vinyl Ethers."

(30) L. N. Owen, *J. Chem. Soc.*, 385 (1945).

(31) C. Moureu, *Bull. soc. chim.*, [3] **31**, 493 (1904).

(32) E. Ott and G. Dittus, *Ber.*, **76**, 80 (1943).

(33) Reppe probably thought of vinylation in similar terms but he wrote undissociated species NaOCH₃ and CH₃OCH=CHNa.[10] He also considered the alkali alkoxide to be more associated the greater the acidity of the parent hydroxy compound and used this idea to explain the lower rate of vinylation of phenols as compared with alcohols. We use ionic species and emphasize the nucleophilicity of the alkoxide.

(34) E. Hagglund and A. Ringbom, *Z. anorg. Chem.*, **169**, 96 (1928).

(35) T. L. Jacobs and W. R. Scott, Jr., THIS JOURNAL, **75**, 5497 (1953).

(36) A. L. Henne and M. Nager, *ibid.*, **74**, 650 (1952).

(37) J. F. Bunnett and R. E. Zahler, *Chem. Revs.*, **49**, 273 (1951).

(38) R. Adams and R. S. Ludington, THIS JOURNAL, **67**, 794 (1945).

(39) J. Loevenich, J. Losen and A. Dierichs, *Ber.*, **60**, 950 (1927).

(40) J. O. Edwards, THIS JOURNAL, **76**, 1540 (1953).

(41) P. Tarrant and J. A. Young, *ibid.*, **75**, 932 (1953); see W. K. R. Muskgrave, *Quart. Revs.*, **8**, 331 (1954), for related references.

(42) E. R. Alexander, "Principles of Ionic Organic Reaction," John Wiley and Sons, Inc., New York, N. Y., 1950, pp. 147–150.