

min. showed the same composition by v.p.c. as did the product obtained after 2 hr.) Work-up of the reaction mixture in the usual way yielded VII (11%), VIII (55%), IX (27%), and X (7%). No XI was observed.

B. Kinetic Conditions with Methylation in Tetrahydrofuran (THF).—Trityllithium was prepared as described above by the addition of triphenylmethane, 8.30 g. (0.034 mole), in 100 ml. of anhydrous ether to lithium amide (from 0.236 g., 0.034 g.-atom, of lithium) in 75 ml. of liquid ammonia. To the red solution was added dropwise with stirring 2.69 g. (0.024 mole) of VII in 25 ml. of ether over 30 min. The liquid ammonia then was removed in the usual way (the red color of the excess trityllithium disappeared at this point) and was replaced by 100 ml. of THF. The ether was distilled from the reaction mixture until the temperature of the distillate reached 50°. The reaction mixture was cooled to room temperature, 16.0 g. (0.12 mole) of methyl iodide was added, and the mixture refluxed for 2 hr. After work-up of the reaction mixture and equilibration of the 2,6-dimethylcyclohexanones with 10% hydrochloric acid, analysis of the products gave VII (35%), VIII (47%), IX (<10%), and X (13%).

C. Equilibrium Conditions with Methylation in 1,2-Dimethoxyethane.—Trityllithium was made by addition of 8.30 g. (0.034 mole) of triphenylmethane in 100 ml. of ether to lithium amide (from 0.236 g., 0.034 g.-atom, of lithium) in 75 ml. of liquid ammonia and 3.36 g. (0.030 mole) of VII in 25 ml. of ether was added dropwise with stirring over 30 min. When the last few drops of ketone were added, the disappearance of the red color of the trityllithium indicated that a slight excess of ketone to this base was present. After the liquid ammonia had been removed and 100 ml. of 1,2-dimethoxyethane added to replace it, ether was distilled from the reaction mixture until the temperature of the distillate reached 70°. After cooling to room temperature and the addition of 16.0 g. (0.12 mole) methyl iodide, the reaction mixture was refluxed for 2 hr. Work-up in the usual way yielded a mixture of ketones which contained VII (14%), VIII (13%), and IX (73%). No other methylation products were observed.

Acknowledgment.—The author is sincerely grateful to Professor Gilbert Stork for his advice and assistance throughout the course of the work.

The Reaction of Lithium Acetylide-Ethylenediamine with Ketones

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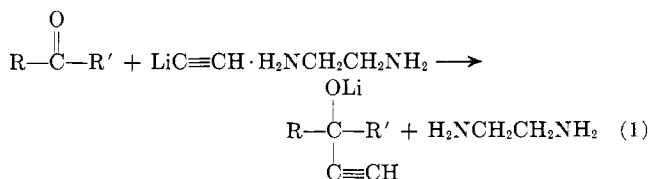
Received December 5, 1963

The reaction between lithium acetylide-ethylenediamine and a variety of ketones has been studied in several organic solvents under argon and acetylene atmospheres. High yields of ethynylcarbinols were obtained. A relationship between the yield of ethynylcarbinol and the dielectric constant of the solvent is discussed.

In a recent paper¹ we reported the preparation and some properties of lithium acetylide-ethylenediamine. This crystalline complex is stable up to about 45°, in contrast to uncomplexed lithium acetylide which is stable only in liquid ammonia at -33°. ²

This new reagent with its higher stability has a potential of being used over a wide range of temperatures in a variety of organic solvents and in standard equipment. In this paper, this new versatility is discussed, and the effect of some of the variables on the reaction with ketones to form ethynylcarbinols is shown.

Lithium acetylide-ethylenediamine was found to add readily across a ketonic linkage to produce the lithium salt of the corresponding ethynylcarbinol.



The yield obtained was found to vary widely, depending upon the reaction conditions and the solvent.

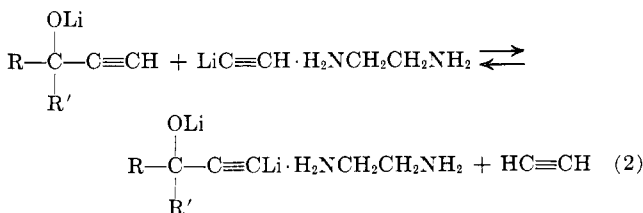
Table I summarizes the results obtained when stoichiometric quantities of lithium acetylide-ethylenediamine were allowed to react with the various ketones. Yields are based on starting materials added, and no correction is made for recovered ketone. Several runs were made with 10% excess acetylide where low yields were experienced with stoichiometric quantities. Yield was determined by analysis, not by isolation. Duplicate runs gave yields varying up to 2%.

If the yields given in Table I are plotted against the dielectric constant of the solvent, an interesting curve is obtained for each ketone. These curves can be grouped into several different types (see Fig. 1-4) and reflect two major side reactions.

In low dielectric solvents (such as benzene) there is usually a drop in yield. In most cases this loss is due mainly to base-catalyzed enolization. Evidence for this is the fact that after hydrolysis all of the starting ketone can be accounted for either as ethynylcarbinol or as unchanged ketone. Additional evidence is the relationship between the yields obtained in benzene and the base-catalyzed enolization constants determined by H. Shechter, *et al.*,³ and listed in Table II.

The two marked exceptions to this simplification are the diaromatic ketones benzophenone and 9-fluorenone. Although it is impossible for them to enolize, they have the most dramatic drop in yield in low dielectric solvents. In fact, 1,1,4,4-tetraphenyl-2-butyne-1,4-diol is the major product obtained from benzophenone in benzene. This anomaly will be discussed in more detail under metalation.

At the high end of the dielectric scale (and to a lesser extent over the entire range), the reduction in yield appears to be due to metalation of the resulting ethynylcarbinol. This product may react further with an-



(1) O. F. Beumel, Jr., and R. F. Harris, *J. Org. Chem.*, **28**, 2775 (1963).

(2) M. Corbellini and L. Turner, *Chim. Ind. (Milan)*, **42**, 251 (1950); *Chem. Abstr.*, **54**, 19,250 (1960).

(3) H. Shechter, M. J. Collins, R. Dessy, Y. Okuzumi, and A. Chen *J. Am. Chem. Soc.*, **84**, 2095 (1962).

TABLE I
YIELDS OF ETHYNYLCARBINOL FROM LITHIUM ACETYLIDE·ETHYLENEDIAMINE^a

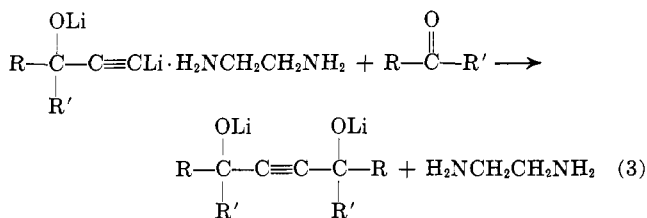
| | —Benzene ^b — | | Tetrahydrofuran-benzene ^c | | Tetrahydrofuran ^c | | N,N-Dimethylacetamide-benzene ^b | | N,N-Dimethylacetamide ^d | |
|--|--|-----|--|--------------------|--|-----|--|--------------------|--|-----|
| | C ₂ H ₂ ^e | Ar | C ₂ H ₂ ^e | Ar | C ₂ H ₂ ^e | Ar | C ₂ H ₂ ^e | Ar | C ₂ H ₂ ^e | Ar |
| Cyclopentanone | 76 | 65 | 88 89 ^f | 76 | 82 86 ^f | 72 | 81 | 68 | 74 | 16 |
| Cyclohexanone | 89 | 91 | 98 | 90 | 90 | 84 | 100 | 84 | 89 | 73 |
| Cycloheptanone | | 98 | | | 100 | 99 | | 97 | 98 | 85 |
| Acetone | 62 | 55 | 92 | 69 | 75 86 ^f | 74 | 99 | 78 | 75 | 50 |
| 2-Butanone | 89 | 76 | 99 | 81 | 98 | 83 | 100 | 96 | 87 | 61 |
| 3-Pentanone | 94 | 87 | 99 | 96 | 96 | 94 | 100 | 87 | 95 | 66 |
| 2-Octanone | 96 | 82 | 98 | 90 | 95 | 90 | | 100 | 90 | 69 |
| 3-Octanone | 97 | 91 | 100 | 98 | 97 | 94 | 100 | 92 | 92 | 63 |
| Diisopropyl ketone | | 100 | | 99 | | 100 | | | | 100 |
| 2-Cyclohexylcyclohexanone ^g | | 91 | | 92 | 100 | 91 | | | | |
| 2-Cyclohexylcyclohexanone | | 69 | | | 64 | | | | 79 | |
| Methyl vinyl ketone ^h | 27 | 20 | 75 | 61 | 86 98 ^f | 75 | 68 | 45 | 41 | 34 |
| Methyl vinyl ketone | | 13 | | | 53 | 43 | | | | |
| Isophorone ^g | 81 | 78 | 87 93 ^f | 86 | 58 | 46 | 32 | 11 | 0 | 0 |
| Isophorone | | 74 | | 73 | 41 | 44 | | 9 | 8 | 0 |
| Mesityl oxide | | 80 | | 93 | 97 | 99 | | 63 | 25 | 25 |
| Benzal acetone | | 99 | | 100 | 100 | 100 | | 100 | 93 | 79 |
| Dibenzal acetone | | 97 | | 97 | | 97 | | | | 95 |
| Acetophenone | 55 | 46 | 64 | 53 | 57 79 ^f | 57 | 75 80 ^f | 60 | 64 | 37 |
| Propiophenone | 81 | 73 | 88 | 84 | 80 98 ^f | 78 | 76 | 67 | 47 | 37 |
| Benzophenone | 47 | 46 | 50 | 62 | 62 | 58 | 81 | 71 | 92 96 ^f | 77 |
| 9-Fluorenone | | 33 | 40 | 42 56 ^f | 47 | 77 | 82 | 82 90 ^f | 76 | |
| 1-Indanone | 66 | 45 | 74 | 69 | 82 83 ^f | 70 | 76 | 41 | 63 | 39 |

^a Mixed solvents were 50:50 vol.%; yield was based on analysis; stoichiometric quantities, 0.25-hr. addition, and 1 M concentration were used unless otherwise specified. ^b Reaction temperature 35°, reaction time 1.75 hr. ^c Reaction temperature 35°, reaction time 2.75 hr. ^d Reaction temperature 25°, reaction time 1.75 hr. ^e The solvent was presaturated with acetylene and acetylene was bubbled through the mixture throughout the reaction. ^f A 10% excess of lithium acetylide·ethylenediamine was used. ^g Reaction temperature 45°, reaction time 6 hr. ^h Concentration 0.25 M, addition time 2.5 hr., reaction time 3 hr.

TABLE II
EFFECT OF BASE-CATALYZED ENOLIZATION ON YIELD

| Ketone | Base-catalyzed enolization constant ^a $k^{40^\circ} \times 10^7$ | Yield with LiC ₂ H·H ₂ NCH ₂ CH ₂ NH in benzene-acetylene |
|--------------------|---|---|
| Acetophenone | 2200 | 55 |
| Cyclopentanone | 680 | 76 |
| Propiophenone | 490 | 81 |
| Cyclohexanone | 100 | 89 |
| Cycloheptanone | 19 | 98 |
| Diisopropyl ketone | 0.6 | 100 |

other molecule of ketone to form an acetylenic glycol or the reaction may stop here depending on the ketone and the reaction conditions. In either case, a loss in yield of ethynylcarbinol occurs if equimolar quantities of acetylide and ketone are used.



Although nothing could be done about enolization, except to change solvents, metalation could be minimized or eliminated. The use of a solvent presaturated with acetylene is sufficient to increase the yield markedly. The use of an acetylene atmosphere in addition to saturating the solvent will sometimes give an additional increase. The use of acetylene is felt to reverse eq. 2.

Interestingly, with benzophenone and 9-fluorenone, not only were the corresponding acetylenic glycols

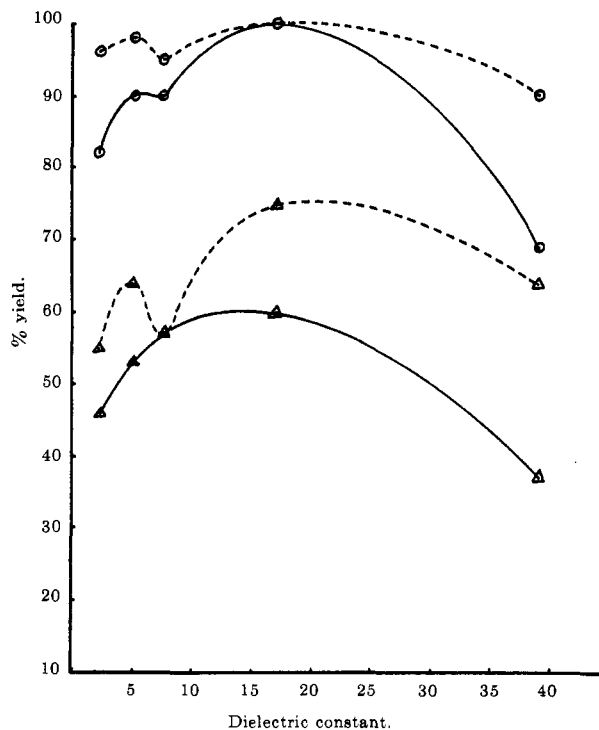


Fig. 1.—Yield of ethynylcarbinol vs. dielectric constant of the solvent: O, from 2-octanone; Δ, from acetophenone; -----, acetylene atmosphere; ———, argon atmosphere.

formed in all solvent but the formation was far greater at low dielectrics. It was possible to minimize this acetylenic glycol formation in high dielectric solvents through the use of acetylene, but this did not help in low dielectric solvents. Either a different mechanism

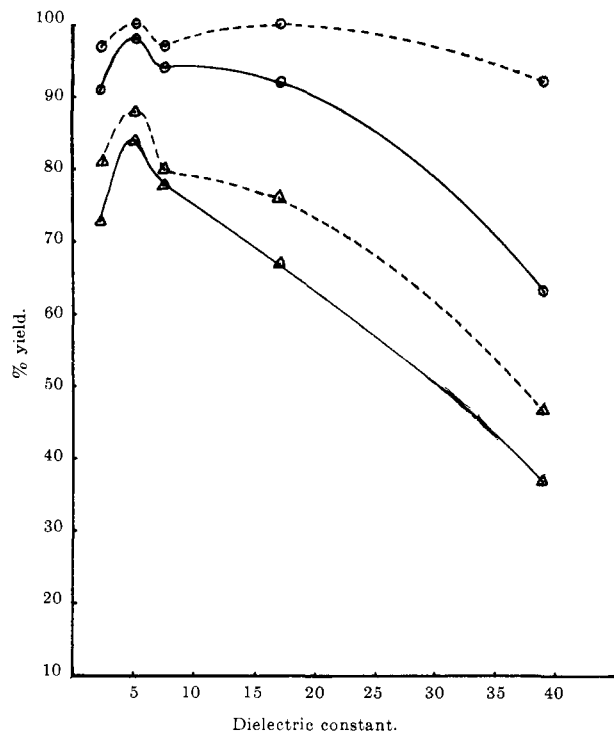


Fig. 2.—Yield of ethynylcarbinol *vs.* dielectric constant of the solvent: O, from 3-octanone; Δ, from propiophenone; -----, acetylene atmosphere; ———, argon atmosphere.

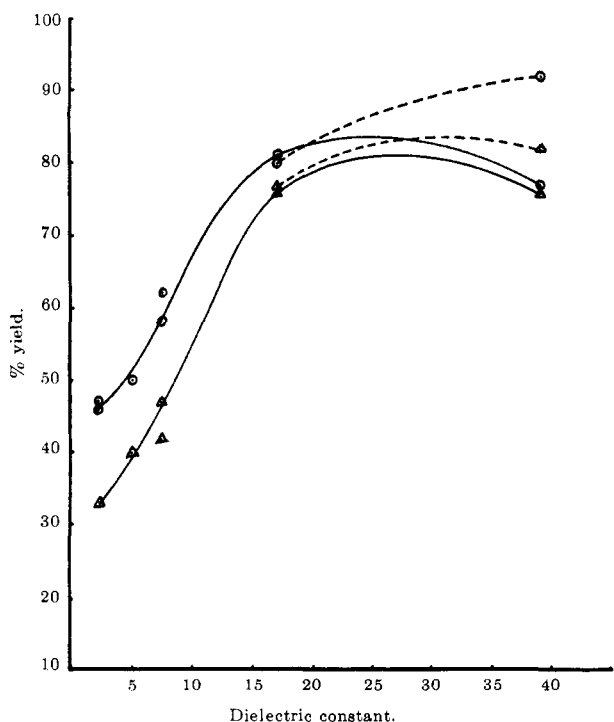


Fig. 3.—Yield of ethynylcarbinol *vs.* dielectric constant of the solvent: O, from benzophenone; Δ, from 9-fluorenone; -----, acetylene atmosphere; ———, argon atmosphere.

is responsible for the formation of these acetylenic glycols at low dielectrics or for some unknown reason acetylene fails to prevent metalation of the corresponding diaromatic ethynylcarbinols. Possibly the failure of excess acetylene to prevent metalation in the low dielectric solvents may be attributed to the low solubility of acetylene in these solvents.

The problem of steric hindrance was experienced only with 2-cyclohexylcyclohexanone, and forcing conditions (6 hr. at 45°) were necessary in order to obtain yields over 80%. It was not possible to use these conditions with *N,N*-dimethylacetamide as the solvent, since it reacts appreciably with the acetylide at this temperature.

It usually takes about an hour longer for the reaction between lithium acetylide-ethylenediamine and ketones to go to completion in tetrahydrofuran than in any other solvent. During this period, any side reaction has a greater opportunity to compete with the main reaction. This is apparently the reason why many of the ketones give a lower yield in tetrahydrofuran than would be predicted by a smooth yield *vs.* dielectric constant curve (Fig. 1 and 2).

Three of the ketones used in this study are subject to polymerization. When the standard conditions used to ethynylate the other ketones were used with methyl vinyl ketone, isophorone, and mesityl oxide, polymerization did occur to a considerable extent, especially in high dielectric solvents. It was found that with slow addition of the ketone, combined with greater dilution, it was possible to minimize polymerization. Lowering the reaction temperature lowered the yield.

Table I gives results using both sets of conditions for methyl vinyl ketone and isophorone. For mesityl oxide this change was felt unnecessary since excellent yields could be obtained in tetrahydrofuran using standard conditions.

Lithium acetylide-ethylenediamine appears to be an excellent reagent for the ethynylation of ketones. It offers high yields combined with the convenience of storage stability and simplicity of use. It should be possible, with the aid of Table I, to obtain good yields of ethynylcarbinol from most ketones.

Experimental

General.—The lithium acetylide-ethylenediamine used was all from the same lot. The analysis¹ was lithium acetylide-ethylenediamine, 92.3%; dilithium acetylide, 0.2%; *N*-lithio-ethylenediamine, 2.7%; lithium hydroxide, 0.6%; ethylenediamine, 2.8%; and 1.4% unknown.

All liquid ketones were distilled prior to use except for methyl vinyl ketone and 2-cyclohexylcyclohexanone.⁴ Solid ketones were used as received. Benzene was thiophene-free and dried over sodium wire. Tetrahydrofuran (refined) and *N,N*-dimethylacetamide were used as received. Acetylene (welding) was purified by passage through columns containing activated alumina.

Reaction of Lithium Acetylide-Ethylenediamine with Ketones.

—A 1-l., three-necked flask fitted with a dropping funnel, condenser, stirrer, and thermometer served as the reactor; a glass "T" above the condenser served as a means for argon cover and as an exit for escaping gas.

Lithium acetylide-ethylenediamine (40.1 g., 0.40 mole) was placed in the argon-flushed reactor, followed by 400 ml. of solvent. Stirring was started and the mixture was warmed to 35°. Ketone (0.40 mole) was added dropwise over a period of 15 min. while maintaining 35° by cooling. The mixture was stirred at room temperature for an additional 1.75 hr.

Water (100 ml.) was added slowly to hydrolyze the mixture. The contents were brought to gentle reflux and held for 1 hr. to remove any dissolved acetylene. After cooling to room temperature, the two layers were separated, weighed, and analyzed.

Solid ketones were dissolved in a minimum amount of solvent for the addition. This solvent was subtracted from the 400-ml. initial solvent charge.

(4) Obtained from Allied Chemical Co.

The procedure was the same for all solvents under argon with the following exceptions.

(1) In *N,N*-dimethylacetamide-benzene, 200 ml. of each solvent was used. (2) In tetrahydrofuran, 2.75 hr. was allowed for the reaction to go to completion instead of 1.75 hr. (3) In tetrahydrofuran-benzene, 200 ml. of each solvent was used and 2.75-hr. reaction time was allowed. (4) In *N,N*-dimethylacetamide, the reaction temperature was 25°.

Reactions under acetylene were carried out in the same manner as specified above for each solvent system except that the solvents were presaturated with acetylene and acetylene was bubbled through the solution throughout the reaction.

The following modifications were employed in a second set of runs for methyl vinyl ketone and isophorone: (1) 1600 ml. of solvent was used in a 2-l. reactor; (2) the ketone was added over a period of 2.5 hr.; and (3) the mixture was stirred at room temperature for an additional 3 hr.

For 2-cyclohexylcyclohexanone, the reaction temperature was raised to 45° and maintained for 6 hr. in all solvent systems except *N,N*-dimethylacetamide and benzene-*N,N*-dimethylacetamide.

With Benzophenone and 9-Fluorenone.—Benzophenone (0.327 mole) dissolved in benzene (120 ml.) was added to a slurry of lithium acetylide-ethylenediamine (0.327 mole) in benzene (207 ml.) at 35° over a period of 15 min. The resultant slurry was stirred at room temperature for 1.75 hr., hydrolyzed with water (100 ml.), refluxed for 1 hr., cooled to room temperature, and filtered.

Analysis of the filtrate indicated a 46% yield of 1-ethynyl-diphenylcarbinol. The white, crystalline solid was air-dried, giving m.p. 156–160°, 28.1 g. (44%). After recrystallization from methanol-water, it had m.p. 191–192°; lit.⁵ (for 1,1,4,4-tetra-phenyl-2-butyne-1,4-diol) m.p. 192°.

Anal. Calcd. for C₂₃H₂₂O₂: C, 86.12; H, 5.68. Found: C, 86.06; H, 5.82.

Similarly, using 9-fluorenone, 9,9'-ethynylenebis-9-fluorenone was obtained as an orange, crystalline solid, m.p. 236°, lit.⁶ m.p. 238°.

Anal. Calcd. for C₂₃H₁₈O₂: C, 87.02; H, 4.69. Found: C, 86.78; H, 4.63.

With 2-Cyclohexylcyclohexanone.—1-Ethynyl-2-cyclohexylcyclohexanol is a previously unreported compound, b.p. 115° (1 mm.).

Anal. Calcd. for C₁₄H₂₂O: C, 81.49; H, 10.75. Found: C, 81.73; H, 10.93.

With Isophorone.—1-Ethynyl-3,5,5-trimethyl-2-cyclohexenol is a previously unreported compound, b.p. 82° (3 mm.).

Anal. Calcd. for C₁₁H₁₆O: C, 80.44; H, 9.82. Found: C, 80.36; H, 9.87.

Determination of Dielectric Constants of Mixed Solvents.—Equipment consisted of a Q meter type 260-A from the Boonton Radio Corp., operating at 700 kc. with a 30-mmfd. capacitor detuned to 4.20 mmfd. The dielectric constants found were benzene, 2.31; benzene-tetrahydrofuran (50:50 vol. %), 4.98; tetrahydrofuran, 7.55; benzene-*N,N*-dimethylacetamide (50:50 vol. %), 16.90; and *N,N*-dimethylacetamide, 39.40.

Method of Analyses. A. Introduction.—The ethynyl alcohols were analyzed *in situ* by measuring the acetylenic hydrogen function.⁷ It was necessary to determine the solvent conditions and reaction time for each ethynyl alcohol.

Ketones were analyzed by the hydroxylamine hydrochloride method.⁸

B. Procedure for Ethynyl Alcohol Determination.—A weighed sample of solution to be analyzed was placed in a 400-ml. beaker containing 100 ml. of proper solvent mixture (Table III) and equipped with a pH meter and magnetic stirrer. The solution was neutralized with 0.1 *N* sulfuric acid (2 *N* sulfuric acid used if considerable basic material present) to pH 4.00. Silver nitrate solution, 10% by weight (10 ml. per 25-ml. titration), was added and the liberated acid was titrated to pH 4.00 with 0.1 *N* sodium hydroxide.

Care must be exercised in determining the final end point, since tailing is prevalent in many compounds (Table III). The electrode tips tend to gum over and must be cleaned before the

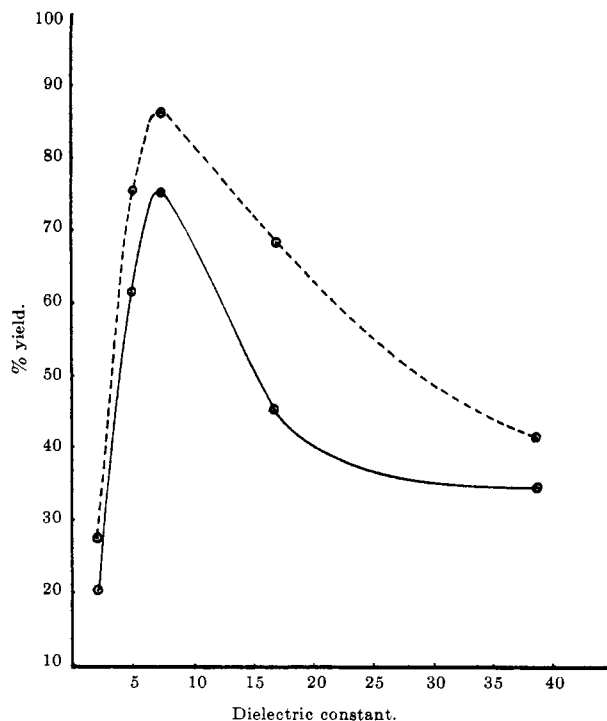


Fig. 4.—Yield of ethynylcarbinol vs. dielectric constant of the solvent: O, from methyl vinyl ketone; -----, acetylene atmosphere; —, argon atmosphere.

TABLE III

CONDITIONS USED FOR THE ANALYSIS OF ETHYNYLCARBINOLS

| Parent ketone | Volume of water, ml. | Volume of methanol, ml. | Time, ^a min. |
|---------------------------|----------------------|-------------------------|-------------------------|
| Cyclopentanone | 50 | 50 | 20 |
| Cyclohexanone | 100 | 0 | 10 |
| Cycloheptanone | 50 | 50 | 20 |
| Acetone | 50 | 50 | 45 |
| 2-Butanone | 50 | 50 | 45 |
| 3-Pentanone | 50 | 50 | 30 |
| 2-Octanone | 40 | 50 | 30 |
| 3-Octanone | 50 | 50 | 30 |
| Diisopropyl ketone | 25 | 75 | 10 |
| Methyl vinyl ketone | 50 | 50 | 150 |
| Isophorone | 100 | 0 | 150 |
| Mesityl oxide | 50 | 50 | 60 |
| Benzal acetone | 25 | 75 | 30 |
| Dibenzal acetone | 25 | 75 | 30 |
| Acetophenone | 25 | 75 | 15 |
| Propiophenone | 50 | 50 | 20 |
| Benzophenone | 50 | 50 | 20 |
| 9-Fluorenone | 25 | 75 | 45 |
| 1-Indanone | 25 | 75 | 45 |
| 2-Cyclohexylcyclohexanone | 25 | 75 | 30 |

^a Total time to reach end point due to tailing.

final end point is taken. The per cent yield was determined with the following equation.

$$\% \text{ yield} = \frac{\text{wt. of layer} \times \text{ml. of NaOH} \times N \text{ of NaOH}}{\text{wt. of sample} \times \text{moles of ketone} \times 10}$$

Blanks were run under the various solvent conditions using 1-ethynylcyclohexanol as standard and were found to be negligible. A blank was also run with lithium acetylide-ethylenediamine and *N,N*-dimethylacetamide at 35° for 2.5 hr. After working the mixture in the usual manner, no acetylenic hydrogen could be detected.

Table IV is a summary of the method applied to several pure ethynylcarbinols.

(5) A. Babyan, *Izv. Akad. Nauk Arm. SSR*, **5/6** (10/11), 121 (1941).

(6) E. Bergmann, H. Hoffmann, and D. Winter, *Ber.*, **66B**, 46 (1933).

(7) T. L. Jacobs, *Org. Reactions*, **5**, 45 (1960).

(8) J. Mitchell, Jr., "Organic Analysis," Vol. 1, Interscience Publishers, Inc., New York, N. Y., 1953, p. 243.

TABLE IV
ANALYTICAL RESULTS FROM PURE ETHYNYLCARBINOLS

| Parent ketone | B.p., °C. | M.p., °C. | Assay, % |
|---------------------------|-------------------|-----------|------------|
| Cyclohexanone | 178 | 32-33 | 99.5 ± 0.1 |
| Diisopropyl ketone | 163-165 | ... | 98.7 ± 0.2 |
| Acetophenone | 85 (3 mm.) | ... | 99.2 ± 0.1 |
| 2-Butanone | 119-121 | ... | 99.5 ± 0.1 |
| 2-Cyclohexylcyclohexanone | 115 (1 mm.) | ... | 98.3 ± 0.2 |
| Methyl vinyl ketone | 50-51 (54 mm.) | ... | 99.9 ± 0.1 |
| 2-Octanone | 72-73 (4 mm.) | ... | 99.9 ± 0.1 |
| 1-Indanone | ... | 70.1 | 99.9 ± 0.1 |
| 9-Fluorenone | ... | 107 | 98.4 ± 0.1 |

C. Procedure for Ketone Determinations.—A weighed sample of solution to be analyzed was placed in a 400-ml. beaker containing 200 ml. of water and equipped with a pH meter and magnetic stirrer. The solution was neutralized to pH 4.00 with 0.1 N hydrochloric acid and 0.8 N hydroxylamine hydrochloride was added (10 ml. per 40-ml. titration). The liberated hydrochloric acid was back-titrated with 0.1 N sodium hydroxide.

This method was applied to cyclohexanone, acetone, cyclopentanone, 2-butanone, 3-pentanone, and 2-octanone.

Acknowledgment.—We wish to thank Dr. Ralph G. Verdieck for determining the dielectric constants and John G. Maroski for his assistance in carrying out many of the analyses.

Fluoro Ketones. II. Reactions with Trialkyl Phosphites

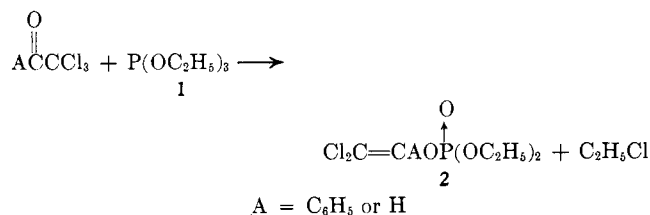
D. W. WILEY AND H. E. SIMMONS

Contribution No. 924 from the Central Research Department, Experimental Station,
E. I. du Pont de Nemours and Company, Wilmington 98, Delaware

Received December 11, 1963

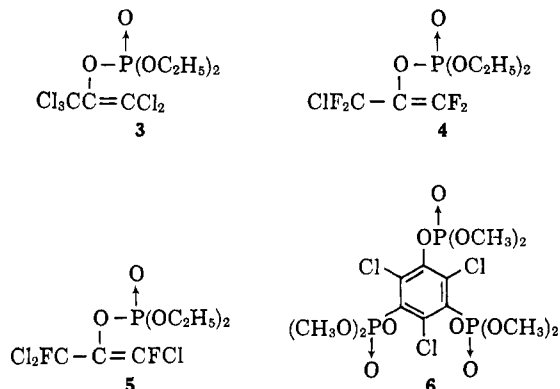
sym-Dichlorotetrafluoroacetone and *sym*-difluorotetrachloroacetone have been found to undergo the Perkow reaction with trialkyl phosphites to give the corresponding dialkyl perhaloisopropenyl phosphate and alkyl chloride. Perfluoro ketones undergo a new reaction with trialkyl phosphites to yield alkyl enol ethers of the ketones and dialkyl phosphorofluoridate.

The reaction of α -halogenated aldehydes, ketones, esters, and amides with phosphites containing at least one alkyl ester group yields vinyl phosphates.¹⁻³ For example, the reaction of chloral^{2,3} or trichloroacetophenone² with triethyl phosphite (1) yields the dichlorovinyl esters 2 and ethyl chloride.



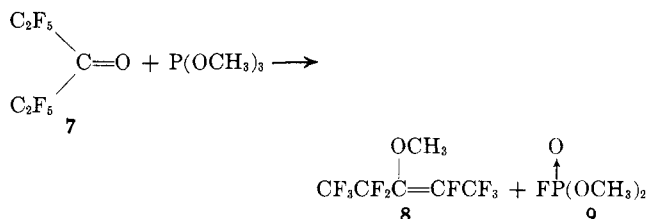
This paper describes some examples of reaction of alkyl phosphites with perhalogenated ketones and the abnormal reaction products from perfluorinated ketones.

When hexachloro-, *sym*-dichlorotetrafluoro-, or *sym*-difluorotetrachloroacetone react with triethyl phosphite,



phite, the corresponding diethyl perhaloisopropenyl phosphates (3, 4, and 5) are formed along with ethyl chloride. Interestingly, no ethyl fluoride was formed in the latter two reactions. With 3 moles of trimethylphosphite, hexachloro-1,3,5-cyclohexanetrione⁴ gave the aromaticized product 6. The isopropenyl phosphates are sensitive to water, react with bromine, and appear to undergo S_N2' reactions with anions such as iodide and cyanide.

Surprisingly, the perfluorinated ketones were found to react exothermically at 0° with trialkyl phosphites with no alkyl fluoride evolution to give the alkyl enol ether of the starting ketone and a dialkyl phosphorofluoridate. For example, perfluoro-3-pentanone (7) reacted with trimethyl phosphite to give 3-methoxyperfluoro-2-pentene (8) and dimethyl phosphorofluoridate (9). The enol ether 8 was obtained as a 1:1 mixture of *cis* and *trans* isomers, separable by gas chro-



matography. The proof of structure requires comment only in that the isomer with methoxy and fluorine groups *trans* had no infrared absorption in the region associated with C=C stretching frequency in marked contrast to the *cis* isomer (Fig. 1). Both isomers showed C=C Raman absorptions. The structural assignment is based on the interpretation of the I¹⁹ n.m.r. spectra (Fig. 2) given in Experimental.

The reaction appeared to be quite general for perfluoro ketones giving enol ethers with perfluoro-4-hep-

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(2) M. S. Kharasch and I. S. Bengelsdorf, *J. Org. Chem.*, **20**, 1356 (1955).

(3) W. Perkow, *Ber.*, **87**, 755 (1954).

(4) T. Zincke and O. Kegel, *ibid.*, **22**, 1467 (1889).