Wadsworth W S, Jr. & Emmons W D. The utility of phosphonate carbanions in olefin synthesis. *J. Amer. Chem. Soc.* **83**:1733-8, 1961.
[Rohm and Haas Co., Philadelphia, PA]

The reaction of phosphonate carbanions containing electron-withdrawing groups with aldehydes or ketones in an aprotic solvent constitutes a useful olefin synthesis. These reagents are, in general, more reactive than the analogous 'Wittig' reagents and have a number of special features which enhance their utility. [The *SCI*® indicates that this paper has been cited in over 510 publications since 1961.]

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"*This paper represented a cumulation of* work carried out for a number of years prior to publication. The research was performed while I was employed as a chemist at Rohm and Haas Co. William Emmons, the coauthor, was director of the laboratory and my immediate superior.

"Our objective was not to discover a new olefin synthesis but to prepare for study a series of vinyl phosphonates which could possibly act as monomers. It was hoped that copolymers containing phosphorus would give flame retardance to articles fabricated from such polymers. We began by attempting to prepare diethyl α-cyano-vinylphosphonate. The base catalyzed condensation of diethyl cyanomethylphosphonate with formaldehyde in an aprotic solvent gave upon distillation a small amount of liquid which immediately polymerized to a clear *self-extinguishing, nearly nonflammable* plastic. The distillation was particularly annoying for polymerization would occur even in the cooling condenser. The polymer being insoluble was difficult to remove which required the ultimate disposal of quantities of ground glass equipment.

"After many attempts to stabilize the initial monomer (we never were successful), it was decided to carry out the condensation under conditions which would give a less reactive product. Consequently, benzaldehyde was substituted for formaldehyde and since the former is insoluble in water, an aprotic solvent was necessary. It was somewhat of a surprise to find that, during the course of the reaction, a precipitate (sodium diethyl phosphate) formed which was easily removed by filtration. Upon removal of solvent a high yield of phenyl acrylonitrile was obtained. From this it was simple to deduce that a 'Wittig' type reaction had taken place. The betaine formed in the aprotic solvent collapsed to a dialkyl phosphate salt and olefin. The reaction was exploited to prepare numerous classes of alkenes. In addition, cyclopropanes were prepared by the addition of epoxides to phosphonate carbanions.

"Our procedure as finally developed has a *number of advantages over the 'Wittig' reaction.* Phosphonates, prepared primarily via the Arbuzov reaction, are much simpler to synthesize than triarylphosphoranes; phosphonate anions are more reactive toward aldehydes and ketones than are the phosphoranes; reactions are run under much milder conditions which result in fewer undesirable side products. Perhaps the biggest advantage, however, is the ease of work-up of reaction mixtures.

"Near the completion of our work, Horner and co-workers, University of Mainz, published a paper which described the formation of olefins from phosphine oxides and aldehydes,[1] a much less convenient procedure than that which we described. In their paper they reported the condensation of diethyl benzylphosphonate with benzaldehyde to give stilbene. Their conditions were unnecessarily *harsh and the reaction was not* expanded or exploited. Controversy, of course, arose as to who first discovered the reaction, a controversy which has been solved by calling the reaction by a number of names: the Wadsworth-Emmons reaction, the Horner modification, and even a combination of the proper names.

"A review article has been written which adequately describes the many uses of the reaction and which gives a multitude of examples."[2]

1. **Horner L, Hoffmann H, Wippell H G & Klahre G.** Phosphinoxyde als Olefinierungsreagenzien. *Chem. Ber.* **92**:2499-505, 1959.
[The *SCI* indicates that this paper has been cited in over 110 publications since 1961.]
2. **Wadsworth W S, Jr.** Synthetic applications of phosphoryl-stabilized anions. *Organic Reactions* **25**:73-253, 1977.