We thank Professor Working for calling this to our attention.

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# The Action of Sodium Phenylacetylene on α,β-Unsaturated Esters

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It has been reported[1] that esters of formic acid react with sodium phenylacetylene producing an unsaturated aldehyde. Nef,[2] however, was unable to obtain even a trace of the corresponding ketone from ethyl acetate or benzoate, although the acid chloride and anhydride gave positive results. Because of these contradictory results and because little is known concerning the activity of acetylenic salts with unsaturated systems, an investigation was made with several unsaturated esters.

It was found that phenylcinnamylacetylene is obtained readily by the interaction of sodium phenylacetylene and ethyl cinnamate the result probably of 1,2-addition followed by the elimination of sodium alcoholate. This ketone, containing as it does a double and triple bond conjugated with a carbonyl group, has interesting possibilities as a vehicle for testing the selective reactivity of reagents for such conjugate systems. Actually the accumulation of unsaturated groups appears to hinder rather than promote the normal reactivity of the carbonyl group. Attempts to force a reaction result in the formation of nontractable tars, while more powerful reagents such as the Grignard cause the ketone to act as an enol.

## Experimental

**Cinnamylphenylacetylene.**—To 0.2 gram mole of sodium phenylacetylene suspended in dry ether and connected to a reflux condenser was added the equivalent of ethyl or methyl cinnamate. Heat sufficient to cause gentle boiling was evidenced for a few minutes. A slow but steady evolution of hydrogen took place even after long standing, due to secondary reactions. The deeply colored mixture was allowed to evaporate in a stream of air after addition to cracked ice containing a slight excess of acetic acid. The resulting oil quickly became crystalline if seeded: yield, after washing with a small volume of cold alcohol, 21 g. It separated from benzene–petroleum ether mixtures in the form of small lustrous needles melting at 140–141°.

*Anal.* Calcd. for $C_{17}H_{12}O$: C, 88.0; H, 5.1. Found: C, 87.9; H, 5.3.

It responded to the usual tests for unsaturation, but the addition products, with bromine for example, were obtained only as intractable mixtures. The original substance was sensitive to acids and even dilute acetic acid caused tar formation on long standing at room temperature. A purple color formed when a trace of the ketone was dissolved in cold sulfuric acid, subsequently becoming greenish-fluorescent in appearance. While more stable toward alkaline reagents, hot solutions eventually caused resinification. Traces of phenylacetylene and benzaldehyde were detected. No reactions were observed with hydroxylamine or hydrazine even after long heating. The use of higher temperatures with sealed tubes produced tars. A crystalline product quickly formed with both methyl- and phenylmagnesium halide, but on decomposition with dilute acid the original ketone was recovered. It liberated hydrogen on contact with sodium and displaced sodium from sodium phenylacetylene, thus explaining the secondary reactions observed in the original preparation. Benzoic acid and benzaldehyde were identified among the oxidation products of the ketone with permanganate. Ethyl crotonate reacted even more vigorously with sodium phenylacetylene, but the product was obtained only as a thick oil. Benzoyl methyl acrylate yielded an amorphous powder that was not further examined.

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[1] Moureu and Delage, *Compt. rend.*, **133**, 105 (1901).

[2] *Ann.*, **308**, 279 (1899).