Reactions of Sodium Diethyl Phosphite with Some Aryl Halides

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Under photostimulation, aryl halides react with diethyl phosphite ion to form arylphosphonate esters:

$$\bigcirc -I + (EtO)_2PO^{-} \xrightarrow{h\nu} \bigcirc -P^{\circ}_{OEt} + I^{-}$$

These and related reactions occur in excellent yield, and are useful for synthesis. They are believed to occur by the radical chain,  $S_{RN}$ l mechanism. Studies of the behavior of dihalobenzenes have furnished a remarkable set of observations that are intelligible in terms of the postulated mechanism. o-Haloiodobenzenes react under photostimulation in the usual  $S_{RN}$ l fashion, but they also react in the dark by an ionic mechanism that itself has some interesting features.