Figure 1477 continued . . .

In 1941, an organic chemist named Morris Kharasch reported that adding 1 mole percent of copper to a Grignard reagent caused the formation of the 1,4-addition product (Figure 1478).

By 1952, Henry Gilman had identified an organocopper reagent whose properties were distinct from either organolithium or Grignard reagents. The Gilman reagent, as it is sometimes called, is an organometallic reagent known as a cuprate (Figure 1479). From earlier work, it was well known that when traditional organometallic reagents were combined with cuprous iodide (Cul), a 1:1 reaction occurs to give an organocopper (RCu) compound. These RCu compounds are often highly colored and quite insoluble, and they give reactions that are comparable to the other organometallic reagents. In the 1950s, however, Gilman reported that when a second equivalent of the original organometallic reagent is added, the colored solid dissolves and the solution goes colorless. The cuprate reagent in solution is an ionic compound with the formula R<sub>2</sub>CuLi. Gilman reported that these reagents not only gave 1,4-addition products with  $\alpha,\beta$ -unsaturated carbonyl compounds, by they could also give the product from substitution reactions.

## Figure 1479

## Formation and reaction of lithium dialkylcuprates (Gilman, 1952).