Reaction of Diphenylmethyl-lithium with 3,3-Dichloro-1,2-diphenylcyclopropene to give Tetraphenylbutenyne[1]

By G. MELLONI and J. CIABATTONI*

(*Department of Chemistry, Brown University, Providence, Rhode Island* 02912)

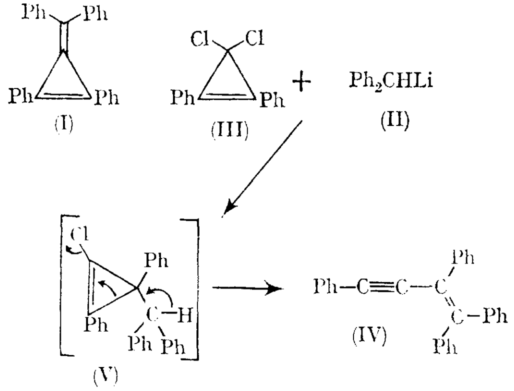
OUR interest in synthetic approaches to tetraphenyltriafulvene (I)[2] prompted our investigation of the reaction of diphenylmethyl-lithium (II) with 3,3-dichloro-1,2-diphenylcyclopropene (III).[3] In view of Bergmann and Agranat's[4] successful synthesis of hexaphenyltriapentafulvalene by the reaction of tetraphenylcyclopentadienyl-lithium with (III) this pathway seemed suitable. We report the anomalous formation of an isomer of hydrocarbon (I) derived from unexpected attack of (II) on the double bond of (III).

Reaction of (II) with (III) (*ca.* 1 : 1, inverse addition) in tetrahydrofuran at $-70°$ under nitrogen afforded, after chromatography on alumina (benzene : hexane 1 : 10), a white crystalline hydrocarbon (53%), m.p. 135—136° (needles from 95% ethanol), identified as tetraphenylbutenyne (IV) on the basis of its microanalysis and the following spectral data: mass spectrum *m/e* 356; ν(KBr) 3050m, 1595m, 1570w, 1480m, 1440m; λ_{max} (C_6H_{12}); 337 (log ϵ 4·29), 252 (4·40), 239sh mμ (4·33); λ_{min} (C_6H_{12}) 2·95(3·93); n.m.r. (CCl_4) δ 6·9—7·7 (complex multiplet).

Conclusive structural evidence was provided by an unambiguous synthesis of (IV) in 43% yield by the reaction of phenylethynylmagnesium bromide with $\alpha\alpha$-diphenylacetophenone[5] in ether, followed by hydrolysis and finally dehydration of the intermediate acetylenic alcohol with refluxing 20% aqueous sulphuric acid.

The proposed mechanism involves attack of (II) on the carbon–carbon double bond of (III) with expulsion of chloride ion to give the nonisolable chlorocyclopropene intermediate (V). Subsequent spontaneous dehydrochlorination with concomitant rupture of the cyclopropene nucleus affords (IV).

The initial attack of the lithium reagent on the double bond of (III) is in contrast to previous work in which nucleophilic substitution at carbon-bearing chlorine was found.[4,6] The dehydrohalogenation has analogy in the work of Shields, Gardner, and their co-workers[7] who observed the formation of enyne products from the reaction of *gem*-dichlorocyclopropanes with potassium t-butoxide in dimethyl sulphoxide.



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