Base-catalysed Isomerization of Triphenylmethyl Dimer

By ROBERT D. GUTHRIE* and G. R. WEISMAN

(*Department of Chemistry, University of Kentucky, Lexington, Kentucky* 40506)

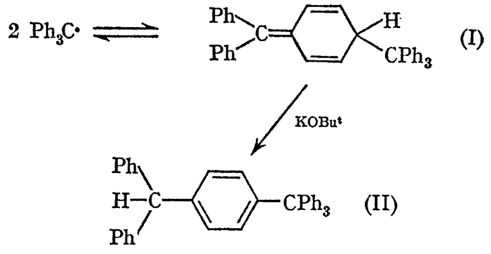
Summary The dimer of the triphenylmethyl radical is unambiguously shown to be 1-diphenylmethylene-4-tritylcyclohexa-2,5-diene.

THE recent suggestion[1] that the dimer of triphenylmethyl radical is not hexaphenylethane but 1-diphenylmethylene-4-tritylcyclohexa-2,5-diene (I) prompts us to report a reaction which serves as an unambiguous demonstration of the presence of (I).

When a solution of triphenylmethyl radical in benzene[2] was treated with an equal volume of 0·5 N-potassium t-butoxide in t-butyl alcohol at room temperature for 24 hr., a precipitate was formed which proved to be αααα′α′-pentaphenylxylene[3] (II) (71% yield after two recrystallizations). The supernatant liquid gave no precipitate when treated with oxygen. By comparison, the same experiment substituting t-butyl alcohol without potassium t-butoxide gave no precipitate in the same reaction time and gave ditrityl peroxide on subsequent treatment with oxygen (63% yield). These observations are explicable in terms of dimerization of triphenylmethyl radical to form (I) followed by base-catalysed isomerization to (II) (see Scheme).

Previous preparations of (II) have involved treatment of solutions of triphenylmethyl radical with acid,[4] a reaction which probably proceeds through protonation of (I). Alternative mechanisms for the acid-catalysed reaction are possible and its value as a demonstration of the presence of (I) has apparently not been appreciated. Observation of a base-catalysed reaction requires the intermediacy of (I).

In support of our mechanistic assignment, we have run the reaction using Me$_3$COD and observed 52% of one atom of D in (II)† Cram has observed 50% intramolecularity in a nearly identical base-catalysed 1,5-hydrogen migration in Me$_3$COD.[5]



This work has no direct bearing on the question of the existence of hexaphenylethane and gives no indication of the concentration of (I) present. It nevertheless supports the arguments of Lankamp, Nauta, and MacLean.[1]

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† Deuterium analysis by mass spectrometry.

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[4] M. Gomberg, *Ber.*, 1903, **36**, 376.

[5] D. J. Cram, R. Willey, H. P. Fisher, and D. A. Scott, *J. Amer. Chem. Soc.*, 1964, **86**, 5370.