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2,2,3,3-TETRAPHENYLBUTANE: A TRUE HEAD-TO-HEAD "ETHANE" DIMER

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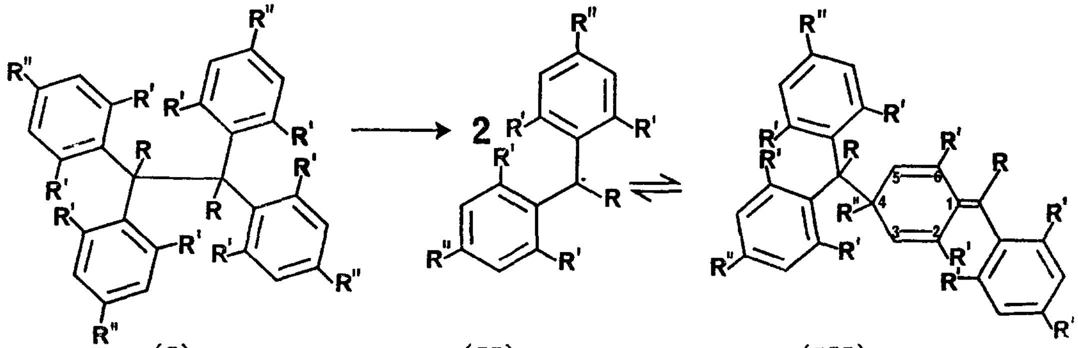
The intriguing question of the structure of substituted ethanes has received considerable attention for many years, more particularly since 1968 when Nauta and co-workers[1] verified the methylene-cyclohexadiene structure for hexaphenylethane. This subject has been reviewed[2] recently and "The Hexaphenylethane Riddle" explored in a historical context.

Dialkylarylmethyl radicals are known[3] to dimerise at 5-10° to give an ethane as the major product. The minor products include the methylene-cyclohexadiene form and at elevated temperature this is converted to the more stable ethane dimer. By contrast, diaryl- and triaryl-methyl radicals dimerise to give methylene-cyclohexadiene compounds (III). However there are two examples of the unequivocal synthesis[1] of tetraarylethanes (I). These are tetra(2,6-dimethylphenyl)ethane [R and R''=H,R'=CH_3] and tetra(2,4,6-trimethylphenyl)ethane [R=H,R' and R''=CH_3]. Both these compounds undergo dissociation in a high-boiling solvent to give the corresponding diarylmethyl radicals which then recombine to the more favoured methylene-cyclohexadiene form (III).



(I) (II) (III)

It has recently been shown by ^{1}H NMR[4] and ^{13}C NMR[5] spectroscopy that 9-phenylfluorenyl radicals associate to give the true ethane dimer, 9,9'-diphenyl-9,9'-bifluorenyl. I now report the first example of the association of diphenylmethyl-type radicals yielding a true ethane dimer.

2,2,3,3-Tetraphenylbutane was prepared (by reaction of lithium metal with 1,1-diphenylethyl chloride[6]) to provide a convenient thermal source of tertiary carbon radicals. It was shown conclusively to exist in the ethane form by a ^{1}H NMR investigation. The spectrum is composed of a single absorption due to six methyl protons at 2.02ppm and a multiplet absorption due to twenty aromatic protons at 6.85-7.25ppm and is consistent only with the ethane structure (I) [$R=CH_3$,R' and R"=H]. There is no evidence for the methylene-cyclohexadiene form and, despite a number of attempts, it has not proved possible to synthesize this compound.

The UV spectrum of 2,2,3,3-tetraphenylbutane exhibits a broad absorption with λ_{max} = 265mu and log ε = 3.06 in cyclohexane. This is in agreement with the findings of Nauta[1] for true symmetrical ethanes, and is in contrast to the extinction coefficients observed for methylene-cyclohexadiene structures.[1,7,8]

It is perhaps surprising that the relatively simple 1,1-diphenylethyl radical (II) {$R=CH_3$,R' and R"=H], with no aromatic substituents, dimerises to give the ethane. This is in direct contrast to the behaviour of triaryl, and other diarylmethyl radicals for example triphenylmethyl[1] and 2- and 4-substituted diphenylmethyl radicals[1], all of which form dimers of the methylene-cyclohexadiene type.

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