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A NEW INTERPRETATION OF THE MONOMER-DIMER EQUILIBRIUM OF TRIPHENYLMETHYL- AND ALKYLSUBSTITUTED-DIPHENYL METHYL-RADICALS IN SOLUTION

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Introduction

The discussions in the beginning of this century about the triphenylmethyl radical discovered by Gomberg (1) lead ultimately to the supposition that dimerisation of this radical leads to hexaphenylethane, a conviction which has gone unchallenged by later investigators: Schlenk (2), Marvel (3), Ziegler (4). An analogous dimerisation, leading to (alkylsubstituted)tetraphenylethanes was accepted by Coops (5), Nauta (5), Theilacker (6) and Fleurke (7) fortheir (alkylsubstituted) diarylmethyl radicals. However in several instances results were obtained that were hard to explain in this way such as:

a. the prohibited association of the tri(4-t.butylphenyl)methyl radical (Selwood (8)) and of the di(2,5-t.butylphenyl)methyl radical (Theilacker (6^c)).

b. the influence of para alkyl substituents in the di(2,6-dimethylphenyl)-methyl radical: introduction of one para group being without effect, whereas two para groups cause almost complete inhibition of dimerisation (9).

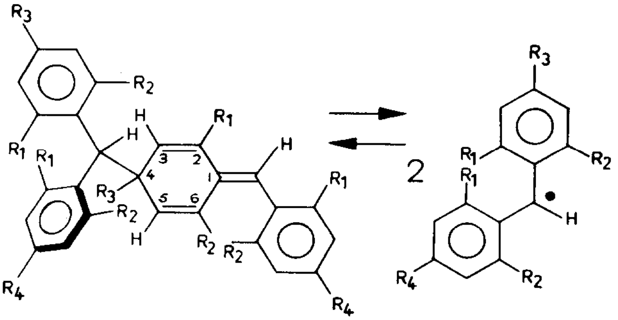
From investigations to be described in this and subsequent publications it must be concluded that the supposed ethanes, so far described, comprise two types of dimerisation products.

Those ethanes which do not split into radicals or do so only with great difficulty (for instance, di-, (unsubstituted) tetra- and pentaphenylethane and also those tetraphenylethanes carrying a moderate number of ortho alkylgroups (see (7)) are to be regarded as true ethanes.

The dimers, however, which are in equilibrium with their free radicals in solution are no ethanes as appears from UV and NMR investigations, but molecules in which one radical is attached, by means of its central carbonatom, to a para carbon atom in one of the phenyl nuclei of the second radical. These dimers therefore have a methylene-cyclohexadiene structure.

New structures

According to this concept for the "tetraphenylethanes" I-IV, which dissociate in solution, the equilibrium must be represented as follows:



compound no.	R_1	R_2	R_3	R_4	m.p. °C
I(5,7)	methyl	methyl	H	H	120
II(5,9)	methyl	methyl	H	methyl	115
III(9)	methyl	methyl	methyl	methyl	137
IV(6^b)	t.butyl	H	H	H	-

Physical properties of the dimers I-IV

It should be noted that all four dimers have a low melting point; also, the dimers I, II and IV dissociate in solution to about the same degree. When brought in solution III dissociates completely in dimesitylmethyl radicals; it can only be prepared from dimesityl carbinol with the use of V^{2+} or Cr^{2+} in aceton sulfuric acid at low temperature (9).

The methylene-cyclohexadiene structure of the above mentioned dimers is in agreement with their UV and NMR spectra: a strong absorption in the UV in the range near 300 mμ and the appearance of aliphatic and olefinic protons in the NMR spectra.

Dimer I

UV: broad absorption with λmax = 273 mμ in a KBr pellet and λmax = 270 mμ in cyclohexane; the radical concentration is too low to interfere and the extinction can readily be measured: log ε mol = 4.46.
These values are in line with the data of the unsubstituted methylene-cyclohexadiene (Plieninger (10)) and 4-methylene-1,1,2,3,5,6-hexamethyl-2,5-cyclohexadiene (von Doering (11)).

NMR*: phenylprotons at 6,8-6,9 ppm; olefinic proton of the 1-methylene group 6,3 ppm; olefinic protons at the 3 and 5 position at 5,4-5,5 ppm; a signal of the aliphatic proton at the 4 position almost at the same value as that of the tertiary proton of the diarylmethylgroup at 4,2-4,4 ppm; protons of the olefinic methylgroup at the 2-position at 1,95 ppm and the absorption of the other group at the 6-position shifted by the neighboring phenylgroup to higher field at 1,2 ppm.

True sym. tetraarylethanes

The question why these remarkable dimers arise from the radicals in solution instead of the expected ethanes is under investigation. For the sake of comparison the synthesis of the corresponding true ethanes seemed to be indicated. So far, sym-tetra(2,6-dimethylphenyl)ethane (E I)** and sym-tetra-(2,4,6-trimethylphenyl)ethane (E III) were synthesized.

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*Varian A-60, solvent: CCl_4, temperature: 36°C, TMS as internal standard, chemical shifts are reported as δ-values.

**Numbers have been given in analogy to those of the none-ethane dimers with the E of ethane added.

Synthesis and physical properties of the true ethanes

Preparation by means of the well-known process: diarylchloromethane with molecular silver is impossible. However, reaction of the diarylcarbinols with excess V^{2+} or Cr^{2+} in acetone-HCl solution at roomtemperature affords the ethanes in 10 - 20% yield (9); metal-organic complexes seem to play a dominating part here. In contrast with the dimers I and III the ethanes E I and E III show high melting points (227 - 228°C and 230 - 231°C respectively). The true ethanes dissociate only with difficulty into radicals.

If a solution of E I in a high boiling solvent e.g. decylbenzene, is heated at 220 - 240°C for a few seconds and than cooled quickly to roomtemperature it yields the well known radical-dimer I equilibrium, whereas from E III under these circumstances the unassociated dimesitylmethyl radical is obtained since in solution the concentration of dimer III is zero.

The last result is, to our opinion, in contrast with the properties of the supposed tetramesitylethane of Golstein (12).

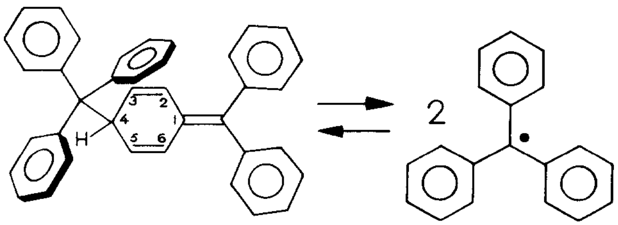
UV: E I: λmax = 270 mμ, log ε mol = 2.96 in cyclohexane

E III: λmax = 274 mμ, log ε mol = 3.06 in cyclohexane

NMR: A single absorption of the two protons at the central carbon atoms at 5 ppm; many absorptions of the protons of the aromatic methylgroups between 1.75 and 2.20 ppm, owing to hindered rotation of the phenyl rings (9).

Hexaphenylethane of Gomberg

In accordance with the above concept for the dimerisation of diarylmethyl-radicals the equilibrium: hexaphenylethane ⇄ 2 triphenylmethyl radicals, should be represented as:



In this equilibrium the dimer has the 1-diphenylmethylene-4-trityl-2.5-cyclohexadiene structure, advocated temporarily by Jacobson and Gomberg sixty years ago, but rejected later on (13).

Preliminary investigations indicate that the dimer prepared from triphenylchloromethane and molecular silver in tetrachloromethane has indeed the suggested structure.

UV: broad absorption with λmax = 315 mμ, measured in a KBr pellet; in solution the absorption of the triphenylmethyl radical interferes but the maximum of the dimer absorption can still be measured: λmax = 313 mμ.

NMR: signals of the protons of the phenylgroups at 6,8 - 7,4 ppm; a quartet of the olefinic protons at the 2,3,5 and 6 positions between 5,8 and 6,4 ppm and a signal of the aliphatic proton at the 4 position at 5 ppm.

The implications of these findings are further investigated in several directions a.o. in an effort to synthesize a true hexaphenylethane.

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