Slow Rotation in Tetra-arylmethanes

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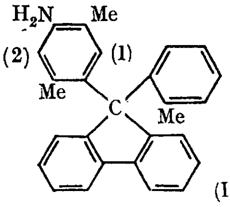
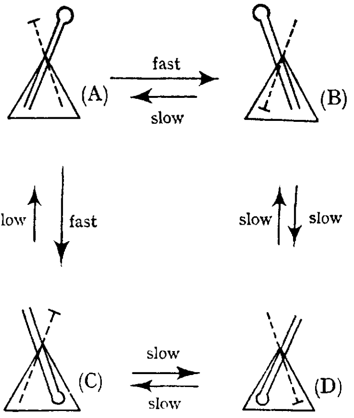
ADAMS AND CAMPBELL[1] suggested that tetra-arylmethanes containing the fluorene nucleus might be resolvable because of slow rotation around the bonds to the central carbon atom. However, they were unable to resolve the compounds that they prepared, which included as the most hindered example, compound (I).



(I)

We prepared the compounds according to their directions, and obtained proton magnetic resonance spectra with a Varian A-60 spectrometer at several temperatures. When dissolved in CH_2Cl_2, compound (I) has three separate methyl resonances at 22°; four methyl resonances are observed at $-55°$. We interpret these as two complete sets of methyl resonances with overlap of three of the resonances. This interpretation is confirmed by the occurrence of two clear but unequal sets of signals for protons (1) and (2) at $-55°$ with only one set at 22°. We further interpret these two sets of signals as evidence for the existence, on the ^1H n.m.r. time scale, of two isomers of (I). Approximate signal shape analysis[2] gives the free energy of activation for isomer interconversion as 13 ± 1 kcal./mole at $-30°$.

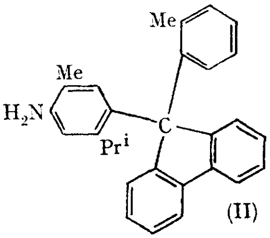
Compound (I) is capable of existence as four geometric isomers in a manner completely analogous to the situation with *o*-substituted diphenylacetic acids.[3] The isomers can be represented as follows:



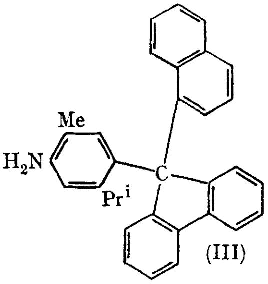
The fluorene nucleus is represented by the triangle and is viewed in the plane of the paper; the circle in one symbol (in front of the paper, and the bar in the other (behind the paper) represent methyl groups *ortho* to the carbon atom that is bonded to the central carbon atom.

One of the isomers [probably (B), (C), or (D)] is separated from the others by barriers of 13 kcal. mole^{-1}. The barrier occurs as the benzene rings are rotated synchronously, without passing each other, through about 90° and an *o*-methyl group is forced past an ortho-hydrogen atom of the fluorene nucleus. Racemization, however, must occur by a different mechanism—one that requires the benzene rings to be rotated past each other.

The behaviour of compounds (II) and (III) indicates that they are resolvable (or at least the barrier to racemization is high). When dissolved in toluene or in $CHCl_2 \cdot CHCl_2$, two doublets of equal intensity are observed for the β-methyl protons of the 2-propyl group. A single set of signals is observed for all other protons. These doublets persist, and even become sharper, up to the boiling point of these solvents (111° and 146°). For the β-methyl groups to be nonequivalent (each with its own doublet), there can be no symmetry plane between the β-methyl groups. If there is no symmetry plane between these groups, the molecule as a whole lacks a symmetry plane and may be resolvable. The barrier to racemization is probably greater than 20 kcal. mole^{-1}.



(II)



(III)

We have also observed rotational isomerism in triarylmethanes that is similar to that of the tetraarylmethanes.

This work was supported by the U.S. Atomic Energy Commission.

(*Received, June 10th, 1968; Com.* 759.)

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[1] R. Adams and J. Campbell, *J. Amer. Chem. Soc.*, 1950, **72**, 153.

[2] T. Nakagawa, *Bull. Chem. Soc. Japan*, 1966, **39**, 1006. Signal overlap and poor resolution at low temperature with this large molecule prevent refined application of Nakagawa's method.

[3] O. S. Akkerman and J. Coops, *Rec. Trav. chim.*, 1967, **86**, 755.