Tetrahedron Letters No.48, pp. 5011-5014, 1968. Pergamon Press. Printed in Great Britain.

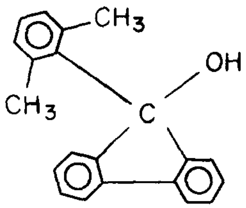
SLOW INTERNAL MOTION IN A TRIARYL CARBINOL

by T. H. Siddall, III and W. E. Stewart

Savannah River Laboratory, E. I. du Pont de
Nemours and Co., Aiken, South Carolina 29801

(Received in USA 27 June 1968; received in UK for publication 2 September 1968)

This communication reports the observation, by means of proton magnetic resonance (PMR), of nonequivalence of the methyl groups in the triaryl carbinol



(I)

It also discusses the preliminary investigation of the mechanism of the identity exchange that causes the separate signals for these methyl groups to merge into one signal at about 200° in solution with hexachlorobutadiene.

Compound I was prepared as described by Adams and Campbell (1), and was purified by vacuum distillation (10^{-3} mm, ~170°) followed by repeated crystallization, first from hexane, then from acetone, and finally from methylcyclohexane to give a white solid. The identity and purity of I were confirmed by a combination of PMR and IR spectroscopy and by elemental analysis. We were motivated by the work of Adams and his students to investigate I, and similar compounds and derivatives, as molecules with possible slow internal motion.

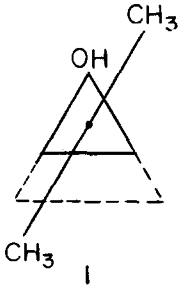
At 40°, I shows two separate methyl resonances in a variety of solvents: (a) 1.20 ppm and 2.92 ppm from TMS in $CDCl_3$; (b) 1.23 and 3.03 in CD_3 $COCD_3$; (c) 1.13 and 2.99 in CD_3CN; (d) 1.20 and 2.92 in $CHCl_2CHCl_2$; (e) 1.17 and 2.87 in hexachlorobutadiene — all obtained with a Varian A-60 spectrometer. The -OH signal was located at rather high field in solvents (a), 2.07 ppm; (d), 2.13; and (e), 1.78; but at much lower field in (b), 4.46; and (c), 5.73. This shift to low field we take as evidence for hydrogen bonding. The separate methyl signals remain sharp in (b) at 50°, but are slightly broadened in (c) at 80°.

Signal broadening is evident in (d) and (e) at 100° and above. Signal coalescence occurs over a wide range and is not complete at 200° in (e). When dissolved in trifluoroacetic acid, the two methyl signals are coalesced even at 40°.

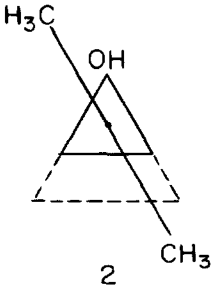
Signal shape analysis (2) gave E_a = 17 kcal/mole, log A_o = 11, and $\Delta F^*_{180^\circ}$ = 21.6 kcal/mole. The results were obtained with 250 mg of I made up to 1 ml with (e). Very similar signal shape dependence on temperature was obtained at 68 mg/ml. At this lower concentration, the signal-to-noise ratio was too poor to permit quantitative rate determinations. However, the exchange mechanism does appear to be first order.

The signal pattern for the aromatic protons also changes with temperature. In particular, a group of small signals at about 6.9 ppm coalesces into a single broad signal, while other signals are little changed. However, signal overlap prevents this phenomenon from having easy quantitative utility.

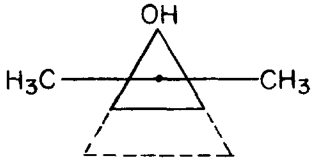
The general conformation of I in its ground state is uniquely determined, subject to elementary considerations of potential energy and symmetry. The fluorene nucleus is well fixed by the bond between its rings. However, the third benzene ring is free to seek the angle of rotation, around its bond to the central carbon atom, that provides the lowest potential energy. The favorable angles of rotation can be described with conventional Newman diagrams



1



2



3

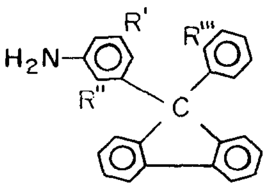
The fluorene nucleus is symbolized by /-------\ , and the third benzene ring is viewed end-on down its bond to the central carbon atom. Conformations 1 and 2 are mirror images, and consequently are identical in terms of PMR spectroscopy. However, the methyl groups are nonequivalent in 1 and 2. Conformer 3 potentially has a PMR identity separate from 1 and 2, but lacks separate identity for the two methyl groups within that conformer identity. The combination

1 and 2 is the conformer species observed by PMR spectroscopy. Conformer 3, if present, is below the limits of detection (probably about one part in one hundred). Other possible or more detailed conformations do not seem plausible or well defined. General consideration of chemical shifts is consistent with the assignment to Conformers 1 and 2.

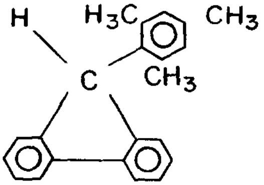
There are two internal motions that would interchange the identities of o-methyl groups in Conformer 1 and 2, and thereby correspond to symmetry operations. Rotation by 180° around the bond to the central carbon atom is one of these, and inversion of the central carbon atom is the other. The simple observation that the methyl groups are nonequivalent at low temperature, but equivalent at high temperature, is not sufficient to decide between these two alternatives. It is necessary to turn to other observations.

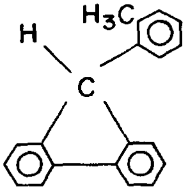
Coalescence of the separate methyl signals in trifluoroacetic acid indicates that an ionic activated state, and that inversion as the mechanism of site exchange, prevail in that solvent. The maintenance of two separate signals in the solvents of high dielectric constant (acetone and acetonitrile) is an argument against an ionic activated state in those solvents and the chlorocarbons. Tentatively, we conclude that there are two actual mechanisms of site exchange. One or the other prevails, depending on circumstances.

We are continuing these investigations to obtain more precise kinetic quantities, and to provide more insight into the exchange mechanism. One particularly fruitful approach may be to attempt to separate isomers of compounds similar to I, but that have unsymmetrical substitution in the third benzene ring. There is also a wide range of interesting derivatives of triaryl carbinols. We have already observed slow exchange for compounds of types represented by



(II)





We will report our preliminary studies of these phenomena shortly. Although Adams was unable to confirm his expectations of isomerism in compounds of type II by polarimetry, evidence is available from PMR.

ACKNOWLEDGMENT

The information contained in this article was developed during the course of work under Contract AT(07-2)-1 with the U. S. Atomic Energy Commission.

REFERENCES

1. R. Adams and J. Campbell, J. Am. Chem. Soc. **72**, 153 (1950).
2. T. Nakagawa, Bull. Chem. Soc. Japan **39**, 1006 (1966)