Tetrahedron Letters No. 6, pp 527 - 530.
©Pergamon Press Ltd. 1979. Printed in Great Britain.

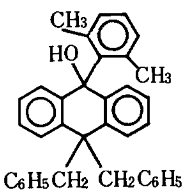
0040-4039/79/0201-0527$02.00/0

RESTRICTED ROTATION INVOLVING THE TETRAHEDRAL CARBON. XXIV. 10,10-DIBENZYL-9-ARYL-10,10-DIHYDROANTHRACEN-9-OLS: A NEW SYSTEM WHICH EXHIBITS A HIGH BARRIER TO ROTATION ABOUT A C_{sp^3}-C_{sp^2} BOND.[1)]

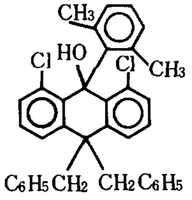
Mikio Nakamura
Department of Chemistry, School of Medicine, Toho University,
Ōmorinishi, Ota-ku, Tokyo 143
Michinori Ōki
Department of Chemistry, Faculty of Science, The University of Tokyo,
Hongo, Bunkyo-ku, Tokyo 113

Barriers to rotation about the C_9-C_{ar} bond of 9-arylfluorene derivatives are extraordinarily high and in some cases rotational isomers have been isolated as stable entities at room temperature.[2)] In contrast, barriers to rotation of structurally similar 9-arylxanthene derivatives are lower than those of the corresponding fluorene derivatives by more than 10 kcal/mol. McKinley et al.[3)] explained the sharp contrast in those barriers to rotation on the basis of the difference in the direction of the substituents: the aryl group in the xanthene system takes an axial conformation both in the ground state and in the transition state for rotation. If the aryl group is axial in the boat form of the 9,10-dihydroanthracene type molecules,[4)] the steric repulsion between 1,8-hydrogens of the xanthene ring and 2',6'-substituents of the aryl ring will not increase in the transition state for rotation in contrast to the case of the 9-arylfluorene system.

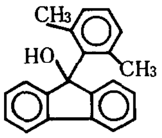
This means that the barrier to rotation of the 9-arylxanthene system may be increased if the 9-aryl group is forced to take an equatorial conformation. Although it is impossible to realize such a situation in the 9-arylxanthene system, it becomes possible in carbon analogs, 9-aryl-9,10-dihydroanthracene derivatives, by the introduction of two substituents in the 10 position. If a bulky group in the 9 position takes an axial conformation, it oposes a substituent in the 10 position which is also axial. Therefore introduction of two bulky substituents, which assure that one of the two groups is always axial irrespective to the ring inversion, in the 10 position, a bulky substituent in the 9 position will inevitably take the equatorial conformation. Under such expectation, we synthesized 9-(2,6-xylyl)-10,10-dibenzyl-9,10-dihydroanthracen-9-ol (1) and its 1,8-dichloro derivative (2), measured the barriers to rotation about the C_9-C_{ar} bond by the DNMR method and compared the results with those of 9-(2,6-xylyl)fluoren-9-ol (3) and 9-(2,6-xylyl)xanthen-9-ol (4).



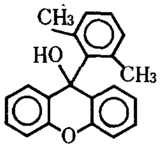
(1)



(2)

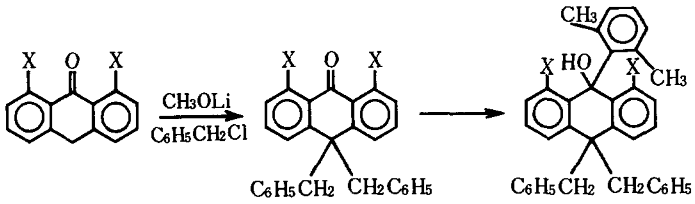


(3)



(4)

The syntheses of the required compounds were accomplished in the following manner. Anthrone and its dichloro derivative (5)[5] were treated with lithium methoxide and benzyl chloride to afford 10,10-dibenzylanthrone (6).[6] Reaction of the dibenzylanthrone with 2,6-dimethylphenyllithium produced desired 10,10-dibenzyl-9-(2,6-xylyl)anthracen-10-ols: 1, mp 216 – 217 °C; 2, mp 283 – 285 °C.



(5) (6) (1) : X=H

(2) : X=Cl

The ^{1}H NMR spectrum of compound 1 in $CDCl_3$ at room temperature showed two methyl signals at δ 0.26 and 2.55, indicating that the rotation about the C_9-C_{ar} bond is frozen on the NMR time scale (Fig. 1). It is noteworthy that one of the methyl signals appeared at quite a high field (δ 0.26) compared with those of the corresponding fluorene (3, δ 1.15) and xanthene (4, δ 1.35) derivatives. The abnormally high methyl signal together with the high chemical shift of the OH (δ -0.2) may be the results of the anisotropy of the benzene ring of the benzyl group in the 10 position. That is, two benzyl groups are arranged in such a manner that the two bulky benzene rings take the conformation anti to each other to avoid the steric repulsion. As a result one benzene ring of the benzyl group faces the methyl group in the 2' position and another the OH group, making these protons shift to quite a high field.

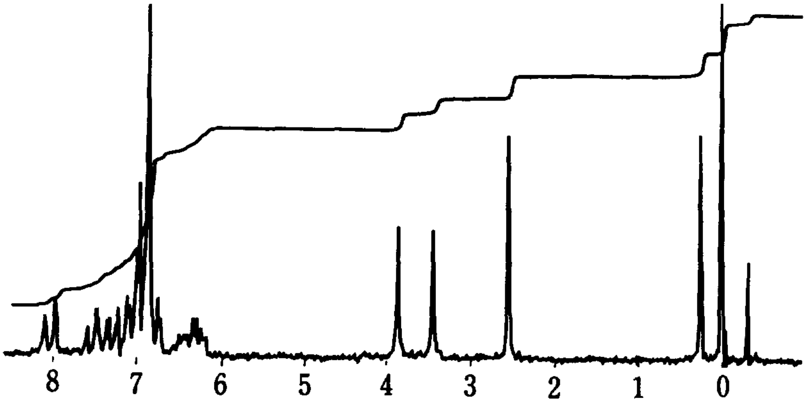


Fig. 1 ^{1}H NMR Spectrum of Compound 1 at Room Temperature

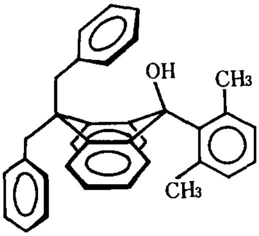


Fig. 2 A Plausible Conformation of Compound 1

When the temperature of a hexachlorobutadiene solution of 1 was raised, the two methyl signals broadened and coalesced at 137.8°C. Thus the rate for rotation at this temperature was calculated to be 305 s^{-1} and the free energy of activation 19.6 kcal/mol. Although the barrier to rotation of this compound is a little smaller than those of the corresponding fluorene derivative (3) (Tc = 163°C and $\Delta G_c^{\ddagger}$ = 21.1 kcal/ol),[7] as expected, it is ca. 9 kcal/mol higher than the xanthene derivative (4) (Tc = -20°C, and $\Delta G_c^{\ddagger}$ = 10.9 kcal/mol).[3]

The 2,6-xylyl group might take an axial conformation and rotate as such in the transition state of rotation. We cannot rigorously exclude the possibility at the present stage, but believe that the rotation takes place in the 2,6-xylyl-equatorial conformation because of the congested state in the 2,6-xylyl-axial conformation. The following substituent effect may be taken as evidence for the equatorial conformation in the transition state also.

Introduction of substituents in 1 and 8 positions may increase the barrier to rotation, as in the case of fluorene derivatives,[8] if the 2,6-xylyl group assumes the equatorial conformation. ^{1}H NMR spectra of compound 2 were measured at various temperatures. Although two methyl signals at δ 2.78 and 0.39 broadened considerably at high temperatures, they resisted to coalescence even at 200°C. Thus the barrier to rotation about the C_9-C_{ar} bond must be higher than 22.7 kcal/mol.

From our experiences, the signal shapes are judged to suggest that the coalescence temperature will be higher than 200°C by 25-35°C. If we assume that the Tc of the methyl signals is 230°C, then the barrier to rotation is calculated as 23.5 kcal/mol. The results indicate that isolation of rotational isomers at room temperature will be possible, if we introduce different substituents in the 2' and 6' positions of the phenyl group in this system. A work on this line is in progress.

References

1) Preceding paper: M. Nakamura, H. Kihara, N. Nakamura, and M. Ōki, Org. Magn. Reson., submitted.

2) (a) M. Ōki, Angew. Chem. Int. Ed. Engl., 15, 87 (1976); (b) M. Nakamura, N. Nakamura, and M. Ōki, Bull. Chem. Soc. Jpn., 50, 1097 (1977); (c) M. Nakamura, N. Nakamura, and M. Ōki, Bull. Chem. Soc. Jpn., 50, 2986 (1977).

3) S. V. McKinley, P. A. Grieco, A. E. Young, and H. H. Freedman, J. Am. Chem. Soc., 92, 5900 (1970).

4) (a) A. W. Brinkmann, M. Gordon, R. G. Harvey, P. W. Rabideau, J. B. Stothers, and A. L. Ternay, Jr., J. Am. Chem. Soc., 92, 5912 (1970); (b) P. W. Rabideau, Acc. Chem. Res., 11, 141 (1978).

5) E. de Barnett and M. A. Matthews, J. Chem. Soc., 123, 2549 (1923).

6) D. Y. Curtin, R. C. Tuites, and D. H. Dybvig, J. Org. Chem., 25, 155 (1960).

7) K. Albert and A. Rieker, Chem. Ber., 110, 1804 (1977).

8) W. T. Ford, T. B. Thompson, K. A. J. Snoble, and J. M. Timko, J. Am. Chem. Soc., 97, 95 (1975).

(Received in Japan 11 November 1978)