

HINDERED ROTATION IN 1,3-DIPHENYL ALLYL ANION

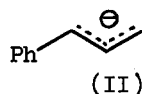
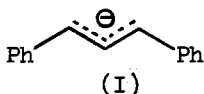
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^1H n.m.r. studies of substituted 1,3-diphenyl allyl anions¹ showed that phenyl rotation is on the n.m.r. time scale but the spectra were so complex that it was difficult to obtain rates. In the proton decoupled ^{13}C n.m.r. spectra no such problems exist. The sodium salt of trans,trans-1,3-diphenyl allyl anion (I) in liquid ammonia at -10° shows signals at 90.3 (-CH-CH-CH), 112.1 (para-C), 118.6 (ortho-C), 128.8 (meta-C), 129.0 (?-CH-CH-CH-), and 146.7 (phenyl-1-C) (δ from T.M.S.)². As the temperature is lowered the signal due to the ortho carbons broadens and splits into two peaks at 115.4 and 121.3 δ . The coalescence temperature of -40° corresponds to a barrier to phenyl rotation $\Delta G_{\text{rot}}^\ddagger$ of 10.9 kcal/mol and computer assisted fitting of ten spectra between -36° and -59° gives Arrhenius parameters of $\log_{10} A = 11.46 \pm 0.63$ and $E_a = 9.60 \pm 0.65$ kcal/mol. These are in the same region as barriers for phenyl aldehydes and ketones³ and close to the barrier for phenyl rotation of the lithium salt of 1-phenyl allyl anion (II) in T.H.F.⁴ In the latter case, however, the barrier is found to vary with the nature of the counter-ion and it seems likely that in this medium either (II) exists as contact ion pairs or that rotation occurs via a contact ion pair^{5,6}. ^1H n.m.r.⁷ (Na and Li salts, -10°) and u.v.⁸ (Li, Na and K salts, 25° to -60°) studies of anion (I) in liquid ammonia revealed only the presence of solvent separated ion pairs and ^{13}C n.m.r. studies of the Li and K salts gave rotational rates within experimental error of those determined for the Na salt. This seems to eliminate the possibility of a contact ion pair

intermediate. The barrier to rotation in (I) was also shown to be independent of the concentration of excess NH_2^- (up to 30%) eliminating the possibility of a protonation/deprotonation mechanism⁹. Comparison with other barriers to rotation in group-I organo-metallic compounds is difficult as in most cases no reliable test was made of the mechanism¹⁰ or there were definite indications of an intermediate contact ion pair^{1,4-6,11}.



References

1. J.W. Burley and R.N. Young, J.C.S. Perkin II, 1972, 1843.
2. J.P.C.M. van Dongen, H.W.D. van Dijkman, and M.J.A. de Bie, Rec.Trav.Chim., 1974, 92, 29.
3. F.A.L. Anet and M. Ahmad, J.Amer.Chem.Soc., 1964, 86, 119; N. Nakamura and M. Oki, Bull.Chem.Soc. Japan, 1972, 45, 2565.
4. V.R. Sandel, S.V. McKinley and H.H. Freedman, J.Amer.Chem.Soc., 1968, 90, 495.
5. G. Fraenkel, J.G. Russell and Y.-H. Chen, J.Amer.Chem.Soc., 1973, 95, 3208.
6. F.J. Kronzer and V.R. Sandel, J.Amer.Chem.Soc., 1972, 94, 5750.
7. R.J. Bushby and G.J. Ferber, Chem.Comm., 1973, 407.
8. U.V. studies in ether solvents have been made by J.W. Burley and R.N. Young, J.Chem.Soc. (B), 1971, 1018; J.C.S. Perkin II, 1972, 1006.
9. G.J. Heiszwolf, J.A.A. van Drunen, and H. Kloosterziel, Rec.Trav.Chim., 1969, 88, 1377.
10. R.B. Bates, D.W. Gosselink and J.A. Kaczynski, Tet.Let., 1967, 205; G.J. Heiszwolf and H. Kloosterziel, Rec.Trav.Chim., 1967, 86, 1345; P. West, J.I. Purmort and S.V. McKinley, J.Amer.Chem.Soc., 1968, 90, 797; H. Kloosterziel and J.A.A. van Drunen, Rec.Trav.Chim., 1968, 87, 1025; 1970, 89, 270; S. Brownstein and D.J. Worsfold, Canad.J.Chem., 1972, 50, 1246; R.B. Bates, S. Brenner, and C.M. Cole, J.Amer.Chem.Soc., 1972, 94, 2130; and H. Kloosterziel, Rec.Trav.Chim., 1973, 92, 1167.
11. The work in reference 9 may be an exception but compare reference 6.