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HINDERED ROTATION IN 1,3-DIPHENYL ALLYL ANION

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^{1}H n.m.r. studies of substituted 1,3-diphenyl allyl anions[1] 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 ($-\underline{C}H-CH-\underline{C}H$), 112·1 (*para*-C), 118·6 (*ortho*-C), 128·8 (*meta*-C), 129·0 (?$-CH-\underline{C}H-CH-$), 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 $\Delta G^{\neq}_{rot.}$ of 10·9 kcal/mol and computer assisted fitting of ten spectra between -36° and -59° gives Arrhenius parameters of $\log_{10}A = 11{\cdot}46 \pm 0{\cdot}63$ and $E_a = 9.60 \pm 0{\cdot}65$ kcal/mol. These are in the same region as barriers for phenyl aldehydes and ketones[3] 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]. ^{1}H 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 mechanism[9]. 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 mechanism[10] or there were definite indications of an intermediate contact ion pair[1,4-6,11].

(I)

(II)

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11. The work in reference 9 may be an exception but compare reference 6.