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CONFIGURATIONAL AND CONFORMATIONAL ANALYSIS OF CIS- AND TRANS-9,10-DIHYDRO-9,10-DIPHENYLPHENANTHRENE BY ESR: VICINAL DIAXIAL PHENYL SUBSTITUENTS IN THE TRANS ISOMER

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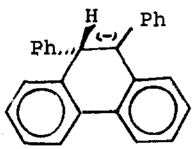
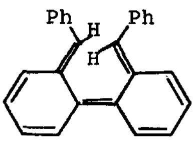
Two stereoisomers of 9,10-dihydro-9,10-diphenylphenanthrene (I) have been synthesized and their stereochemistry tentatively assigned on the bases of (now obsolete) mechanistic considerations.[1] We wish to report an unequivocal structure proof by esr spectroscopy of c- and t-$I^{\dot{-}}$ which controverts the earlier assignment and reveals t-$I^{\dot{-}}$, and therefore presumably t-I, to have diaxial vicinal phenyl substituents. Electrocyclic cleavages of the two anion radicals have also been observed.

Isomer A, obtained by protonic quenching of the dianion of 9,10-diphenylphenanthrene and earlier assigned the *trans* configuration, has nmr (CCl_4) τ 5.61(2H,s), 3.33(4H,m), 2.9(12H,m), 2.1(2H,m) and mp 130°. Reduction of A by K/THF/crown ether at -78° gave the green, biphenyloid anion radical:esr hfs a_p=5.4(2H), a_o=2.7 (2H), a_β=2.7(1H). These hfs may be compared to those of the biphenyl anion radical: a_p=5.46(2H), a_o=2.73(4H), a_m=0.43(4H).[2] The single β proton splitting must be assigned to a lone axial hydrogen: $A^{\dot{-}}$ must be c-$I^{\dot{-}}$. Note that ring inversion is slow on the esr time scale even at 0° presumably because it entails passage through a high energy torsional state wherein the *cis* phenyls become eclipsed. Isomer B, produced by the action of phenyl lithium on *o,o*´-bis (α-bromobenzyl) biphenyl, has nmr ($CDCl_3$) τ 5.61(2H), 2.9(16H), and 2.1(2H) and mp 168°. Note the exact coincidence of the saturated methine signals of A and B. This isomer, upon potassium reduction, gives an anion radical with esr hfs: a_p=5.4(2H), a_o=2.7(2H). No beta hfs are present. Since the magnitude of a^{β}_{ax} is established in *cis*-$I^{\cdot -}$ (2.7G), it is clear that no axial protons are present in *t*-$I^{\cdot -}$. The phenyl substituents therefore occupy the axial positions. Though unusual, this circumstance is readily comprehended when thought is given to the *anti* character of the phenyl groups in this conformer as contrasted to their gauche character in the diequatorial conformer and upon noting the absence of conventional 1,3 diaxial repulsions in the cyclohexadienoid system of I. The diaxiality of the phenyl substituents in *t*-I, incidentally, does not vitiate the usual *trans*>*cis* stability sequence for 1,2 disubstitution on a cyclohexyl ring. Refluxing in cyclohexylamine/lithium cyclohexylamide converts *c*-I to *t*-I. Moreover, as expected, the *trans* isomer is higher melting than the *cis*.

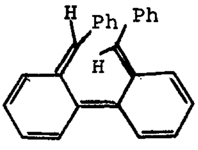
These findings are also mechanistically enlightening. The formation of *c*-I in the dianion quenching can now be understood as preferential protonation, for steric reasons, on the side of the intermediate anion (II) *trans* to the neighboring phenyl group. Other *cis* diprotonations have been observed in this laboratory.[3] The formation of *t*-I in the other reaction eliminates III as a possible intermediate, since it should close disrotatorily, giving *c*-I. Although IV would



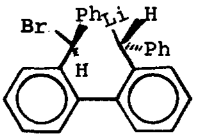
II



III



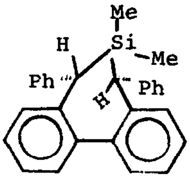
IV



V

account for the formation of *t*-I, it has such severe steric problems as to appear unlikely to be formed, especially in preference to III. A more creditable mechanism is an internal Sn2 displacement involving the organolithium V, which could directly yield the more stable *trans* isomer.

The anion radicals of *c*- and *t*-I are relatively stable at -20°, but their color and esr signal fades at 0°. Larger scale potassium/THF reductions of both isomers at 0° yield the yellow-brown dianion III^{-2}. Protonic quenching (H_2O or CH_3OH) yields *o,o*′-dibenzylbiphenyl, and dimethyldichlorosilance gives the cyclic silane VI: nmr ($CDCl_3$) τ 9.93(3H,s) , 9.87(3H,s) , 6.29(1H,s) , 6.13(1H,s) , 2.9 (18H,m). The *cis* stereochemistry of VI was assigned on the basis of variable



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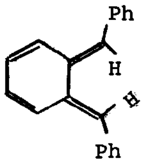

VII

temperature mnr studies. At 150° (in hexachlorocyclopentadiene) the pair of singlets at τ 6.29 and 6.13 had broadened to coalescence; at 196° they collapsed to a singlet at τ 6.2. Meanwhile, the two silane methyl singlets remained unchanged. Re-cooling to 100° restored the original spectrum. For equivalent methines, only the cis silane isomer may have nonequivalent methyls. The nonequivalence of the methines at ambient temperature seems to reflect unsymmetrical twisting in the seven membered cycle. Molecular models also suggest the feasibility of such twisting. Assuming a preferred supraficial addition in the silane quenching reaction III^{-2} may be assigned the E,E configuration. A similar quenching reaction with *E,E* and *Z,E*-VII^{-2} has been shown to be ~85% stereospecific.[4] The absence of stereospecificity in the electrocyclic cleavages producing III^{-2} could be solely a consequence of the relatively high (0°) cleavage temperature allowing rapid equilibration of III^{-2} and IV^{-2}. Alternatively or in addition, the severe steric congestion in IV$^{\dot{-}}$ may stultify the normal symmetrical rotary mode in favor of a semirotatory process at least for that isomer of I$^{\dot{-}}$ which would ordinarily give IV$^{\dot{-}}$.

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