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THE REDUCTIVE CLEAVAGE OF TRIPTYCENE DERIVATIVES

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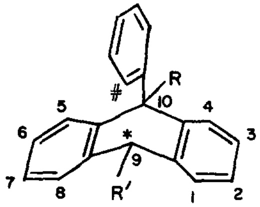
Little is known concerning the details of reductive cleavage reactions of aromatic hydrocarbons, although bond-forming reactions and cleavages of heteromolecules have received attention. We report here results which establish the course of one such reaction.

Tetrahydrofuran solutions of triptycene derivatives yield 9-phenylanthracenes when allowed to contact potassium metal (1). The complexity of the reaction can best be illustrated by consideration of the hypothetical intermediate I, formed by ring fission of an unspecified nature (* and # represent $^{\bullet}$ or -). One more bond must be broken (C-R) and one must be formed (at #) to arrive at the final product.



I

Electron spin resonance spectra of the substituted anthracene radical anions have been obtained in all cases. Attempts to detect the triptycene radical anion, however, have been unsuccessful. Even at -40°, although the time required for appearance of an esr signal increased from a few minutes at room temperature to 36 hours, that signal was due to the product. Smentowski has also tried without success to detect the triptycene radical anion in THF at -80°(2).

The predominant fate of bridgehead hydrogen (R = H) in monosubstituted compounds was determined by investigation of 9-phenyl-10-^{3}H-triptycene. Workup of the reaction mixture by

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**Present address: Department of Chemistry, The Ohio State University, Columbus, Ohio 43210 addition of methanol followed by sulfur aromatization produced 9,10-diphenylanthracene containing only 8% of the activity of the starting material. Thus, 92% of the product is formed by abstraction of hydrogen from the solvent. Product studies of disubstituted derivatives have failed to detect migration from the bridgehead to the #; instead, the group is lost to the medium.

When R is lost, it cleaves as an anion. 9,10-Dibenzyltriptycene was allowed to react with potassium, followed by addition of dry CO_2. Phenylacetic acid was detected both by VPC and by its characteristic odor. Product studies of a series of 9,10-disubstituted derivatives (R, R' = H, CH_3, C_6H_5, and $C_6H_5CH_2$ in all combinations except diphenyl) established the order of cleavage aptitude as benzyl, hydrogen > phenyl > methyl, thus providing direct confirmation of the order reported for cleavage of groups as anions in a variety of reactions (3).

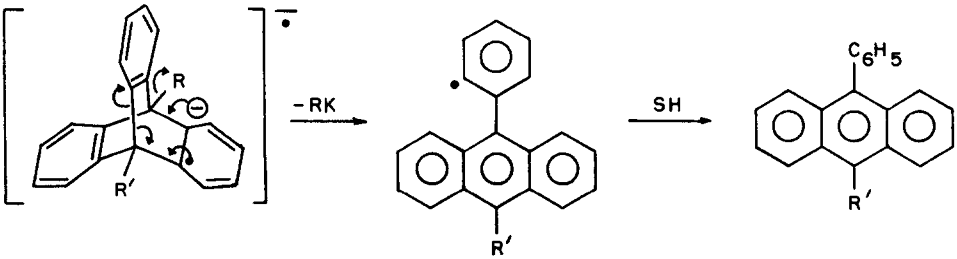
The ring which becomes the phenyl substituent in the product was shown to be other than the one containing the extra electron. 2-Phenyltriptycene yields exclusively 2,9-diphenylanthracene after aromatization, determined by VPC comparison with authentic samples of 2,9- and 2,10-diphenylanthracenes (kindly furnished by Professor Dickerman (4)) and with <u>meta</u>- and <u>para</u>-9-biphenylylanthracenes. Whereas sodium does not react with any of the other compounds studied, even at elevated temperatures (1), it is able to slowly effect cleavage of 2-phenyltriptycene at room temperature. The only esr spectrum observed with either metal, however, is that of the radical anion of the product. Evidently, the extra stability of the biphenyl radical anion enables the reaction to proceed with sodium, in contrast to the parent compound. This can be overdone: 2,3-benzotriptycene radical anion is stable for weeks at room temperature, as are the radical anions of other derivatives with anion-stabilizing substituents reported in the literature (5).

The absence of a detectable amount of 2,10-diphenylanthracene shows that the stabilization of the * in I by the phenyl group is an important factor affecting isomer distribution in the product. Thus, a substantial amount of delocalization must have occurred by the time the transition state of the ring-opening step is reached. An alternative explanation involving an equilibrium between the closed and isomeric open forms can not be completely ruled out, but is considered less likely on steric and energetic grounds.

Two facts argue for ring opening of the radical anion rather than the dianion. The first is the remarkable fact that this cleavage occurs at all at room temperature, since radical anions of <u>ortho</u>-xylene are not detectable at temperatures appreciably above -80° (6). The second is that sodium is able to effect cleavage of 2-phenyltriptycene despite the known reluctance of the biphenyl radical anion to undergo further reduction (7). It must be emphasized, however, that dianion intermediacy can not be rigorously excluded, since the reduction occurs on a metal surface, and it is not inconceivable that a very small amount of extremely reactive dianion could be formed.

The effect of the 2-phenyl substituent on product distribution was utilized to determine the nature of the *. 2-Methyltriptycene reacts readily with potassium to yield, after aromatization, a mixture of two compounds shown to be 2-methyl-9-phenyl- and 2-methyl-10-phenylanthracenes (VPC, mp) in the ratio of 1:2. The former involves a transition state or intermediate in which the * can be located on the methyl-bearing carbon; the latter does not. The methyl group thus appears to destabilize the *, indicating that it is an anion, and thus the ǂ is most likely a radical. Loss of a bridgehead group thus produces a neutral anthracene system, which is subsequently reduced to the radical anion, as shown in Figure I.

FIG. I



One set of compounds deserves separate mention. 9,10-Disubstituted triptycenes in which one substituent is CH_3 afforded intermediate esr spectra which changed to those of the products when the solution was allowed to stand without further contact with the potassium mirror. For example, 9,10-dimethyltriptycene afforded a spectrum analyzable as arising through the interaction of three pairs of hydrogens with the odd electron. This intermediate is considered to be II or one of the species in equilibrium with it (8), in which the four meta hydrogens of the diphenylethylene system do not affect the esr spectrum. Loss of phenyl eventually leads to the observed product, 9,10-dimethylanthracene. This intermediate can be pictured as arising through an intramolecular hydrogen shift from the methyl group, in contrast to compounds losing hydrogen from the bridgehead. The hydrogen which would change position here, if this were indeed the case, is on the side of the molecule appropriate for intramolecular migration (cf. I). Further experiments are planned to test this point.

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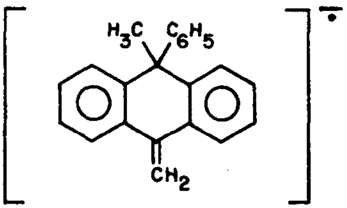

II

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