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REDUCTION OF 1-(2-BROMOPHENYL)-1,2,2-TRIPHENYLETHYLENE BY NAPHTHALENE RADICAL ANION

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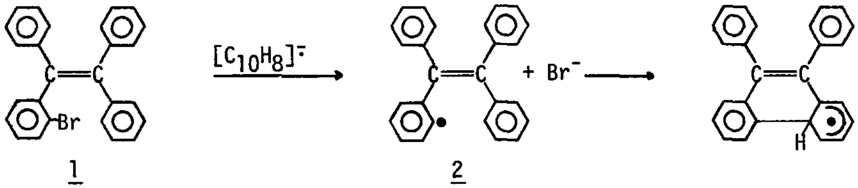
The mechanism of reduction of halobenzenes by naphthalene radical anions is a matter of current interest and controversy[1,2]. As part of our continuing interest in utilizing intramolecular rearrangement reactions as probes for radical intermediates[3-5], the reduction of 1-(2-bromophenyl)-1,2,2-triphenylethylene[6] (1) by the naphthalene radical anion has been investigated.

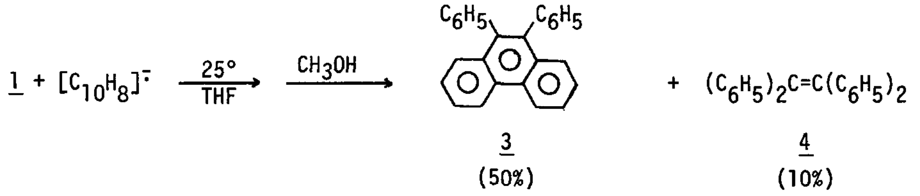
The proposed mechanisms for naphthalene radical anion reductions of aryl and alkyl halides invoke the intermediacy of the corresponding radicals[1,2,7]. If radicals were generated in the radical anion reduction of 1, it was anticipated that the corresponding o-(1,2,2-triphenylvinyl)phenyl radical (2) would undergo ring closure to the 9,10-diphenylphenanthrene ring system (eq 1) by analogy with the Pschorr cyclization and related intramolecular arylation reactions[8,9].



1 2

(1)

Preliminary experiments involving the reaction of 1 with sodium or lithium naphthalene in tetrahydrofuran (THF) resulted in formation of significant amounts of the ring-closed product, 9,10-diphenylphenanthrene (eq 2)[10]. The apparent efficiency of this ring closure reaction



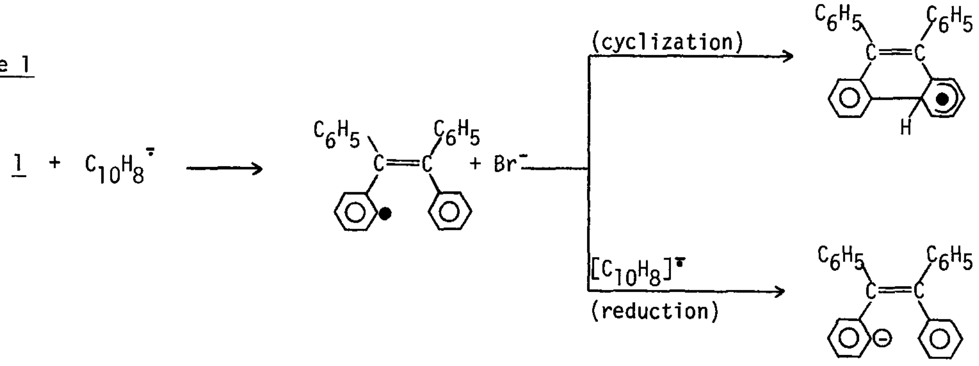
3 (50%)
4 (10%)

(2)

prompted us to carry out some preliminary investigations concerning the mechanism of radical anion reactions with aryl halides. On the basis of the general mechanism proposed for the reaction of alkyl halides with naphthalene radical anion (and advocated by Sargent[2] for the analogous halobenzene reaction), it was anticipated that the amount of ring closure to yield

9,10-diphenylphenanthrene would be dependent on the concentration of naphthalene radical anion, since ring-closure would compete with reduction of the radical to the anion as shown in Scheme 1[12].

Scheme 1



Contrary to these predictions and results obtained in the naphthalide reduction of 5-hexenyl fluoride[13] and related reactions[14,15], the amount of ring-closure to 9,10-diphenylphenanthrene and 9,10-dihydro-9,10-diphenylphenanthrene shows little sensitivity to the concentration of naphthalide or the mode of addition as shown by the data in Table 1. The amount of ring closure actually increases (for either mode of addition) with increasing concentration of naphthalene radical anion. These results appear to be inconsistent with the mechanism outlined in Scheme 1[16].

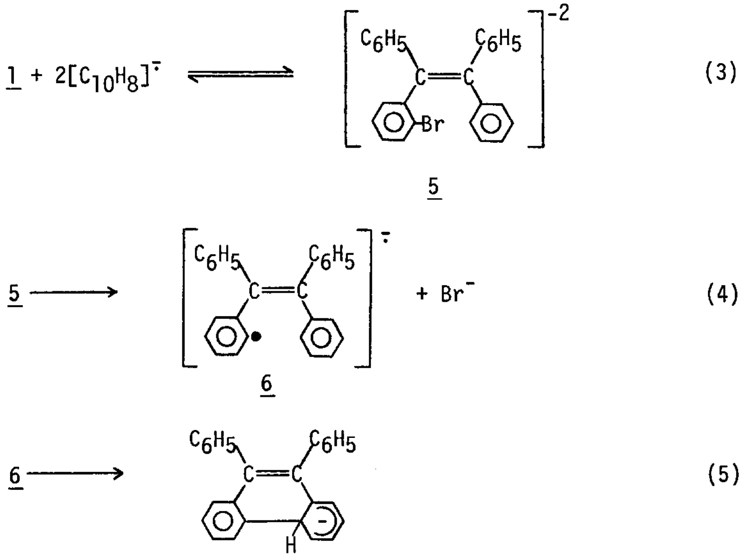
Table 1. Reactions of 1 with Naphthalide in THF at 25°C.

Run	Mole Ratio of Bromide 1 to Naphthalide.[a]	Addition Mode [b]	Counter Ion	% Yield Ring-Closed Products (9,10-Diphenylphenanthrene)[c]
1.	1:1	Normal	Na^+	36
2.	1:1	Inverse	Na^+	49
3.	1:2.5	Normal	Na^+	52
4.	1:2.5	Inverse	Na^+	48 [d]
5.	1:2.5	Normal	Li^+	51
6.	1:2.5	Inverse	Li^+	50
7.	1:5	Normal	Na^+	59
8.	1:5	Inverse	Na^+	61
9.	1:10	Normal	Na^+	27 [e]
10.	1:10	Inverse	Na^+	46 [e]

[a] Each component diluted with 40 ml THF. The initial concentration of 1 was *ca.* 10^{-2} *M*. [b] Normal addition involves dropwise addition of 1 to the naphthalide solution followed by quenching with methanol. [c] Determined by vpc. Estimated error ± 2%. Other observed products are tetraphenylethylene and 1,2-dihydro-1,1,2,2-tetraphenylethane (7-26%). [d] 20% of the ring-closed product was 9,10-dihydro-9,10-diphenylphenanthrene. [e] Actual ring-closed product was 9,10-dihydro-9,10-diphenylphenanthrene.

A reasonable alternative or competing mechanism, consistent with the dependence on naphthalide concentration, is shown in Scheme 2. This mechanism invokes the intermediacy of the dianion 5 of the tetraphenylethylene system[18]. The tetraphenylethylene dianion is known

Scheme 2



to be the predominant species in the rapidly established[19] disproportionation equilibrium of the tetraphenylethylene radical anion (eq 6,K = 400 at 20°C)[20]. Polarographic half-wave potentials for tetraphenylethylene (-2.0 v, 2e$^-$) and naphthalene (-2.5 v) support the electron transfer process shown in eq 3[21,22]. Some precedent for the existence of species such as 5 is available from studies of halobenzene[23] and alkyl halide[18] reductions by aromatic radical anions and

$$2[(C_6H_5)_2C{=}C(C_6H_5)_2]^{\dot{-}} \rightleftharpoons [(C_6H_5)_2C{=}C(C_6H_5)_2]^{-2} + \underline{4} \qquad (6)$$

dianions, respectively. The ring closure step (eq 5) is simply the intramolecular analog of the step proposed for the alkylation of naphthalene in reactions of alkyl halides with naphthalide[7] and related reactions[24,25]. Thus, each step in the mechanisms outlined in Scheme 2 seems reasonable; however, it will remain for further studies to provide convincing evidence for this mechanism and its generality. With regard to the generality of the ring-closure reaction, it is significant to note that analogous ring closure is not observed in the naphthalene radical anion reduction of either o-bromobenzophenone or o-bromodiphenylmethane.

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