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PHOTOREDUCTION OF AROMATIC COMPOUNDS VIA AMINE EXCIPLEXES[1]

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Abstract: Many cata and peri condensed polynuclear aromatic compounds were reduced smoothly by sodium borohydride in absolute ethanol in the presence of a tertiary amine to give products in good yields.

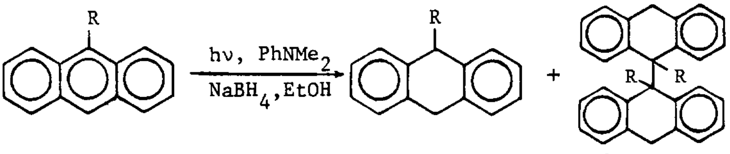
The common method for the reduction of aromatic compounds is the Birch Reduction which is usually carried out in liquid ammonia either with or without a cosolvent. A limitation of the Birch Reduction is the low solubility of many polynuclear aromatic compounds in liquid ammonia. Although photoexcited aromatic compounds are known to react with borohydrides to yield reduction products via radical ion intermediates, few of these reactions appear to have any practical applications.[2-6] Photoreduction of aromatic compounds with amines has been studied in a number of laboratories but the reaction was complicated by the formation of amination products.[7-9] In connection with our interest in the chemistry of exciplexes, the photoreduction of polynuclear aromatic hydrocarbons and their halogenated derivatives by sodium borohydride in the presence of a tertiary amine was explored as an alternate method to the Birch Reduction. We found that many cata and peri condensed polynuclear aromatic compounds were reduced smoothly in absolute ethanol to give products in good yields. The reaction is exemplified by the photoreductions of anthracene and pyrene, and the results are summarized in the Table.

A solution of anthracene (0.505 g, 2.83 mmol), N,N-dimethylaniline (3.41 g, 28 mmol) and $NaBH_4$ (0.25 g, 6.6 mmol) in 110 ml of absolute ethanol was irradiated with a Hanovia 450-w lamp through a uranyl glass filter for 2 hr. Tlc and uv analyses of the reaction mixture indicated that the reduction was complete. 9,10,9',10'-Tetrahydro-9,9'-bianthryl (1, 220 mg, 44%), mp 251-3° (HOAc),[10] precipitated during the reaction, was collected by filtration. The mixture was washed with 10% aq. HCl to remove the amine. The reduction products were isolated by chromatography over neutral alumina (Activity II, 100 g). 9,10-Dihydroanthracene (2, 67 mg, 13%) mp 107-8° (ethanol),[11] was isolated from the petroleum ether eluate, while an additional amount of 1 (60 mg, 12%) was recovered from the ether-petroleum ether (1:19) eluate. Variable amounts of anthracene (5-10%), which were presumably derived from the air oxidation of the products during the work-up, were also isolated from the chromatography. Diethylaniline may be substituted for dimethylaniline, and sodium cyanoborohydride for sodium borohydride. No amination product of anthracene was detected in the chromatographic fractions or in the aqueous HCl extracts. Under similar conditions, the photoreduction of pyrene was less efficient (6 hr).

TABLE

Hydrocarbon[a]	Amine	Filter	Products and Yields		
			Dihydro[b]	Others[b]	Φ[c]
Anthracene	$PhNMe_2$	uranyl	9,10; 11-17%[d]	2a; 52-61%	0.11
9-Methylanthracene	$PhNMe_2$	uranyl	9,10; 15%[d]	2b; 54%	0.14
9,10-Dimethylanthracene	$PhNMe_2$	uranyl	9,10; 63%[d,e]	--	0.12
Benzo[a]anthracene[f]	$PhNMe_2$	uranyl	7,12; 61%[d]	--	0.12
Dibenzo[a,h]-anthracene	$PhNMe_2$	uranyl	7,14; 58%[d]	--	0.15
Pyrene	$PhNMe_2$	uranyl	4,5; 59-69%	4, 11-16%	0.013
Acenaphthylene	$PhNMe_2$	uranyl	Acenaphthene; 22%	Dimers; 77%[g]	0.002[h]
Naphthalene[i]	Et_3N	Corex	1,4; 17%[d,j] 1,2; 3%	$(C_{10}H_9)_2$; 49%[k]	0.024
Phenanthrene	Et_3N	Pyrex	9,10; 36%	$(C_{14}H_{11})_2$; 27%[l] $(C_{14}H_{10})_2$; 12%[l] polymeric; 25%	0.002[h]
t-Stilbene	Et_3N	Pyrex	Dibenzyl; 32%	*c*-Stilbene; 11% polymeric; 45%	0.002[h]

[a] Reactions were carried out in absolute ethanol unless otherwise noted. [b] Products were identified by comparison with authentic samples. [c] Determined with the aid of a benzophenone-benzhydrol secondary actinometer. [d] 5-10% of the hydrocarbon was also recovered. [e] A mixture of *cis* and *trans* isomers (6:5). [f] Solvent was ethanol:dichloromethane (9:2). [g] A mixture or *cis* and *trans* isomers (1:1). [h] Estimated. [i] Solvent was methanol:diglyme (2:3). [j] Estimated by nmr. The pure 1,4-isomer was isolated by a second chromatography. [k] A mixture of *meso* and *d,l* isomers (4:5). [l] Structure determined by spectroscopic means only.



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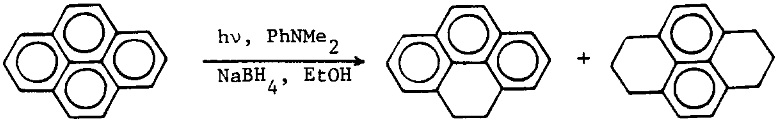
2a R = H

2b R = CH_3



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The products isolated were 4,5-dihydropyrene (3, 59-69%, mp 131-2° (ethanol),[12] and 1,2,3,6,7,8-hexahydropyrene (4, 13-16%), mp 132-4° (ethanol).[13]

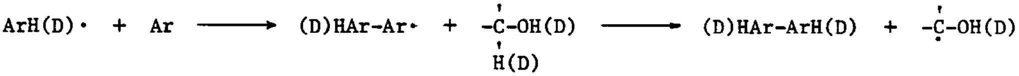
The mechanism of photoreduction of anthracene was investigated by the use of various deuterium labeled reagents. We found that approximately one atom of D was incorporated into the 9(10) position of 1 and 2 when ethanol-0-d was used as the solvent, while no appreciable amount of deuterium was incorporated when either $NaBD_4$ or $PhN(CD_2CH_3)_2$ was used instead of $NaBH_4$ or $PhN(C_2H_5)_2$ in the reduction. However, approximately two atoms of D were incorporated into 1 and 2 when CD_3OD was used as the solvent. The results are consistent with the following mechanism:[14]

$$\mathrm{Ar} \xrightarrow{h\nu} \mathrm{Ar}^{*}$$

$$\mathrm{Ar} + \mathrm{amine} \longrightarrow [\mathrm{exciplex}] \longrightarrow \mathrm{Ar}^{\overline{\cdot}} + \mathrm{amine}^{\dot{+}}$$

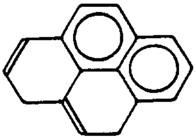
$$\mathrm{Ar}^{\overline{\cdot}} + \mathrm{ROH(D)} \longrightarrow \mathrm{ArH(D)\cdot} + \mathrm{RO}^{-}$$

$$\mathrm{ArH(D)\cdot} + \mathrm{-\overset{|}{\underset{H(D)}{C}}-OH(D)} \longrightarrow \mathrm{ArH_2(D_2)} + \mathrm{-\overset{|}{\underset{\bullet}{C}}-OH(D)}$$



$$\mathrm{ArH(D)\cdot} + \mathrm{Ar} \longrightarrow \mathrm{(D)HAr\text{-}Ar\cdot} + \mathrm{-\overset{|}{\underset{H(D)}{C}}-OH(D)} \longrightarrow \mathrm{(D)HAr\text{-}ArH(D)} + \mathrm{-\overset{|}{\underset{\bullet}{C}}-OH(D)}$$

The CD_3OD recovered from the photoreduction of pyrene in the presence of $NaBH_4$ was enriched in protium as shown by mass spectrometry. Sodium borohydride apparently serves as a scavenger for the radicals derived from the solvent and for the radical anion (and radical) derived from the amine in this reaction to prevent the formation of byproducts. The photoreduction products of pyrene in ethanol-0-d are labeled at the 1- and 3-positions in addition to the 4- and 5-positions. The reduction apparently proceeds successively via 1-hydropyrenyl radical, 1,9-dihydropyrene (5) and other metastable dihydropyrenes as the intermediates.[15] 1,9-Dihydropyrene and its 1,5-isomer (6) may be isomerized to the more stable 3, while the 1,6- and 1,8-isomers (7 and 8) may be further reduced to 4. The lower quantum yield (0.013) of the photoreduction of pyrene than those of anthracenes may be attributed to the presence of metastable dihydropyrene intermediates (5-8) which may function as quenchers of the photoexcited pyrene.



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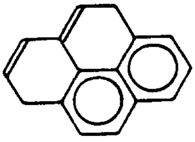

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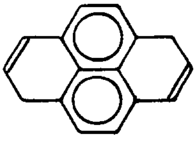

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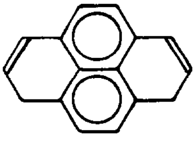

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Since it is known that chloroarenes or bromoarenes may be photoreduced to the corresponding arenes by $NaBH_4$ with high efficiency,[16] our procedures may be applied equally well to the photoreduction of these compounds. The product compositions are virtually identical to those derived from the unsubstituted arenes. The method has been successfully applied to the reduction of 1-bromopyrene, 1,6-dibromopyrene, 1,8-dibromopyrene, 9-chloroanthracene, 9-bromoanthracene, 9,10-dichloroanthracene, 9,10-dibromoanthracene, 1-chloronaphthalene and 2-chloroanaphthalene. Unsubstituted arenes were demonstrated to be the intermediates in the reduction by chromatographic techniques, but our attempts to interrupt the reduction at the arene stage were not successful.

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References and Notes

1. This work is also identified as "Chemistry of Exciplexes 19."
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