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Photochemical Reactions of Hydroarenes with *N*-Bromosuccinimide

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The photochemical reactions of 1,2,3,4-tetrahydronaphthalene (THN), 9,10-dihydrophenanthrene (DHP), 9,10-dihydroanthracene (DHA), and acenaphthene (AN) with *N*-bromosuccinimide (NBS) were investigated under N_2 atmosphere at room temperature. The results show that the relative reactivities of the hydroarenes toward a photochemical reaction with NBS are THN $<$ DHP $<$ AN $<<$ DHA, which is consistent with the stabilities of the radicals produced by benzylic hydrogen abstraction from the hydroarenes. Photochemical reactions of THN and DHP mainly afforded dehydrogenated products, while the photobrominations of the dehydrogenated products from AN and DHA with NBS proceeded readily.

As an important reagent for organic synthesis, *N*-bromosuccinimide (NBS) has been widely used in bromination,[1,2] dehydrogenation,[3] and other reactions.[4,5] When using methylarenes as substrates, a bromine atom of NBS can substitute for either an aromatic or a benzylic hydrogen atom, depending on the substrate types and the reaction conditions. It is necessary for the efficient use of NBS to understand the reactivities and reaction mechanisms of different substrates with NBS under mild conditions.

Futamura and Zong[6] investigated the photobromination of some mono- and dimethylarenes with NBS at room temperature, finding that the benzylic hydrogen atom of mono- and dimethylarenes can be selectively replaced with Br from NBS to afford bromomethyl-, (bromomethyl)methyl- and bis(bromomethyl)arenes. Can the benzylic hydrogen of other compounds be photochemically replaced with Br from NBS? To answer this, we investigated the photochemical reactions of 1,2,3,4-tetrahydronaphthalene (THN), 9,10-dihydrophenanthrene (DHP), 9,10-dihydroanthracene (DHA), and acenaphthene (AN) with NBS.

Experimental

Materials. All of the reagents used were commercially purchased. NBS was used as received without additional purification. The impurities in THN were removed by washing in turn with 5% aqueous H_2SO_4, 5% Na_2CO_3, and water followed by distillation under nitrogen. DHP was purified by silica-gel column chromatography using hexane as an eluate. The purifications of DHA, AN, and biphenyl were performed by recrystallization from ethanol.

General Procedure. A substrate (1 mmol), biphenyl (0.5 mmol, used as internal standard), benzene (20 mL, used as solvent), and NBS (2.2 mmol) were put into a 100 mL, spherical-bottom flask. After replacing air in the flask with nitrogen, the flask was covered up with a gum cap and then irradiated at room temperature with a 200-W high-pressure mercury arc while the solution in the flask was being stirred magnetically. After being irradiated for a prescribed period of time, the solution was sampled with a syringe through the gum cap. The substrate and products in the solution sampled were identified by GC-MS (Shimadzu QP-5000) if necessary and quantified by GC (Shimadzu GC-17A).

Results and Discussion

Time profiles of the substrate conversions and product yields are provided as Figs. 1–4. It can be seen that in the initial step, the reactivities of the substrates in the photochemical reaction decreased in the order DHA $>>$ AN $>>$ DHP $>>$ THN.

THN, DHP, and DHA are routinely used as hydrogen donors, since their benzylic hydrogen atoms are readily abstracted. Studies show that their rates of benzylic hydrogen abstraction decrease in the order DHA $>>$ AN $>$ DHP $>$ THN.[7–10] It can be deduced from the data in Table 1 that once a benzylic hydrogen atom is abstracted, an adjacent β-hydrogen atom (as for THN) or a hydrogen atom on another benzylic carbon (as for DHP and DHA) is more readily abstracted. Therefore, the abstraction of the first benzylic hydrogen atom should be the rate-determining step. The reactivities of the compounds toward a photochemical reaction with NBS thus decrease in the order DHA $>>$ DHP $>$ THN.

The relative reactivities of alkylarenes toward benzylic hydrogen abstraction can be evaluated in terms of the stabilities of the resulting radicals. The resonance energy (RE), based on structure-resonance theory, is considered to be an important index for comparing the radical stabilities. Hence, the relative reactivities of alkylarenes toward benzylic hydrogen abstraction can be compared by the RE values of the corresponding radicals, i.e., the larger is the RE value of a radical, the more easily does benzylic hydrogen abstraction from its precursor alkylarenes proceed. When a benzylic hydrogen is abstracted, DHP, AN, and DHA are converted to 9,10-dihydrophenanthren-9-yl, acenaphthen-1-yl, and 9,10-dihydroanthracen-9-yl

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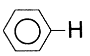
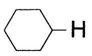
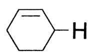
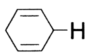
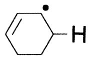
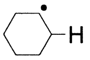
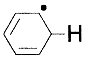
Table 1. Dissociation Energies (kJ mol^{-1}) of the C–H Bond in Some Hydrocarbons and Radicals.[11]

Structure							
BDE	431.0	395.4	342.9	306.9	198.7	167.4	100.4

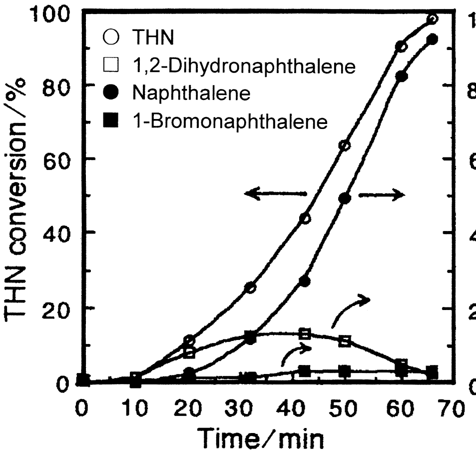


Fig. 1. Time profile of THN conversion and product yields.

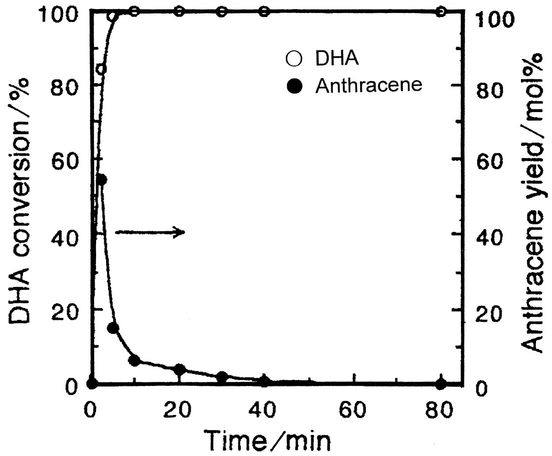


Fig. 3. Time profile of DHA conversion and anthracene yield.

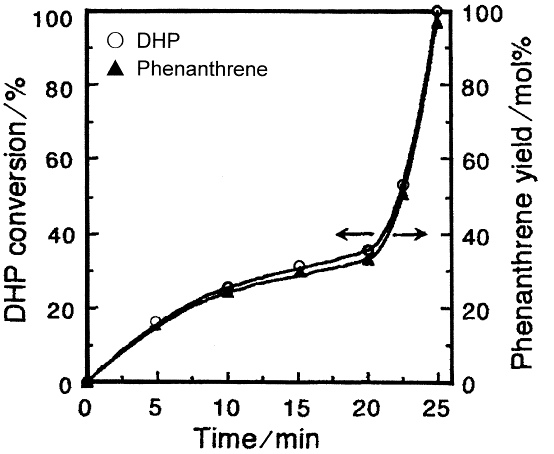


Fig. 2. Time profile of DHP conversion and phenanthrene yield.

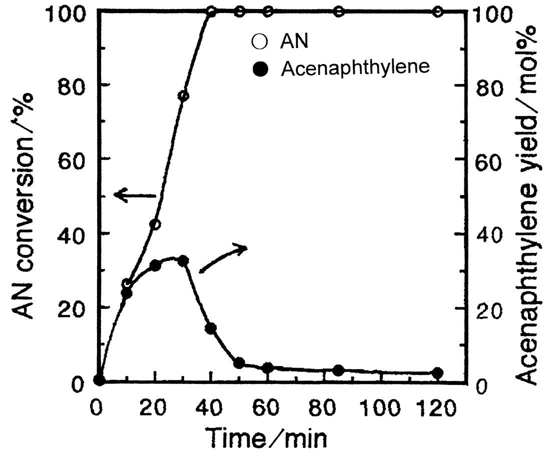


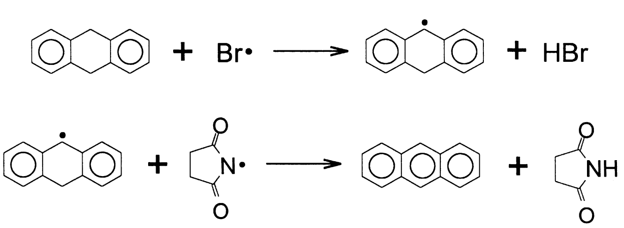
Fig. 4. Time profile of AN conversion and acenaphthylene yield.

radicals, respectively. The radicals can be structurally classified into benzyl, 1-naphthylmethyl, and diphenylmethyl radicals, respectively, the RE values (kJ mol^{-1})[12] of which increase in the order benzyl (30.6) < 1-naphthylmethyl (44.4) < diphenylmethyl (54.6). The above theoretical analysis further interprets the difference among the substrates in reactivity toward a photochemical reaction with NBS.

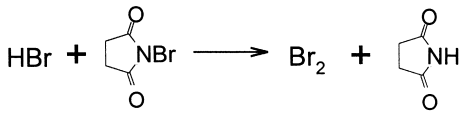
DHA is very reactive toward a photochemical reaction with NBS, the conversion being more than 80% on irradiation for only 2 min. In the initial step, DHA is mainly dehydrogenated to anthracence by bromic and *N*-succinimidyl radicals derived from NBS decomposition (Scheme 1).

The reaction of the resulting HBr with NBS produces Br_2 (Scheme 2).

The reaction of Br_2 with 9,10-dihydroanthracen-9-yl radical affords 9-bromo-9,10-dihydroanthracene (BDHA) and Br (Scheme 3).



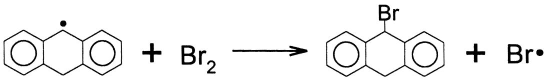
Scheme 1.



Scheme 2.

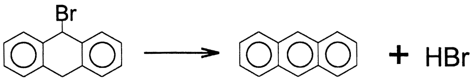
Table 2. Yields of the Products from the Photochemical Reactions of Some Hydroarenes with NBS for 2 h

Substrate	Product yield/mol%			
	Main product		By product	
THN	Naphthalene	97.1	1-Bromonaphthalene	2.9
DHP	Phenanthrene	94.5	9-Bromophenanthrene	5.5
DHA	9-Bromoanthracene	88.9	9,10-Dibromoanthracene	11.1
AN	1-Bromoacenaphthylene	68.2	1,2-Dibromoacenaphthylene	31.8



Scheme 3.

The resulting BDHA decomposes to anthracene and HBr due to its lability (Scheme 4).



Scheme 4.

Therefore, unlike mono- and dimethylarenes, BDHA, as the bromo derivative of DHA, was produced only as an intermediate. A similar reaction mechanism can be presumed for the other substrates.

After 2 h-irradiation, all of the substrates were completely converted. However, as shown in Table 2, THN and DHP were primarily converted to dehydrogenation products, whereas the main products from the photochemical reactions of DHA and AN with NBS were monobromo derivatives of polycyclic arenes with small amounts of dibromo derivatives, indicating that the photobrominations of the dehydrogenation products from DHA and AN proceeded significantly.

Taking DHA as an example, photobromination of its dehydrogenated product, anthracence, may proceed either by the addition of $Br^\bullet$ and subsequent hydrogen abstraction or by the addition of Br_2 and subsequent removal of HBr to afford 9-bromoanthracene (9-BA). Some of the resulting 9-BA may be converted to 9,10-dibromoanthracene via further photobromination followed by hydrogen abstraction or by the removal of HBr.

A similar process could be inferred for acenaphthylene, the dehydrogenation product of acenaphthene, but the photobrominations of naphthalene and phenanthrene are difficult. As quantum-chemical measures of the reactivities of unsaturated hydrocarbons toward radical, electrophilic or nucleophilic reactions, superdelocalizability (S_r) values[13] have been used to interpret the differences in the reactivity among various diarylmethanes toward hydrogenolysis[14] and hydrocracking,[15] i.e., a carbon atom in an aromatic ring with a larger S_r value accepts a hydrogen atom more readily. During bromination, an arene accepts radical $Br^\bullet$ or electrophilic Br_2, and the abilities of arenes to accept radical $Br^\bullet$ or electrophilic species Br_2 can be analogously predicted by their S_r values: anthracene (9-position: 1.314) $>>$ phenanthrene (9-position: 1.026) $>$ naphthalene (1-position: 0.994).[13] Therefore, the photochemical reactions of THN and DHP afforded only small amounts of the corresponding bromoarenes.

Dehydrogenation is an important synthetic reaction. Conventional dehydrogenation is usually conducted at high temperature and in the presence of a catalyst, and entails disadvantages, such as low product yield, difficult product separations and catalyst deactivation by carbonaceous deposit. The photochemical reaction with NBS provides an effective method for the dehydrogenation of some hydroarenes under mild conditions.

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