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CARBOCYCLIZATION BY HOMOLYTIC SUBSTITUTION (S_H' PROCESS). A NEW ROUTE TO DIHYDROINDOLE OR DIHYDROBENZOFURAN

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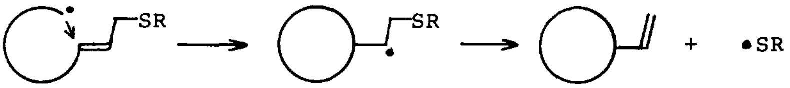
Summary; N-(4-Phenylthio-2-butenyl)-2-bromoaniline reacted with tributyltin hydride to give 3-vinyl-2,3-dihydroindole in 96% yield via hitherto unknown intramolecular S_H' process, some other examples and remarkable dilution effect on these homolytic carbocyclizations were described.

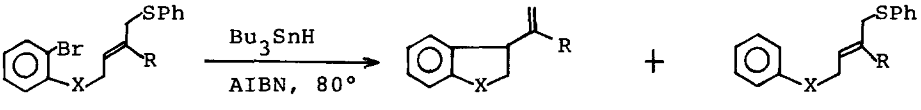
We wish to report here a synthetically useful and first example of intramolecular S_H' process free from the serious side reactions.[1] Our approach in this direction is based on the following working hypotheses;

1) An active carbon radical generated initially should be trapped immediately by intramolecular fashion to minimize the side reactions.
2) In the final step of the reaction, splitting of the relatively stable radical is desired to prevent the further second reaction.
3) The total reaction should proceed by radical chain reactions.

These three hypotheses led us to the following synthetic design.



To visualize our idea , we first examined the possibility of the homolytic cyclization of N-(4-phenylthio-2-butenyl)-2-bromoaniline (1a). Thus, 1a was allowed to react with twice the molar amount of tributyltin hydride (Bu$_3$SnH) in presence of azobisisobutyronitrile (AIBN) in refluxing benzene (0.02 M concentration of Bu$_3$SnH) under argon for 3-4 h to produce the desired 3-vinyl-2,3-dihydroindole (2a)in 96% yield (bp. 110°/30 mmHg).



1 2 3

a R=H X=NH 96%
b R=Me X=NH 56%
c R=H X=O 75%

Similarly, dihydroindole 2b or benzofuran 2c was obtained in 56% or 75% yield, respectively [2b bp. 157-159°/27 mmHg (Kugelrohr); 2c bp. 131-134°/4 mmHg (Kugelrohr)].

When the same reaction was carried out in more higher concentration of Bu_3SnH, simple reduction product 3 was also obtained in addition to 2. A characteristic aspect in this cyclization was a remarkable dilution effect on the product distribution (2 vs 3) (Table 1).

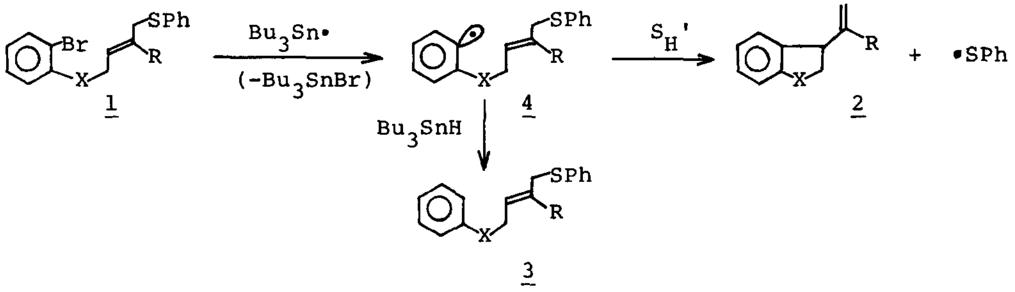
Table 1. Dilution effect on the product distribution (2a vs 3a)[2]

Concentration Bu_3SnH[a]	Yield(%)[b] 2a	3a	Product ratio 2a/3a
0.020 M	96	—	~100/0
0.062	73	6	93/7
0.250	52	28	65/35
0.500	51	44	54/46
0.062[c]	20	64	24/76

[a] The ratio of 1a and Bu_3SnH was 1:2 in all cases. [b] GPC yield.

[c] Tetrahydrofuran (THF) was used in place of benzene.

Similarly, the compound 1c gave cyclized product 2c exclusively at 0.02 M concentration of Bu_3SnH, while, at 0.50 M concentration, 2c and 3c were obtained in 40 and 48% yield, respectively.
These data suggest the following reaction scheme.



The intermediate radical 4 cyclizes to 2 with liberation of phenylthiyl radical.[3] In concentrated medium or THF, radical 4 abstracts hydrogen intermolecularly either from tin hydride or THF to afford the reduction product 3.

References and notes

1) For intermolecular S_H' reactions, see, (a) T. Migita, M. Kosugi, K. Takayama, Y. Nakagawa, Tetrahedron, 29,51(1973);M. Kosugi, K. Kurino, K. Takayama, T. Migita, J. Organomet. Chem., 56,C11(1973).(b)Y. Ueno, S. Aoki, M. Okawara, J. Am. Chem. Soc., 101,5414(1979).

2) All new compounds obtained had satisfactory spectral and analytical data.

3) Phenylthiyl radical was trapped by tin hydride to give thiostannane (Bu_3Sn-SPh).[1b]

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