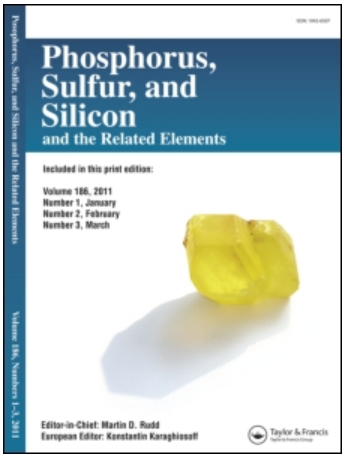

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Cyclic Amination onto Aromatic Ring via Radical Pathway with (Diacetoxyiodo)arenes

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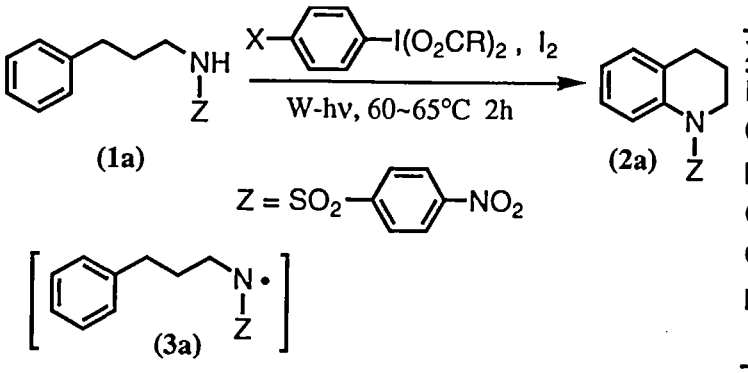
Sulfonamides of primary amine bearing an aromatic ring at γ-position were treated with (diacetoxyiodo)arene and iodine under irradiation conditions with a tungsten lamp to give the corresponding 1,2,3,4-tetrahydroquinoline derivatives in moderate to good yields.

Tetrahydroquinoline alkaloids such as virantmycin and 1,2,3,4-tetrahydro-4-quinolinones have high biological activities.[1] Therefore, extensive studies on the preparation of these skeletons have been carried out, mainly with condensation and cycloaddition methods. However, study on the radical cyclization onto the aromatic ring via an aminyl radical is extremely limited, *i.e.*, the formation of an aminium radical generated by the photolytic or ferrous ion-catalyzed decomposition of N-chloroamines in strong acidic media,[2] and the yields in these reactions are poor.

Here, as a part of our study on the reactivity of (diacetoxyiodo)arenes as radical precursors,[3] we report a good preparation method of six-membered cyclic aromatic amine from primary amine bearing an aromatic ring at γ-position, through the radical amination onto the aromatic ring. Previously, we have reported that the treatment of alcohols containing an aromatic ring at γ-position with (diacetoxyiodo)arene and iodine gave the corresponding 6-iodochroman derivatives in moderate to good yields via the corresponding oxygen-cented radicals.[4] While, when sulfonamide **1a** was treated with (diacetoxyiodo)benzene and iodine under the same conditions, the cyclized product **2a**, N-protected 1,2,3,4-tetrahydroquinoline, without iodination was obtained in good yield. The present reaction did not proceed at all, with other protecting group such as acetyl or phosphoryl group, without irradiation with a tungsten lamp (400W) or room light (fluorescent lighting, 40W), or without (diacetoxyiodo)arene. The system with bromine instead of iodine also did not give the cyclized product. Next, the substituent effect of the aromatic ring in (diacetoxyiodo)arene was studied under the same conditions as shown in Table 1. However, no big difference between the nitro and methoxy groups was observed. Moreover, the reactivity of (diacetoxyiodo)benzene and

TABLE 1

Substituent effect of (diacetoxyiodo)arenes.



X	R	Yield / %
NO_2	CH_3	71
Cl		66
H		67
CH_3		65
CH_3O		61
H	CF_3	0
	CH_2CH_3	64

(dipropionoxyiodo)benzene was same, though [bis(trifluoroacetoxyiodo)]benzene did not give the cyclized product. Probably, the formation of sulfonamidyl radical **3a** is not the rate-determining step. Then, the other sulfonamides were treated with (diacetoxyiodo)benzene and iodine under the same conditions. The sulfonamides derived from primary and secondary alkyl branched amines were converted to the corresponding sulfonamides of the cyclic aromatic amines in moderate yields. Thus, the present method is very useful for the preparation of 1,2,3,4-tetrahydroquinoline derivatives, because the reaction proceeds by a simple operation, and under mild and neutral conditions.

REFERENES

1. S. Omura, A. Nakagawa, H. Hashimoto, R. Oiwa, Y. Iwai, A. Hirano, N. Shibukawa, and Y. Kojima, *J. Antibiotics*, **33**, 1395 (1980); A. Nakagawa, Y. Iwai, H. Hashimoto, N. Miyazaki, R. Oiwa, Y. Takahashi, A. Hirano, N. Shibukawa, Y. Kojima, and S. Omura, *ibid.*, **34**, 1408 (1981); A. B. Daruwala, J. E. Gearien, W. J. Dunn, P. S. Benoit, and L. Bauer, *J. Med. Chem.*, **17**, 819 (1974); M. S. Atwal, L. Bauer, S. N. Dixit, J. E. Gearien, M. Megahy, R. Morris, and C. Pokorny, *ibid.*, **12**, 994 (1969).
2. Amination onto aromatic ring via aminyl radical: F. Minisci and R. Galli, *Tetrahedron Lett.*, 2531 (1966); S. A. Glover, A. Goosen, and H. A. H. Laue, *J. Chem. Soc., Perkin 1*, 1647 (1973); Amination onto aromatic ring via iminyl radical: A. R. Forrester, M. Gill, and R. H. Thomson, *J. Chem. Soc., Chem. Commun.*, 677 (1976); A. R. Forrester, M. Gill, J. S. Sadd, and R. H. Thomson, *ibid.*, 291 (1975); Hofmann-Löffler reaction: E. J. Corey and W. R. Hertler, *J. Am. Chem. Soc.*, **82**, 1657 (1860); W. R. Hertler and E. J. Corey, *J. Org. Chem.*, **24**, 572 (1959); P. Buchschacher, J. Kalvoda, D. Arigoni, and O. Jeger, *J. Am. Chem. Soc.*, **80**, 2905 (1958).
3. H. Togo, M. Aoki, and M. Yokoyama, *Tetrahedron*, **49**, 8241 (1993); H. Togo, R. Taguchi, K. Yamaguchi, and M. Yokoyama, *J. Chem. Soc., Perkin 1*, 2135 (1995); H. Togo, T. Muraki, and M. Yokoyama, *Synthesis*, 155 (1995); idem, *Tetrahedron Lett.*, **36**, 7089 (1995).
4. T. Muraki, H. Togo, and Y. Masataka, *Tetrahedron Lett.*, **37**, 2441 (1996).