Ipso Selectivity in the Reductive Iodonio-Claisen Rearrangement of Allenyl(*p*-methoxyaryl)iodinanes

Masahito Ochiai,* Takao Ito and Yukio Masaki
Gifu Pharmaceutical University, 5-6-1 Mitahora Higashi, Gifu 502, Japan

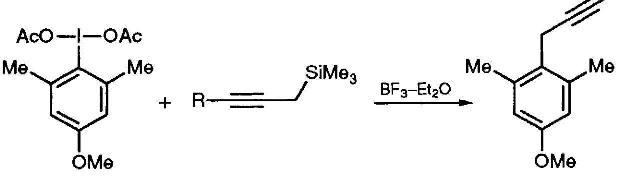
Allenyl(aryl)iodinanes, generated from *p*-methoxy(diacetoxyiodo)arenes by the reaction with propyn-2-yl(trimethyl)silanes in the presence of BF_3–Et_2O in dichloromethane, undergo reductive *ipso* iodonio-Claisen rearrangement selectively at −20 °C yielding *ipso*-substituted propynylarenes.

Claisen rearrangements involving oxygen, nitrogen, sulfur and phosphorus atoms of groups 15 and 16 have been well precedented.[1] Recently, we reported Claisen rearrangement involving an iodine atom of group 17 in which allenyl(aryl)iodinanes, generated by S_E2' reaction of aryliodinanes with propynylsilanes in the presence of BF_3–Et_2O, undergo reductive iodonio-Claisen rearrangement at −20 °C yielding *ortho*-propynyliodoarenes in good yield.[2] The lack of the crossover products in the reaction argues for intramolecularity of the rearrangement.

When both *ortho* positions of aryliodinanes were occupied with alkyl substituents, the reductive iodonio-Claisen rearrangement of the allenyl(aryl)iodinanes affords *meta* substitution products although a free *para* position is available, which is in marked contrast to the results of Claisen rearrangement of *ortho*-disubstituted phenyl allyl ethers.[3] We report herein *ipso* iodonio-Claisen rearrangement of allenyl(aryl)iodinanes generated from *p*-methoxy(diacetoxyiodo)arenes yielding *ipso*-propynylarenes.

Reaction of 2,6-dimethyl-4-methoxy(diacetoxyiodo)benzene **1**† with 1.2 equiv. of 1,3-bis(trimethylsilyl)propyne **2b** in the presence of BF_3–Et_2O afforded the *ipso*-substituted alkyne **3b** selectively in 25% yield, along with the formation of 2,6-dimethyl-4-methoxyiodobenzene (34%). With the use of 2 equiv. of **2b**, the yield of **3b** was much improved: thus, treatment of **1** with 2 equiv. of **2b** in the presence of BF_3–Et_2O (1 equiv.) and $MgSO_4$ in dichloromethane at −20 °C for 1 h gave a 67% yield of **3b**. In these reactions, formation of the *meta*-rearranged product, 3-(2,4-dimethyl-3-iodo-6-methoxyphenyl)-1-(trimethylsilyl)prop-1-yne **19** (R = $SiMe_3$), was detected but in only less than 0.5% yield.

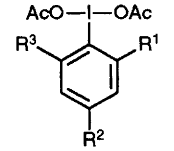
The results of the *ipso* propynylation are summarized in Table 1. Again, the use of two- or five-fold excess of **2c** gave a good yield of the *ipso* product **3c** (compare runs 4–6). The reactions of Table 1 showed the exclusive formation of the



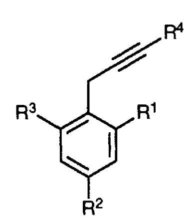
1 **2a–d** **3a–d**

a; R = H, **b**; R = $SiMe_3$, **c**; R = cyclo-C_6H_{11}, **d**; R = $CH(OH)CHMe_2$

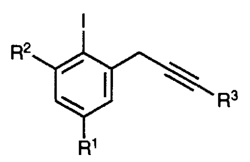
Scheme 1



4; R^1 = OMe, R^2 = R^3 = H
5; R^1 = R^3 = H, R^2 = OMe
6; R^1 = R^2 = R^3 = Bu^t



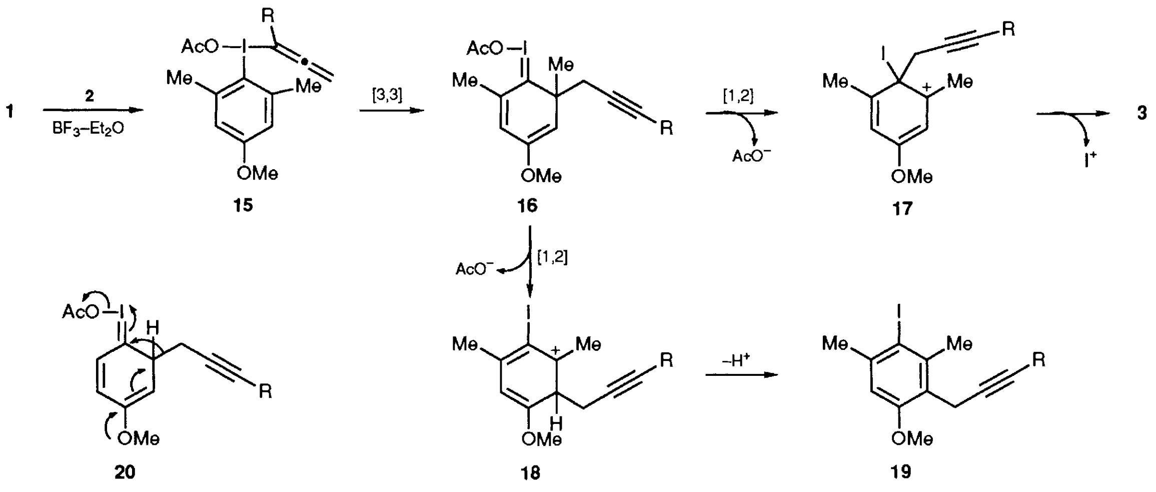
7; R^1 = OMe, R^2 = R^3 = R^4 = H
8; R^1 = R^3 = R^4 = H, R^2 = OMe
9; R^1 = R^3 = H, R^2 = OMe, R^4 = $SiMe_3$
10; R^1 = R^2 = R^3 = Bu^t, R^4 = $SiMe_3$



11; R^1 = R^3 = H, R^2 = OMe
12; R^1 = OMe, R^2 = R^3 = H
13; R^1 = OMe, R^2 = H, R^3 = $SiMe_3$
14; R^1 = R^2 = Bu^t, R^3 = $SiMe_3$

---

† The iodinane **1** was prepared by sodium perborate oxidation of 2,6-dimethyl-4-methoxyiodobenzene according to the method developed by McKillop and Kemp.[4] *Selected spectroscopic data* for **1**: m.p. 153–154 °C (decomp.); IR ν_{max}/cm^{-1} ($CHCl_3$) 3015, 1640, 1585, 1465, 1360, 1320, 1280, 1160, 1070, 1005, 920 and 860; ^1H NMR (270 MHz; $CDCl_3$) δ 1.97 (6H, s), 2.73 (6H, s), 3.83 (3H, s), and 6.79 (2H, s).



Scheme 2

ipso-substituted alkyne **3** and, in all cases, **3** was obtained in more than 98% selectively.

Competition between the *ipso* substitution and the normal *ortho* rearrangement of allenyliodinanes was observed in the reaction of 2-methoxy- **4** or 4-methoxy(diacetoxyiodo)benzene **5**. Reaction of 2-methoxyiodinane **4** with **2a** (2 equiv.) gave a 30 : 70 mixture of the *ipso* alkyne **7** and the *ortho* alkyne **11** (63%). In the reaction of 4-methoxyiodinane **5**, however, the *ipso* substitution became the major reaction course and a 55 : 45 mixture of **8** and **12** was obtained by the reaction with **2a** in 75% yield. Similarly, the reaction of **5** with **2b** afforded a 55 : 45 mixture of **9** and **13** (62%). Furthermore, the reaction of 2,4,6-tri-*tert*-butyl(diacetoxyiodo)benzene **6**[5] with **2b** gave a 1 : 1 mixture of **10** and **14** (67%).

The exclusive *ipso* substitution of **1** involves an intermediate formation of the allenyl(aryl)iodinane **15**‡ and will be rationalized in terms of a facile 1,2-rearrangement of the propynyl group of **16**, generated by [3,3]-sigmatropic rearrangement of **15** (Scheme 2). Since the 1,2-rearrangement of **16** involves an energetically preferable reduction of trivalent iodine to univalent iodine, it should be a low energy process. Of the two possible 1,2-rearrangement pathways of the propynyl group of **16** to *ipso* and *meta* sites, the transition state of the former process leading to the cation **17** will be more efficiently stabilized than that of the latter process leading to the cation **18** by the π-donor *p*-methoxy group.[6] Subsequent deiodination of **17** will afford the *ipso*-substituted product **3**.[7]

Thus, the presence of a *p*-methoxy group of aryliodinanes will be essential to the success for the regioselective *ipso* propynylation. This was further supported by the observation that the reaction of **5** affords large amounts of the *ipso* products **8** and **9**, in which the rate of the 1,2-migration of propynyl groups to the *ipso* site, assisted by the *p*-methoxy group as shown in **20**, is larger than that of the deprotonation of **20** leading to the normal *ortho* products **12** and **13**, whereas the reaction of (diacetoxyiodo)benzene gives *o*-propyn-2-yliodoarenes exclusively.[2]

Table 1 Reductive *ipso* propynylation of **1** by the reaction with propynylsilanes **2**

Run	**2** (Equiv.)	**3** [Yield (%)][a]
1	**2a** (2)	**3a** (57)
2	**2b** (1.2)	**3b** (25)
3	**2b** (2)	**3b** (67)
4	**2c** (1.2)	**3c** (15)
5	**2c** (2)	**3c** (51)
6	**2c** (5)	**3c** (61)
7	**2d** (3)	**3d** (34)

[a] Isolated yield.

This work was supported in part by the Grant-in-Aid for Scientific Research on Priority Area of Organic Unusual Valency No. 02247101 from the Ministry of Education, Science and Culture, Japan.

Received, 16th September 1991; Com. 1/04785J

References

1 S. J. Rhoads, in *Molecular Rearrangements*, ed. P. de Mayo, Interscience, New York, 1963, vol. 1, p. 655; S. J. Rhoads and N. R. Raulins, *Org. React. (NY)*, 1975, **22**, 1; D. S. Tarbell, *Org. React. (NY)*, 1944, **2**, 2; R. P. Lutz, *Chem. Rev.*, 1984, **84**, 205; F. E. Ziegler, *Chem. Rev.*, 1988, **88**, 1423; D. I. Loewus, *J. Am. Chem. Soc.*, 1981, **103**, 2292.

2 M. Ochiai, T. Ito, Y. Takaoka and Y. Masaki, *J. Am. Chem. Soc.*, 1991, **113**, 1319.

3 D. S. Tarbell and J. F. Kincaid, *J. Am. Chem. Soc.*, 1940, **62**, 728; I. A. Pearl, *J. Am. Chem. Soc.*, 1948, **70**, 1746; D. Y. Curtin and H. W. Johnson, *J. Am. Chem. Soc.*, 1956, **78**, 2611; M. Schmid, H.-J. Hansen and H. Schmid, *Helv. Chim. Acta*, 1973, **56**, 105; H. Katayama, M. Ohkoshi and K. Kaneko, *Chem. Pharm. Bull.*, 1984, **32**, 1770.

4 A. McKillop and D. Kemp, *Tetrahedron*, 1989, **45**, 3299.

5 M. Ochiai, K. Oshima, T. Ito, Y. Masaki and M. Shiro, *Tetrahedron Lett.*, 1991, **32**, 1327.

6 K. Kaneko, H. Katayama, Y. Saito, N. Fujita and A. Kato, *J. Chem. Soc., Chem. Commun.*, 1986, 1308; L. I. Kruse and J. K. Cha, *J. Chem. Soc., Chem. Commun.*, 1982, 1333.

7 C. D. Hurd and C. N. Webb, *J. Am. Chem. Soc.*, 1936, **58**, 2190; D. S. Tarbell and J. W. Wilson, *J. Am. Chem. Soc.*, 1942, **64**, 1066.

---

‡ J. R. Norton (Colorado State University) has established the intermediacy of the allenyl(aryl)iodinanes in the reductive *ortho* propynylation of aryliodinanes by variable temperature ^{13}C NMR spectroscopy experiments (personal communication).