CHEMISTRY LETTERS, pp. 457-458, 1989.

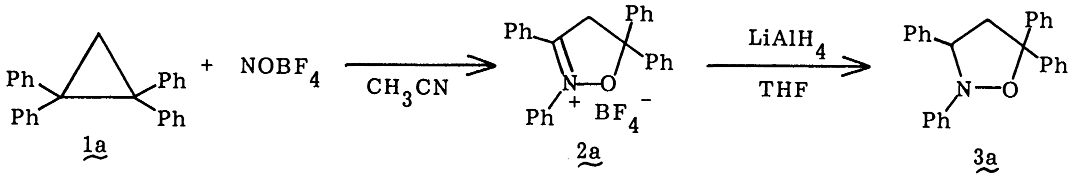
Formation of 2-Substituted 2-Isoxazolinium Salts by the Reaction of 1,1,2,2-Tetrasubstituted Cyclopropanes with $NOBF_4$

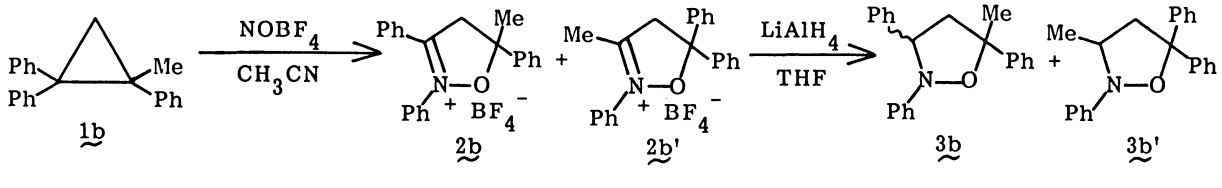
Nobuyuki ICHINOSE, Kazuhiko MIZUNO,* and Yoshio OTSUJI*
Department of Applied Chemistry, College of Engineering,
University of Osaka Prefecture, Sakai, Osaka 591

The reaction of 1,1,2,2-tetraphenyl- and 1-methyl-1,2,2-triphenylcyclopropanes with $NOBF_4$ gave 2-phenyl-2-isoxazolinium tetrafluoroborates via the phenyl migration from 3-phenyl-2-isoxazolidinium or 1-isoxazolinium intermediates.

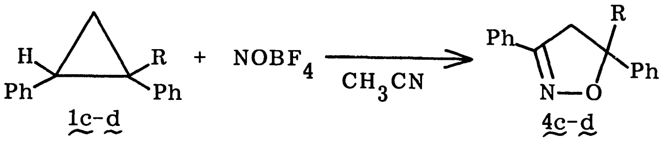
Previously, we have reported that the reaction of 1,2-diarylcyclopropanes with $NOBF_4$ affords 3,5-diaryl-2-isoxazolines via the NO insertion into the cyclopropane ring.[1,2] However, the examination of chemical behavior of 1,1,2,2-tetrasubstituted cyclopropanes toward $NOBF_4$ led to the finding of a new migration of phenyl group from carbon to nitrogen. We now report that the reaction of 1,1,2,2-tetraphenyl- and 1-methyl-1,2,2-triphenyl-cyclopropanes (1a, 1b) with $NOBF_4$ gives 2-phenyl-2-isoxazolinium salts via the phenyl migration from 3-phenyl-2-isoxazolidinium or 1-isoxazolinium intermediates.

To an acetonitrile solution (20 cm^3) of 1a (0.5 mmol) was added 1.2 equiv. of $NOBF_4$ under argon atmosphere at room temperature. The solution immediately turned dark purple and then gradually yellow in 20-30 min. The solvent was evaporated under reduced pressure. The residue was triturated with THF and filtered to give 2,3,5,5-tetraphenyl-2-isoxazolinium tetrafluoroborate 2a in an 89% yield as yellow solid. The structure was determined by its spectral properties and elemental analysis,[3] and also by its chemical conversions. The reduction of 2a with $LiAlH_4$ in THF gave 2,3,5,5-tetraphenylisoxazolane 3a in a quantitative yield.[4,5] When 1b was treated with $NOBF_4$ in a similar manner, two isomeric 2-isoxazolinium salts (2b, 2b') were obtained in a 5 : 3 ratio in almost quantitative yield. They gave a mixture of two isomeric isoxazolane derivatives (3b, 3b') upon treatment with $LiAlH_4$.





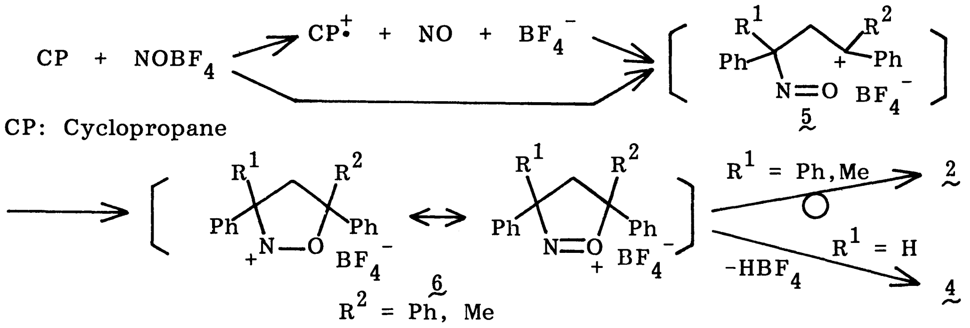
However, the reaction of 1,1,2-triphenylcyclopropane (**1c**) and 1-methyl-1,2-diphenylcyclopropane (**1d**) with $NOBF_4$ under similar conditions gave the isoxazoline derivatives **4c** and **4d** in 72% and 84% yields, respectively.



c: R = Ph

d: R = Me

A plausible mechanism for these reactions is shown in Scheme 1. The first step is a one-electron transfer from cyclopropanes (CP) to $NOBF_4$ to give the radical cations $CP^{+\cdot}$ and NO.[2)] The attack of NO on $CP^{+\cdot}$ gives 2-isoxazolidinium or 1-isoxazolinium intermediate **6** via **5**. However, the possibility that the direct electrophilic attack of NO^+ toward the cyclopropane ring produces **5** and **6** can not be ruled out at present. When no hydrogen is present at the the C-3 position of **6**, the phenyl group at that position preferentially migrates to the cationic nitrogen to give 2-phenyl-2-isoxazolinium salts **2**. On the other hand, when hydrogen is present at the C-3 position, deprotonation from **6** occurs to afford 2-isoxazolines **4**.



Scheme 1.

This work was partially supported by a Grant-in-Aid for Scientific Research on Priority Areas from the Ministry of Education, Science and Culture of Japan (No. 63607527).

References

1) N. Ichinose, K. Mizuno, T. Tamai, and Y. Otsuji, Chem. Lett., 1988, 233.

2) N. Ichinose, K. Mizuno, K. Yoshida, and Y. Otsuji, Chem. Lett., 1988, 723.

3) Spectral data for **2a**: decomp 136-139 °C; ^1H NMR ($CDCl_3$) δ 5.15 (s, 2H), 7.30-7.80 (m, 20H); ^{13}C NMR ($CDCl_3$) δ 50.8 (t), 95.4 (s), 122.5 (s), 126.0 (d), 126.9 (d), 129.2 (d), 129.8 (d), 129.9 (d), 131.0 (d), 131.1 (d), 133.7 (d), 133.9 (d), 136.0 (d), 137.8 (s), 166.0 (s); IR (KBr) 3000, 1580, 1430, 1360, 1180, 1020, 870, 830, 750, 670 cm^{-1}; MS (20 eV) m/z 375 (M^+-HBF_4). Found: C, 69.58; H, 4.63; N, 2.99%. Calcd for $C_{27}H_{22}NOBF_4$: C, 70.00; H, 4.78; N, 3.02%.

4) A. Cerri, C. De Micheli, and R. Gandolfi, Synthesis, 1974, 710; G. Bianchi, C. De Micheli, and R. Gandolfi, J. Chem. Soc., Perkin Trans. 1, 1976, 1518.

5) I. Bruning, R. Grashey, H. Hauck, R. Huisgen, and H. Seidl, Org. Synth., Coll. Vol. 5, 1124 (1973).

(Received December 19, 1988)