

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

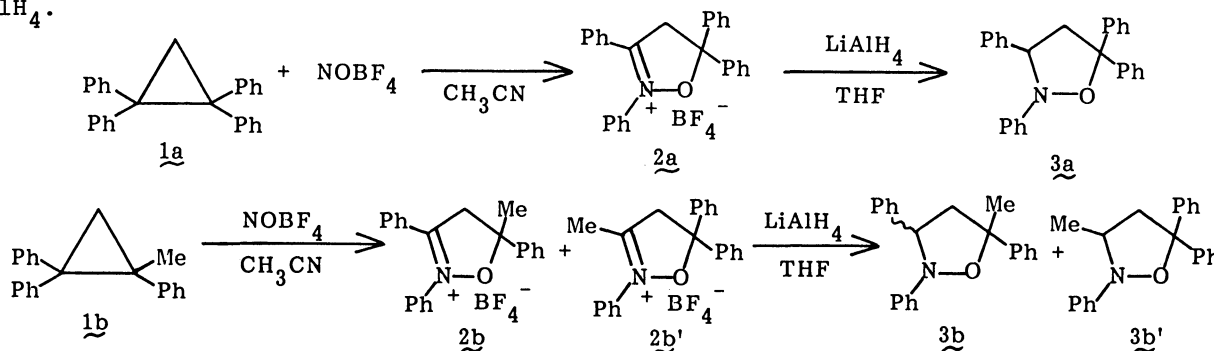
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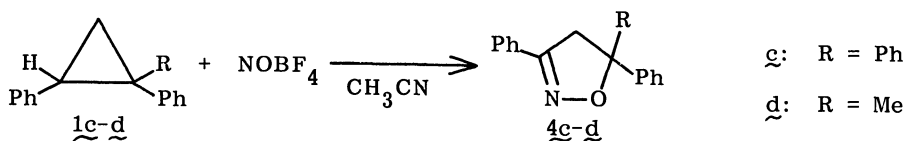
The reaction of 1,1,2,2-tetraphenyl- and 1-methyl-1,2,2-triphenylcyclopropanes with NOBF_4 gave 2-phenyl-2-isloxazolinium tetrafluoroborates via the phenyl migration from 3-phenyl-2-isloxazolidinium or 1-isloxazolinium intermediates.

Previously, we have reported that the reaction of 1,2-diarylcyclopropanes with NOBF_4 affords 3,5-diaryl-2-isloxazolines 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-triphenylcyclopropanes (1a, 1b) with NOBF_4 gives 2-phenyl-2-isloxazolinium salts via the phenyl migration from 3-phenyl-2-isloxazolidinium or 1-isloxazolinium intermediates.

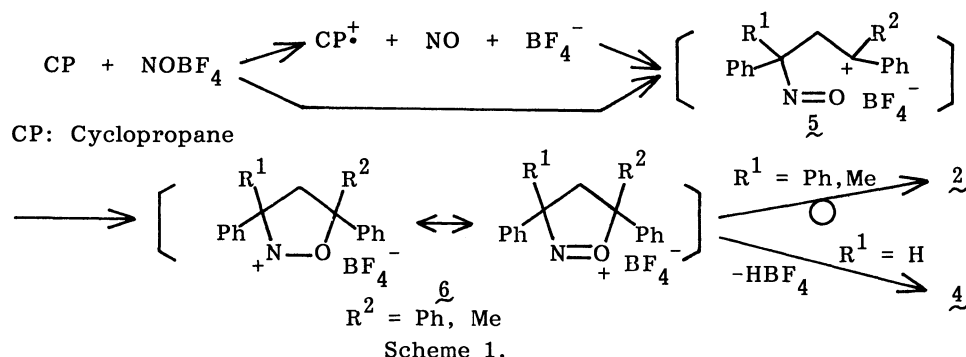
To an acetonitrile solution (20 cm³) of 1a (0.5 mmol) was added 1.2 equiv. of NOBF_4 under argon atmosphere at room temperature. The solution immediately turned dark purple and then gradually yellow in 20-30 min. The solvent was evaporated under reduced pressure. The residue was triturated with THF and filtered to give 2,3,5,5-tetraphenyl-2-isloxazolinium 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-tetraphenylisoxazoline 3a in a quantitative yield.^{4,5)} When 1b was treated with NOBF_4 in a similar manner, two isomeric 2-isloxazolinium salts (2b, 2b') were obtained in a 5 : 3 ratio in almost quantitative yield. They gave a mixture of two isomeric isoxazoline 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.



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 $\text{CP}^{\cdot+}$ and $\text{NO}^{\cdot}$.²⁾ The attack of NO on $\text{CP}^{\cdot+}$ 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.



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

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- 3) Spectral data for 2a: decomp 136-139 °C; ¹H NMR (CDCl_3) δ 5.15 (s, 2H), 7.30-7.80 (m, 20H); ¹³C 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 ($\text{M}^+ - \text{HBF}_4$). Found: C, 69.58; H, 4.63; N, 2.99%. Calcd for $\text{C}_{27}\text{H}_{22}\text{NOBF}_4$: C, 70.00; H, 4.78; N, 3.02%.
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(Received December 19, 1988)