

A convenient preparative method for the synthesis of 2-cyclopropyloxirane and 2-cyclopropyl-2-methyloxirane

V. A. Dokichev,^{a*} I. O. Maidanova,^a Yu. V. Tomilov,^{b*} G. A. Tolstikov,^a and O. M. Nefedov^b

^aInstitute of Organic Chemistry, Ufa Research Center of the Russian Academy of Sciences,
71 prosp. Oktyabrya, 450054 Ufa, Russian Federation.

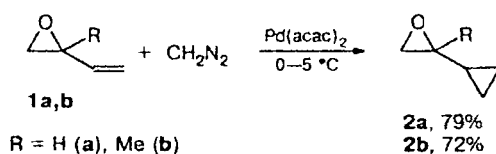
Fax: +7 (347 2) 35 6066. E-mail: root@chemorg.ufanet.ru

^bN. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,
47 Leninsky prosp., 117913 Moscow, Russian Federation.

Fax: +7 (095) 135 6390. E-mail: tom@ioc.ac.ru

Cyclopropyloxiranes are highly reactive compounds, which can serve as promising intermediates in the synthesis of heterocyclic compounds^{1,2} and isoprenoids with the *E*-configuration of the double bond.³ The methods for their synthesis used most frequently are based on the oxidation of vinylcyclopropanes with potassium permanganate⁴ and methylenation of cyclopropyl ketones with dimethylsulfonium methylide.³ In addition, it is known⁵ that the reaction of diazomethane with vinyl-oxirane in the presence of catalytic quantities of CuI, CuCl₂, or [C₃H₅PdCl]₂ also affords cyclopropyloxirane, but as a component of a difficultly separable mixture with 5,6-dihydro-2*H*-pyran and 3-vinylloxetane.

We developed a convenient method for the synthesis of 2-cyclopropyloxirane (**2a**) and 2-cyclopropyl-2-methyloxirane (**2b**), based on the catalytic cyclopropanation of vinyloxiranes (**1a,b**) with diazomethane in the presence of Pd(acac)₂.



Thus the Pd(acac)₂-catalyzed reaction of **1a** with a 2.5-fold molar excess of CH₂N₂ at 0–5 °C in diethyl ether gives cyclopropyloxirane (**2a**), and that of **1b** affords 2-cyclopropyl-2-methyloxirane (**2b**) in 72–79% yields. Since almost no by-products are formed, the resulting cyclopropyloxiranes are readily separated from the unreacted vinyloxirane by effective rectification. The cyclopropyloxiranes **2** thus obtained were identified by

comparing their physicochemical characteristics with those reported in the literature.⁶

When Pd(OAc)₂, (PhCN)₂PdCl₂, Cu(OTf)₂, or Rh₂(CF₃COO)₂ are used as catalysts, the yields of oxiranes **2** decrease, and the mixture of reaction products contains predominantly compounds resulting from intramolecular isomerization of oxiranes **1**, namely, *trans*-but-2-enal and 2-methylbut-2-enal.⁷ Thus, unlike Pd(OAc)₂ and (PhCN)₂PdCl₂, which are normally used for cyclopropanation of olefins with diazomethane,⁸ Pd(acac)₂ not only acts a "softer" catalyst of deazotation of CH₂N₂ but also ensures a virtually complete retention of the oxirane ring in the initial and final reaction products, which accounts for its successful use for the synthesis of cyclopropyloxiranes **2**.

References

1. J. A. Donnelly, J. Y. Hoey, S. O. Braien, and I. O'Ciardy, *J. Chem. Soc., Perkin Trans. I*, 1973, 2030.
2. J. A. Donnelly and J. Y. Hoey, *J. Chem. Soc., Perkin Trans. I*, 1975, 2364.
3. H. Nakamura, H. Yamamoto, and H. Nozaki, *Tetrahedron Lett.*, 1973, 111.
4. W. Kirmse and B. Kornrumpf, *Angew. Chem., Int. Edit.*, 1969, 8, 75.
5. M. Kapps and W. Kirmse, *Angew. Chem., Int. Edit.*, 1969, 8, 75.
6. M. Kim and Y. J. Kim, *J. Chem. Soc., Chem. Commun.*, 1991, 326.
7. M. Suzuki, Y. Oda, and R. Noyori, *J. Am. Chem. Soc.*, 1979, 101, 1623.
8. Yu. V. Tomilov, V. A. Dokichev, U. M. Dzhemilev, and O. M. Nefedov, *Usp. Khim.*, 1993, 62, 847 [*Russ. Chem. Rev.*, 1993, 62, 799 (Engl. Transl.)].

Received January 30, 1998