PERFLUOROPROP-2-ENYLSILVER

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Perfluoro-olefins combine with silver(I) fluoride in acetonitrile at room temperature to yield perfluoroalkylsilver compounds [e.g., CF_3 . $CF:CF_2 + AgF \longrightarrow (CF_3)_2CFAg$], which are much more stable thermally than silver alkyls and can be isolated as solvates [e.g., $(CF_3)_2CFAg$.MeCN].¹ Application of this nucleophilic addition reaction to perfluorobut-2-yne yields <u>trans</u>-perfluoro-(1-methylpropenyl)silver, $CF_3.CF:C(CF_3)Ag$, a white solid isolable by sublimation at $150^{\circ}/0.05$ mmHg.²

The lower homologue, perfluoroprop-2-enylsilver, has now been synthesised from tetrafluoroallene and isolated in 66% yield by vacuum sublimation at $160-180^{\circ}$.

CF₂:C:CF₂ + AgF _acetonitrile CF₃.C(Ag):CF₂

The structure of perfluoroprop-2-enylsilver was established by elemental analysis and i.r. (C:C str. 6.12μ m; mull) and 19 F n.m.r. spectroscopy (three band systems of relative intensities 3:1:1 at -30.1, -28.0, and -17.6 p.p.m. relative to external trifluoroacetic acid), and by the conversions shown in the annexed scheme. The orientation of addition of silver fluoride to one of the π -systems in tetrafluoroallene is consistent with a nucleophilic addition mechanism.³

$$CF_{3} \cdot C(Ag): CF_{2} \xrightarrow{H_{2}^{0}, 20^{\circ}} CF_{3} \cdot CH: CF_{2} (99\%)$$

$$\xrightarrow{Br_{2}, 20^{\circ}} CF_{3} \cdot CH: CF_{2} (88\%)$$

$$CF_{3} \cdot C(Ag): CF_{2} \xrightarrow{300-350^{\circ}} CF_{2}: C(CF_{3}) \cdot C(CF_{3}): CF_{2} (56\%)$$

$$\xrightarrow{MeI, 20^{\circ}} CF_{3} \cdot CMe: CF_{2} (95\%)$$

$$\xrightarrow{MeI, 20^{\circ}} CF_{3} \cdot CMe: CF_{2} (95\%)$$

$$\xrightarrow{Me_{3}SIC1, 20^{\circ}} CF_{3} \cdot C(SIMe_{3}): CF_{2} (99\%)$$

The products shown in the scheme were characterised by elemental analysis and spectroscopic methods (i.r., n.m.r., and mass).

References

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