Reaction of Trifluoromethanesulphonyl Chloride with Alkenes catalysed by a Ruthenium(II) Complex

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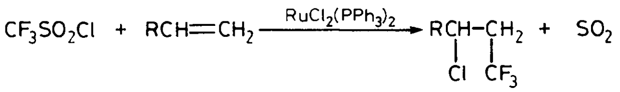
The reaction of trifluoromethanesulphonyl chloride with alkenes in the presence of dichlorotris(triphenylphosphine)ruthenium(II) gives 1 : 1 adducts with extrusion of sulphur dioxide.

Recently, fluoroalkylated compounds have received much attention in medicine and material chemistry.[1] However, it is difficult to introduce a fluoroalkyl group into alkenes or aromatic compounds by ordinary alkylating methods *via* carbocationic intermediate because of the high electron-withdrawing character of fluorine. New methods of fluoroalkylation have been developed: *e.g.* fluoroalkylation of alkenes or aromatic compounds by perfluoroalkanoyl peroxide,[2] metal complexes of fluoroalkyl halides,[3] perfluorocarboxylic acids mediated by xenon difluoride,[4] fluoroalkyl halide with metal complex catalysts,[5] and electrochemical method with trifluoroacetic acid[6] have been used. However, these methods do not give satisfactory yields of the products, and often suffer from side reactions. We have already reported the reaction of trichloromethanesulphonyl chloride with alkenes in the presence of ruthenium(II) complex to give 1 : 1 adducts in good yields with evolution of sulphur dioxide.[7] During our systematic investigations on the reactions of sulphonyl chlorides with alkenes in the presence of a catalytic amount of a ruthenium(II) complex, we found that the reaction of trifluoromethanesulphonyl chloride (**1**) with alkenes in the presence of a ruthenium(II) complex proceeded smoothly under mild conditions to afford the corresponding 1 : 1 adducts in high yields with extrusion of sulphur dioxide.



$$CF_3SO_2Cl + RCH{=}CH_2 \xrightarrow{RuCl_2(PPh_3)_2} \underset{Cl}{RCH}-\underset{CF_3}{CH_2} + SO_2$$

(**1**) (**2**) (**3**)

Typically, a solution containing (**1**) (2.0 mmol), styrene (**2a**) (5.0 mmol), and dichlorotris(triphenylphosphine)ruthenium(II) (0.02 mmol) in 4.0 ml of benzene was degassed and heated at 120 °C in a sealed tube for 16 h. Flash column chromatography on Florisil using benzene and then the gel permeation chromatography using chloroform gave 3-chloro-1,1,1-trifluoro-3-phenylpropane (**3a**) in 84% yield. Other metal catalysts,

$$CF_3SO_2Cl + Ru^{II} \rightarrow [CF_3SO_2Cl]^{\cdot -} + Ru^{III}$$
$$[CF_3SO_2Cl]^{\cdot -} \rightarrow CF_3SO_2\cdot + Cl^-$$
$$Ru^{III} + Cl^- \rightarrow Ru^{III}\text{–}Cl$$
$$CF_3SO_2\cdot \rightarrow \cdot CF_3 + SO_2$$
$$\cdot CF_3 + RCH{=}CH_2 \rightarrow R\dot{C}HCH_2CF_3$$
$$R\dot{C}HCH_2CF_3 + Ru^{III}\text{–}Cl \rightarrow RCHClCH_2CF_3 + Ru^{II}$$

Scheme 1

Table 1. The reaction of (**1**) with alkenes in the presence of $Ru(PPh_3)_3Cl_2$.

R	(**2**), (mmol)	Reaction time /h	Product, % Yield[a]
(**2a**) Ph	5	16	(**3a**), 84
(**2b**) *p*-ClC_6H_4	4	16	(**3b**), 74
(**2c**) *m*-$NO_2C_6H_4$	4	16	(**3c**), 79
(**2d**) *p*-MeC_6H_4	10	16	(**3d**), 46[b]
(**2e**) $Me(CH_2)_5$	4	14	(**3e**), 66
(**2f**) $Me(CH_2)_7$	4	14	(**3f**), 72
(**2g**) $Me(CH_2)_9$	4	15	(**3g**), 70
(**2h**) EtO_2C	10	14	(**3h**), 70
(**2i**) $PhCO_2$	6	24	(**3i**), 49

[a] The yields were determined by g.c. [b] $CF_3CH{=}CHC_6H_4Me$-*p* was obtained in 16% yield together with (**3d**).

e.g. $Pd(OAc)_2$, $Rh(PPh_3)_3Cl$, $Pd(PPh_3)_4$, $Ni(PPh_3)_2Cl_2$, or $RuCl_3$, were much less effective, (**3a**) being obtained in very low yield from (**1**) and (**2a**). Results for the reaction of (**1**) with other alkenes (styrene derivatives, acyclic alkenes, ethyl acrylate, and vinyl benzoate) using the ruthenium(II) catalyst are summarized in Table 1.

The reaction of (**1**) with styrenes possessing an electron-withdrawing group (*p*-Cl, *m*-NO_2) on the aromatic nucleus afforded the 1 : 1 adducts (**3**) in good yields, as did the acyclic alkenes (**2e**—**g**) and the alkenes (**2h**) and (**2i**) containing an electron-withdrawing group. Interestingly, the propene $CF_3CH{=}CHC_6H_4Me$-*p* was obtained in 16% yield together with the propane (**3d**) (46%) in the reaction of (**1**) with (**2d**). The product (**4d**) seems to be produced from (**3d**) formed initially, by the dehydrochlorination catalysed by the ruthenium(II) complex. Ruthenium(II) catalysed dehydrochlorination was found in the reaction of (**2d**) with β-styrylsulphonyl chloride.[8]

The reaction may be accounted for by Scheme 1 involving a redox transfer mechanism as we have proposed in the reaction of trichloromethanesulphonyl chloride with alkenes catalysed by the ruthenium(II) complex.[7]

The ruthenium(II) catalysed reaction of (**1**) is useful in that trifluoromethylation can be performed with alkenes containing electron-donating and electron-withdrawing groups. The adducts (**3**) can be readily converted to the corresponding alkenes by dehydrochlorination on treatment with base. For example, reaction of (**3a**) with potassium hydroxide at 50 °C afforded 3,3,3-trifluoro-1-phenylpropane in 62% yield. The reaction of (**1**) with alkenes should be useful synthetically for introducing a trifluoromethyl group on alkenyl carbon atoms, since (**1**) (b.p. 32 °C) can be easily handled at room temperature, whereas a trifluoromethylating reagent such as trifluoromethyl iodide (b.p. −23 °C) is a gas at atmospheric pressure and difficult to handle.

Received, 24th April 1989; Com. 9/01694E

References

1 M. Hudlicky, 'Chemistry of Organic Fluorine Compounds,' Ellis Horwood, New York, 1976; R. Filler and Y. Kobayashi, 'Biomedicinal Aspects of Fluorine Chemistry,' Kodansha/Elsevier, New York, 1982.

2 M. Yoshida, K. Moriya, H. Sawada, and M. Kobayashi, *Chem. Lett.*, 1985, 755.

3 Y. Kobayashi, K. Yamamoto, and I. Kumadaki, *Tetrahedron Lett.*, 1979, 4071; T. Kitazume and N. Ishikawa, *Chem. Lett.*, 1982, 1453; C. Francèse, M. Tordeux, and C. Wakselman, *Tetrahedron Lett.*, 1988, 1029.

4 Y. Tanabe, N. Matsuo, and N. Ohno, *J. Org. Chem.*, 1988, **53**, 4582.

5 T. Fuchikami and I. Ojima, *Tetrahedron Lett.*, 1984, 303; T. Ishihara, M. Kuroboshi, and Y. Okada, *Chem. Lett.*, 1986, 1895; Q. Y. Chen, Z. Y. Yang, C. X. Zhao, and Z. M. Qiu, *J. Chem. Soc., Perkin Trans. 1*, 1988, 563.

6 K. Uneyama and K. Ueda, *Chem. Lett.*, 1988, 853; C. J. Brookes, P. L. Coe, D. M. Owen, A. E. Pedler, and J. C. Tatlow, *J. Chem. Soc., Chem. Commun.*, 1974, 323.

7 N. Kamigata, H. Sawada, N. Suzuki, and M. Kobayashi, *Phosphorus Sulfur*, 1984, **19**, 199.

8 N. Kamigata, J. Ozaki, and M. Kobayashi, *J. Org. Chem.*, 1985, **50**, 5045.