

# Carbenoid Reactions of Organoelemental Compounds Containing Trifluoromethyl Groups: VII.\* Difluorocyclopropanation of Olefins and Dienes with a System Tris(trifluoromethyl)bismuth—Aluminum Chloride\*\*

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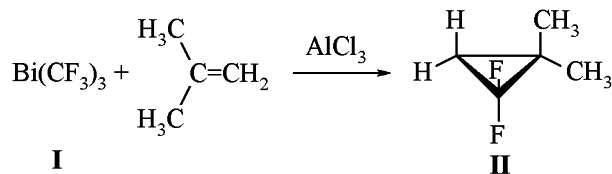
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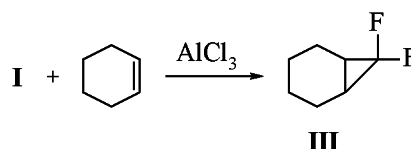
**Abstract**—Tris(trifluoromethyl)bismuth generates difluorocarbene at  $-30^{\circ}\text{C}$  in the presence of aluminum chloride. By reaction of the difluorocarbene with isobutylene, styrene, cyclohexene, and 2,3-dimethylbutadiene the corresponding substituted difluorocyclopropanes were obtained.

Quite a few methods of difluorocarbene generation are known by now [2]. It reacts with olefins to afford difluorocyclopropanes extensively used as intermediate products in organic synthesis [3]. One among the principal methods of difluorocarbene generation is based on the use of organoelemental compounds containing trifluoromethyl groups, as organocopper, organotin, organocadmium, organosilicon, and organophosphorus derivatives. The most often is applied trifluoromethylphenylmercury that does not afford difluorocarbene as a result of thermal degradation but cleanly affords it when treated with sodium iodide at  $80^{\circ}\text{C}$  [4–6]. Recently an extensive application found the preparation of difluorocarbene from trifluoromethyltin by heating to  $150^{\circ}\text{C}$  [7, 8] or at lower temperature by treating with sodium iodide [9]. Mild thermal sources of the difluorocarbene among the organoelemental compounds are trifluoromethyltrifluorosilane [10] and tris(trifluoromethyl)difluorophosphorane [11–15]. All the procedures for difluorocarbene generation from organoelemental compounds mentioned above require high temperature and cannot be used in reactions with thermally unstable compounds. Therefore the search for mild sources of difluorocarbene generation is continued.

We showed before that the tris(trifluoromethyl)bismuth in the presence of aluminum chloride behaved as a selective difluoromethylating agent with respect to tertiary amines, phosphines, and arsines [1, 16]. The target of the present study was to elucidate whether it was possible to carry out difluorocyclopropanation of olefins and dienes in reaction with tris(trifluoromethyl)bismuth in the presence of  $\text{AlCl}_3$ . We found that with tris(trifluoromethyl)bismuth (I) in the presence of aluminum chloride reacted with isobutylene in acetonitrile at  $-20^{\circ}\text{C}$  to afford 2,2-dimethyl-1,1-difluorocyclopropane (II) in 75% yield. The monitoring of difluorocyclopropane II formation in the process of the reaction is easily performed with the use of  $^{19}\text{F}$  NMR spectroscopy by appearance of the difluoromethylene group triplet in the region  $-139$  ppm [17].



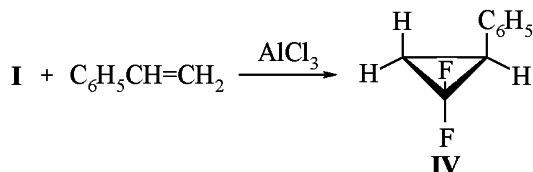
Reactions of tris(trifluoromethyl)bismuth (I) with cyclohexene and styrene in the presence of  $\text{AlCl}_3$  at  $-20^{\circ}\text{C}$  result in 7,7-difluoronorcarane (III) and



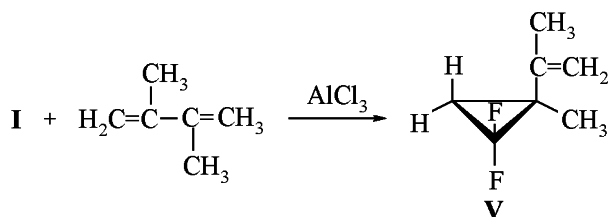
\* Previous communication see [1].

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2-phenyl-1,1-difluorocyclopropane (**IV**) in 40 and 60% yield respectively.



2,3-Dimethylbutadiene reacts with the tris(trifluoromethyl)bismuth in the presence of  $\text{AlCl}_3$  at  $-20^\circ\text{C}$  to provide a product of difluorocarbene addition only across one double bond, 2-isopropenyl-2-methyl-1,1-difluorocyclopropane **V** in 75% yield.



Compound **V** is a colorless fluid; its composition and structure are confirmed by  $^1\text{H}$ ,  $^{19}\text{F}$ , and  $^{13}\text{C}$  NMR spectra, mass spectrum, and elemental analysis. In the  $^{19}\text{F}$  NMR spectrum appears a single resonance of the fluorine atoms of the difluoromethylene group in  $-137.75$  ppm region in the form of triplet of quartets with the coupling constants  $^3J_{\text{FH}}$  8.8 and  $^4J_{\text{FH}}$  2.3 Hz.  $^{19}\text{F}$  NMR spectrum of compound **V** at  $-55^\circ\text{C}$  contains two signals of fluorine atoms from the  $\text{CF}_2$  group at  $-135.62$  ppm and  $-136.58$  ppm respectively with a geminal coupling constant  $^2J_{\text{FF}}$  158 Hz.

This the tris(trifluoromethyl)bismuth in the presence of aluminum chloride can be applied to difluorocyclopropanation of olefins and dienes. The mild conditions of the reaction are favorable for preparation of thermally unstable compounds.

## EXPERIMENTAL

$^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{19}\text{F}$  NMR spectra were recorded on spectrometer Bruker AC 200 at operating frequencies 200, 50.3, and 188.3 MHz respectively, internal references TMS ( $^1\text{H}$ ,  $^{13}\text{C}$ ) and  $\text{CCl}_3\text{F}$  ( $^{19}\text{F}$ ). The mass spectrum was measured on Varian CH-5 instrument at  $180^\circ\text{C}$ .

All reactions were carried out in argon atmosphere. Acetonitrile was distilled over  $\text{P}_2\text{O}_5$ . The tris(trifluoromethyl)bismuth (**I**) was prepared from bis(trifluoromethyl)cadmium complex [18].

## 1,1-Difluoro-2,2-dimethylcyclopropane (**II**).

To a solution of 0.82 g (1.97 mmol) of tris(trifluoromethyl)bismuth (**I**) in 5 ml of anhydrous acetonitrile at  $-20^\circ\text{C}$  at vigorous stirring was added 0.166 g (2.96 mmol) of isobutylene and 0.376 g (2.78 mmol) of fine powder of aluminum chloride. The mixture was stirred at this temperature for 1 h, and then gradually warmed to room temperature. The reaction mixture was poured into water, the precipitate was filtered off, the reaction products were twice extracted into benzene, and the benzene extract was dried with magnesium sulfate. On distilling off benzene the fractional distillation afforded 0.16 g of 1,1-difluorocyclopropane (**II**), yield 75%, bp  $41\text{--}42^\circ\text{C}$ . The boiling point and spectral characteristics of compound **II** are consistent with the published data [17].

**7,7-Difluoronorcarane (**III**)** was similarly prepared from 0.92 g (2.21 mmol) of tris(trifluoromethyl)bismuth (**I**), 0.182 g (2.21 mmol) of cyclohexene, and 0.306 g (2.26 mmol) of aluminum chloride. Yield 0.12 g (40%), bp  $122^\circ\text{C}$ . The boiling point and spectral characteristics of compound **III** are consistent with the published data [19].

**2-Phenyl-1,1-difluorocyclopropane (**IV**)** was prepared in the same way as compound **II** from 0.649 g (1.56 mmol) of tris(trifluoromethyl)bismuth (**I**), 0.162 g (1.56 mmol) of styrene, and 0.223 g (1.65 mmol) of aluminum chloride. Yield of compound **IV** 0.14 g (60%), bp  $64\text{--}65^\circ\text{C}$  (25 mm) [17].

**2-Isopropenyl-2-methyl-1,1-difluorocyclopropane (**V**)** was prepared as compound **II** from 0.84 g (2.02 mmol) of tris(trifluoromethyl)bismuth (**I**), 0.166 g (2.02 mmol) of 2,3-dimethylbutadiene, and 0.47 g (3.47 mmol) of aluminum chloride. Yield of compound **V** 0.2 g (75%), bp  $58^\circ\text{C}$ .  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ,  $\delta$ , ppm), at  $-30^\circ\text{C}$ : 4.88 d (2H,  $\text{CH}_2=$ ,  $^2J_{\text{HH}}$  9 Hz), 1.76 s (3H,  $\text{CH}_3$ -vinyl), 1.25 m (3H,  $\text{CH}_3$ -cycle,  $^4J_{\text{HF}}$  2.3 Hz), 1.44 d.m (1H cycle,  $^2J_{\text{HH}}$  10,  $^3J_{\text{HF}}$  8.8 Hz), 1.12 d.m (1H cycle,  $^2J_{\text{HH}}$  10,  $^3J_{\text{HF}}$  8.8 Hz).  $^{19}\text{F}$  NMR spectra: (1) ( $\text{CDCl}_3$ ,  $\delta_{\text{F}}$ , ppm), at  $20^\circ\text{C}$ :  $-137.75$  t.q (2F,  $\text{CF}_2$ ,  $^3J_{\text{FH}}$  8.8,  $^4J_{\text{FH}}$  2.3 Hz); 2) ( $\text{CDCl}_3$ ,  $\delta_{\text{F}}$ , ppm), at  $-55^\circ\text{C}$ :  $-135.62$  d.m (1F,  $\text{CF}_2$ ,  $^2J_{\text{FF}}$  158 Hz),  $-136.58$  d.m (1F,  $\text{CF}_2$ ,  $^2J_{\text{FF}}$  158 Hz).  $^{13}\text{C}$  NMR spectrum ( $\text{CD}_3\text{CN}$ ,  $\delta_{\text{C}}$ , ppm): 17.55 t ( $\text{CH}_3$ -cycle,  $^3J_{\text{CF}}$  2 Hz), 20.34 ( $\text{CH}_3$ -vinyl), 21.56 t ( $\text{CH}_2$ ,  $^2J_{\text{CH}}$  10 Hz), 32.03 t (C cycle,  $^2J_{\text{CF}}$  10 Hz), 113.41 ( $\text{CH}_2=$ ), 114.94 t ( $\text{CF}_2$ ,  $^1J_{\text{CF}}$  288 Hz), 142.26 (C vinyl). Mass spectrum ( $180^\circ\text{C}$ ),  $m/z$ : 132  $[\text{M}]^+$ .

## REFERENCES

1. Kirij, N.V., Pasenok, S.V., Yagupolskii, Yu.L., Fitzner, A., Tyrre, W., and Naumann, D., *J. Fluor.*

- Chem.*, 1999, vol. 94, no. 2, pp. 207–212.
2. Brahms, D.L.S. and Dailey, P., *Chem. Rev.*, 1996, vol. 96, no. 5, pp. 1585–1632.
  3. Weyerstahl, P., Schwarzkopff, U., and Nerdel, F., *Lieb. Ann.*, 1973, no. 12, pp. 2100–2110.
  4. Seyferth, D. and Hopper, S.P., *J. Organometal. Chem.*, 1971, vol. 26, no. 2, pp. 62–64.
  5. Seyferth, D., Hopper, S.P., and Darragh, K.V., *J. Am. Chem. Soc.*, 1969, vol. 91, no. 23, pp. 6536–6537.
  6. Seyferth, D. and Hopper, S.P., *J. Org. Chem.*, 1972, vol. 37, no. 25, pp. 4070–4075.
  7. Cullen, W.R. and Waldman, M.C., *Canad. J. Chem.*, 1969, vol. 47, no. 17, pp. 3093–3098.
  8. Cullen, W.R. and Waldman, M.C., *J. Fluor. Chem.*, 1971/72, vol. 1, no. 2, pp. 151–163.
  9. Seyferth, D., Dertouzos, H., Suzuki, R., and Mui, J.Y.P., *J. Org. Chem.*, 1967, vol. 32, no. 10, pp. 2980–2984.
  10. Sharp, K.G. and Coyle, T.D., *J. Fluor. Chem.*, 1971/72, vol. 1, no. 2, pp. 249–251.
  11. Birchall, J.M., Haszeldine, R.N., and Roberts, D.W., *Chem. Commun.*, 1967, no. 6, pp. 287–288.
  12. Mahler, W., *J. Am. Chem. Soc.*, 1968, vol. 90, no. 2, pp. 523–524.
  13. Mahler, W., *J. Am. Chem. Soc.*, 1962, vol. 84, no. 23, pp. 4600–4601.
  14. Birchall, J.M., Haszeldine, R.N., and Roberts, D.W., *J. Chem. Soc., Perkin Trans. I*, 1973, no. 10, pp. 1071–1078.
  15. Birchall, J.M., Fields, R., Haszeldine, R.N., and Kendall, N.T., *J. Chem. Soc., Perkin Trans. I*, 1973, no. 16, pp. 1773–1779.
  16. Pasenok, S.V., Kirij, N.V., Yagupolskii, Yu.L., Naumann, D., Tyrra, W., and Fitzner, A., *Z. Anorg. Allg. Chem.*, 1999, vol. 625, p. 834.
  17. Kamel, M., Kimpenhaus, W., and Buddrus, J., *Chem. Ber.*, 1976, vol. 109, no. 7, pp. 2351–2369.
  18. Lange, H. and Naumann, D., *J. Fluor. Chem.*, 1984, vol. 26, no. 1, pp. 1–18.
  19. Knunyants, I.L., Komissarov, Ya.F., Dyatkin, B.L., and Lantseva, L.T., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1973, no. 4, pp. 943–945.