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Preliminary communication

An improved organomercury route to difluorocarbene

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In a recent communication[1] we reported the preparation of phenyl(trifluoromethyl)mercury by fluorination of phenyl(tribromomethyl)mercury with phenylmercuric fluoride/hydrogen fluoride. Although phenyl(trifluoromethyl)mercury remained undecomposed after it had been heated in cyclooctene solution at reflux for 10 days, the sodium iodide procedure served excellently in releasing CF_2 from this reagent under mild conditions, and high *gem*-difluorocyclopropane yields could be realized when this reaction was carried out in the presence of olefins.

Although our published synthesis of phenyl(trifluoromethyl)mercury gives pure product in good yield, the prior preparation of both PhHgF and $PhHgCBr_3$ is required, and for this reason a more convenient route to this mercurial was sought. Other routes to trifluoromethyl–mercury compounds are known. The original preparation of trifluoromethylmercuric iodide used the UV irradiation of iodotrifluoromethane and elemental mercury in a sealed Pyrex tube[2]. Long reaction times (7–8 days), the use of an excess of mercury, the requirement of vigorous shaking of the reaction tube, the photolability of CF_3HgI and the potential hazards associated with the possible violent rupture of sealed tubes containing mercury combined to make this procedure rather unattractive. The reaction of iodotrifluoromethane with cadmium amalgam in a Pyrex tube at room temperature, which gave $(CF_3)_2Hg$ in reasonable yield[3], was an improvement, but a procedure not based on the reaction of the volatile (b.p. 22.5°) and expensive CF_3I with elemental mercury was desirable.

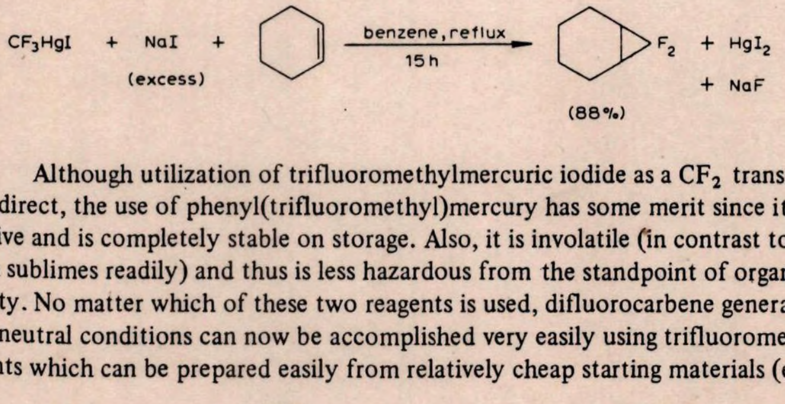
A du Pont patent[4] disclosed the thermal decarboxylation of mercury(II) trifluoroacetate at 300° to give trifluoromethylmercuric trifluoroacetate. We find that this reaction proceeds readily and that its product can be converted easily to the desired phenyl(trifluoromethyl)mercury by procedures based on the facile substituent exchange common in mercury chemistry. A direct preparation of $PhHgCF_3$ was possible (eq.1), but separation of the products required column chromatography (silicic acid, CH_2Cl_2

$$CF_3HgO_2CCF_3 + Ph_2Hg \xrightarrow[\text{reflux}]{\text{benzene or hexane}} PhHgCF_3 + PhHgO_2CCF_3$$

eluent) and the isolated yields of pure $PhHgCF_3$ were only 50–60%. It was found operationally advantageous to convert the $CF_3HgO_2CCF_3$ to trifluoromethylmercuric iodide by treatment with sodium iodide and to treat the CF_3HgI thus obtained with diphenylmercury to give $PhHgCF_3$ and PhHgI. The following procedure was used.

Crude $CF_3HgO_2CCF_3$ (m.p. 93–100°, ν(C=O) 1675 cm^{-1}), obtained in 53% yield based on initially charged mercuric oxide using Aldrich's procedure, was dissolved in diethyl ether and an equimolar amount of $NaI \cdot 2H_2O$ in 1,2-dimethoxyethane was added dropwise with stirring to the refluxing mercurial solution. After 30 min an equimolar amount of 1*M* aq. HCl was added, the reaction mixture was stirred vigorously and the organic phase was separated. Evaporation of the latter at reduced pressure gave crude CF_3HgI which was sublimed twice to give material of good purity in 78% yield. Treatment of trifluoromethylmercuric iodide with an equimolar quantity of diphenylmercury in benzene solution (3 h at reflux, under nitrogen) precipitated phenylmercuric iodide. The benzene solution was evaporated and the residue crystallized from hexane to give phenyl(trifluoromethyl)mercury, m.p. 141–143° (pure by TLC), in 75% yield. The phenylmercuric iodide yield was 95%.

The application of phenyl(trifluoromethyl)mercury in *gem*-difluorocyclopropane synthesis has been demonstrated[1]. We have found that trifluoromethylmercuric iodide serves equally well (eq.2). The mercurial was treated with a three-fold excess of well-dried sodium iodide[5] in the presence of a three-fold excess of cyclohexene in benzene (50 ml for 10 mmol of CF_3HgI), with stirring at reflux, under nitrogen, for 15 h. During this time red mercury(II) iodide precipitated nearly quantitatively. Filtration was followed by trap-to-trap vacuum distillation and GLC analysis of the distillate. Using this procedure, 1,1-difluoro-2-trimethylsilylmethylcyclopropane was prepared from allyltrimethylsilane in 78% yield.



(2)

Although utilization of trifluoromethylmercuric iodide as a CF_2 transfer agent is more direct, the use of phenyl(trifluoromethyl)mercury has some merit since it is not light-sensitive and is completely stable on storage. Also, it is involatile (in contrast to CF_3HgI which sublimes readily) and thus is less hazardous from the standpoint of organomercurial toxicity. No matter which of these two reagents is used, difluorocarbene generation under mild, neutral conditions can now be accomplished very easily using trifluoromethyl–mercury reagents which can be prepared easily from relatively cheap starting materials (eq.3–6).

$$2\,CF_3CO_2H + HgO \xrightarrow{\text{water}} (CF_3CO_2)_2Hg + H_2O \qquad (3)$$

$$(CF_3CO_2)_2Hg \xrightarrow{300^\circ} CF_3HgO_2CCF_3 + CO_2 \qquad (4)$$

$$CF_3HgO_2CCF_3 + NaI \rightarrow CF_3HgI + CF_3CO_2Na \qquad (5)$$

$$CF_3HgI + Ph_2Hg \rightarrow PhHgCF_3 + PhHgI \qquad (6)$$

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REFERENCES

1 D. Seyferth, S.P. Hopper and K.V. Darragh, *J. Amer. Chem. Soc.*, 91 (1969) 6536.
2 H.J.Emeléus and R.N. Haszeldine, *J. Chem. Soc.*, (1949) 2948.
3 H.J. Emeléus and R.N. Haszeldine, *J. Chem. Soc.*, (1949) 2953.
4 P.E. Aldrich, *U.S. patent* 3,043,859 (1962).
5 D. Seyferth, M.E. Gordon, J.Y.-P. Mui and J.M. Burlitch, *J. Amer. Chem. Soc.*, 89 (1967) 959.

Reaction of p-tolyl(bromodichloromethyl)mercury with "PhHgF · HF"

p-Tolyl(bromodichloromethyl)mercury was prepared by our improved procedure for aryl(trihalomethyl)mercurials[24]. The product obtained in 81% yield (0.1 mol scale reaction) had m.p. 126–127° (dec.). (Found: C, 20.83; H, 1.31. $C_8H_7BrCl_2Hg$ calcd.: C, 21.14; H, 1.55%.) NMR (CS_2; Varian A60): 7.10 (s, 4 H, aryl) and 2.33 ppm (s, 3 H, CH_3). This compound had been prepared previously by the original phenyl(trihalomethyl)mercurial procedure and a m.p. of 116–117° (dec.) had been reported[25].

The usual fluorination procedure was used in the reaction of 6.55 g (20.8 mmol) of "PhHgF · HF" and 9.1 g (20 mmol) of *p*-tolyl(bromodichloromethyl)mercury in 125 ml of toluene in the presence of 1 ml of 48% HF at room temperature for 2 h. The reaction mixture was filtered to give 8.6 g of white solid. Brominolysis showed this to contain 12.1 mmol of phenyl groups and 9.55 mmol of *p*-tolyl groups. The filtrate was evaporated and the residual solids also were brominated. The yields of bromobenzene and *p*-bromotoluene obtained indicated the presence of 6.83 mmol of phenyl groups and 7.87 mmol of *p*-tolyl groups in the benzene solubles.

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REFERENCES

1 D. Seyferth, R. A. Woodruff, D. C. Muell Lambert, Jr., *J. Organometal. Chem.*, 43 (1972) 55.
2 D. Seyferth, *Accounts Chem. Res.*, 5 (1972) 65.
3 H. C. Clark and C. J. Willis, *J. Amer. Chem. Soc.*, 82 (1960) 1888.
4 D. Seyferth, H. Dertouzos, R. Suzuki and J. Y.-P. Mui, *J. Org. Chem.*, 32 (1967) 2980.
5 H. J. Emeléus and R. N. Haszeldine, *J. Chem. Soc.*, (1949) 2948.
6 H. J. Emeléus and R. N. Haszeldine, *J. Chem. Soc.*, (1949) 2953.
7 K. V. Darragh, Ph. D. Thesis, Mass. Inst. of Technology, 1968.
8 D. Seyferth and K. V. Darragh, *J. Org. Chem.*, 35 (1970) 1297.
9 D. Seyferth, M. E. Gordon and K. V. Darragh, *J. Organometal. Chem.*, 14 (1968) 43.
10 G. F. Wright, *J. Amer. Chem. Soc.*, 58 (1936) 2653.
11 D. Seyferth, C. K. Haas and S. P. Hopper, *J. Organometal. Chem.*, 33 (1971) C1.
12 (a) A. L. Henne and T. Midgley Jr., *J. Amer. Chem. Soc.*, 58 (1936) 884;
(b) A. L. Henne, *J. Amer. Chem. Soc.*, 59 (1937) 1200;
(c) A. L. Henne, *J. Amer. Chem. Soc.*, 60 (1938) 1569.
13 D. Seyferth and H. Shih, *Organometal. Chem. Syn.*, 1 (1972) 41.
14 D. Seyferth, J. Y.-P. Mui and J. M. Burlitch, *J. Amer. Chem. Soc.*, 89 (1967) 4953.
15 D. Seyferth, J. Y.-P. Mui and R. Damrauer, *J. Amer. Chem. Soc.*, 90 (1968) 6182.
16 D. Seyferth and D. C. Mueller, *J. Organometal. Chem.*, 25 (1970) 293.
17 A. Ledwith and L. Phillips, *J. Chem. Soc.*, (1962) 3796.
18 D. Seyferth, H. D. Simmons Jr. and H. Shih, *J. Organometal. Chem.*, 29 (1971) 359.
19 D. Seyferth, M. E. Gordon, J. Y.-P. Mui and J. M. Burlitch, *J. Amer. Chem. Soc.*, 89 (1967) 959.
20 D. Seyferth and S. P. Hopper, *J. Organometal. Chem.*, 26 (1971) C62.
21 D. Seyferth, S. P. Hopper and G. J. Murphy, *J. Organometal. Chem.*, in press.
22 A. J. Bloodworth, *J. Organometal. Chem.*, 23 (1970) 27.
23 N. Allen and N. H. Furman, *J. Amer. Chem. Soc.*, 54 (1932) 4625.
24 D. Seyferth and R. L. Lambert Jr., *J. Organometal. Chem.*, 16 (1969) 21.
25 D. Seyferth, J. Y.-P. Mui and R. Damrauer, *J. Amer. Chem. Soc.*, 90 (1968) 6182.