BIS(TRIFLUOROMETHYL)MERCURY AS A READILY AVAILABLE SOURCE OF DIFLUOROCARBENE

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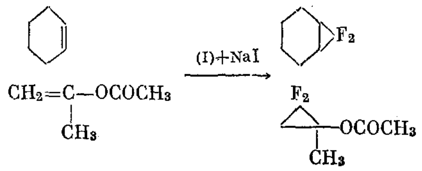
Phenyltrifluoromethylmercury was obtained [1] by the reaction of phenylmercury fluoride with phenyltribromomethylmercury and was used as a source of difluorocarbene. Later a communication appeared [2] on the use of trifluoromethylmercury iodide for this purpose, which, according to the data given in [2], is obtained in good yield by the reaction of $NaI \cdot 2H_2O$ with trifluoromethylmercury acetate, which was synthesized by the pyrolysis of mercury trifluoroacetate [3]. This method is apparently less laborious than the method given in [1] (a description of the experiment is absent in [2]). However, besides certain difficulties that are associated with the preparation of trifluoromethylmercruy iodide, it also has the disadvantage that only one of the two CH_3 groups of the starting mercury bis(trifluoroacetate) is used. From this standpoint bis(trifluoromethyl)mercury (I) can be a better source of difluorocarbene; however, up to now it was difficultly available; the sole method for its preparation was the symmetrization of trifluoromethylmercury iodide with amalgams [4].

We found that (I) can be obtained in nearly quantitative yield by the pyrolysis of mercury trifluoroacetate in vacuo in the presence of fused K_2CO_3. Phenyltrifluoromethylmercury is obtained in a similar manner from phenylmercury trifluoroacetate.

$$\begin{array}{ccc} (CF_3COO)_2Hg & \xrightarrow[180-200^\circ]{K_2CO_3} & (CF_3)_2Hg\ (I) \\ C_6H_5HgOCOCF_3 & & C_6H_5HgCF_3 \end{array}$$

Bis(trifluoromethyl)mercury is a good generator of difluorocarbene. Its reaction with cyclohexene in the presence of NaI in THF gave difluoronorcarane, while reaction with isopropenyl acetate gave 1,1-difluoro-2-methyl-2-acetoxycyclopropane (the preparative yield in both cases was 35%).



EXPERIMENTAL METHOD

The ^{19}F NMR spectra were obtained on a Hitachi-60 spectrometer at 56.4 MHz. The chemical shifts are indicated in ppm from CF_3COOH, which was used as the external standard.

Mercury Trifluoroacetate. To a stirred solution of 14 g of technical CF_3COOH in 45 ml of water was added 12 g of mercury oxide in small portions. The mixture was heated for 3-5 min at 50-60°, evaporated in vacuo, and the residue was dried in vacuo at 100°.

Phenylmercury Trifluoroacetate. To a stirred mixture of 57 g of CF_3COOH and 39 g of benzene was added 108 g of mercury oxide in small portions. The reaction mass was stirred for 5 min at 50-60°. After cooling, the precipitate was filtered and dried in vacuo over conc. H_2SO_4.

Bis(trifluoromethyl)mercury (I). A mixture of 14.1 g of $(CF_3COO)_2Hg$ and 10.0 g of fused K_2CO_3 was placed in a flask, equipped with a wide side outlet that was cooled, and heated up to 180-200° at 20-30 mm. The formed (I) sublimes and crystallizes in the cooled outlet, and also on the walls of the flask. The yield of (I) was 10.3 g (92.5%), mp 163-166° [4].

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Phenyltrifluoromethylmercury. In the same manner as the preceding experiment, a mixture of 10.0 g of phenylmercury trifluoroacetate and 5.0 g of K_2CO_3 was heated up to 220-230° at 20-30 mm. We obtained 6.2 g (70%) of phenyltrifluoromethylmercury with mp 137-138° [1]. ^{19}F NMR spectrum: singlet with a chemical shift of −40.6 ppm, and the mercury satellites, $J_{^{199}Hg-^{19}F} = 1030$ Hz (from heptane).

7,7-Difluoronorcarane. To a stirred mixture of 9.0 g of fused NaI, 7.4 g of cyclohexene and 12 ml of absolute THF at 80-82° was added in 1 h a solution of 10.2 g of (I) in 5 ml of absolute THF, after which the mixture was stirred at this temperature for another 7 h, an additional 3.0 g of NaI was added, and the stirring was continued at 80-82° until the signal of (I) in the ^{19}F NMR spectrum of the reaction mixture had disappeared completely. Then all of the volatile portion of the reaction mixture was vacuum-distilled into a trap, cooled to −80°, and the trap contents were fractionally distilled. We obtained 2.8 g (35%) of 7,7-difluoronorcarane with bp 122° [5], which was identified by GLC by comparison with an authentic sample.

1,1-Difluoro-2-methyl-2-acetoxycyclopropane. To a stirred mixture of 10.2 g of freshly distilled isopropenyl acetate, 10 ml of dry dimethoxyethane and 10.0 g of fused NaI at 92-94° was added in drops a solution of 12.0 g of (I) in 10 ml of dimethoxyethane (in 3 h). The stirring at this temperature was continued for 2 days until the signal of (I) in the ^{19}F NMR spectrum of the reaction mixture had disappeared completely. Then the volatile portion was vacuum-distilled (into a trap at −80°), the trap contents were poured into water, and the organic layer was separated and dried over $MgSO_4$. Fractional distillation gave 3.2 g (35.1%) of 1,1-difluoro-2-methyl-2-acetoxycyclopropane with bp 124°. Infrared spectrum (ν, cm^{-1}): 740 m, 760 m, 870 w, 965 m, 985 m, 1065 m, 1080 w, 1120 s, 1270-1280 s, 1355 w, 1465 w, 1500 m, 1595 w, 1770-1790 s. ^{19}F NMR spectrum (AB system): $\delta_{F(A)}$ 60.4 ppm; $\delta_{F(B)}$ 62.6 ppm; $J_{F(A)-F(B)} = 163$ Hz. Each component represents a triplet of quartets, $J_{F-CH_2} = 10$ Hz, $J_{F-CH_3} = 2.1$ (A) and 2.4 Hz (B). Mass spectrum: M^+ with m/e 150. Found, %: C 47.53; H 5.24; F 25.31%. $C_6H_8F_2O_2$. Calculated, %: C 48.04; H 5.38; F 25.33%.

CONCLUSIONS

1. The pyrolysis of mercury trifluoroacetate and phenylmercury trifluoroacetate in the presence of K_2CO_3 respectively gave bis(trifluoromethyl)mercury and phenyltrifluoromethylmercury in high yields.

2. Bis(trifluoromethyl)mercury can serve as a source of difluorocarbene.

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