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LETTERS TO THE EDITOR

Addition of Trifluoroacetic Acid to (*R*)-(+)-Limonene in the Presence of $Mo_2(OOCCF_3)_4$

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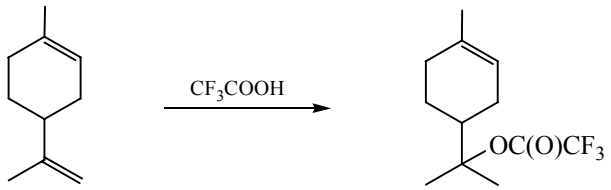
Addition of trifluoroacetic acid to alkenes proceeds readily according to the Markovnikov's rule, which allows preparation of the corresponding trifluoroacetates. Thus, the reaction of propylene with trifluoroacetic acid led to the formation of isopropyl trifluoroacetate with a yield of ~100% [1]. Similarly limonene **I** added trifluoroacetic acid at 20–30°C in toluene or cyclohexane at exocyclic C=C bond to form α-terpinyl trifluoroacetate **II** [2–4], while the other, endocyclic C=C bond, was not involved into the reaction (Scheme 1).

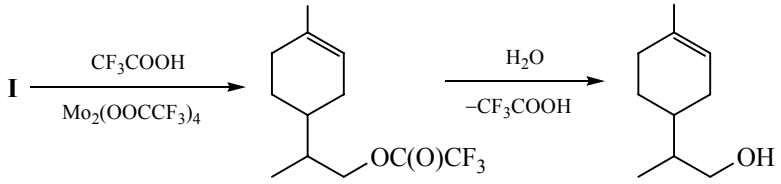
At the same time, in the presence of molybdenum(II) trifluoroacetate dimer, $Mo_2(OOCCF_3)_4$, the reaction of trifluoroacetic acid with propylene proceeded against the Markovnikov's rule to afford *n*-propyl trifluoroacetate with 90–100% selectivity [5]. Accordingly, it is presumable that in the presence of $Mo_2(OOCCF_3)_4$ the reaction of limonene with trifluoroacetic acid would yield 2-(4-methylcyclohex-3-en-1-yl)propyl trifluoroacetate **III**, hydrolysis of which would lead to terpene alcohol **IV** (Scheme 2).

Scheme 1.



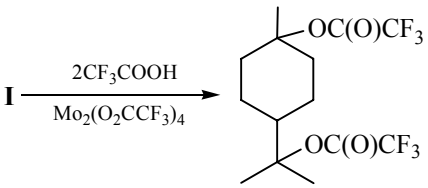
I **II**

Scheme 2.



III **IV**

Scheme 3.



V

Alcohol **IV** has been obtained earlier from limonene by hydroboration and subsequent oxidation [6, 7].

In contrast to the expected, we found that the reaction of trifluoroacetic acid with (*R*)-(+)-limonene (toluene, 20–30°C) in the presence of molybdenum(II) trifluoroacetate (0.1 mol per 1 mol of limonene) afforded almost exclusively terpin bistrifluoroacetate **V** as a result of acid addition at both C=C bonds according to the Markovnikov's rule. By ^{1}H NMR data, only half of limonene was consumed when the reagents ratio of 1 : 1 was used. In contrast, a complete conversion of limonene was observed when two-fold excess of trifluoroacetic acid was used. According to ^{1}H and ^{19}F NMR, terpin bistrifluoroacetate **V** was obtained as the only reaction product (Scheme 3).

Analytically pure terpin bistrifluoroacetate **V** was isolated as colorless liquid by vacuum distillation with a yield of 69%. Its physicochemical and spectral (IR, ^{1}H, ^{13}C, ^{19}F NMR) characteristics were identical to the characteristics of the same compound we had first synthesized from limonene and trifluoroacetic acid using sulfuric acid as a catalyst [4].

In summary, $Mo_2(OOCCF_3)_4$ is an effective catalyst for adding TFA to both C=C bond of limonene according to the Markovnikov's rule. Probably, this catalyst can be used for the addition of perfluoroalkanecarboxylic acids to the endocyclic bonds of another cycloalkenes.

The following reagents were used: (+)-(*R*)-Limonene (97%, Acros), trifluoroacetic acid (99%, Acros), and trifluoroacetic anhydride (99%, Acros Organics). Toluene and *n*-pentane were purified and dried by standard procedures [8].

Molybdenum(II) trifluoroacetate dimer was obtained by a known method [9]. All operations were carried out under argon atmosphere. A mixture of 2.0 g of molybdenum(II) acetate [10], 30 mL of trifluoroacetic acid, and 3 mL of trifluoroacetic anhydride was heated at 120°C for 2 h, and then centrifuged. The precipitate was separated by decantating, washed with 5 mL of *n*-pentane, and dried in a vacuum. Yield 2.1 g (69.7%), yellow powder. IR spectrum, ν, cm^{-1}: 3037 w, 3025 w, 2906 w, 1601 s, 1577 s, 1464 s, 1253 m, 1193 br, 860 s, 787 m, 772 m, 730 s, 520 br, 495 m [9].

1-Methyl-1-{4-methyl-3-[(trifluoroacetyl)oxy]-cyclohexyl}ethyl trifluoroacetate (terpin bistrifluoroacetate) (V). Trifluoroacetic acid, 8.5 g (0.074 mol), was added dropwise to a mixture of 1.0 g of $Mo_2(OOCCF_3)_4$, 7 mL of toluene, and 5.0 g (0.037 mol) of (*R*)-(+)-limonene under argon atmosphere. The resulting mixture was stirred at 20–30°C for 2.5 h, and then separated by decantating. The precipitate was washed with water (10 mL), 5% aqueous sodium hydrogen carbonate (10 mL) and 5% aqueous sodium chloride solution (10 mL). The organic layer was dried over magnesium sulfate. After the solvent removal, the residue was distilled in vacuum. Yield 9.3 g (69.0%), bp 79–80°C (1 mmHg), n_D^{20} 1.3974. IR spectrum, ν, cm^{-1}: 1772 (C=O), 1224, 1235 (C–F). ^{1}H NMR spectrum, δ, ppm: 1.34–1.44 m (4H, C^3H_2, C^5H_2), 1.53 s (6H, C^9H_3, $C^{10}H_3$), 1.58 s (3H, C^7H_3), 1.60–1.68 m (2H, $C^2H_2^a$, $C^6H_2^a$), 1.93 m (1H, C^4H), 2.42–2.47 m (2H, $C^2H_2^e$, $C^6H_2^e$). ^{13}C NMR spectrum, δ_C, ppm: 21.52 (C^3, C^5), 22.68 (C^9, C^{10}), 25.14 (C^7), 35.35 (C^2, C^6), 45.82 (C^4), 86.78 (C^8), 91.10 (C^1), 114.4 q (CF_3, $^1J_{CF}$ 287.1 Hz), 156.0 q and 155.9 q (C=O, $^2J_{CF}$ 41.2 Hz). ^{19}F NMR spectrum, δ_F, ppm: –76.60, –76.56.

^{1}H and ^{13}C NMR spectra of the $CDCl_3$ solutions were recorded on an Avance 400 spectrometer (400.13 and 100.61 MHz, respectively). ^{19}F NMR spectrum was registered on a Bruker AM-500 spectrometer (470.6 MHz) using $CDCl_3$ as a solvent $CFCl_3$ as a reference. IR spectra (film) were recorded on a Shimadzu FTIR-8400S spectrometer.

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