Bull. Chem. Soc. Jpn., 57, 1431—1432 (1984)

An Easy Preparation of Triphenylmethyl Carboxylates

Shun-ichi HASHIMOTO, Masahiko HAYASHI, and Ryoji NOYORI*
Department of Chemistry, Nagoya University, Chikusa, Nagoya 464
(Received December 27, 1983)

Synopsis. A new recipe for triphenylmethylation of carboxylic acids and phenol is disclosed.

Triphenylmethylation of carboxylic acids has been conventionally achieved by heating triphenylmethyl bromide and metal carboxylates in nonpolar solvents.[1] Sensitive, polymerizable acrylic acids, however, can be esterified only using the expensive silver salts.[2] We found that condensation of economically accessible trimethylsilyl carboxylates (**1**) and triphenylmethyl fluoride (**2**) proceeds smoothly at room temperature in acetonitrile containing a catalytic amount of tetrafluorosilane (**3**). This facile procedure allows the easy synthesis of triphenylmethyl methacrylate (**4a**),[3] an important material for the preparation of the chiral liquid chromatographic stationary phases.[4,5]

$$\underset{\mathbf{1}}{RCOOSi(CH_3)_3} + \underset{\mathbf{2}}{(C_6H_5)_3CF} \xrightarrow{SiF_4} \underset{\mathbf{4}}{RCOOC(C_6H_5)_3} + (CH_3)_3SiF$$

a: $R=CH_2=C(CH_3)$, **b**: $R=n\text{-}C_9H_{19}$, **c**: $R=C_6H_5$

In a like manner, the tetrafluorosilane-catalyzed reaction of phenyl trimethylsilyl ether and the fluoride **2** gave phenyl triphenylmethyl ether in a high yield.

Experimental

All melting points were uncorrected. IR spectra were recorded on a JASCO IRA-1 spectrometer. ^{1}H NMR spectra were measured with a JEOL JNM FX-90Q (90 MHz) spectrometer using tetramethylsilane as an internal standard. Mass spectra were determined with a Hitachi RMU-6C mass spectrometer, operating with an ionization energy of 70 eV. Tetrafluorosilane (**3**) was purchased form Matheson Co. Triphenylmethyl fluoride (**2**) was prepared by the reported method.[6] Acetonitrile was distilled from CaH_2 before use. All products are known compounds and gave consistent spectral data.

Triphenylmethyl Methacrylate(4a). To a solution of **1a** (1.25 g, 7.91 mmol) and **2** (2.07 g, 7.91 mmol) in dry acetonitrile (2 cm^3) was added a 0.08 mol dm^{-3} solution of **3** in acetonitrile (4.9 cm^3, 0.396 mmol) at 14 °C under argon atmosphere. After 6-h stirring at this temperature, the resulting yellow mixture was poured into a vigorously stirred, pH 7.4 phosphate buffer (80 cm^3) containing KF (8.0 g) which was kept at 0 °C. The whole mixture was extracted with a 2:1 mixture of ether and hexane (50 cm^3×2), and the combined organic layers were washed with aq $NaHCO_3$ and brine, dried over anhydrous Na_2SO_4, and evaporated *in vacuo*. The residual solid was recrystallized from hexane to give **4a** (2.42 g, 94% yield) as colorless prisms: Mp 98—99 °C (lit,[7] 101—102 °C); IR (CCl_4) 1725, 1490, 1140 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.99 (3H, dd, J=1.0, 1.4 Hz), 5.60 (1H, m), 6.23 (1H, m), 7.2—7.5 (15H, m); MS m/z 328 (M$^+$), 260, 259, 243, 183, 165, 105, 85, 83, 77.

The above reaction was carried out in acetonitrile-d_3 for 6 h, and the reaction mixture was subjected to ^{1}H NMR analysis, which indicated the production of the theoretical amount of trimethylfluorosilane[8] (δ=0.21, d, $J_{CH_3,F}$=7.5 Hz) in addition to **4a**.[9]

Triphenylmethyl Decanoate (4b). A mixture of **1b** (232 mg, 0.95 mmol), **2** (249 mg, 0.95 mmol), and **3** (0.08 mol dm^{-3} in acetonitrile, 0.62 cm^3, 0.05 mmol) in acetonitrile (2.5 cm^3) was stirred at 16 °C for 6 h. The reaction mixture was worked up as described above, and the oily residue was chromatographed on silica gel, which had been treated with triethylamine (2%), using a 5:1 mixture of hexane and ether as an eluent. Pure **4b** was obtained as a colorless oil (361 mg, 88%): IR (CCl_4) 1760, 1500, 1150 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.87 (3H, br t, J=6.0 Hz), 1.07—1.73 (14H, m) 2.43 (2H, t, J=6.8 Hz) 7.1—7.4 (15H, m); MS m/z 414 (M$^+$), 260, 259, 244, 243, 165, 78, 77.

Triphenylmethyl Benzoate (4c). A mixture of **1c** (372 mg, 1.92 mmol), **2** (503 mg, 1.92 mmol), and **3** (0.08 mol dm^{-3} in acetonitrile, 1.2 cm^3, 0.1 mmol) in acetonitrile (4 cm^3) was stirred at 16 °C for 4 h. Workup followed by recrystallization from a 10:1 mixture of hexane and benzene afforded **4c** (671 mg, 96%) as colorless plates: Mp 170—171 °C (lit,[1] 168—170 °C); IR (CCl_4) 1740, 1600, 1500, 1270 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=7.1—7.6 (18H, m), 8.13 (2H, J=1.5, 7.8 Hz); MS m/z 364 (M$^+$), 260, 259, 244, 243, 85, 83.

Phenyl Triphenylmethyl Ether. A mixture of phenyl trimethylsilyl ether (166 mg, 1.0 mmol), **2** (262 mg, 1.0 mmol), and **3** (0.08 mol dm^{-3} in acetonitrile, 0.63 cm^3, 0.05 mmol) in acetonitrile (2 cm^3) was stirred at 15 °C for 24 h. Aqueous workup followed by column chromatography on 2% triethylamine-treated silica gel using a 30:1 mixture of hexane and ether as an eluent, afforded the product (286 mg, 85%) as a colorless oil. This oil crystallized as colorless prisms from ethanol solution: Mp 103—104 °C (lit,[10] 103 °C); IR (CCl_4) 1600, 1500, 1450, 1220 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=6.6—7.1 (5H, m) 7.1—7.5 (15H, m); MS m/z 244, 243, 165, 94.

References

1) K. D. Berlin, L. H. Gower, J. W. White, D. E. Gibbs, and G. P. Sturm, *J. Org. Chem.*, **27**, 3595 (1962).

2) H. Yuki, K. Hatada, Y. Kikuchi, and T. Niinomi, *J. Polym. Sci. Part B*, **6**, 753 (1968).

3) For the preparation of **4a** from **1a** and triphenylmethyl trimethylsilyl ether, see: S. Murata and R. Noyori, *Tetrahedron Lett.*, **22**, 2107 (1981).

4) Y. Okamoto, K. Suzuki, K. Ohta, K. Hatada, and H. Yuki, *J. Am. Chem. Soc.*, **101**, 4763 (1979); H. Yuki, Y. Okamoto, and I, Okamoto, *ibid.*, **102**, 6356 (1980); Y. Okamoto, I. Okamoto, and H. Yuki, *Chem. Lett.*, **1981**, 835; Y. Okamoto, I. Okamoto, and H. Yuki, *J. Polym. Sci. Polym. Lett. Ed.*, **19**, 451 (1981); Y. Okamoto, S. Honda, I. Okamoto, H. Yuki, S. Murata, R. Noyori, and H. Takaya, *J. Am. Chem. Soc.*, **103**, 6971 (1981); R. Noyori, N. Sano, S. Murata, Y. Okamoto, H. Yuki, and T. Ito, *Tetrahedron Lett.*, **23**, 2969 (1982); Y. Kawada, H. Iwamura, Y. Okamoto, and H. Yuki, *ibid.*, **24**, 791 (1983).

5) A column of (+)-poly(triphenylmethyl methacrylate) coated on macroporous silica gel (Chiralpak OT) is available from Japan Spectroscopic Co. Ltd., Ishikawa-cho, Hachioji,

Tokyo.

6) G. A. Olah, J. T. Welch, Y. D. Vankar, M. Nojima, I. Kerekes, and J. A. Olah, *J. Org. Chem.*, **44**, 3872 (1979).

7) N. A. Adrova and L. K. Prokhorova, *Vysokomol. Soedin.*, **3**, 1509 (1961); *Chem. Abstr.*, **56**, 10384 (1962).

8) A. E. Newkirk, *J. Am. Chem. Soc.*, **68**, 2736 (1946).

9) Other Lewis acids such as BF_3, $AlCl_3$ (in CH_3CN), and $TiCl_4$ (in CH_2Cl_2) also acted as catalyst of this reaction.

10) A. Baeyer, *Ber.*, **42**, 2625 (1909).