Alkylation of bromoarenes with 4-methylbicyclo[2.2.2]octan-1-ol and 8-methyltricyclo[4.4.0.0^{3,8}]decan-1-ol in methanesulfonic acid

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Alkylation of bromoarenes with 4-methylbicyclo[2.2.2]octan-1-ol or 8-methyltricyclo-[4.4.0.0^{3,8}]decan-1-ol (twistanol) in methanesulfonic acid gives the corresponding bromine-containing 1-aryl-4-methylbicyclo[2.2.2]octanes and 1-aryl-8-methyltricyclo[4.4.0.0^{3,8}]-decanes.

Key words: bicyclo[2.2.2]octanes, tricyclo[4.4.0.0^{3,8}]decanes (twistanes), the Friedel—Crafts reaction, liquid crystals, alkylation, bromoarenes.

Disubstituted bicyclo[2.2.2]octanes and twistanes are of interest as elements of liquid-crystal structures.[1,2] Earlier,[3,4] we have found that 4-alkylbicyclo[2.2.2]octan-1-ols and 8-alkyltwistan-1-ols can alkylate benzene and bromobenzene at the *para*-position in conc. H_2SO_4 according to the Friedel—Crafts reaction pattern, the yields of the alkylation products being >90%. However, this method is of limited application to other benzene, naphthalene, and biphenyl derivatives liable to sulfonation.

In the present work, we demonstrated that the use of methanesulfonic acid instead of sulfuric acid allows rapid, high-yielding, and highly selective alkylation of bromobenzene, bromobiphenyl, and 2-bromonaphthalene with 4-methylbicyclo[2.2.2]octan-1-ol and 8-methyltwistan-1-ol (Scheme 1).

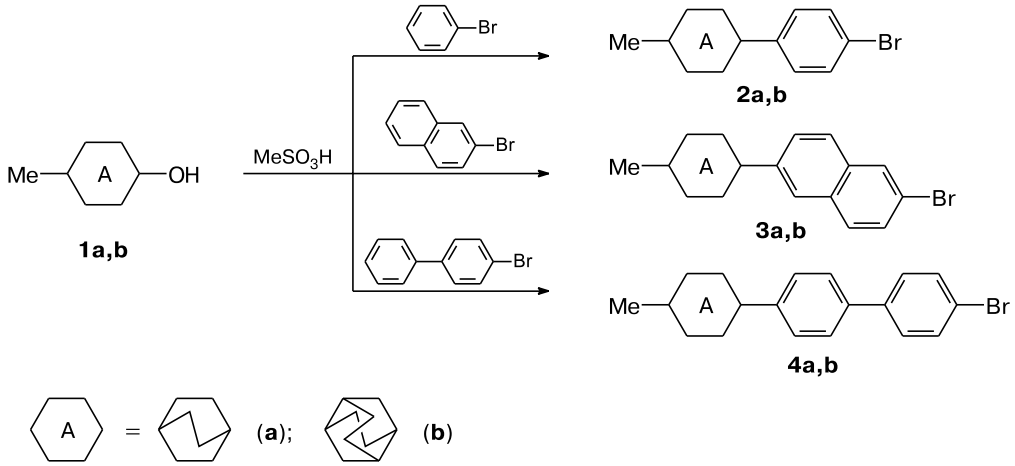
The procedure we developed is of preparative value and can be used for the synthesis of other arenes containing bicyclo[2.2.2]octane and twistane substituents.

Experimental

The starting 4-methylbicyclo[2.2.2]octan-1-ol (**1a**) and 8-methyltricyclo[4.4.0.0^{3,8}]decan-1-ol (**1b**) were prepared according to known procedures.[5,6]

The course of all reactions was monitored by TLC on silica gel (Merck, Kieselgel 60, and F254). Spots were visualized under UV light (λ = 254 nm). The melting points of the starting compounds and the reaction products were determined on a Mettler-FP-90 instrument fitted with an Olympus BH-2 polarizing microscope. ^{1}H NMR spectra were recorded on Bruker AM-300 and Bruker Avance II 300 spectrometers. Chemical

Scheme 1



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shifts δ are referenced to Me_4Si. Mass spectra were recorded on a Kratos MS-30 instrument (ionizing energy 70 eV; mass numbers are cited for the ^{79}Br isotope).

Synthesis of 1-bromoaryl-4-methylbicyclo[2.2.2]octanes (2a—4a) and 8-bromoaryl-1-methyltwistanes (2b—4b) (general procedure). Compound **1a** or **1b** (1 mmol) was added to a vigorously stirred mixture of a bromoarene (1 mmol) and methanesulfonic acid (0.5 mL). The reaction mixture was stirred at 20—25 °C for 10 h and poured onto ice. The product was extracted with ether. The combined extracts were washed with water, dried over Na_2SO_4, and concentrated. The residue was recrystallized from appropriate solvents.

1-(4-Bromophenyl)-4-methylbicyclo[2.2.2]octane (2a). Yield 95%, m.p. 86—87 °C (MeOH) (*cf.* Ref. 1: m.p. 85—86 °C (EtOH)).

1-(4-Bromophenyl)-8-methyltricyclo[4.4.0.0^{3,8}]decane (2b). Yield 92%, m.p. 81—82 °C (MeOH) (*cf.* Ref. 6: m.p. 82—83 °C (EtOH)).

1-(6-Bromonaphthalen-2-yl)-4-methylbicyclo[2.2.2]octane (3a). Yield 96%, m.p. 166—168 °C (MeOH). ^1H NMR ($CDCl_3$), δ: 7.90 (s, 1 H); 7.71—7.62 (m, 3 H); 7.55 (d, 1 H, J = 13.7 Hz); 7.51 (d, 1 H, J = 13.7 Hz); 1.95—1.86 (m, 6 H, CH_2); 1.59—1.51 (m, 6 H, CH_2); 0.88 (s, 3 H, Me). MS, m/z (I_{rel} (%)): 328 $[M]^+$ (42), 258 $[M - C_5H_{10}]^+$ (36), 179 $[M - C_5H_{10} - Br]^+$ (100). Found (%): C, 69.42; H, 6.41. $C_{19}H_{21}Br$. Calculated (%): C, 69.30; H, 6.43.

1-(6-Bromonaphthalen-2-yl)-8-methyltricyclo[4.4.0.0^{3,8}]decane (3b). Yield 94%, m.p. 152—154 °C (MeOH). ^1H NMR ($CDCl_3$), δ: 7.96 (s, 1 H); 7.72—7.65 (m, 3 H); 7.57—7.48 (m, 2 H); 2.18—2.09 (m, 2 H); 1.93—1.84 (m, 1 H); 1.82—1.14 (m, 11 H); 0.94 (s, 3 H, Me). MS, m/z (I_{rel} (%)): 354 $[M]^+$, 258 $[M - C_7H_{12}]^+$ (54), 179 $[M - C_7H_{12} - Br]^+$ (100). Found (%): C, 71.28; H, 6.50. $C_{21}H_{23}Br$. Calculated (%): C, 70.99; H, 6.52.

[4-(4-Bromophenyl)phenyl]-4-methylbicyclo[2.2.2]octane (4a). Yield 90%, m.p. 205—207 °C (MeOH) (*cf.* Ref. 1: m.p. 207—208 °C ($HOCH_2CH_2OCH_3$)).

[4-(4-Bromophenyl)phenyl]-8-methyltricyclo[4.4.0.0^{3,8}]decane (4b). Yield 93%, m.p. 166—168 °C (MeOH). ^1H NMR ($CDCl_3$), δ: 7.57—7.40 (m, 8 H); 2.14—2.04 (m, 2 H); 1.88—1.78 (m, 1 H); 1.77—1.43 (m, 8 H); 1.41—1.27 (m, 2 H); 1.20—1.12 (m, 1 H); 0.93 (s, 3 H, Me). MS, m/z (I_{rel} (%)): 380 $[M]^+$ (69), 365 $[M - Me]^+$ (12), 284 $[M - C_7H_{12}]^+$ (100), 284 $[M - C_7H_{12} - Br]^+$ (61), 230 $[M - MeTW]^+$ (19). Found (%): C, 72.62; H, 6.59. $C_{23}H_{25}Br$. Calculated (%): C, 72.44; H, 6.61.

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