(2*S*,3*S*)-3-(4-Chlorophenyl)-2-(2,4-dichlorophenyl)-3-methoxypropane-1,2-diol (14b). A mixture of the epoxide **8b** (1.20 g, 3.64 mmol), BF_3-Et_2O (0.52 g, 3.64 mmol) in MeOH (24 mL) was refluxed for 6 h. The mixture was diluted with CH_2Cl_2 and washed with aqueous $NaHCO_3$ solution. The organic layer was dried (Na_2SO_4), evaporated, and chromatographed. Elution with hexane/AcOEt (8/2) gave **14b** (756 mg, 57%) as an oil: IR (film) 3450 cm^{-1}; NMR δ 7.40–6.85 (7 H, m, ArH × 7), 5.12 (1 H, s, C_3-H), 4.48 and 4.24 (each 1 H, each d, J = 12 Hz, CH_2O), 3.90 (2 H, brs, OH × 2), and 3.26 (3 H, s, OMe); $[\alpha]^{25}_D$ −73.9° (*c* 1.00, $CHCl_3$). Anal. Calcd for $C_{16}H_{15}O_3Cl_3$: C, 53.13; H, 4.18; Cl, 29.41. Found: C, 52.86; H, 4.16; Cl, 29.09.

(2*S*,3*R*)-2,3-Bis(4-chlorophenyl)-3-methoxy-1-[(*p*-tolylsulfonyl)oxy]propan-2-ol (10a). A mixture of the diol **9a** (1.51 g, 4.62 mmol), *p*-TsCl (0.88 g, 4.62 mmol), and pyridine (15 mL) was stirred at 0 °C for 15 h. The mixture was poured into ice and extracted with Et_2O. The organic layer was washed with brine, dried (Na_2SO_4), and evaporated. The residue was chromatographed (hexane/AcOEt, 8/2) to give **10a** (1.99 g, 90%) as an oil, which was used in the next step without further purification: NMR δ 7.75–6.70 (12 H, m, ArH × 12), 4.50 and 4.16 (each 1 H, each d, J = 12 Hz, CH_2O), 4.42 (1 H, s, C_3-H), 3.15 (3 H, s, OMe), and 2.42 (3 H, s, $ArCH_3$).

(2*S*,3*S*)-3-(4-Chlorophenyl)-2-(2,4-dichlorophenyl)-3-methoxy-1-[(*p*-tolylsulfonyl)oxy]propan-2-ol (15b). Tosylation of the diol **14b** (640 mg, 1.77 mmol) as above afforded **15b** (690 mg, 76%): mp 157–159 °C (Et_2O–hexane); NMR δ 7.75–6.85 (11 H, m, ArH × 11), 5.08 and 4.70 (each 1 H, each d, J = 12 Hz, CH_2O), 4.96 (1 H, s, C_3-H), 3.44 (1 H, s, OH), 3.22 (3 H, s, OMe), and 2.42 (3 H, s, $ArCH_3$); $[\alpha]^{23}_D$ −72.9° (*c* 1.00, $CHCl_3$). Anal. Calcd for $C_{23}H_{21}O_5Cl_3S$: C, 53.55; H, 4.10; Cl, 20.62; S, 6.22. Found: C, 53.27; H, 4.07; Cl, 20.91; S, 5.93.

(2*S*,3*R*)-2,3-Bis(4-chlorophenyl)-3-methoxy-1-(1*H*-1,2,4-triazol-1-yl)propan-2-ol (11a). A mixture of the tosylate **10a** (1.90 g, 3.95 mmol), 1,2,4-triazole (0.55 g, 7.90 mmol), NaH (50% mineral oil dispersion, 0.379 g, 7.90 mmol), and DMF (10 mL) was stirred at 70 °C for 2 h. The mixture was poured into ice and extracted with CH_2Cl_2. The organic layer was dried (Na_2SO_4) and evaporated to leave an oil which was chromatographed. Elution with CH_2Cl_2/MeOH (95/5) gave **11a** (1.25 g, 84%) as an oil: NMR δ 8.00 and 7.80 (each 1 H, each s, triazole H × 2), 7.30–6.70 (8 H, m, ArH × 8), 4.72 and 4.55 (each 1 H, each d, J = 12 Hz, CH_2N), 4.02 (1 H, s, C_3-H), and 3.16 (3 H, s, OMe). Oxalate: mp 159–161 °C (Et_2O); $[\alpha]^{23}_D$ −82.0° (*c* 1.02, EtOH). Anal. Calcd for $C_{20}H_{19}N_3O_6Cl_2$: C, 51.29; H, 4.09; N, 8.97; Cl, 15.14. Found: C, 51.29; H, 4.06; N, 9.01; Cl, 15.38.

(2*S*,3*S*)-3-(4-Chlorophenyl)-2-(2,4-dichlorophenyl)-3-methoxy-1-(1*H*-1,2,4-triazol-1-yl)propan-2-ol (16b). Similar reaction of the tosylate **15b** (690 mg, 1.34 mmol) as above gave **16b** (440 mg, 80%) as an oil: NMR δ 7.96 and 7.76 (each 1 H, each s, triazole H × 2), 7.30–6.80 (7 H, m, ArH × 7), 5.52 and 4.94 (each 1 H, each d, J = 15 Hz, CH_2N), 5.18 (1 H, s, C_3-H), 4.54 (1 H, s, OH), and 3.32 (3 H, s, OMe). Oxalate: mp 92–94 °C (AcOEt/Et_2O); $[\alpha]^{23}_D$ −11.3° (*c* 1.01, EtOH). Anal. Calcd for $C_{20}H_{19}N_3O_6Cl_3$: C, 47.68; H, 3.80; N, 8.34; Cl, 21.12. Found: C, 47.44; H, 3.96; N, 8.21; Cl, 21.36.

(2*S*,3*R*)-2,3-Bis(4-chlorophenyl)-1-(1*H*-1,2,4-triazol-1-yl)propane-2,3-diol (12a). A mixture of **11a** (1.30 g, 3.44 mmol), $AlCl_3$ (1.37 g, 10.3 mmol), and NaI (1.55 g, 10.3 mmol) in MeCN (10 mL) was refluxed for 8 h. The mixture was diluted with CH_2Cl_2 and washed with aqueous $Na_2S_2O_3$ solution. The organic layer was dried (Na_2SO_4) and evaporated, and the residue was chromatographed. Elution with CH_2Cl_2/MeOH (95/5) gave the starting material **11a** (340 mg, 26%). Further elution afforded **12a** (640 mg, 51%): mp 181–183 °C (Et_2O); NMR δ 7.94 and 7.74 (each 1 H, each s, triazole H × 2), 7.30–6.80 (8 H, m, ArH × 8), 4.76 and 4.46 (each 1 H, each d, J = 13 Hz, CH_2N), 4.55 (1 H, s, C_3-H); $[\alpha]^{25}_D$ −0.7° (*c* 1.01, $CHCl_3$). Anal. Calcd for $C_{17}H_{15}N_3O_2Cl_2$: C, 56.06; H, 4.15; N, 11.54; Cl, 19.47. Found: C, 55.98; H, 4.19; N, 11.42; Cl, 19.18.

(2*S*,3*S*)-3-(4-Chlorophenyl)-2-(2,4-dichlorophenyl)-1-(1*H*-1,2,4-triazol-1-yl)propane-2,3-diol (17b). Similar reaction of **16b** (340 mg, 0.82 mmol) as above yielded **17b** (254 mg, 78%): mp 164–166 °C (Et_2O); NMR (Me_2SO-d_6) δ 8.32 and 7.54 (each 1 H, each s, triazole H × 2), 7.40–6.90 (7 H, m, ArH × 7), 5.90 (1 H, s, C_2-OH), 6.26 (1 H, d, J = 5 Hz, C_3-OH), 5.60 (1 H, d, J = 5 Hz, C_3-H), 5.46 and 4.84 (each 1 H, each d, J = 15 Hz, CH_2N); $[\alpha]^{23}_D$ −47.1° (*c* 1.00, MeOH). Anal. Calcd for $C_{17}H_{14}N_3O_2Cl_3$: C, 51.21; H, 3.54; N, 10.61; Cl, 26.68. Found: C, 51.31; H, 3.61; N, 10.53; Cl, 26.75.

(*S*)-(+)-2,3-Bis(4-chlorophenyl)-3-oxo-1-(1*H*-1,2,4-triazol-1-yl)propan-2-ol [(*S*)-(+)-1a]. Me_2SO (1 mL) was added dropwise to a stirred solution of oxalyl chloride (127 mg, 1 mmol) in CH_2Cl_2 (2 mL) at −78 °C. Diol **12a** (364 mg, 1 mmol) was added and the solution was stirred at −78 °C for 15 min. Et_3N (2 mL) was added, and the solution was stirred at room temperature for 15 min. The mixture was diluted with CH_2Cl_2 and washed with brine, and the organic layer was dried (Na_2SO_4) and evaporated. The residue was chromatographed (CH_2Cl_2/MeOH, 98/2), yielding (*S*)-(+)-(**1a**) (293 mg, 81%): mp 161–163 °C (Et_2O); IR ($CHCl_3$) 1720 cm^{-1}; NMR δ 8.02 and 7.86 (each 1 H, each s, triazole H × 2), 7.90–7.20 (8 H, m, ArH × 8), 6.30 (1 H, brs, OH), 5.03 and 4.37 (each 1 H, each d, J = 13 Hz, CH_2N); $[\alpha]^{23}_D$ +117.3° (*c* 1.00, $CHCl_3$). Anal. Calcd for $C_{17}H_{13}N_3O_2Cl_2$: C, 56.38; H, 3.62; N, 11.60; Cl, 19.58. Found: C, 56.43; H, 4.01; N, 11.95; Cl, 19.83.

(*S*)-(+)-3-(4-Chlorophenyl)-2-(2,4-dichlorophenyl)-3-oxo-1-(1*H*-1,2,4-triazol-1-yl)propan-2-ol [(*S*)-(+)-1b]. Oxidation of the diol **17b** (127 mg, 1 mmol) as above provided (*S*)-(+)-**1b** (122 mg, 81%): mp 200–202 °C (Et_2O); IR ($CHCl_3$) 1720 cm^{-1}; NMR 7.88 and 7.66 (each 1 H, each s, triazol H × 2), 7.80–7.20 (7 H, m, ArH × 7), 6.75 (1 H, brs, OH) 5.12 and 4.84 (each 1 H, each d, J = 15 Hz, CH_2N); $[\alpha]^{23}_D$ +282.0° (*c* 1.01, $CHCl_3$). Anal. Calcd for $C_{17}H_{12}N_3O_2Cl_3$: C, 51.47; H, 3.05; N, 10.59; Cl, 26.82. Found: C, 51.41; H, 3.21; N, 10.61; Cl, 26.91.

Facile De-*tert*-butoxycarbonylations of β-Keto Esters and Mixed Malonate Esters Using Water in Dimethyl Sulfoxide

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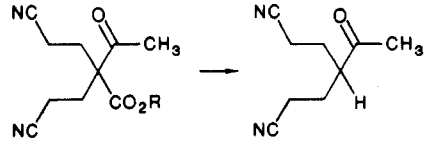
Dealkoxycarbonylations of malonate esters, β-keto esters, and α-cyano esters (and other related activated substrates) to esters, ketones, and cyanides, respectively, using water or water/LiCl (or other salts) in dipolar aprotic solvents such as Me_2SO are important synthetic reactions.[1]

During the course of preparation of 4-acetylheptane-1,7-dinitrile (**2**), we have investigated the dealkoxycarbonylations of the β-keto esters **1a** and **1b** under several reaction conditions.



1a, R = CH_2CH_3
b, R = $C(CH_3)_3$

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On heating the β-keto ester **1a** with water/Me_2SO/LiCl for 5 h at reflux, the dinitrile **2** could be isolated in a 60% yield. In the absence of the LiCl only about 10% reaction occurred under reflux for 3 days.

(1) (a) Krapcho, A. P. *Synthesis* **1982**, 805. (b) Krapcho, A. P. *Synthesis* **1982**, 893.

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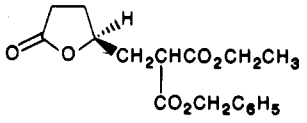
On the other hand, when **1b** is heated in water/Me_2SO/LiCl or in water/Me_2SO alone, **2** could readily be obtained in yields of 90% and 60%, respectively. Based on these observations, it can be concluded that the de-*tert*-butoxycarbonylation occurs more readily than the deethoxycarbonylation in water/Me_2SO in the absence of salts such as LiCl.

When di-*tert*-butyl malonate is refluxed in water/Me_2SO, *tert*-butyl acetate and *tert*-butyl alcohol are formed rapidly. The mixed malonate ester, *tert*-butyl ethyl malonate on heating in water/Me_2SO or water/Me_2SO/LiCl gives an ethyl acetate to *tert*-butyl acetate ratio of 10 and 6, respectively. Both reaction conditions lead to a selective de-*tert*-butoxycarbonylation.

One is tempted to conclude that the selective loss of the *tert*-butyl ester is based on an oxygen–alkyl cleavage of these esters to form a tertiary carbocation intermediate under the conditions of water/Me_2SO. The increased proportion of deethoxycarbonylation found in the water/Me_2SO/LiCl reaction is suggestive of more S_N2 cleavage of the ethyl ester functionality which would lead to a higher proportion of *tert*-butyl acetate.

One case of a selective removal of an ester functionality from a mixed malonate ester has been reported recently.[2] The reaction of **3** (or its enantiomer) with water/Me_2SO/NaCl apparently leads only to **4** (90%), this product arising from selective attack of the carbethoxy functionality.



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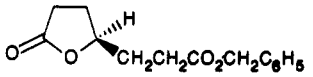

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In addition an α-cyano-*tert*-butyl ester has recently been reported as undergoing a de-*tert*-butoxycarbonylation on treatment with water/NaCl/Me_2SO.[3] It might be expected on the basis of the foregoing results that this could also be effectively accomplished by water/Me_2SO alone.

The results are of potential usefulness for the future construction of molecules of the activated types discussed here which will allow for the facile chemoselective removal of tertiary ester groups using only water in dipolar aprotic solvents.

Experimental Section

Preparation of 2. (a) From 1b, Water, and LiCl/Me_2SO. A mixture of **1b**[4] (60.0 g, 0.227 mol), Me_2SO (300 mL), water (4.5 g, 0.25 mol), and LiCl (10.6 g, 0.25 mol) was heated at reflux for 5 h. The reaction mixture was cooled, water (200 mL) was added, and the mixture was extracted with methylene chloride (3 × 150 mL). The extract was dried over $MgSO_4$ and the solvent removed in vacuo. Distillation under reduced pressure removed *t*-BuOH and Me_2SO, and the dinitrile **2** was collected at 173–175 °C (0.5 mmHg) as a light yellow viscous oil (33.5 g, 90%).

(b) From 1b and Water/Me_2SO. A mixture of **1b** (6.0 g, 0.0227 mol), Me_2SO (30 mL), and water (0.45 g, 0.025 mol) was heated under reflux for 3 h. The workup and purification procedure was the same as in the procedure a above. Compound **2** was obtained (2.23 g, 60%).

(c) From 1a and Water/Me_2SO. A mixture of **1a**[5] (1.56 g, 0.0066 mol), Me_2SO (9 mL), and water (0.2 mL) was refluxed for 96 h. Workup and purification as in a above led to 0.09 g (8%) of **2**.

(d) From 1a and Water/Me_2SO/LiCl. A mixture of **1a** (53.64 g, 0.227 mol), Me_2SO (300 mL), water (4.5 g, 0.25 mol), and LiCl (10.6 g, 0.25 mol) was refluxed for 5 h. Workup and purification as in procedure a above gave **2** (21.50 g, 59%).

***tert*-Butyl Ethyl Malonate Reactions. (a) Water/Me_2SO/LiCl.** A mixture of *tert*-butyl ethyl malonate (2.0 g, 0.01 mol), Me_2SO (8 mL), water (0.21 g, 0.012 mol), and LiCl (0.5 g, 0.12 mol) was heated under reflux for 4 h. The reaction mixture was distilled at atmospheric pressure and the analysis of the distillate performed by proton NMR analysis to determine the product ratios. For this analysis the singlets at δ 2.02 (CH_3CO_2Et), 1.95 (CH_3CO_2-*t*-Bu), or 1.42 ($MeCO_2C(CH_3)_3$) were used.

(b) Water/Me_2SO. Performed as above without LiCl.

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Nafion-H† Catalyzed De-tert-butylation of Aromatic Compounds[1a]

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It has been previously reported that the *tert*-butyl group could serve as a positional protective group for the preparation of some phenolic compounds,[2-8] diarylalkanes,[9] dibenzocycloheptadiene[10] 4-hydroxyphenyl aryl ether,[11] dimethyl- and dihydroxy[2.2]metacyclophanes,[12-13] 1,2-di- and 1,2,3-trisubstituted benzenes,[14] and 2-mono and 2,2-disubstituted biphenyls.[15]

The transalkylation (including trans tert-butylation) of aromatic compounds is usually carried in the liquid phase using sulfuric acid and Lewis acid halides, mainly $AlCl_3$, as catalyst. Although the conversions are high, generally complex workup procedures are necessary involving quenching of complexes (which often result in multistep workup procedures for Lewis acids like $AlCl_3$, $AlBr_3$, BF_3, etc.) or washing the products repeatedly for acid removal. Furthermore, *tert*-butyl-substituted aromatic compounds that contain hydroxyl, methoxy, carbonyl, and amino groups, etc., are easily complexed with Lewis acids. To obtain optimum yields in such cases, more than the molar equivalent of catalyst is required.

Over the years we have shown that Nafion-H,[16] a superacidic perfluororesinsulfonic acid is a convenient catalyst for a variety of acid-catalyzed synthetic transformations. The selectivity, high catalytic activity, and its ease of re-

† Nafion-H is a registered trademark of Du Pont.

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