SUPPORTING INFORMATION

Unusual and Unexpected Reactivity of t-Butyl Dicarbonate (Boc₂O) with Alcohols in the Presence of Magnesium Perchlorate. A New and General Route to t-Butyl Ethers.

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General Methods. The ^1H and ^{13}C NMR spectra were recorded at 400 MHz and 100 MHz, respectively. The chemical shifts (δ) are given in ppm relative to the signals of the solvent (CHCl_3) or TMS. Coupling constants are given in Hz. Carbon types were determined by DEPT ^{13}C NMR experiments. The following abbreviations are used to indicate the multiplicity: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), bs (broad signal).

Purification of reaction products was carried out by flash chromatography on silica gel (230-400 mesh). Optical rotations are reported as follows: $[\alpha]_D^{25}$ (c in g per 100 mL, solvent).

Materials. Commercial grade reagents and solvents were used without further purification.

All starting alcohols, anhydrous $\text{Mg}(\text{ClO}_4)_2$ and Boc_2O were purchased from Aldrich and used as received.

General Procedure for the Synthesis of t-Butyl Ethers.

All the reactions were carried out in CH_2Cl_2 or without solvent. Anhydrous $\text{Mg}(\text{ClO}_4)_2$ was heated under vacuum (0.1 Torr) at 130°C for 2h before use to enhance its activity.

In a two necked flask equipped with a magnetic stirring bar and a condenser coil, $\text{Mg}(\text{ClO}_4)_2$ (0.10 mmol) and the alcohol **1** (1.0 mmol) were dissolved in 1.5 mL of CH_2Cl_2 . Then Boc_2O (2.3 mmol) was added and a bubbling was immediately observed. The mixture was stirred at reflux until the TLC analysis revealed the presence of Boc_2O . The crude reaction mixture was diluted with water and extracted with CH_2Cl_2 . The organic layer was separated, dried over MgSO_4 , filtered and the solvent was removed by rotary evaporation. The t-butyl ether was separated from the residual alcohol by flash chromatography on silica gel with a mixture of petroleum ether/ Et_2O =9:1.

When the reaction was carried out without solvent, the alcohol **1** and the catalyst are mixed together, then Boc_2O was added and the mixture was heated at 40°C until the TLC analysis revealed the presence of Boc_2O .

1-t-Butoxy-4-methoxybenzene¹ **3h** and (S)-Ethyl 2-t-butoxypropanoate² **3r** are known compounds completely characterized. t-Butyl 2-nitroethyl ether **3p** is a commercial product. ^1H and ^{13}C NMR data for other compounds follow.

1-t-Butoxyoctane 3a: ^1H NMR³: δ (ppm)= 0.88 (t, $J_{\text{HH}}=6.8$, 3H), 1.19 (s, 9H), 1.20-1.40 (m, 10H), 1.45-1.55 (m, 2H), 3.32 (t, $J_{\text{HH}}=6.6$, 2H).

^{13}C NMR : δ (ppm)= 14.0 (CH_3), 22.6 (CH_2), 26.2 (CH_2), 27.5 (CH_3), 29.3 (CH_2), 29.5 (CH_2), 30.7 (CH_2), 31.8 (CH_2), 61.6 (CH_2), 72.3 (C).

1-t-Butoxybenzene 3b: ^1H NMR : δ (ppm)= 1.35 (s, 9H), 6.95-7.00 (m, 2H), 7.05-7.10 (m, 1H), 7.25-7.30 (m, 2H).

^{13}C NMR⁴: δ (ppm)= 29.4 (CH_3), 78.3 (C), 123.3 (CH), 124.2 (CH), 128.8 (CH), 131.9 (C).

2-t-Butoxyoctane 3c: ^1H NMR: δ (ppm)= 0.88 (t, $J_{\text{HH}}=6.8$, 3H), 1.10 (d, $J_{\text{HH}}=6.2$, 3H), 1.18 (s, 9H), 1.25-1.50 (m, 10H), 3.50-3.60 (m, 1H).

^{13}C NMR: δ (ppm)= 14.1 (CH_3), 22.6 (CH_2), 23.0 (CH_3), 26.1 (CH_2), 28.6 (CH_3), 29.5 (CH_2), 31.9 (CH_2), 39.0 (CH_2), 67.4 (CH), 76.6 (C).

t-Butoxycyclopentane 3d: ^1H NMR⁵: δ (ppm)= 1.18 (s, 9H), 1.40-1.50 (m, 4H), 1.60-1.85 (m, 4H), 3.95-4.05 (m, 1H).

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^{13}C NMR: δ (ppm)= 23.7 (CH_2), 28.6 (CH_3), 34.9 (CH_2), 72.8 (CH), 73.5 (C).

(1S, 2R, 4R)-2-t-Butoxy-1-isopropyl-4-methylcyclohexane 3e: ^1H NMR: δ (ppm)= 0.72 (d, $J_{\text{HH}}=6.9$, 3H), 0.80-1.00 (m, 3H), 0.88 (d, $J_{\text{HH}}=6.4$, 3H), 0.90 (d, $J_{\text{HH}}=6.8$, 3H), 1.05-1.15 (m, 1H), 1.21 (s, 9H), 1.30-1.40 (m, 1H), 1.60-1.65 (m, 2H), 1.95-2.00 (m, 1H), 2.20-2.25 (m, 1H), 3.21 (dt, $J_{\text{HH}}=4.4$, $J_{\text{HH}}=10.3$, 1H).

^{13}C NMR: δ (ppm)= 16.2 (CH_3), 21.7 (CH_3), 22.5 (CH_3), 23.3 (CH_2), 24.7 (CH), 29.3 (CH_3), 31.8 (CH), 34.6 (CH_2), 45.4 (CH_2), 49.2 (CH), 71.5 (CH), 73.1 (C).

$[\alpha]_{\text{D}}^{25} = -50$ (c=1, CHCl_3)

1-(t-Butoxymethyl) benzene 3f ^1H NMR⁶: δ (ppm)= 1.31 (s, 9H), 4.47 (s, 2H), 7.25-7.40 (m, 5H).

^{13}C NMR: δ (ppm)= 27.7 (CH_3), 64.1 (CH_2), 73.4 (C), 127.1 (CH), 127.4 (CH), 128.3 (CH), 139.9 (C).

2-t-Butoxy-1,2-diphenylethanone 3g: ^1H NMR⁷: δ (ppm)= 1.25 (s, 9H), 5.62 (s, 1H), 7.20-7.55 (m, 8H), 8.05-8.10 (m, 2H).

^{13}C NMR: δ (ppm)= 28.0 (CH_3), 76.0 (C), 79.7 (CH), 126.1 (CH), 127.6 (CH), 128.1 (CH), 128.5 (CH), 130.0 (CH), 132.7 (CH), 135.2 (C), 138.6 (C), 200.1 (C).

1-t-Butoxy-3-chlorobenzene 3i: ^1H NMR: δ (ppm)= 1.35 (s, 9H), 6.88 (ddd, $J_{\text{HH}}=1.0$, $J_{\text{HH}}=2.2$, $J_{\text{HH}}=8.1$, 1H), 7.00 (t, $J_{\text{HH}}=2.2$, 1H), 7.05 (ddd, $J_{\text{HH}}=1.0$, $J_{\text{HH}}=2.2$, $J_{\text{HH}}=8.1$, 1H), 7.18 (t, $J_{\text{HH}}=8.1$, 1H).

^{13}C NMR: δ (ppm)= 28.8 (CH_3), 79.2 (C), 122.2 (CH), 123.4 (CH), 124.3 (CH), 129.6 (CH), 134.0 (C), 156.4 (C).

1-t-Butoxy-4-fluorobenzene 3j: ^1H NMR: δ (ppm)= 1.31 (s, 9H), 6.93 (s, 2H), 6.94 (s, 2H).

^{13}C NMR: δ (ppm)= 28.7 (CH_3), 78.5 (C), 115.2 (d, $J_{\text{CF}}=22.4$, CH), 125.5 (d, $J_{\text{CF}}=8.2$, CH), 151.1 (C), 159.1 (d, $J_{\text{CF}}=240.3$, C).

1-t-Butoxynaphthalene 3k: ^1H NMR: δ (ppm)= 1.46 (s, 9H), 7.10 (dd, $J_{\text{HH}}=1.0$, $J_{\text{HH}}=7.6$, 1H), 7.33 (t, $J_{\text{HH}}=7.8$, 1H), 7.40-7.45 (m, 2H), 7.50 (d, $J_{\text{HH}}=8.3$, 1H), 7.75-7.80 (m, 1H), 8.20-8.25 (m, 1H).

^{13}C NMR: δ (ppm)= 29.1 (CH_3), 79.7 (C), 116.3 (CH), 122.3 (CH), 123.4 (CH), 125.1 (CH), 125.4 (CH), 125.9 (CH), 127.5 (CH), 130.0 (C), 134.8 (C), 152.1 (C).

2-t-Butoxynaphthalene 3l: ^1H NMR: δ (ppm)= 1.41 (s, 9H), 7.18 (dd, $J_{\text{HH}}=2.4$, $J_{\text{HH}}=8.7$, 1H), 7.35-7.45 (m, 3H), 7.65-7.80 (m, 3H).

^{13}C NMR: δ (ppm)= 28.9 (CH_3), 78.9 (C), 119.7 (CH), 124.4 (CH), 125.0 (CH), 125.9 (CH), 127.2 (CH), 127.9 (CH), 128.5 (CH), 130.3 (C), 134.1 (C), 152.2 (C).

(E)-1-(3-t-Butoxy-2-methylprop-1-enyl) benzene 3m: ^1H NMR: δ (ppm)= 1.27 (s, 9H), 1.88 (d, $J_{\text{HH}}=1.4$, 3H), 3.95 (d, $J_{\text{HH}}=1.0$, 2H), 6.54 (bs, 1H), 7.15-7.20 (m, 1H), 7.25-7.35 (m, 4H).

^{13}C NMR: δ (ppm)= 15.6 (CH_3), 27.6 (CH_3), 68.0 (CH_2), 73.2 (C), 125.6 (CH), 126.1 (CH), 128.0 (CH), 129.9 (CH), 136.5 (C), 138.0 (C).

t-Butyl cholesteryl ether 3n: ^1H NMR: δ (ppm)= 0.67 (s, 3H), 0.85-1.70 (m, 34H), 1.19 (s, 9H), 1.80-1.90 (m, 2H), 1.95-2.00 (m, 2H), 2.10-2.15 (m, 1H), 2.25-2.30 (m, 1H), 3.25-3.35 (m, 1H), 5.3 (bs, 1H).

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^{13}C NMR: δ (ppm)= 11.8 (CH₃), 18.7 (CH₃), 19.4 (CH₃), 21.1 (CH₂), 22.6 (CH₃), 22.8 (CH₃), 23.8 (CH₂), 24.3 (CH₂), 28.0 (CH), 28.2 (CH₂), 28.5 (CH₃), 31.3 (CH₂), 31.9 (CH), 32.0 (CH₂), 35.8 (CH), 36.2 (CH₂), 36.6 (C), 37.8 (CH₂), 39.5 (CH₂), 39.8 (CH₂), 42.1 (CH₂), 42.3 (C), 50.3 (CH), 56.2 (CH), 56.8 (CH), 71.5 (CH), 73.3 (C), 120.9 (CH), 142.0 (C).
[α]_D²⁵ = -35 (c=1, CHCl₃)

(Z)-1-t-Butoxyhex-3-ene 3o: ^1H NMR: δ (ppm)= 0.88 (t, $J_{\text{HH}}=6.8$, 3H), 1.19 (s, 9H), 1.20-1.40 (m, 6H), 2.00-2.05 (m, 2H), 2.20-2.35 (m, 2H), 3.33 (t, $J_{\text{HH}}=7.2$, 2H), 5.30-5.50 (m, 2H).
 ^{13}C NMR: δ (ppm)= 14.0 (CH₃), 22.6 (CH₃), 27.3 (CH₂), 27.6 (CH₃), 29.0 (CH₂), 29.4 (CH₂), 31.5 (CH₂), 61.5 (CH₂), 72.6 (C), 125.7 (CH), 131.8 (CH).

1-Bromo-3-t-butoxynonane 3q: ^1H NMR: δ (ppm)= 1.18 (s, 9H), 1.30-1.35 (m, 8H), 1.40-1.55 (m, 4H), 1.80-1.90 (m, 2H), 3.32 (t, $J_{\text{HH}}=6.7$, 2H), 3.40 (t, $J_{\text{HH}}=7.0$, 2H).
 ^{13}C NMR: δ (ppm)= 26.1 (CH₂), 27.5 (CH₃), 28.1 (CH₂), 28.6 (CH₂), 29.32 (CH₂), 29.33 (CH₂), 30.6 (CH₂), 32.8 (CH₂), 33.9 (CH₂), 61.5 (CH₂), 72.3 (C).

Benzyl 4-(t-butoxy)butyl ether 3s: ^1H NMR : δ (ppm)= 1.17 (s, 9H), 1.55-1.70 (m, 4H), 3.35 (t, $J_{\text{HH}}=6.4$, 2H), 3.49 (t, $J_{\text{HH}}=6.8$, 2H), 4.50 (s, 2H), 7.25-7.35 (m, 5H).
 ^{13}C NMR: δ (ppm)= 26.6 (CH₂), 27.3 (CH₂), 27.5 (CH₃), 61.3 (CH₂), 70.3 (CH₂), 72.5 (C), 72.8 (CH₂), 127.5 (CH), 127.6 (CH), 128.3 (CH), 138.6 (C).

4-(t-Butoxy) butyl tri-isopropylsilyl ether 3t: ^1H NMR : δ (ppm)= 1.05-1.10 (m, 21H), 1.18 (s, 9H), 1.55-1.60 (m, 4H), 3.35-3.40 (m, 2H), 3.65-3.70 (m, 2H).
 ^{13}C NMR: δ (ppm)= 12.0 (CH), 18.0 (CH₃), 27.1 (CH₂), 27.8 (CH₃), 29.9 (CH₂), 61.5 (CH₂), 63.4 (CH₂), 72.4 (C).

t-Butyl 2-t-butoxyethylcarbamate 3u: ^1H NMR : δ (ppm)= 1.18 (s, 9H), 1.45 (s, 9H), 3.20-3.25 (m, 2H), 3.41 (t, $J_{\text{HH}}=4.8$, 2H), 4.88 (bs, 1H).
 ^{13}C NMR: δ (ppm)= 27.5 (CH₃), 28.4 (CH₃), 41.2 (CH₂), 60.6 (CH₂), 73.0 (C), 79.1 (C), 156.1 (C).

General Procedure for the Deprotection of t-Butyl Ethers.

The reactions were carried out in undistilled CH₃CN without any precautions to exclude water. In a two necked flask equipped with a magnetic stirring bar and a condenser coil, CeCl₃·7H₂O (1.0 mmol), NaI (1.0 mmol) and the ether **3** (1.0 mmol) were dissolved in 2 mL of CH₃CN. The mixture was stirred and heated at the desired temperature until the TLC analysis revealed the disappearance of the starting material. The crude reaction mixture was diluted with water and extracted with CH₂Cl₂. The organic layer was separated, dried over MgSO₄, filtered and the solvent was removed by rotary evaporation. The alcohol was purified by flash chromatography on silica gel with a mixture of petroleum ether/Et₂O=9:1.

INDEX	FREQUENCY	PPM	HEIGHT
1	4547.171	61.600	32.6
2	2401.009	31.826	27.3
3	2315.557	30.693	34.3
4	2224.002	29.480	33.9
5	2209.353	29.286	29.3
6	2075.682	27.514	108.5
7	1979.243	26.236	35.0
8	1707.018	22.627	25.2
9	1058.195	14.027	24.0

INDEX	FREQUENCY	PPM	HEIGHT
1	5775.915	76.560	15.2
2	5079.483	67.329	17.3
3	2945.018	39.036	23.1
4	2404.841	31.876	20.0
5	2223.561	29.473	20.8
6	2155.810	28.575	65.9
7	1969.036	26.100	23.0
8	1736.485	23.017	20.8
9	1705.967	22.613	18.4
10	1061.416	14.069	17.9

INDEX	FREQUENCY	PPM	HEIGHT
1	7130.034	71.437	32.6
2	4560.727	45.355	42.5
3	4560.727	45.351	42.5
4	3480.032	34.605	42.0
5	3159.942	31.820	37.9
6	2948.994	29.324	141.8
7	2477.859	24.640	32.7
8	2340.243	23.271	40.7
9	2260.911	22.482	44.7
10	2176.722	21.645	38.1
11	1629.493	16.204	40.2
12	100.330	0.998	42.0

INDEX	FREQUENCY	PPM	HEIGHT
1	13027.929	123.548	34.5
2	13028.511	123.439	86.1
3	12413.511	122.439	86.1
4	12287.228	122.183	81.5
5	7956.875	79.222	30.3
6	2894.489	28.782	220.9

INDEX	FREQUENCY	PPM	HEIGHT
1	12626.369	125.555	93.7
2	12618.274	125.475	91.6
3	11579.541	113.348	63.2
4	11577.541	113.348	63.2
5	2881.493	28.653	343.3
6	100.018	0.995	53.9

INDEX	FREQUENCY	PPM	HEIGHT
1	9696.683	128.530	35.6
2	9619.166	127.502	36.4
3	9593.530	127.163	36.8
4	9500.754	125.933	39.0
5	9426.289	124.946	32.0
6	9387.225	124.428	40.0
7	9031.989	119.719	28.9
8	2181.194	28.912	79.0

INDEX	FREQUENCY	PPM	HEIGHT
1	1378.53	138.011	28.9
2	13725.552	138.466	28.8
3	12965.852	128.931	60.6
4	12868.711	127.965	73.1
5	12682.524	126.114	47.8
6	12625.858	125.550	37.4
7	7775.277	77.317	50.7
8	7743.706	77.003	55.5
9	7711.326	76.681	53.3
10	7363.237	73.219	30.5
11	2941.392	29.527	181.0
12	2941.392	29.527	181.0
13	1570.386	15.616	23.2

INDEX	FREQUENCY PPM	HEIGHT
1	1215.866	13.4
2	1215.849	23.8
3	7775.244	16.5
4	7742.864	16.1
5	7711.293	16.6
6	7369.680	12.4
7	7185.521	39.7
8	5714.233	44.3
9	5647.853	42.6
10	5056.511	44.1
11	4236.306	41.5
12	4204.549	39.4
13	4004.549	39.4
14	3973.787	45.0
15	3799.743	39.4
16	3678.316	26.4
17	3639.460	42.9
18	3597.365	42.5
19	3214.467	44.9
20	3208.801	45.8
21	3151.325	13.6
22	2878.855	13.6
23	2838.855	42.5
24	2815.379	30.7
25	2442.195	40.3
26	2395.244	38.6
27	2293.245	40.9
28	2267.341	35.5
29	2116.772	38.2
30	1945.966	35.2
31	1881.205	37.3
32	1106.583	37.0
33	100.284	44.9

INDEX	FREQUENCY	PPM	HEIGHT
1	9942.341	131.786	28.6
2	9483.953	125.710	26.0
3	5841.264	77.426	19.6
4	5809.525	77.005	22.4
5	5777.175	76.577	22.9
6	5478.704	72.620	5.5
7	4635.783	61.447	35.5
8	2376.803	31.505	29.9
9	2214.444	29.353	31.4
10	2186.367	28.980	32.0
11	2078.942	27.556	120.3
12	2060.631	27.314	31.2
13	1701.733	22.557	23.8
14	1059.624	14.045	22.7
15	75.707	1.004	30.1

INDEX	FREQUENCY	PPM	HEIGHT
1	729.13	72.95	46.3
2	629.19	62.95	46.0
3	3405.534	33.864	35.5
4	3293.822	32.753	57.2
5	3078.492	30.612	60.8
6	2949.780	29.332	62.2
7	2948.161	29.316	60.0
8	2880.162	28.640	52.0
9	2824.306	28.085	54.5
10	2766.022	27.505	164.3
11	2628.405	26.137	64.7

180 160 140 120 100 80 60 40 20 ppm

INDEX	FREQUENCY PPM	HEIGHT
1	1293.804	6.8
2	12902.002	32.4
3	12832.575	62.1
4	12816.384	28.1
5	7776.378	12.8
6	7743.598	12.9
7	7712.427	13.6
8	7323.862	38.5
9	7288.244	11.9
10	7068.057	32.6
11	5160.337	157.2
12	2743.657	158.6
13	2743.657	39.0
14	2674.849	37.9

INDEX	FREQUENCY	PPM	HEIGHT
1	7775.942	77.323	36.1
2	7713.591	76.087	36.0
3	7713.591	76.087	36.9
4	7343.664	73.025	29.0
5	6098.638	60.644	64.2
6	4139.625	41.164	21.3
7	2854.124	28.381	252.5
8	2760.221	27.447	247.2