Introduction

Following the 1945 report by Newman on the utility of Trifluoroacetic Acid (TFA) as a condensing agent for the acylation of anisole with acetic anhydride [1], TFA has found enormous utility in organic synthesis [1-3]. For example, TFA is useful in protecting group removal, as a solvent for radical and polymer processes, oxidations, reductions, and other reactions [2]. Some years ago, we described the reduction of diarylmethanols to the corresponding diarylmethanes using the novel combination of NaBH₄ and trifluoroacetic acid [4]. During this study we observed the unexpected side reactions shown in Scheme 1, which obviously involve the TFA-promoted self-condensation of the initial reduction products 4, 6, and 8 with the carbocations derived from alcohols 1, 2, and 3 to give 5, 7, and 9, respectively. Although serendipitous, given hindsight this alkylation is not surprising given that TFA is strongly ionizing and poorly nucleophilic, and hence capable of stabilizing, in particular, benzylic carbocations.

Despite the intervening years, this simple TFA-promoted Friedel-Crafts alkylation of benzylic alcohols has not been pursued.
We now describe this alkylation as a simple alternative to the numerous other methods that have been reported for the benzylic alkylation of arenes with benzyl alcohols (e.g., HF [5], TsOH [6], Nafion-H [7] other cation-exchange resins [8], Sc(OTf)3 [9-11], NiOP04·3H2O [12,13], La(OTf)3 [10], Yb(OTf)3 [10,11], TiOH [10], Hf(OTf)4 [10], rare earth (III) (OSO2CF3)3 [14], zeolites [15-17], IrCl4·4H2O [18], l-Sn complex [19,20], 12-tungstophosphoric acid [21], I2 [22], IrCp* complexes [23], MoO6 [24], NaHSO4/SiO2 [25], Ph3P(OTf)2 [26], Fe(III)-porphyrin [27], BF3·H2O [28], Hf0.5[TEAPS]PW12O40 [29], choline chloride-(TOH)2 [30], and B(C6F5)3 [31]. Our method is eco-friendly as the only by-product is water and the TFA can be recycled. A summary of our results is depicted in Table 1. The reactions are not optimized. For example, in one case a 10-fold excess of TFA afforded a 93% yield of 17. In addition, we observed the benzylic alcohol and related alkylation shown in Scheme 2. Interestingly, an attempt to ambush the carbocation from alcohol 32 with NaBH4 [4] was unsuccessful and gave only 9-phenylfluorene [32].

**Table 1**: TFA-Promoted arene alkylation with benzyl alcohol (10).

<table>
<thead>
<tr>
<th>Arone</th>
<th>Product</th>
<th>Yield (%)</th>
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<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>70%</td>
</tr>
<tr>
<td>13</td>
<td>14</td>
<td>70%</td>
</tr>
<tr>
<td>15</td>
<td>17</td>
<td>70%</td>
</tr>
<tr>
<td>18</td>
<td>19</td>
<td>70%</td>
</tr>
<tr>
<td>12</td>
<td>20</td>
<td>70%</td>
</tr>
<tr>
<td>22</td>
<td>23</td>
<td>70%</td>
</tr>
<tr>
<td>25</td>
<td>26</td>
<td>47%</td>
</tr>
</tbody>
</table>

Note: A: Reactions were conducted with a 5-fold excess of arene and TFA as solvent at reflux; B: Yield of distilled product based on benzyl alcohol 10 or 25; C: A ten-fold excess of TFA and 2 grams of benzyl alcohol (10); D: Equimolar amounts of naphthalene (22) and benzyl alcohol (22); E: Yield of crude product.

To minimize the concentration of TFA, we diluted it with acetic acid (in a ratio of 1:10), but these alkylation conditions of benzene (11) with benzyl alcohol (10) only yielded benzyl acetate, consistent with the enhanced nucleophilicity of acetic acid vis-à-vis TFA. Given the propensity of TFA to promote rearrangements [32,33] in a control experiment we heated 1,4-dibenzy1benzene (20) in TFA for 12 h, but it was recovered unchanged. In the alkylations of toluene (13), biphenyl (12), and naphthalene (22) (Table 1) the expected isomeric mixtures were obtained, and the ratios were estimated by proton NMR integration. In summary, we have described a simple trifluoroacetic-promoted alkylation of aromatic hydrocarbons with benzyl alcohols. The reaction is exceptionally simple, the...
yields are satisfactory, the byproduct is water, and the TFA can be recycled. Neat TFA enjoys an ideal blend of ionizing power and low nucelophility to fulfill a successful arene alkylation of benzylic alcohols.

**Experimental Section**

Thin-layer chromatography was performed using oven-dried Silica gel G plates; benzene was used as a solvent system unless specified otherwise. Spots were observed under ultraviolet light (UVS-11), measuring Rf's from the top of the spot. Gas chromatography analysis was done on a Varian 2800 GC instrument, using CHCl3 or ether as a solvent; T = 150 °C unless otherwise indicated. Infrared spectra were recorded with neat films on NaCl plates, and chloroform solution cells for solids, recorded on a Perkin-Elmer 257 or 137 spectrometers. Polystyrene film was used for calibration. Nuclear magnetic resonance spectra were recorded on a Hitachi Perkin-Elmer R-24 spectrometer, using 5% TMS in CDCl3 as a solvent. Melting points were taken in capillary tubes using a Thomas-Hoover melting point apparatus; they were uncorrected.

**General Procedure for the Alkylation of Arenes with Benzyl Alcohol**

To a stirred solution of distilled trifluoroacetic acid (10 ml) and arene (0.09 mol) under nitrogen at rt was added a mixture of benzyl alcohol (1.00 g, 0.00926 mol) and arene (0.02 mol). The reaction was initially concentrated by rotary evaporation (to recover TFA and unreacted arene), and then distilled under vacuum to isolate the diary methane product. In some cases column chromatography was used for calibration. Nuclear magnetic resonance spectra were recorded on a Varian 2800 GC instrument, using CHCl3 as a solvent. Melting points were taken in capillary tubes using a Thomas-Hoover melting point apparatus; they were uncorrected.

**Characterization Data for Compounds**

**Diphenylmethane (12):** Colorless oil; Yield 64%; bp 88 °C/0.05 Torr (Lit [34], bp 165 °C/24 Torr), which slowly solidified (Lit [34], mp 24.5 °C); IR (film) 3110–3050, 740, 695 cm⁻¹ (Lit [35] IR (film) 3062, 733, 699 cm⁻¹); NMR (CDCl3) δ 7.5–6.8 (m, 10H), 3.7 (s, 2H), 2.3 (s, 3H); GC showed a single peak. This material was identical to an authentic sample [4].

**1-Benzyl-4-Methylbenzene (14) and 1-Benzyl-2-Methylbenzene (15):** Colorless oil (mixture); Yield 78%; bp 69 °C/0.05 Torr (Lit [7] bp 120–122 °C/3 Torr); IR (film) 3110–2940, 790, 745, 725, 695 cm⁻¹ (Lit [22] IR (film) 3063, 3025, 789, 743, 724, 697 cm⁻¹); NMR (CDCl3) δ 7.3–6.8 (m, 18H), 3.9 (s, 2H), 3.6 (s, 2H), 2.2 (s, 3H), 2.0 (s, 9H) (in a ~1:1 ratio) (Lit [22], for 14 NMR (CDCl3) δ 7.29–7.08 (m, 9H), 3.93 (s, 2H), 2.30 (s, 3H); GC showed a single peak. This material was identical to authentic sample [4].

**2-Benzyl-1,3,5-Trimethylbenzene (19):** Colorless oil; Yield 73%; bp 105 °C/0.05 Torr (Lit [7], bp 142-144 °C/5 Torr); IR (film) 3015–2880, 850, 725, 695 cm⁻¹ (Lit [35], IR (film) 3020, 2922, 852, 727 cm⁻¹); NMR (CDCl3) δ 7.2–6.8 (m, 7H), 4.0 (s, 2H), 2.4 (s, 3H), 2.2 (s, 6H) (Lit [18]), NMR (CDCl3) δ 7.24–7.11 (m, 5H), 6.88 (s, 4H), 4.01 (s, 2H), 2.28 (s, 3H), 2.20 (s, 6H); GC showed one peak. This material was identical to a known sample [4].

**1,4-Dibenzy1benzene (20) and 1,2-Dibenzy1benzene (21):** White solid (mixture from EtOH); Yield 68%; mp 58–64 °C (Lit [38], for 20, mp 85-86 °C; for 21, mp 78 °C); NMR (CDCl3) δ 7.7–7.0 (m, 28H), 4.45 (s, 4H), 3.90 (s, 4H); the latter peaks in a 3:1 ratio; (Lit [39], for 20) NMR (CDCl3) δ 7.30 (m, 4H), 7.23 (m, 6H), 7.16 (m, 4H), 3.99 (s, 4H); GC also showed two peaks in a ratio of 3:1. The major isomer (20) agreed by comparison with an authentic sample as prepared below.

**1,4-Dibenzy1benzene (20):** To a rt mixture of 1,4-diformylbenzene (Aldrich) (10.0 g, 0.0746 mol) in 95% EtOH (530 ml) and water (150 ml) was added NaBH₄ (1.00 g, 0.26 mol) over 1 h with stirring. After stirring for 3 h at rt, 6N HCl was added (100 ml). Concentration in vacuo to a volume of 200 ml induced formation of a white solid. Recrystallization from EtO affored colorless needles of 1,4-bis(hydroxymethyl)benzene, mp 119-120 °C (Lit [40], mp 117.5-118.5 °C). To a solution of TFA (15 ml) and benzene (25 ml) at rt was added the above diol (1.00 g, 0.00725 mol) in portions over 30 min. The mixture was refluxed for 24 h. The usual workup afforded an oil (2.23 g) that solidified. Crystallization from EtOH gave colorless crystals (0.439 g in two crops) of 20, mp 84-85 °C (Lit [38], mp 85-86 °C). This material was identical to the major isomer 20 as prepared above from diphenylmethane.

**1-Benzynaphthalene (23) and 2-Benzynaphthalene (24):** Colorless oil (mixture); Yield 25%; bp 80 °C/0.25 Torr (Lit [41] 217-230 °C/20 Torr); NMR (CDCl3) δ 8.1–6.9 (m, 15H), 4.4 (s, 2H), 4.1 (s, 2H), the latter peaks in a ratio of 4:1 (23:24); Lit [41], NMR (CDCl3) for 24, δ 7.7–7.0 (m, 7H), 7.08 (s, 5H), 3.92 (s, 2H); Lit [4] (for 23) mp 57.5-59.5 °C. The major isomer (23) was identical to authentic sample by TLC and NMR [4]. 4-Benzylbiphenyl (26). Solid; Yield 47%; mp 84-92 °C after crystallization from EtO (Lit [42], mp 85 °C) [4] mp 86.5-87 °C; NMR (CDCl3) δ 7.6-6.8 (m, 14H), 4.0 (s, 2H). This material was identical to authentic material [4].
References