Alkylation of deactivated arenes by alkanes in the presence of aprotic organic superacid $CBr_4 \cdot 2AlBr_3$

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Deactivated arenes (di- and tri-halobenzenes, acetophenone, benzophenone and methylbenzoate) have been shown to be alkylated by alkanes and cycloalkanes (propane, n-butane, cyclopentane) in the presence of superacid $CBr_4 \cdot 2AlBr_3$ in the range –40 to 0 °C; in some cases selective and effective mono- or di-alkylation can be achieved.

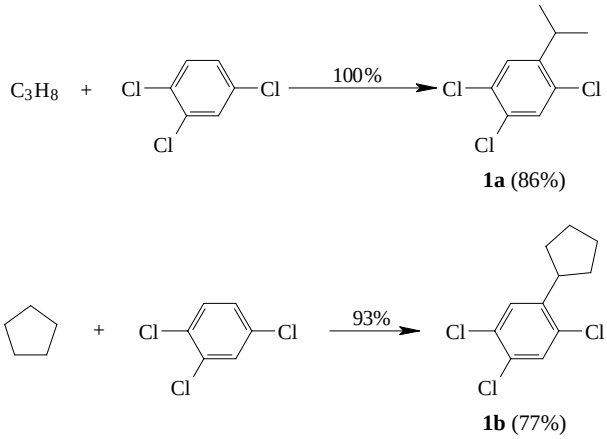
Alkylation of arenes is an important reaction from both fundamental and industrial points of view. In addition to traditional agents for Friedel–Crafts alkylation,[1] such as alkyl halides, olefins and alcohols, saturated hydrocarbons in the presence of aprotic superacids under mild conditions have also been used.[2,3] Obviously, saturated hydrocarbons are the most promising alkylating agents because of their availability and higher stability towards strong electrophiles, which minimizes side reactions.

Schmerling was the first to report on the alkylation of benzene and toluene with isoalkanes, methylcyclohexane, decahydronaphthalene and cyclohexane at *ca.* 30 °C,[2] induced by a $CuCl_2 + AlCl_3$ mixture. These reactions were not effective and selective. For example, the reaction of cyclohexane with benzene yielded only traces of cyclohexylbenzene, although the addition of minor amounts of isopentane increased the yield up to 10% based on initial $CuCl_2$ (20% based on benzene).

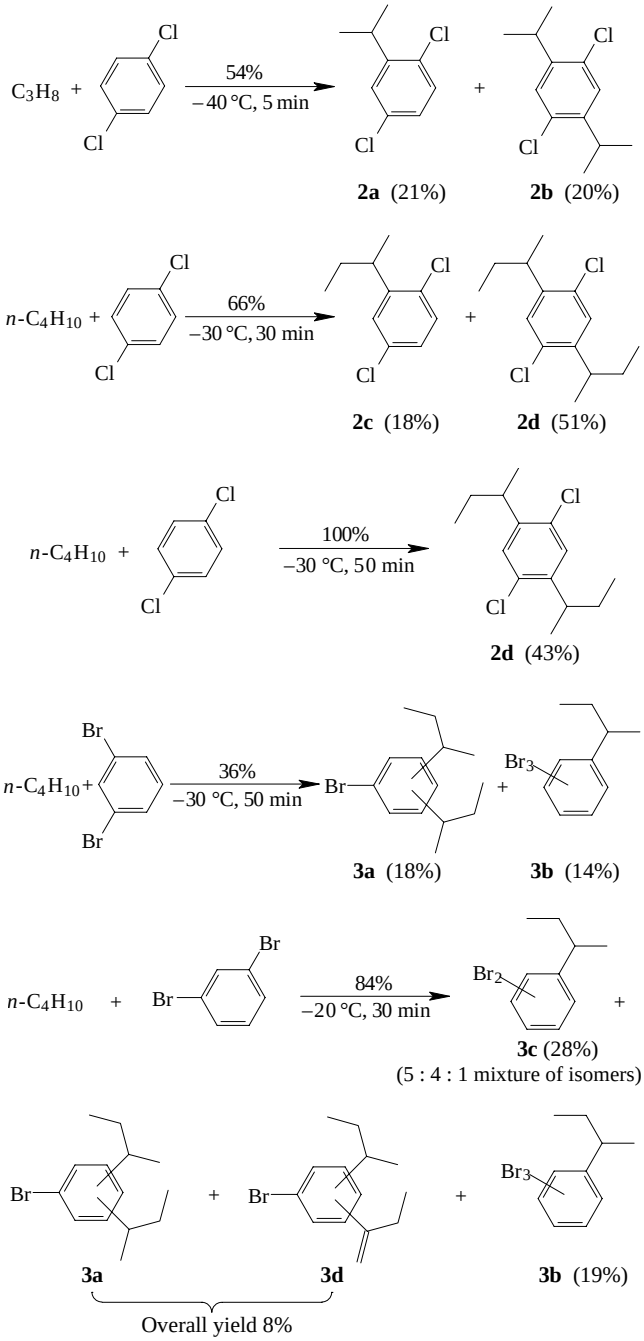
Recently we have reported the alkylacylation reaction of benzene and bromobenzene by alkanes (including n-butane) and cycloalkanes in the presence of $RCO^+Al_2X_7^-$ complexes at 0–20 °C.[3] These simple single-stage reactions allow in some cases the preparation of products with yields of 70–90% and good selectivity. It is to be stressed that alkylation of aromatics, even with traditional alkylating agents, has so far been limited to activated arenes[1] and fluoroaromatics[4] displaying specific properties. In ref. 5 it is stated that 'alkylation of aromatics more passivated than halobenzenes is impossible'. To the best of our knowledge the alkylation of dihalobenzenes, and especially trihalobenzenes, as well as other aromatics studied in this work has not been reported earlier even with traditional alkylating agents. Undoubtedly, alkylation of deactivated arenes by alkanes and cycloalkanes was previously unknown.

In continuation of our studies on the *polyhalomethane* $n AlBr_3$ superacid-initiated transformations of alkanes and cycloalkanes[6–8] we have found that passivated arenes can be alkylated by propane, butane and cyclopentane in the presence of $CBr_4 \cdot 2AlBr_3$ superacid in CH_2Br_2 solution at –40 to 0 °C.

Unexpectedly, the alkylation of trichlorobenzene has been found to occur more effectively and selectively than that of less passivated dihalobenzenes. The reaction of both propane and cyclopentane with 1,2,4-trichlorobenzene at –20 °C results in a single monoalkylated product in high yield (Scheme 1;



Scheme 1 Alkylation of 1,2,4-trichlorobenzene (–20 °C, 30 min).



Scheme 2 Alkylation of dihalobenzenes.

elsewhere the yields are given based on ArH; numbers over arrows indicate conversion of ArH).

The reactions with dihalobenzenes are less selective. Alkylation often leads to mixtures of mono- and di-alkylated products, and noticeable amounts of non-volatile tar are simultaneously formed. Moreover, alkylation of *p*-dibromobenzene (in contrast with *p*-dichlorobenzene) with more labile C–Br bonds is accompanied by disproportionation to yield alkylated mono- and tri-bromides. The reason for the low effeciency of dihalobenzene alkylation is mostly due to the rather high reactivity of the initial, and especially of the forming, alkylated dihalobenzenes towards the superacid. Indeed, the conversions of *p*-dichlorobenzene amount to 90–100% at –40 to –30 °C for 20–50 min, while the overall yield of alkylated products in some reactions does not exceed 45%. Nevertheless, taking into account the fact that mono- and di-alkylated products can be separated, some dichlorobenzene alkylation reactions may be considered to be of interest for laboratory preparations (Scheme 2).‡

The next group of reactions represents the alkylation of monosubstituted benzenes with a rather strong electron-withdrawing substituent (σ^+ constant up to +0.466), Scheme 3.‡,[9]

Since the formation of cations[10] and even dications[11] of aromatics under the action of powerful oxidizing agents has been proven, one may suggest that the key-stage in the considered reactions represents arene hydride ion abstraction by the superacid, similarly to reactions of alkanes with superacids. The arene cation then either directly attacks an alkane[10] or is added to an olefin generated from an alkane to form alkylated aromatics.

However, using the $CBr_4 \cdot 2AlBr_3$ superacid as the hydride ion trapping agent, we have shown that these pathways can be ruled out. Indeed, when 0.45 g of *m*-dibromobenzene was stirred with 0.62 g of CBr_4 and 1.1 g of $AlBr_3$ in 3.5 ml of CH_2Br_2 at 30 °C for 20 min no reduction product, $CHBr_3$, was found. It is interesting to note that without an arene under similar conditions the reduction of CBr_4 by CH_2Br_2 alone occurs to give $CHBr_3$ with a yield *ca*. 20% (Scheme 4).

The suppressing effect of the arene on hydride ion abstraction from CH_2Br_2 can be interpreted by supposing that in the presence of arene electrophilic attack of CBr_3^+ cation on arene is the dominant pathway. Thus, dibromobenzene is the worse donor of hydride ion than alkanes and dihalomethanes.

Therefore, for the reactions under discussion a mechanistic scheme similar to that common to electrophilic substitution of arenes can be proposed (Scheme 5).

The results of the present work deny the view that arenes more passivated than halobenzenes, are incapable of being alkylated.

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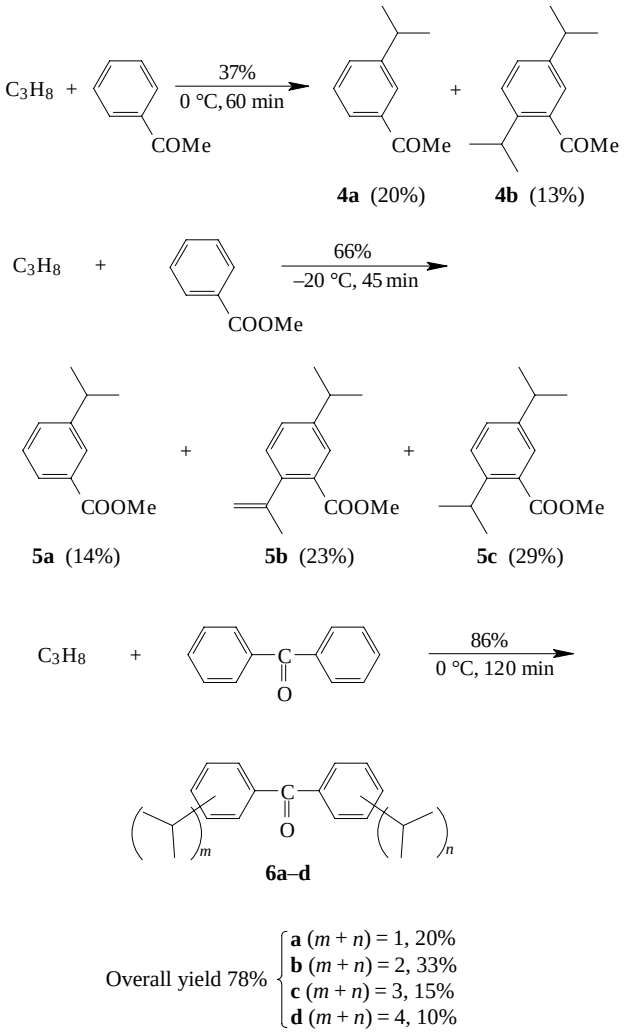
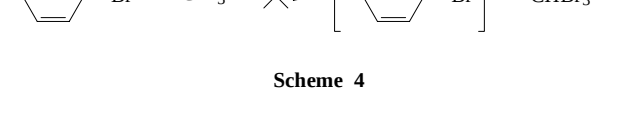


Scheme 3 Alkylation of monosubstituted deactivated arenes.



Scheme 4

† *Typical procedure*. A mixture of 1.0 g (3.75 mmol) $AlBr_3$, 0.62 g (1.87 mmol) CBr_4 and 2 ml of dried CH_2Br_2 was placed into a 100 ml two-necked round-bottomed flask and stirred until a homogeneous solution was formed. The mixture was cooled to –20 °C, then the reaction flask was filled with dry propane. A solution of 0.11 g (0.62 mmol) of 1,2,4-trichlorobenzene in 0.5 ml of CH_2Br_2 was then added under a propane atmosphere. The mixture was stirred at –20 °C over 0.5 h under a slight extra pressure of propane, then hydrolysed with ice-water, extracted with ether, washed with aqueous $NaHCO_3$, dried with anhydrous $MgSO_4$ and analysed. According to GC, a single product **1a** was formed, yield 0.125 g (0.56 mmol), 90% based on $C_6H_3Cl_3$.

‡ GC quantitative analyses were carried out with an internal standards using a Model 3700 gas chromatograph equiped by FID and quartz capillary column [l = 30 m, i.d. = 0.22 mm, stationary phase SE-54, temperature program 60 (0) - 8/min - 260 (5)]. Identification of reaction products was carried out by GC-MS method using a similar capillary column.

Selected mass spectral data of obtained compounds, m/z (I_{rel}, %):

1a: 222 (M^+, 28), 207 (100), 187 (6), 171 (18);

1b: 248 (M^+, 50), 219 (22), 213 (63), 206 (100), 193 (20), 159 (34), 149 (38), 55 (30);

2a: 230 (M^+, 29), 215 (100), 135 (6), 43 (31), 41 (5);

2c: 202 (M^+, 25), 173 (100), 159 (11), 137 (20), 102 (19);

2d: 258 (M^+, 18), 229 (100), 215 (7), 173 (13), 151 (8), 128 (12);

3a: 268 (M^+, 22), 239 (100);

3b: 368 (M^+, 11), 339 (100), 260 (15), 180 (12), 115 (11);

3c: 290 (M^+, 19), 261 (59), 180 (35), 115 (12), 100 (38), 77 (18);

3d: 266 (M^+, 75), 237 (100), 223 (12), 195 (9), 150 (33), 143 (40), 128 (22), 115 (22);

4a: 162 (M^+, 34), 147 (100), 119 (17), 103 (7), 91 (16), 77 (10);

4b: 204 (M^+, 25), 189 (100), 161 (13), 91 (9), 43 (50);

5a: 178 (M^+, 44), 163 (100), 147 (22), 131 (21), 119 (28), 91 (20), 77 (11), 59 (13);

5b: 218 (M^+, 80), 203 (100) 187 (20), 159 (22), 91 (8), 59 (8);

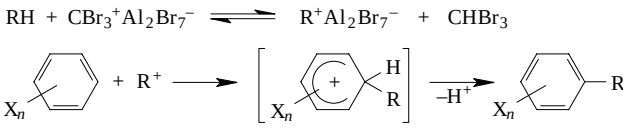
5c: 220 (M^+, 37), 205 (100), 189 (13), 177 (23), 161 (13), 131 (9), 91 (9), 59 (5);

6a: 224 (M^+, 88), 209 (70), 181 (24), 147 (90), 119 (17), 105 (100), 90 (13), 77 (68);

6b: 266 (M^+, 73), 251 (100), 223 (27), 189 (47), 161 (25), 105 (87), 91 (11), 77 (47);

6c: 308 (M^+, 77), 293 (100), 265 (39), 189 (50), 161 (81), 147 (60), 118 (16), 103 (14);

6d: 350 (M^+, 95), 335 (100), 307 (52), 189 (87), 173 (10), 160 (29), 131 (14), 91 (19).



Scheme 5

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