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Unprecedented Alkylation of Pentafluorobenzene with Propane.

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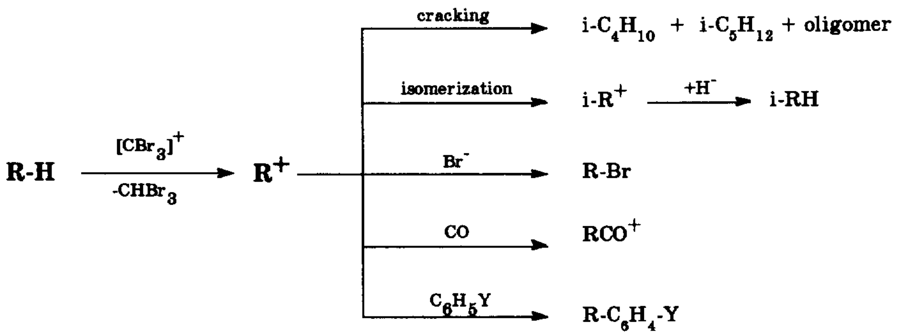
Abstract: Propane has been found to alkylate pentafluorobenzene in the presence of aprotic organic superacids $CBr_4 \cdot nAlBr_3$ (n = 1 or 2) in CH_2Br_2 solution at 0°, giving $C_6F_5Pr^i$ (1) in almost quantitative yield. In the absence of propane at the 20°, pentafluorobenzene reacts with $CBr_4 \cdot 2AlBr_3$ to form $C_6F_5CBr_3$ in 40 % yield. Copyright © 1996 Elsevier Science Ltd

Recently we have found that complexes of polyhalomethanes with aluminium bromide display the properties of aprotic organic superacids[1-5]. In the presence of these superacidic systems, alkane cracking, oligomerization and isomerization[1], ionic bromination of alkanes and cycloalkanes[1,2], carbonylation of alkanes[3] and C_5-C_6 cycloalkanes[4,5] with CO can be effectively achieved under mild conditions. The key stage of alkane transformations seems to be hydride ion transfer from RH to species such as CX_3^+ resulting in corresponding carbocations (R^+) together with the reduction of initial halomethane. The carbocations undergo subsequent transformations, such as cracking and isomerization, or, in the presence of carbocation trapping agents (CO, Br_2, ArH etc.), functionalization and alkylation (Scheme 1):

Scheme 1.

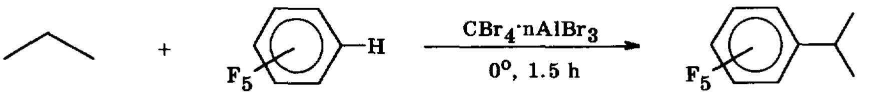


This paper reports of a surprisingly effective and facile alkylation of pentafluorobenzene with propane in the presence of the superacidic systems $CBr_4 \cdot nAlBr_3$ under mild conditions.

The reactions were carried out at 0-20° under propane atmosphere in the presence of $CBr_4 \cdot nAlBr_3$ (n = 1 or 2) in CH_2Br_2. Pentafluorobenzene reacts with propane at 0° in the presence of a four-fold excess of $CBr_4 \cdot 2AlBr_3$ over the arene , to form a single product - $C_6F_5Pr^i$ (1) in an almost quantitative yield for 1,5 hours

(Scheme 2):

Scheme 2.



n = 1 or 2,
C_6F_5H/CBr_4 = 1:4

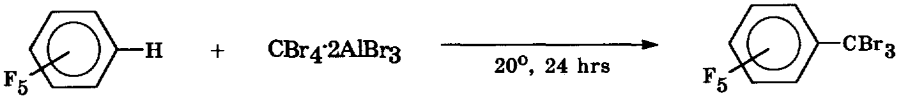
(1)
90-94% based on C_6F_5

Both 1:1 and 1:2 CBr_4·n$AlBr_3$ systems display high and similar activity as was observed earlier for other reactions[1,2]. On the contrary, CCl_4·2$AlCl_3$ is noticeably less active: under similar conditions, the yield of **1** is 27% and equimolar CCl_4·$AlCl_3$ complex is non-active at all.

The reaction promoted by CBr_4·2$AlBr_3$ at 20° is completed over 10 min and affords **1** in 60% yield. Throughout this time CBr_4 disappears completely; instead of it, $CHBr_3$ is formed in 68% yield. The increase of reaction time leads to lowering the yield of **1** due to its subsequent transformations.

In the presence of propane, alkylation products of C_6F_5H with CBr_4 or $CHBr_3$ have not been observed in spite of an excess of polyhalomethane in reaction media. In the absence of propane, however, the interaction of C_6F_5H with CBr_4 2$AlBr_3$ proceeds slowly, resulting in $C_6F_5CBr_3$ (**2**). The yield of **2**, calculated on CBr_4, reaches 40% over 24 hours at room temperature (Scheme 3):

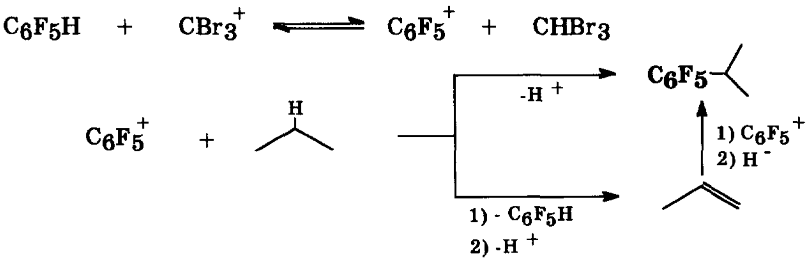
Scheme 3.



(2), 40% based on CBr

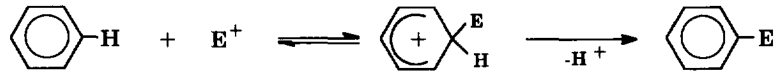
Since the formation of cations[6] and even dications[7] of aromatics under the action of powerful oxydizing agents has been proven, one may suggest that C_6F_5H propylation proceeds *via* hydride ion abstraction from the arene similarly to the reactions of alkanes with these superacids. The formed $C_6F_5^+$ then either attacks propane or adds to propylene generated from the alkane (Scheme 4):

Scheme 4



However, Scheme 4 seems unlikely due to the lack of even the traces of $CHBr_3$ among the products of reaction of C_6F_5H with CBr_4·2$AlBr_3$. Alternatively and more probably, the alkylation of C_6F_5H with both propane and CBr_4 is a the reaction of electrophilic substitution, well-recognized for fluoroarenes[8] (Scheme 5):

Scheme 5.



$E = C_3H_7$, CBr_3

The initial attempts to alkylate C_6F_5H by ordinary Friedel-Craft methods were abortive[9]. Nevertheless, the alkylation of C_6F_5H with CF_3H in the presence of an excess of SbF_5 at 0° for 50 hrs, resulting in the 2:1 mixture of $(C_6F_5)_2CFH$ and $(C_6F_5)_3CH$, respectively, was achieved[9,10]. Similarly, C_6F_5H has been alkylated by 1,1,2-trichlorotrifluoroethane with the formation of a rather complicated mixture of products[10]. In the presence of $AlCl_3$, alkylation of C_6F_5H by CH_2Cl_2 or $CHCl_3$ at 150° over 4,5-8 hrs has been also reported, and $(C_6F_5)_2CH_2$ or $(C_6F_5)_3CH$ were formed in 77 and 92% yields, respectively[9].

Thus, the first example of alkylation of a deactivated arene with a poorly alkylating agent, such as propane, was found. Promoted with aprotic organic superacids $CBr_4{\cdot}nAlBr_3$, the reaction leads to a single product with high yield under mild conditions.

EXPERIMENTAL SECTION.

GC quantitative analyses were carried out with an internal standard using a "Model 3700" gas chromatograph equipped by FID and quartz capillary column (l = 25m/0.23mm, stationary phase - SE-54), temperature program - 60°(0) - 8°/min - 200°(4). Identification of reaction products was carried out by GC-MS and ^1H, ^{19}F-NMR methods by use of VG 7070E and Bruker WP 200SY instruments, respectively. NMR-spectra were recorded in C_6D_6 as a solvent with Me_4Si and $CFCl_3$ as internal and external standards, respectively.

Typical procedures.

Pentafluorobenzene alkylation with propane.

The mixture of 4.0 g (14.9 mmol) $AlBr_3$ and 2.47 g (7.45 mmol) CBr_4 was stirred in 4 ml of CH_2Br_2 until a homogeneous solution was formed. The mixture was cooled to 0° and filled with dry propane. Then the solution of 0.31 g (1.85 mmol) C_6F_5H in 0.5 ml of CH_2Br_2 was quickly added under propane atmosphere. The mixture was stirred over 1.5 hrs under slight extra pressure of propane, then hydrolyzed with ice-water, extracted with CH_2Br_2 (2 x 5 ml) and dried with $MgSO_4$. According to GC-data, 0.37 g (1.75mmol) of $C_6F_5Pr^i$ was formed, 94% based on C_6F_5H.

Pentafluorobenzene alkylation with CBr_4 2$AlBr_3$ in the absence of propane.

0.95 g (3.6 mmol) of $AlBr_3$ and 0.6 g (1.8 mmol) of CBr_4 were mixed in round-bottomed flask equipped with a good magnetic stirrer and an excess of C_6F_5H (0.7 ml, ~1.0 g, 6.5 mmol) was added without any other solvent. The bright red mixture was stirred vigorously at room temperature during 24 hrs, hydrolyzed with ice-water, extracted with ether, dried and analyzed quantitatively. According to GC, the conversion of CBr_4 is 0.4 g (66%) and the yield of $C_6F_5CBr_3$ reaches 40% based on CBr_4.

$C_6F_5Pr^i$, m/z, (I_{rel}, %): **210** (M^+, 41), **195** (100), **175** (21), **155** (9), **81** (14).

$C_6F_5Pr^i$, NMR-^{1}H, δ(ppm), J (Hz): **1.20** (d., 6H), 7; **3.18** (sept.,1H), 7.

$C_6F_5Pr^i$, NMR-^{19}F, δ(ppm), J (Hz): **-84.8** (m., 2F), 22; **-80.4** (m., 1F), 22; **-65.7** (m., 2F), 22.

$C_6F_5CBr_3$, m/z, (I_{rel}, %): **337** (M+ - Br, 40), **259** (81), **179** (100), **80** (89), **79** (55).

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