Functionalization of saturated hydrocarbons
3*. One-step alkylacylation of aromatic hydrocarbons with alkanes (or cycloalkanes) in the presence of aprotic organic superacids

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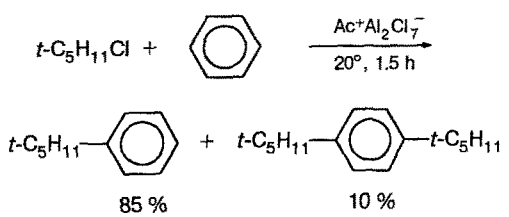
Alkanes and cycloalkanes (isobutane, butane, isopentane, isohexane, and methylcyclopentane) react with benzene or bromobenzene at 0—20 °C in the presence of $RCO^+Al_2X_7^-$ complexes (R = Me, Pr, or Ph; X = Cl or Br) to give products of the alkylacylation of arenes. The yields of alkylated aromatic ketones reach 60—87 % in 5—30 min, whereas the yields of unalkylated aromatic ketones (the competitive reaction) reach 0—40 %. The reactions of isobutane or isopentane with benzene result exclusively in *para* isomers of t-BuC_6H_4COR or a mixture of $Me_2(Et)CC_6H_4COR$ and $Me(i\text{-}Pr)CHC_6H_4COR$ isomers (1:1), respectively. The reaction of isobutane with benzene also proceeds regioselectively and gives only one isomer, 2-Br-t-BuC_6H_4COR.

Key words: saturated hydrocarbons, functionalization of alkanes and cycloalkanes, alkylated aromatic ketones, superelectrophiles.

Selective one-step functionalization of saturated hydrocarbons is of considerable interest for the direct synthesis of organic compounds from available raw hydrocarbons.

It would seem that the ability of aprotic organic superacids $RCO^+Al_2X_7^-$ (R = Alk or Ar; X = Cl or Br) (**1**) (*cf.* Ref. 1) to acylate not only unsaturated compounds[2—5] but also paraffins[1,5,6] under mild conditions should not permit alkylation of aromatic hydrocarbons in their presence. However, it turns out that the acylating ability of complex **1** is suppressed in the presence of excess alkyl halides, and the complex acts as a catalyst for benzene alkylation (Scheme 1).

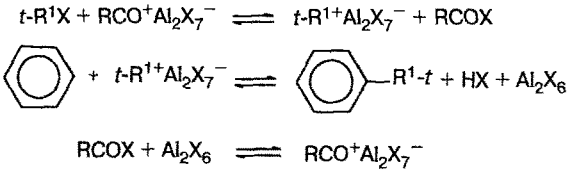
Scheme 1



[PhH] : [t-$C_5H_{11}Cl$] : [**1**] = 180:36:1

Additionally, alkylated aromatic ketones, isomers of p-(t-C_5H_{11})C_6H_4COMe, are formed as byproducts. An increase in the content of the $AcBr \cdot 2AlBr_3$ complex in the initial mixture leads to an increased yield of alkylated aromatic ketones. For instance, at the molar ratio [C_6H_6]:[t-$C_5H_{11}Cl$]:[$AcBr \cdot 2AlBr_3$] = 5:1.5:1, the yield of isomeric p-(t-C_5H_{11})C_6H_4COMe compounds (20 °C, 5 min) is 57 % with respect to the complex. The ratio between mono- and dialkylated products depends on the duration of the reaction. The product of direct acylation of benzene, acetophenone, is practically not formed in the reactions. This direction of the reaction is probably caused by the generation of a carbenium ion, which alkylates benzene (Scheme 2), from the alkyl halide under the action of complex **1**.

Scheme 2



Taking into consideration that complex **1** readily generates carbenium ions from saturated hydrocarbons, we studied the possibility of using the latter as alkylating compounds in reactions with aromatic hydrocarbons. Paraffins and cycloparaffins were found to efficiently alkylate benzene and bromobenzene in the presence of complex **1**. The reactions result in alkylated aromatic ketones. In these reactions, complex **1** acts both as a promotor of alkylation of aromatic compounds with saturated hydrocarbons and, traditionally, as a system for acylating the newly formed alkylbenzenes.

The one-step alkylacylation of benzene with *iso*-, *n*-, or cycloalkanes in the presence of complex **1** proceeds at 0—20 °C (Table 1). The yields of alkylated ketones in

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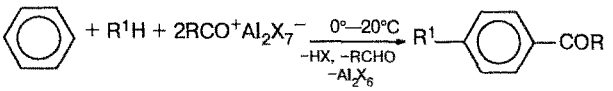
Table 1. One-step alkylacylation of benzene and bromobenzene with paraffins and $RCO^+Al_2X_7^-$ complexes

Experiment	Alkane R^1H	Arene PhY	$RCO^+Al_2X_7^-$ (1) R	X	T/°C	Time (min)	Products (% with respect to ArH) $R^1C_6H_3(Y)COR$	$C_6H_4(Y)COR$
1	*i*-C_4H_{10}*	PhH	Me	Cl	0	30	62	35
2	*i*-C_4H_{10}*	PhH	Me	Cl	20	40	68	35
3	*i*-C_4H_{10}	PhH	Me	Br	0	30	48	41
4	*i*-C_4H_{10}	PhH	Pr	Br	0	30	54	23
5	*i*-C_4H_{10}	PhH	Ph	Cl	0	30	35	18
6	*i*-C_5H_{12}	PhH	Me	Br	20	5	87	3
7	*i*-C_5H_{12}**	PhH	Me	Br	20	5	65	12
8	*n*-C_5H_{12}	PhH	Me	Cl	20	5	81	20
9	*n*-C_5H_{12}***	PhH	Me	Br	20	5	73	3
10	*i*-C_6H_{14}	PhH	Me	Cl	20	5	84	18
11	Me-*cyclo*-C_5H_9	PhH	Me	Cl	20	5	58	11
12	*i*-C_4H_{10}	PhBr	Me	Br	0	60	82	4
13	*i*-C_4H_{10}	PhBr	Me	Cl	0	60	79	22
14	*n*-C_5H_{12}***	PhBr	Me	Cl	0	20	74	Traces
15	*n*-C_4H_{10}***	PhBr	Me	Cl	0	30	40	5

* **1** : arene = 12 : 1. ** **1** : arene = 3 : 1, or 6 : 1 in all the other cases. *** The original *n*-alkanes were previously kept for ~3 h with a catalytic amount of complex **1**.

reactions involving C_5—C_6 alkanes or methylcyclohexane reach 65—87 % in 5 min. The products of the competing reaction, nonalkylated ketones, are formed in 3—20 % yields. Isobutane or *n*-butane may be used as the alkylating agents. Butylated ketones are normally formed in somewhat smaller yields (as high as 68 %) and are also the main reaction products:

Scheme 3



R^1H = *i*-, *n*-C_4H_{10}, *i*-, *n*-C_5H_{12}, 2,3-$Me_2C_4H_8$, *cyclo*-MeC_6H_{11}, *cyclo*-MeC_5H_9
R = Me, Pr, Ph; X = Cl, Br

The alkylacylation can be performed in sufficiently high yields only if one uses an excess of the "alkylating" system (R^1H + $RCO^+Al_2X_7^-$) relative to benzene, with the ratio [R^1H] : [**1**] : [PhH] = (10—15) : (3—12) : 1. A decrease in the [**1**] : [PhH] ratio results in decreased yields of alkylated and increased yields of unalkylated aromatic ketones. In addition, the lowest possible concentration of benzene should be maintained in the reaction mixture, thus a gradual addition of benzene to the R^1H + $RCO^+Al_2X_7^-$ mixture is required. If benzene is added quickly, the yield of nonalkylated aromatic ketones increases abruptly, while the reverse order of reagent addition (the "alkylacylating" system is added to the arene) suppresses alkylation totally and results in PhCOR exclusively.

In order to successfully perform the reaction with normal alkanes, the aromatic hydrocarbon should be introduced only after the mixture of *n*-alkane with complex **1** has been kept for a period sufficient for isomerization of the *n*-alkane (~3 h). The reaction carried out without preliminary isomerization yields almost exclusively the acylation product of the original arene. The lowest alkanes C_1—C_3, which form no stable carbenium ions, do not enter the reaction.

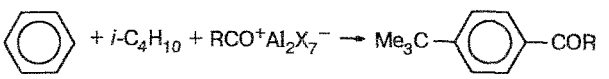
As follows from Table 1, the reaction found is common to various $RCO^+Al_2Cl_7^-$ complexes, although in the case of complex **1** (R = Ph)* the product yields are lower, in analogy with other reactions with the participation of the superacid complexes of the aromatic series.[6]

On the other hand, the use of equimolar $AcBr \cdot AlX_3$ complexes (X = Cl, Br) for the selective alkylacylation of benzene with isobutane or isopentane proved to be unsuccessful. For example, the reaction of isobutane with benzene and $AcBr \cdot AlBr_3$ (molar ratio 10:1:12) in CH_2Br_2 at 20 °C results predominantly in acetophenone: the yields of PhAc and *p*-(*t*-Bu)C_6H_4Ac are 44 % and 10 % respectively after 30 min. An increase in reaction time almost does not change the product yields. When the reaction is carried out with the $AcBr \cdot AlBr_3$ complex under the same conditions, the yields of PhAc and *t*-$C_5H_{11}C_6H_4$Ac are 14 % and 17 % after 5 min, or 22 % and 18 % after 30 min, respectively.

The structures of the resulting products were determined by means of GLC-MS. The relative positions of the substituents were revealed from ^{13}C NMR and were based on the number of types, the nature of the multiplicity of the carbon atoms in the aromatic rings, and the chemical shifts which coincided with the values calculated from incremental schemes.[8]

Reactions of benzene with isobutane or *n*-butane proceed regiospecifically to give only one product, an *n*-(*tert*-butyl)-substituted aromatic ketone (Scheme 4).

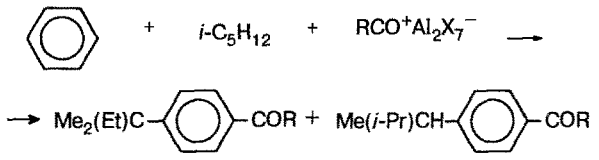
Scheme 4



*Judging by the ^{13}C NMR data, in CH_2Cl_2 the $PhCOCl \cdot 2AlCl_3$ system present only as donor-acceptor complex. However, we believe that reactions with this complex involve acylium cations.

The reactions of benzene with isopentane yield almost equal amounts of two *n*-isomers differing in the structure of the pentyl substituent.

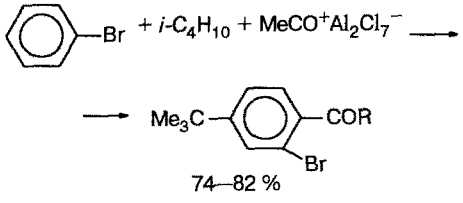
Scheme 5



The reactions with *iso*-hexane, methylcyclopentane, and methylcyclohexane result in a large number of isomers differing in the structure of the alkyl (cycloalkyl) substituents. The structures of the isomers were not studied in more detail.

Alkylacylation of bromobenzene proceeds in high yields (74—82 %) and with higher selectivity than in the case of benzene. The products of bromobenzene acylation are formed in 0—22 % yields (Table 1). Alkylacylation of bromobenzene with isobutane or isopentane also proceeds regiospecifically. The reaction with isobutane results in only one isomer. The nature of the multiplicity of the carbon atoms in the aromatic ring and the chemical shifts provide evidence that the product of bromobenzene butylacylation has the structure of 2-bromo-4-(*tert*-butyl)acetophenone.

Scheme 6



It is likely that in the presence of a strong aprotic superacid, the *n*-(*tert*-butyl)bromobenzene formed initially undergoes isomerization to give the more stable *m*-isomer, whose acylation at the *para* position relative to the *t*-Bu group results in the observed product.

Alkylation of bromobenzene with isopentane, as in the case of benzene, leads to the formation of isomeric ketones with different structures of the amyl substituent.

It should be noted that activated arenes (toluene, naphthalene, and *m*-xylene) also give rise to alkylacylation products, but in yields not exceeding 10 % of the yields of acylation products formed from these arenes. On the other hand, arenes containing strong electron-withdrawing groups (nitrobenzene, acetophenone) do not change under the reaction conditions. This makes it possible to consider that the reaction proceeds as arene alkylation followed by acylation of the alkylated aromatic compound. It is likely that in the case when the aromatic ring is activated for electrophilic attack, acylation and alkylation proceed at comparable rates. Therefore, with an excess of an acylating agent, acylation becomes the predominant process. The difference between the rates of acylation and alkylation becomes stronger for an aromatic compound passivated toward an electrophile. In this case alkylation becomes the predominant, and sometimes the only, direction of the original reaction.

The proposed acylalkylation scheme includes carbenium ion generation from a paraffin, and arene alkylation by the carbenium ion followed by acylation of the aromatic compound (Scheme 7).

Scheme 7

$$R^1H + RCO^+Al_2X_7^- \rightleftharpoons R^{1+}Al_2X_7^- + RCHO$$

$$Y\text{—}C_6H_5 + R^{1+} \overset{-H^+}{\rightleftharpoons} Y\text{—}C_6H_4R^1$$

$$Y\text{—}C_6H_4R^1 + RCO^+ \overset{-H^+}{\rightleftharpoons} Y\text{—}C_6H_3(R^1)COR$$

In contrast to Scheme 2, Scheme 7 does not contain the acylium cation regeneration step. Hence, alkylacylation of arenes with paraffins is not a catalytic reaction. Nevertheless, taking into account the high yields of the target products, the high selectivity and ease of this one-step reaction, and the availability of starting compounds and $RCO^+Al_2Cl_7^-$ complexes (which are prepared by simple mixing of acyl halides with aluminum halides), we feel that this reaction is of interest for laboratory syntheses. It should also be noted that the first step in the traditional method for synthesizing alkylated aromatic ketones, *viz.*, arene alkylation by acid systems, normally provides low selectivity. *tert*-Butylation of aromatic compounds is broadly used as a method to introduce directing groups which ensure selective aromatic substitution.[9,10]

Experimental

"Pure" grade aluminum halides were purified by sublimation *in vacuo* and stored in an inert atmosphere. Acyl halides were purified by distillation over a small amount of PCl_5 or PBr_5; their boiling points agreed with the literature data. Hydrocarbons, bromobenzene, CH_2Cl_2, and CH_2Br_2 were purified according to standard procedures, dried, and distilled.

The GLC analysis was carried out on Biokhrom 1 and Model 3700 chromatographs with a flame-ionization detector and quartz capillary columns (25 m × 0.22 mm), stationary phase SE-30, temperature program 50(2)—6 ° min^{-1}—270 °, with nitrogen as the carrier gas. Spectra were recorded by GLC-MS on a Kratos RF 25 spectrometer with analogous capillary columns. NMR spectra were recorded on a Bruker WP 200 SY spectrometer with working frequencies of 200 and 50.3 MHz for the ^1H and ^{13}C nuclei, respectively.

Alkylated aromatic ketones were synthesized by a standard procedure, according to which a saturated hydrocarbon was added at a fixed temperature to a solution of complex **1** in CH_2Br_2. After this, a solution of an arene in CH_2Br_2 was added dropwise with stirring to the homogeneous solution thus obtained. After the reaction was completed, the cooled reaction mixture was hydrolyzed with water, extracted with ether, and analyzed by GLC and GLC-MS. In some cases, the reaction products were separated from the reaction mixture by vacuum fractionation.

Alkylation and alkylacylation of benzene with *t*-$C_5H_{11}Cl$ in the presence of AcX · 2AlX_3 complexes. ***a.*** To a stirred mixture of benzene (3.66 g, 47 mmol) and *t*-$C_5H_{11}Cl$ (1 g, 9.4 mmol), a solution of the AcBr · $2AlBr_3$ complex (1.3 mL, 0.068 mmol) prepared from AcBr (0.11 g) and $AlBr_3$ (0.84 g) in 16.8 mL of CH_2Br_2 was added dropwise at 20 °C. After 5 min, the mixture

was poured onto ice. The organic layer was extracted with ether, washed with water, and dried with $MgSO_4$. According to GLC-MS, the yields of t-$C_5H_{11}C_6H_5$ (two isomers) and t-$(C_5H_{11})_2C_6H_4$ were 95 % and 4 %, respectively.

b. To a stirred mixture of benzene (1.08 g, 14 mmol) and t-$C_5H_{11}Cl$ (0.45 g, 2.2 mmol), a solution of the $AcBr \cdot 2AlBr_3$ complex prepared from AcBr (0.35 g, 2.8 mmol) and $AlBr_3$ (1.5 g, 5.6 mmol) in 7.5 mL of CH_2Br_2 was added dropwise at −20 °C. The mixture was kept for 40 min at −20 °C and for 5 min at 20 °C and then treated as in the above synthesis. The yield of p-(t-C_5H_{11})C_6H_4COMe was 57 % with respect to $AcBr \cdot 2AlBr_3$. The alkylacylation product contained two isomers, viz., p-$AcC_6H_4CHEt_2$ [MS, m/z (I_{rel} (%)): 161 (100), 133 (17), 162 (15), 190 (2) (M^+), 175 (7)] and p-$AcC_6H_4CHMeCHMe_2$ [MS, m/z (I_{rel} (%)): 147 (100), 148 (50), 190 (25) (M^+), 105 (20), 175 (10)].

c. To a stirred mixture of benzene (10.8 g, 129.5 mmol) and t-$C_5H_{11}Cl$ (2.76 g, 25.9 mmol), a solution of the $AcBr \cdot 2AlCl_3$ complex (0.280 g, 0.72 mmol) in 8 mL of CH_2Br_2 was added dropwise at 20 °C. In order to determine the composition and yields of the products formed, aliquots for GLC were withdrawn at certain time intervals. The yields of t-$C_5H_{11}C_6H_5$ and t-$(C_5H_{11})_2C_6H_4$ after 50 min were 53 % and 20 %, respectively. After 1.5 h, the yield of t-$C_5H_{11}C_6H_5$ reached 80 %, while t-$(C_5H_{11})_2C_6H_4$ was present in trace amounts.

Alkylacylation of benzene with isobutane and the $Ac^+Al_2Cl_7^-$ complex. Liquid isobutane (2 mL, 1.2 g, 20 mmol) was added in one portion to a suspension of the $AcBr \cdot 2AlCl_3$ complex [obtained from $AlCl_3$ (4.0 g, 30 mmol) and AcBr (1.83 g, 15 mmol) in 8 mL of CH_2Br_2 at room temperature] in a 50 mL two-neck flask equipped with a dropping funnel, a Dewar condenser cooled to −30 °C, and a thermometer. Then cooling of the reaction mixture was terminated. When the temperature of the mixture reached 17—19 °C, benzene (0.11 mL, 0.025 g, 1.22 mmol) in 0.9 ml of CH_2Cl_2 was added dropwise over 5 min, and stirring was continued for an additional 35 min at 17—19 °C. The reaction mixture was poured onto ice, and the organic layer was separated, washed with water, and dried with $MgSO_4$. Judging by the GLC data, the yield of BuC_6H_4COMe (M^+ 176) was 0.145 g (68 %), and the yield of acetophenone was 0.05 g (34 %). The solvent and acetophenone were removed by distillation (40 °C, 1 mm Hg), and the residue thus obtained was distilled at 100 °C/1 Torr. The structure of p-(*tert*-butyl)acetophenone was established by the ^{13}C NMR data (CCl_4), δ: 25.8 ($^{13}CH_3CO$), 31.1 ($C(^{13}CH_3)_3$), 34.8 ($^{13}CMe_3$), 124.9 (^{13}CH-arom.), 128 (^{13}CH-arom.), 134.8 (^{13}CH-arom.), 155.4 (^{13}CH-arom.), 194.3 (^{13}CO).

Alkylacylation of benzene with isopentane and the $Ac^+Al_2Br_7^-$ complex. AcBr (0.27 mL, 0.45 g, 3.7 mmol) and CH_2Br_2 (4 mL) were added to $AlBr_3$ (2.0 g, 7.5 mmol) at 20 °C with stirring. The mixture was stirred for 10 min until a homogeneous solution formed. Then isopentane (0.75 mL, 0.45 g, 6.1 mmol) was added, after which benzene (0.05 g, 0.62 mmol) in 0.5 mL of CH_2Br_2 was added dropwise over 2 min. Afterwards, the mixture was stirred for a further 3 min, cooled, hydrolyzed with water, and extracted with ether. The ethereal extracts were dried with $MgSO_4$. This procedure resulted in two isomeric ketones C_5H_{11}—C_6H_4—Ac in the ratio of 1:1, viz., p-(2-methylbutyl-2)acetylbenzene {M^+ 190, m/z 161 [M−Et], 175 [M−Me]} and p-(2-methylbutyl-2)acetylbenzene {M^+ 190, m/z 147 [M−Pr], 175 [M−Me]}. According to GLC data (with CH_3—C_6H_4—Ac as the internal standard), the total yield of amylacetophenones was 87 %, and the yield of PhAc was 3 % with respect to benzene.

Alkylacylation of bromobenzene with isobutane and the $Ac^+Al_2Cl_7^-$ complex. AcBr (0.27 mL, 0.45 g, 3.7 mmol) was added with stirring to $AlCl_3$ (1.0 g, 7.5 mmol) in 2.2 g of CH_2Br_2. The mixture was stirred at 0 °C for 10 min, after which a Dewar condenser cooled to −30 °C was connected to the reaction flask. The suspension of the complex thus obtained was combined with liquid isobutane (1 mL, 0.6 g, 9.0 mmol), and then a solution of bromobenzene (0.094 g, 0.6 mmol) in 0.5 mL of CH_2Br_2 was added dropwise over 5 min. The reaction mixture was stirred at 0 °C for 1 h, hydrolyzed with water (with cooling), and extracted with ether. The ethereal extracts were washed with water and dried with $MgSO_4$ to give a ketone of the molecular formula $C_4H_9C_6H_3(Br)COMe$ {M^+ 254, m/z 239 [M−Me]}. According to GLC data (with $PhCOC_6H_4Br$ as the internal standard), the yield was 82 % with respect to PhBr, and the yield of $CH_3COC_6H_4Br$ was 4 % with respect to PhBr. ^{13}C NMR, δ, for $C_4H_9C_6H_3(Br)COMe$: 30.1 (quint, ^1J = 127 Hz, $^{13}CH_3CO$), 31.3 (q, ^1J = 125 Hz, ^2J = 4 Hz, $^{13}(CH_3)_3C$), 119.5 (m, ^2J = 3 Hz, ^3J = 6 Hz, $^{13}C_{arom}$—Br), 124.4 (dd, ^1J = 160 Hz, ^3J = 6 Hz, $^{13}C_{arom}$—H), 129.5 (d, ^1J = 160 Hz, $^{13}C_{arom}$—H), 130.8 (dd, ^1J = 160 Hz, ^3J = 6 Hz, $^{13}C_{arom}$—H), 139.0 (t, ^3J = 6 Hz, $^{13}C_{arom}$—COMe), 155.2 (d, ^2J = 6 Hz, $^{13}C_{arom}$—Bu), 197.8 (s, $CH_3{}^{13}CO$).

The observed multiplicity of the carbon atoms in the aromatic ring is consistent with the structure of 2-bromo-4(*tert*-butyl)acetophenone. The chemical shifts observed are in accordance with the calculated values given in parentheses:[8] $C_{arom}(2)$—Br 119.5 (122.8), $C_{arom}(4)$—t-Bu 155.2 (157.3), $C_{arom}(1)$—COMe 139.0 (137.9), $C_{arom}(5)$—H 124.4 (123.8), $C_{arom}(6)$—H 129.5 (130.2).

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