OXIDATIVE COUPLING OF AROMATIC COMPOUNDS WITH TRIMETHYLBENZYLSILANE BY THE ACTION OF $MoCl_5$

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We have briefly reported on the high activity of $MoCl_5$ in the cleavage of Si—C bonds in silanes [1]. These reactions are readily accomplished even at −30°C and, as a rule, selectively with the loss of one substituent.

$$Me_3SiR + MoCl_5 \rightarrow Me_3SiCl + [RMoCl_4] \rightarrow \text{products}$$
$$R = Me, Ar, PhCH_2, CH_2 = CH, CH_2 = CH - CH_2.$$

Thus, the benzyl group in trimethylbenzylsilane (TMBS) is selectively eliminated by the reaction of $MoCl_5$ and the conversion is about 40% after 1 h at −30°C. The readiness of this reaction is extremely unexpected since the benzene ring in TMBS is "activated" relative to electrophilic attack due to the hyperconjugation effect of the Me_3Si group [2]. Thus, TMBS is acylated [3], nitrated [4], and chlorosulfonated in high yield; this compound also enters other electrophilic substitution reactions with retention of the $Si—CH_2Ph$ bond.

Carrying out the reaction of TMBS with $MoCl_5$ in an aromatic hydrocarbon leads to facile benzylation of this hydrocarbon with formation of the corresponding diarylmethane (Table 1).

$$Me_3SiCH_2Ph + ArH + MoCl_5 \rightarrow ArCH_2Ph + Me_3SiCl + HCl + MoCl_3$$
$$ArH = PhH, PhMe, 1,3\text{-}Me_2C_6H_4, PhCl, PhF.$$

The yields of the products of the benzylation of arenes are much greater in reactions with the $MoCl_5 \cdot MeNO_2$ complex than with $MoCl_5$ but much less than with WCl_6 and $AlCl_3$.

The reactions proceed readily at 20°C. Thus, the yield of diphenylmethane in the case of benzene is 20% after 2 min and 30% after 5 min.

In order to determine the substrate selectivity of the reaction, we found the ratio of the yields of the products of the benzylation of toluene and benzene under competitive reaction conditions (Table 2).

In this case, the ratio of the yields of tolylphenylmethane and diphenylmethane is about 4. According to Olah et al. [6], the $k_t/k_b = 4.5$ in the benzylation by the action of $PhCH_2Cl$ at 50°C. The positional selectivity of the reaction was studied by ^{13}C and ^1H NMR spectroscopy (Table 3). The NMR spectra of the para and ortho isomers have been reported [7, 8]. The meta isomer was obtained in our laboratory by the reduction of 3-methylbenzhydrone.

The ^{13}C NMR data indicate that the benzylation of toluene by TMBS by the action of $MoCl_5$ gives 15.3% ortho isomer, 47% meta isomer, and 37.7% para isomer. Special experiments showed that isomerization of tolylphenylmethanes occurs under these conditions to give the thermodynamically more stable meta isomer, which is in accord with the work of Olah [9]. In order to suppress isomerization, the benzylation was carried out in the presence of $MoCl_5 \cdot MeNO_2$ [6]. A mixture of ortho and para isomers of tolylphenylmethane (46.3 and 53.7%, respectively) was formed under these conditions. A mixture of 42.4% ortho isomer, 6.2% meta isomer, and 51.4% para isomer was formed upon the benzylation of toluene with benzyl chloride in the presence of $AlCl_3 \cdot MeNO_2$ [6].

Thus, the benzylation of aromatic hydrocarbons by TMBS in the presence of $MoCl_5$ in its substrate and positional selectivity conforms to behavior typical for electrophilic substitution. This reaction is the first example of the oxidative coupling of a heteroorganic compound with an aromatic derivative by the action of $MoCl_5$ whose mechanism was studied.

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TABLE 1. Benzylation of Aromatic Compounds by TMBS in the Presence of $MoCl_5$, $AlCl_3$, and WCl_6, 1 h, 20°C, $[MCl_n]$ = 0.25 M

ArH	MCl_n	$PhCH_2Ar$	Yield of $PhCH_2Ar$, % relative to silane	
			MCl_n	MCl_n $MeNO_2$
PhH	$MoCl_5$	Ph_2CH_2	60	87
PhMe	$MoCl_5$	$PhCH_2C_6H_4Me$	45	88
$1,3\text{-}Me_2C_6H_4$	$MoCl_5$	$PhCH_2C_6H_3Me_2$	37	86
PhCl	$MoCl_5$	$PhCH_2C_6H_4Cl$	21	50
PhF	$MoCl_5$	$PhCH_2C_6H_4$	26	76
PhH	$AlCl_3$	Ph_2CH_2	10	12
PhH	WCl_6	Ph_2CH_2	20	29

TABLE 2. Substrate Selectivity in the Competitive Benzylation of Benzene and Toluene by TMBS in the Presence of $MoCl_5$

Time, min	Yield, %		k_t/k_b	Time, min	Yield, %		k_t/k_b
	Ph_2CH_2	$PhCH_2C_6H_4Me$			Ph_2CH_2	$PhCH_2C_6H_4Me$	
5	4,5	17	3,8	20	7,6	25	3,3
10	6,8	23	3,4	40	10	30	3,0
15	7,8	26	3,3	60	12	48	4,0

TABLE 3. ^{13}C NMR Spectra of Tolylphenylmethanes Obtained by Reactions of TMBS with $MoCl_5$ and with $MoCl_5 \cdot MeNO_2$ in Toluene

Isomer	CH_3 (δ from TMS)		CH_2 (δ from TMS)	
	found	lit. data [7]	found	lit. data [7]
o-	19,5	19,6	39,5	39,5
m-	21,2	21,2*	–	41,9*
p-	20,9	21,0	41,5	41,6

*Our data.

EXPERIMENTAL

Benzene, toluene and m-xylene were purified by distillation over sodium. Chlorobenzene, fluorobenzene and nitromethane were distilled over P_2O_5. TMBS was obtained according to Gorbacheva and Cherkasskaya [10]. Pure-grade samples of $MoCl_5$, $AlCl_3$, and WCl_6 were used without additional purification. The products of the benzylation of arenes, namely, diarylmethanes, were identified by gas-liquid chromatography on an LKhM-8MD chromatograph with a thermal conductance detector on a 1 m × 0.3 mm column packed with SE-30 at 170°C using octadecane as the internal standard and chromato-mass spectrometry on a Finnigan 8200 instrument using a 0.2-mm-diameter capillary column and an 11-μm-thick film with a methylsilicone phase. The mass spectrometer was operated in a continuous scanning mode in the 40-400 mass range at 70 V ionizing voltage. The temperature of the ionization chamber was 200°C. The mass spectra were identified by a library search using the Super INCOS system. Agreement with the library spectra exceeded 0.9.

In order to evaluate the total yields of the reaction products, the arylphenylmethanes were synthesized by benzylation of the corresponding aromatic compounds using benzyl chloride and $AlCl_3$ as the catalyst. The isomeric composition of the tolylphenylmethanes was determined on a Bruker WP 200 SY NMR spectrometer.

Benzylation of Arenes by Trimethylbenzylsilane by the Action of $MoCl_5 \cdot MeNO_2$. A sample of 2.45 ml 20% $MoCl_5$ in $MeNO_2$ was added to a solution of 0.33 g (2 mmoles) TMBS in 6 ml of toluene and stirred for 1 h at 20°C. Then, the mixture was hydrolyzed with saturated aqueous NaCl and cooled to 0°C. The organic layer was separated, neutralized by the addition of sodium carbonate and dried over $CaCl_2$. The excess solvent was distilled off and the solution was passed through alumina to remove traces of molybdenum salts using pentane as the eluent. Gas–liquid chromatographic analysis showed that the total yield of isomeric tolylphenylmethanes was 0.29 g (88%).

CONCLUSIONS

The benzylation of aromatic compounds was carried out efficiently under mild conditions by the action of trimethylbenzylsilane in the presence of $MoCl_5$, $AlCl_3$, or WCl_6 with the formation of the corresponding diarylmethanes. The benzylation in the presence of $MoCl_5$ conforms to behavior typical of electrophilic substitution.

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NEW DATA ON THE REACTION OF TRIALKYL TRITHIOPHOSPHITES WITH ALKYL HALIDES

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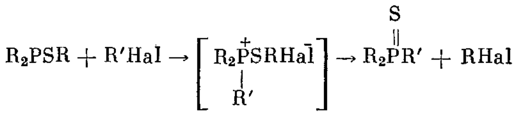
The reaction of phosphonous derivatives of P(III) acid thioesters with alkyl halides studied by A. E. Arbuzov proceeds in accord with the classical scheme and leads to the predominant formation of phosphine sulfides [1]. However, we have shown that substitution of the alkylthio group by a halogen at the P(III) atom in trialkyl trithiophosphites is also possible upon the action of alkyl halide (the products of the Arbuzov reaction were not isolated in this case) [2]. A subsequent study of the reactivity of P(III) acid thioesters showed that the reaction in the case of phosphonite derivatives is accomplished both by the Arbuzov reaction and by substitution of the alkyl thio group and is complicated by a series of secondary processes [3].

Hence, it has become accepted that the reactivity of P(III) acid thioesters relative to alkyl halides varies depending on the environment of the phosphorus atom. In going from phosphonous to phosphite derivatives, there is a shift in the direction of the alkylation of the P—S bond from the phosphorus atom to the sulfide sulfur atom [3-5].



$$R_2PSR + R'Hal \rightarrow \left[\begin{matrix} R_2\overset{+}{P}SR\overline{Hal} \\ | \\ R' \end{matrix}\right] \rightarrow R_2\overset{\overset{S}{\|}}{P}R' + RHal$$

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