Electrophilic aromatic trichloromethylation: intermediates and products

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Based on analysis of experimental data for reactions in solutions and in the gas phase and on the results of quantum-chemical calculations, it was shown that rearomatization stage of cationic σ-complexes formed in the electrophilic trichloromethylation is not deprotonation but dehydrochlorination to form aryldichlorocarbenium ions that are the real products of the reaction under consideration. The geometries and electronic structures of phenyldichlorocarbenium and mesityldichlorocarbenium ions were studied and differences in their reactivities were discussed.

Key words: electrophilic trichloromethylation, mechanism, intermediates; (trichloromethyl)arenium ions, aryldichlorocarbenium ions, trichloromethylarenes.

The use of electrophilic aromatic trichloromethylation for preparative purposes is limited to the synthesis of some specific types of compounds, in which access to the trichloromethyl group is sterically hindered by alkyl substituents[1] or chlorine atoms,[2] to preclude further transformations resulting in diaryldichloromethanes and triarylchloromethanes. In the absence of steric hindrances, the reaction of, *e.g.*, benzene even with excess CCl_4 in the presence of aluminum chloride results in diaryldichloromethane as the main product.[3]

Recently, some new studies on the synthesis of diaryldichloromethanes as precursors of aromatic (first of all, non-symmetric) ketones were reported. Phenyldichlorocarbenium tetrachloroaluminate, $[PhCCl_2]^+AlCl_4^-$ (**1**), was shown to possess high stability (this compound can be stored without changes over a period of two weeks at 25 °C) and to be an efficient electrophile.[4] Based on the ^{13}C NMR spectra (selected spectral parameters are listed in Table 1), it was concluded[4] that the phenyldichlorocarbenium carbocation carries a much larger positive charge than the charge on the carbonyl C atom in the complex of benzoyl chloride with aluminum chloride, $PhCOCl \cdot AlCl_3$ (**2**). It was also suggested that this feature is responsible for the higher reactivity of complex **1** compared to complex **2**. Using the reaction of benzotrichloride in the presence of $AlCl_3$, one can obtain (after hydrolysis of intermediate diaryldichloromethane) high yields of corresponding ketones from various aromatic compounds.[5] Previously,[6] we showed that the use of complex **1** allows introduction of the benzoyl group into the deactivated thiophene and furan derivatives, *viz.*, esters, aldehydes, ketones, and nitriles and into the methyl benzoate ring.

Table 1. Chemical shifts in the ^{13}C NMR spectra of benzoyl chloride, benzotrichloride, and their complexes with $AlCl_3$*

Compound	δ	
	CO	C_p
PhCOCl	167.51	134.88
$PhCOCl \cdot AlCl_3$	191.62	143.01
$PhCCl_3$	97.32	130.01
$PhCCl_2^+AlCl_4^-$	209.53	159.39

* For solutions in 1,2-dichloroethane; the data were taken from Ref. 4.

The electrophilic ability of substituents in the benzene ring can be assessed using the σ_p^+ constants that are linearly related to the chemical shifts C_p. Comparison with the published data[6] shows that the substituent $CCl_2^+AlCl_4^-$ is characterized by extremely high σ_p^+ value (3.6), which is two or three times higher than those of such strong electron acceptors as the acyl groups modified by complexation with aluminum chloride (Table 2).

In this work, we performed semiempirical MNDO, AM1, and PM3 quantum-chemical calculations of two cationic σ-complexes, namely, (trichloromethyl)benzenium (**3**) and 2,4,6-trimethyl-1-(trichloromethyl)benzenium (**4**) ions, their dehydrochlorination products, *viz.*, phenyldichlorocarbenium (**5**) and 2,4,6-trimethylphenyldichlorocarbenium (**6**) cations, and benzotrichloride (**7**) and 2,4,6-trimethylbenzotrichloride (**8**) that are the neutral trichloromethylation products. The results of MNDO calculations carried out using the

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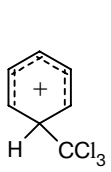
Table 2. σ_p^+-Constants of substituents estimated from the chemical shifts δ_{Cp}

Substituent	σ_p^+	Substituent	σ_p^+
MeO	−0.6	MeO · $AlCl_3$	0.1
CN	0.6	CN · $AlCl_3$	1.2
COOMe	0.6	MeOCO · $AlCl_3$	1.2
PhCO	0.6	PhCO · $AlCl_3$	1.3
MeCO	0.6	MeCO · $AlCl_3$	1.5
NO_2	0.7	NO_2 · $AlCl_3$	1.6
COCl	0.8	ClCO · $AlCl_3$	1.7
HCO	0.8	HCO · $AlCl_3$	1.9
CCl_3	0.3	$CCl_2^+AlCl_4^-$	3.6

Note. The constants of substituents COCl, ClCO · $AlCl_3$, CCl_3, and $CCl_2^+AlCl_4^-$ were calculated from the chemical shifts C_p[1] using an analytical expression for linear $\delta_{C_p} - \sigma_p^+$ correlation in 1,2-dichloroethane: $\Delta\delta_{C_p} = 8.92$, $\sigma_p^+ -1.07$ ($\Delta\delta_{C_p}$ is the chemical shift for *p*-position relative to the chemical shift of unsubstituted benzene); the constants for other substituents were taken from Ref. 6.

MOPAC program package[7] are listed in Table 3. Qualitatively, the results obtained by the AM1 and PM3 methods follow the same pattern (see Fig. 1), though particular energy values and atomic charges differ since the parametrizations of these (related) methods are different.



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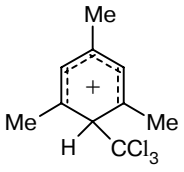

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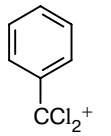

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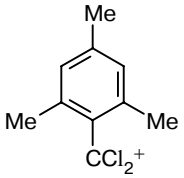

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A common feature of cations **3**—**6** is strong delocalization of the positive charge over the constituent atoms (Table 3). On the other hand, structural differences between the benzene (**3** and **5**) and mesitylene (**4** and **6**) derivatives are rather large. It should be emphasized that ion **5** has a coplanar geometry, while ion **6** is characterized by folding of the benzene ring (the angle between the C(2)—C(1)—C(6) plane and the middle plane C(2)—C(3)—C(4)—C(5)—C(6) is ~5°) and by deviation of the CCl_2 group from the C(2)—C(1)—C(6) plane by an angle of about 35°. According to a commonly ac-

Table 3. Results of MNDO calculations of cations **3**—**6** and **9** and molecules **7** and **8**

Parameter	**3**	**4**	**5**	**6**	**7**	**8**	**9**
ΔH_f/kcal mol^{-1}	210.2	189.7	215.4	204.9	5.4	0.5	189.3
ε_f/eV	−15.6	−14.8	−14.8	−14.2	−10.0	−9.7	−14.8
ε_v/eV	−7.6	−7.2	−7.4	−7.2	−0.9	−1.0	7.1
Atomic charges, *Q*/au:							
C_i	−0.08	−0.04	−0.19	−0.16	−0.15	−0.10	−0.05
C_o	0.14	0.10	0.13	0.09	0.01	−0.03	0.13, 0.11
C_m	−0.16	−0.15	0.12	−0.10	−0.08	−0.05	−0.20, −0.17
C_p	0.28	0.25	0.18	0.14	−0.02	−0.06	0.27
$C_{o\text{-Me}}$	—	0.02	—	0.02	—	0.06	0.01, 0.02
$C_{p\text{-Me}}$	—	0.00	—	0.02	—	0.07	−0.005
C_{CCl}	0.20	0.20	0.28	0.28	0.31	0.31	0.25
H_i	0.14	0.11	—	−	—	−	0.10, 0.11
H_o	0.13	—	0.11	—	0.07	—	—
H_m	0.13	0.12	0.12	0.10	0.07	0.06	0.12
H_p	0.12	—	0.11	—	−0.07	—	—
Cl	−0.04, −0.04, −0.07	−0.05, −0.08, −0.05	0.07, 0.07	0.06, 0.06	−0.12, −0.13, −0.13	−0.12, 0.13, −0.13	−0.08, −0.07, −0.07
$H_{o\text{-Me}}$	—	0.05	—	0.04	—	0.01	0.04, 0.06, 0.07 0.04, 0.06, 0.05
$H_{p\text{-Me}}$		0.06		0.05	—	0.00	0.05, 0.07, 0.06

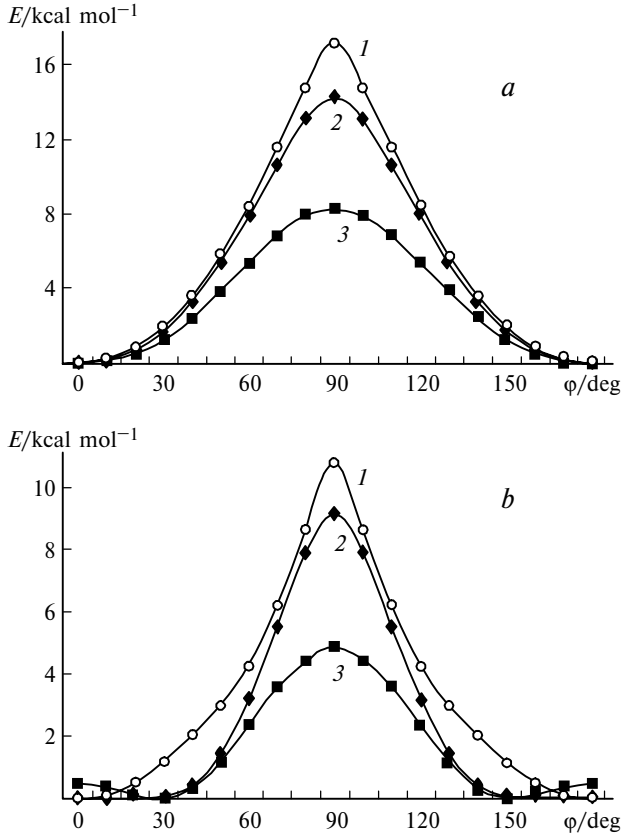

Fig. 1. Profiles of the potential surfaces of rotation for phenyldichlorocarbenium (**5**) (*a*) and 2,4,6-trimethylphenyldichlorocarbenium (**6**) (*b*) ions calculated by different quantum-chemical methods: MNDO (*1*), AM1 (*2*), and PM3 (*3*).

cepted opinion,[8] this value of the inter-plane angle should not lead to appreciable weakening of conjugation between the CCl_2^+ group and aryl fragment. To estimate the energy change due to rotation of these groups, we calculated the profiles of the potential surfaces of rotation for ions **5** and **6** by the MNDO, AM1 and PM3 methods assuming idealized ion geometries with planar aryl rings, the Ar—CCl_2 bond lying in the ring plane, and the constant value of Cl—C—Cl angle (~108°).

According to calculations by different methods, coplanar conformations of ions **5** and **6** (Fig. 1) correspond to the energy minimum, while perpendicular orientation of the ring plane and the CCl_2 group plane corresponds to the energy maximum. It should be noted that, if the angle of rotation does not exceed 20° for ion **5** and 30 to 40° for ion **6**, the energy of the system increases by at most 1 kcal mol^{-1}. In contrast to the AM1 and MNDO methods, PM3 calculations of the sterically hindered ion revealed an energy minimum corresponding to rotation of the CCl_2^+ group by ~30°. However, this minimum is merely 0.5 kcal mol^{-1} deep. It should also be emphasized that the energy profile for phenyldichlorocarbenium ion **5** is much more "steeper," while the energy difference between the conformations with the minimum and maximum energy (this can be considered as a barrier to rotation) is larger than in the case of trimethyl-substituted ion **6**. This can seem to be unexpected; however, it can be explained by pronounced steric strain in the coplanar conformation of ion **6** characterized by conjugation between the aryl fragment and the CCl_2^+ group and by the absence of steric strain in the "perpendicular," conjugation-free conformation.

The above-mentioned barriers to rotation were also estimated using *ab initio* quantum-chemical methods (the Gaussian 94 program package[9]). For each cation, **5** and **6**, we calculated the energies of two conformations, namely, an optimized minimum-energy conformation and a conformation with a fixed value of the angle of rotation of the CCl_2 group about the benzene ring (90°). Our calculations started from the conformation with an angle of 90° between the group CCl_2 plane and the plane passing through the C(2)—C(1)—C(6) atoms and then the aryl fragment geometry was optimized (this results in some flattening of the benzene ring). The basis sets used were STO-3G, 6-31(d,p), 3-21(d,p), and B3LYP/3-21(d,p). The energy differences between the two conformations (Table 4) were also considered as corresponding barrier heights (see above). The results obtained are in qualitative agreement with the results of semiempirical calculations carried out in the same manner as the *ab initio* calculations (see Table 4). Extension of the basis set lowers the height of the barrier to rotation which approaches the values found from semiempirical calculations. Taking phenyldichlorocarbenium cation (**5**) as an example, we have previously shown that calculations with inclusion of electron correlation at the second-order level of perturbation theory (MP2) in the 3-21(d,p) basis set lead to analogous results.

The distinctions between the benzene and mesitylene derivatives are responsible for substantial difference in the ease of dehydrochlorination of ions **3** and **4**. According to MNDO calculations, the reaction **3** → **5** + HCl is exothermic ($\Delta\Delta H_f = -10.0$ kcal mol^{-1}), while the reaction **4** → **6** + HCl is characterized by a negligible heat effect ($\Delta\Delta H_f = -0.1$ kcal mol^{-1}). Of course, the accuracy of these particular numerical values of enthalpy

Table 4. Barriers to internal rotation (in kcal mol^{-1}) of cations **5** and **6** calculated by different quantum-chemical methods

Method	Ion	
	5	**6**
STO-3G	32.6	26.1
6-31(d,p)	23.4	14.1
3-21(d,p)	24.5	14.9
B3LYP/3-21(d,p)	23.7	15.9
MNDO	17.1	10.7
AM1	14.2	9.1
PM3	8.3	4.9

changes should not be overestimated; however, the conclusion that dehydrochlorination of σ-complex **3** proceeds more readily is undoubtful and consistent with the experimental data.

A concept of electrophilic substitution reactions with a sterically hindered rearomatization stage resulting in products with two bulky coplanar substituents was proposed taking trichloromethylation and *tert*-butylation of 2,4-dialkylthiophenes as examples.[10] Trichloromethylation of mesitylene undoubtedly belongs to this type of reactions since the presence of two adjacent methyl groups makes the most favorable (from the viewpoint of conjugation) coplanar arrangement of the CCl_2^+ group with undistorted benzene ring impossible. Here, we consider the α,α-dichlorobenzyl type ion **6** as a reaction product, since even in the case of deprotonation resulting in trichloromethylarene the latter should inevitably undergo a transformation into ion **6** under the action of Lewis acid present in the reaction mixture. In addition, deprotonation was shown to be energetically unfavorable. According to our MNDO calculations of reactions **3** → **7** + H^+ and **4** → **8** + H^+ using the values listed in Table 3 and ΔH_f for proton (326.7 kcal mol^{-1}), the two processes are strongly endothermic ($\Delta\Delta H_f$ = 121.9 and 137.5 kcal mol^{-1}, respectively). As can be seen, deprotonation of 2,4,6-trimethyl-1-(trichloromethyl)benzenium ion (**4**) is much more unfavorable compared to 1-(trichloromethyl)benzenium ion (**3**).

Similar effects were also revealed in the mass spectrometric studies of gas-phase reactions of CCl_3^+ ion with benzene and its homologs (at a pressure of 2 to 4 Torr in the ion source).[11] These reactions resulted only in the "adduct ions," $ArHCCl_3^+$, and products of their dehydrochlorination, $ArCCl_2^+$. In the reaction with benzene small amounts of $PhCCl_2^+$ ion (**5**) were formed only at relatively low temperatures, while only the $PhHCCl_3^+$ ion (**3**) was detected at temperatures above 500 K. In the reaction with mesitylene both types of ions (**4** and **6**) were observed over a wide temperature range. The possibility for partial isomerization of ion **4** into 2,4,6-trimethyl-3-(trichloromethyl)benzenium (**9**) cation to occur has also been discussed.[11] According to our MNDO calculations, the formation energy of **9** (189.3 kcal mol^{-1}) is only 0.4 kcal mol^{-1} lower than that of its isomer **4**, which is consistent with the assumption of the presence of both types of ions and their further dehydrochlorination to give ion **6**.

Thus, based on (i) the experimental data for liquid-phase and gas-phase reactions and (ii) the results of semiempirical quantum-chemical calculations, we showed that the main route of transformations of the intermediates of electrophilic aromatic trichloromethylation, that is, trichloromethylarenium ions, involves their dehydrochlorination with the formation of corresponding α,α-dichlorobenzyl cations rather than deprotonation. Due to steric hindrances to rearomatization, produced by the *ortho*-methyl groups, dehydrochlorination of the 2,4,6-trimethyl-1-(trichloromethyl)benzenium ion proceeds more difficultly than that of sterically unhindered 1-(trichloromethyl)benzenium ion.

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