

SILVER PERCHLORATE PROMOTED REACTIONS: ARYLMETHYLATION OF AROMATICS BY BROMOMETHYLARENES

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Received December 5th, 1975

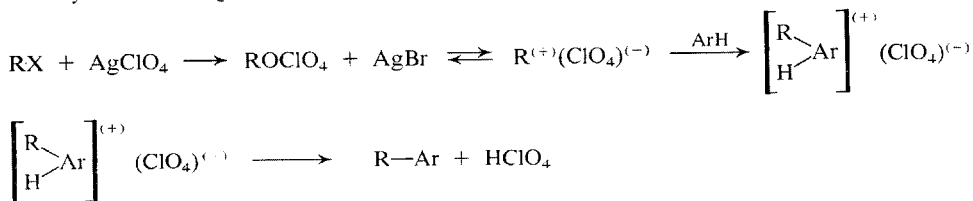
Formation and disproportionation of aryl derivatives $V(a-d)$ – $VIII(a-d)$ was investigated in the title reaction of bromomethyl derivatives I – IV with the aromatic substrates benzene, mesitylene, methoxybenzene and 1,3,5-trimethoxybenzene. The role of perchloric acid (generated in course of the reaction) was elucidated in the two opposing processes by employing calcium carbonate as the acid scavenger. In most cases, suppression of the disproportionation was achieved by the carbonate base without affecting the product-forming step. Importance of polar *vs* steric effects was examined in this context. Synthetic utility of the title reaction is demonstrated by comparison with the related outcomes obtained with aluminium chloride as the standard alkylation catalyst.

Alkylation of aromatics by alkyl halides is performed customarily by the Friedel–Crafts reaction^{1,2} using aluminium chloride or related Lewis acid-metal halides as catalysts. Frequently, however, the presence of Lewis acids brings about complication in the reaction, the subsequent isomerisation^{3,4} and/or disproportionation^{3,5–7} being the most usual obstacle. In some instances, the complications may be avoided by proper selection of reaction conditions or by employing a milder Friedel–Crafts catalyst. Not exceptionally, however, even stringent precautions do not suffice⁵ to preclude the subsequent processes disallowing isolation of the required products.

The silver perchlorate promoted reaction of alkyl halides with aromatics remained so far practically unexplored. It was shown by Burton^{8,9} and Olah³ that *tert*-butyl and isopropyl halides react in presence of stoichiometric amounts of silver perchlorate with benzene or toluene yielding smoothly the corresponding alkylarenes. Methyl and ethyl halides, on the other hand, failed in the alkylation, yielding only the corresponding alkyl perchlorates. Metathesis between silver perchlorate and alkyl halide leading to alkyl perchlorate thus appears to be the preliminary step in the reaction, ionization of the latter alkyl derivative being presumedly the prerequisite for the alkylation process.

An analogy may therefore be postulated between the alkylation promoted by silver perchlorate (Scheme 1a) and that induced by the Friedel–Crafts catalysts (Scheme 1b). However, although silver ion, $Ag^{(+)}$, is obviously electron acceptor and thus

a Alkylation with AgClO_4 :



b Alkylation with AlCl_3 :



SCHEME 1

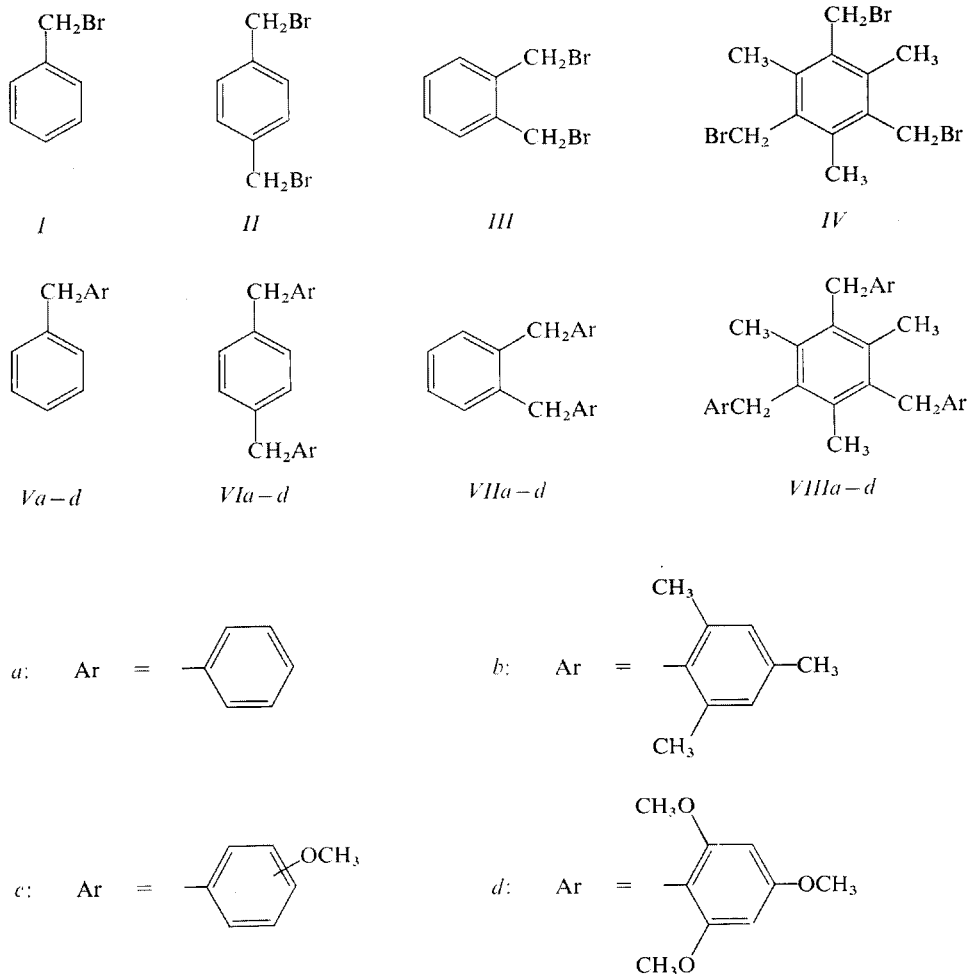
is acid according to Lewis' generalized classification, silver perchlorate has never been found to exert any Lewis acid catalytic activity in the alkylation¹⁰, except for the metathesis with the alkyl halide reagent.* This led us to hope that silver perchlorate could serve as a convenient tool for synthesis of the labile alkylarene compounds which are troublesome in the standard Friedel-Crafts procedures.

To test this view, we examined the silver perchlorate promoted reaction of bromomethylbenzenes *I-IV* with benzene, mesitylene, methoxybenzene and 1,3,5-trimethoxybenzene as the aromatic substrates. The arylmethylbenzenes (*Va-d* to *VIIIa-d*) were expected to result from the reaction (*I* → *Va-d*, *II* → *VIa-d*, *III* → *VIIa-d* and *IV* → *VIIIa-d*) and to differ greatly in their sensitivity towards Lewis acid action. A parallel study in this series employing aluminium chloride as a routine Friedel-Crafts catalyst was performed for comparison (Scheme 2).

EXPERIMENTAL

Materials: Aromatic hydrocarbons, methoxybenzene, benzyl bromide and anhydrous aluminium chloride were commercial products of the highest purity. 1,3,5-Trimethoxybenzene, *o*- and *p*-bis(bromomethyl)benzenes were prepared by known procedures. Silver perchlorate was prepared by treatment of silver oxide with perchloric acid and dehydrated by azeotropic distillation¹³ with benzene. After drying on aspirator at 80°C the product still retained complexed benzene solvent, removable only by prolonged drying at 100°C/0.5 Torr. The benzene-free salt was however very hygroscopic; we therefore employed the benzene-complexed salt in this

* No alkylation of aromatics occurred¹¹ when other Friedel-Crafts alkylating agents (such as ethers or olefins) were used instead of alkyl halides. π -Complex formation between silver perchlorate and aromatic systems seems to be generally a reversible process, unaccompanied by side reactions. Rearrangements of strained non-aromatic (σ -bond) systems by silver perchlorate have however been reported¹².



SCHEME 2

study. No interference of benzene with the other (more reactive) aromatic substrates was noted in the alkylation runs.

2,4,6-Tris(bromomethyl)mesitylene

To a solution of sodium bromide (204.5 g; 2 mol), paraformaldehyde (55 g) and mesitylene (43.5 g; 0.36 mol) in acetic acid (180 ml) was added dropwise a mixture of concentrated sulphuric acid (180 ml) and acetic acid (180 ml). The mixture was stirred at 90–95°C for 6 h. After standing overnight the mixture was diluted with water (2000 ml), the solid was separated and dried *in vacuo* over P₂O₅. Crystallization from dichloroethane yielded 119 g (83%) of the pure product (according to thin-layer chromatography), m.p. 186–188°C. The analytical sample melted after repeated crystallization and sublimation at 189–190°C. For C₁₂H₁₅Br₃ (399.0) calculated: 36.12% C, 3.79% H, 60.09% Br; found: 36.45% C, 3.75% H, 59.93% Br.

TABLE I
Conditions, Separation and Isolated Products in the Silver Perchlorate Promoted Alkylation

Bromide	Aromatic	Base	Separation ^a	Products (yields, %) ^b
<i>I</i>	benzene	—	D	<i>Va</i> (52)
	benzene	CaCO ₃	VPC	<i>Va</i>
	mesitylene	—	D	<i>Vb</i> (72)
	mesitylene	CaCO ₃	VPC	<i>Vb</i>
	methoxybenzene	—	D	<i>Vc</i> (65)
	methoxybenzene	CaCO ₃	VPC	<i>Vc</i>
	trimethoxybenzene	—	TLC	<i>Vd</i>
	trimethoxybenzene	CaCO ₃	CC, S	<i>Vd</i> (55)
<i>II</i>	benzene	—	CC	<i>VIa</i> (80)
	benzene	CaCO ₃	TLC	<i>VIa</i>
	mesitylene	—	TLC	<i>VIIb</i>
	mesitylene	CaCO ₃	CC	<i>VIIb</i> (73), <i>XIIc</i> (10)
	methoxybenzene	—	TLC	<i>VIIc</i>
	methoxybenzene	CaCO ₃	CC	<i>VIIc</i> (66)
	trimethoxybenzene	—	CC	<i>VIIId</i> (25), <i>XIIa</i> (15)
	trimethoxybenzene	CaCO ₃	CC	<i>VIIId</i> (30), <i>XIIa</i> (20)
<i>III</i>	benzene	—	CC	<i>VIIa</i> (75)
	benzene	CaCO ₃	TLC	<i>VIIa</i>
	mesitylene	—	TLC	<i>VIIb</i>
	mesitylene	CaCO ₃	CC	<i>VIIb</i> (90), <i>XIIId</i> (10)
	methoxybenzene	—	CC	<i>VIIc</i> (75)
	methoxybenzene	CaCO ₃	TLC	<i>VIIc</i> (83)
	trimethoxybenzene	—	TLC	<i>VIIId</i> , <i>XIIb</i>
	trimethoxybenzene	CaCO ₃	CC	<i>VIIId</i> (52), <i>XIIb</i> (35)
<i>IV</i>	benzene	—	CC, C	<i>VIIIa</i> (35)
	benzene	CaCO ₃	CC, C	<i>VIIIa</i> (30)
	mesitylene	—	C	<i>IXa</i> (27)
	mesitylene	CaCO ₃	CC, C	<i>VIIIb</i> (58), <i>IXa</i> (2), <i>Xa</i> (8)
	methoxybenzene	—	CC	<i>IXb</i> (70), <i>XIb</i> (30)
	methoxybenzene	CaCO ₃	C	<i>VIIIc</i> (72), <i>IXb</i> (6), <i>XIb</i> (4)
	trimethoxybenzene	—	TLC	<i>IXc</i> , <i>Xc</i> , <i>XIc</i>
	trimethoxybenzene	CaCO ₃	CC, C	<i>IXc</i> (50), <i>Xc</i> (15), <i>XIc</i> (10)

^a Distillation (D), vapour phase chromatography (VPC), column chromatography (CC), thin-layer chromatography (TLC), crystallization (C); ^b after separation and purification.

Alkylation Runs

A. *With silver perchlorate:* Silver perchlorate (1.43 g; 5 mmol calculated for the 1 : 1 AgClO_4 - $-\text{C}_6\text{H}_6$ complex), an excess of aromatic substrate (10 ml of liquid, or, for 1,3,5-trimethoxybenzene, 1 g dissolved in 10 ml of benzene) and precipitated anhydrous calcium carbonate (1 g; 10 mmol: only in the runs indicated in Table I) were stirred for 10 min. An equivalent amount of alkyl bromide was added and stirring was continued for 30 min. Water (20 ml) was added, inorganic salts were filtered off over a short column of silica and washed successively with dichloromethane (20 ml) and ether (20 ml). The organic layers were combined, washed with water and dried by MgSO_4 . Solvents were taken down on aspirator and the residue separated by column chromatography (Silicagel 150–200 g; light petroleum–benzene or light petroleum–ether mixtures as eluents) and/or crystallization. The results are summarized in Tables I and II.

B. *With aluminium chloride:* Equivalent amounts of aluminium chloride and alkyl halide (2–6 mmol of each) were dissolved in an excess of the aromatic substrate (10 ml) and stirred for 5 min. Water (20 ml) was added, organic layer was separated, washed with water, dried over MgSO_4 and taken down on aspirator. Composition of the residue was estimated by thin-layer chromatography using the identified products from the procedure A as reference samples.

Stability of products in presence of AlCl_3 : The arylated derivative VIIIa–c (0.1 mmol) was added to a stirred mixture of aluminium chloride (66 mg; 0.5 mmol) in an appropriate aromatic hydrocarbon (1.5 ml; benzene for VIIIa, mesitylene for VIIIb, methoxybenzene for VIIIc). After 3 min stirring at room temperature the mixture was decomposed by water and worked up as indicated in the procedure B.

Analyses and identification of products: Alkylation runs and isolation procedures were monitored by thin-layer (Silicagel G; light petroleum–benzene–ether eluents) and/or by vapour phase chromatography (SE 30 on Chromosorb W; 160–200°C). Structures of the isolated products were assigned mass-spectrometrically; when necessary, the assignments were supported by the $^1\text{H-NMR}$ spectra (Table III).

RESULTS AND DISCUSSION

Formation and Disproportionation of the Aryl Derivatives V–VIII

Treatment of the bromomethylbenzenes I–IV with stoichiometric amounts of silver perchlorate in benzene led to an instantaneous precipitation of silver bromide and afforded the expected arylmethyl derivatives (Va–VIIIa, respectively) in 50–80% yields, the remainder being higher alkylated products (*vide infra*); no disproportionation or isomerisation has been detected by thin-layer or vapour-phase chromatography.

Similarly, the reaction of mono- and bis(bromomethyl)benzenes I–III with mesitylene in presence of silver perchlorate yielded the corresponding arylated compounds (Vb–VIIb, respectively) accompanied again by higher alkylated products. The reaction of the tris(bromomethyl) derivative IV took, however, a different course. Instead of the trimesitylated derivative VIIIb, dimesitylmethane, m.p. 135°C, was obtained as the sole product (lit.¹⁴, m.p. 133–135°C).

TABLE II
Arylmethylbenzenes

Arylmethyl- benzene	M.p., °C or b.p., °C/Torr	Formula (M.w.)	Calculated/Found	
			%C	%H
<i>Va</i>	120/15 lit. ¹⁵ 141/27	C ₁₃ H ₁₂ (168·2)	92·81 92·75	7·19 7·00
<i>Vb</i>	110/0·5 lit. ¹⁵ 183/11	C ₁₆ H ₁₈ (210·3)	91·37 91·61	8·63 8·60
<i>Vc</i>	95/0·2 ^a lit. ¹⁶ 191/38	C ₁₄ H ₁₄ O (198·3)	84·81 84·49	7·12 6·95
<i>Vd</i>	92—94 lit. ¹⁷ 91—93	C ₁₆ H ₁₈ O ₃ (258·3)	74·40 74·70	7·02 7·10
<i>VIa</i>	86 lit. ¹⁸ 85—86	C ₂₀ H ₁₈ (258·4)	92·98 92·95	7·02 7·14
<i>VIb</i>	182—183 lit. ⁶ 165—166	C ₂₆ H ₃₀ (342·5)	91·17 91·00	8·83 8·71
<i>VIc</i>	88—90 ^a	C ₂₂ H ₂₂ O ₂ (318·4)	82·99 83·01	6·96 7·23
<i>VI d</i>	198—200	C ₂₆ H ₃₀ O ₆ (438·5)	71·21 71·58	6·90 6·95
<i>VIIa</i>	77—78 lit. ¹⁹ 78	C ₂₀ H ₁₈ (258·4)	92·98 92·87	7·02 6·98
<i>VIIb</i>	216 lit. ²⁰ 207—208	C ₂₆ H ₃₀ (342·5)	91·17 91·07	8·83 8·99
<i>VIIc</i>	150—160/0·2 ^{a,b}	C ₂₂ H ₂₂ O ₂ (38·4)	82·99 83·07	6·96 7·01
<i>VII d</i>	181	C ₂₆ H ₃₀ O ₆ (438·5)	71·21 71·65	6·90 6·81
<i>VIIIa</i>	135—136 lit. ²¹ 132	C ₃₀ H ₃₀ (390·6)	92·26 91·95	7·74 8·03
<i>VIIIb</i>	219—221 lit. ⁵ 208—210	C ₃₉ H ₄₈ (516·8)	90·64 90·67	9·36 9·27
<i>VIIIc</i>	142—143 ^c	C ₃₃ H ₃₆ O ₃ (480·7)	82·46 82·44	7·55 7·49
<i>IXa</i>	134—135 lit. ¹⁴ 133—135	C ₁₉ H ₂₄ (252·4)	90·42 90·60	9·58 9·64
<i>IXb</i>	45—50 ^a	C ₁₅ H ₁₆ O ₂ (228·3)	78·92 79·22	7·06 7·04

TABLE II
 (Continued)

Arylmethyl- benzene	M.p., °C or b.p., °C/Torr	Formula (M.w.)	Calculated/Found	
			% C	% H
<i>IXc</i>	116–117	$C_{19}H_{24}O_6$ (348.4)	65.50	6.94
	lit. ²¹ 116–117		65.94	7.00
<i>Xa</i>	155–156	$C_{29}H_{36}$ (384.6)	90.57	9.43
	lit. ⁵ 150–152		90.67	9.11
<i>Xc</i>	166–167	$C_{29}H_{36}O_6$ (480.58)	72.48	7.55
			72.89	7.80
<i>XIb</i>	40–50 ^a	$C_{17}H_{20}O$ (240.3)	84.96	8.39
			85.15	8.15
<i>XIIa</i>	192–193	$C_{43}H_{48}O_9$ (708.85)	73.00	6.80
			73.40	7.00
<i>XIIb</i>	225–227	$C_{43}H_{48}O_9$ (708.85)	73.00	6.80
			73.36	7.10
<i>XIIc</i>	226	$C_{43}H_{48}$ (564.86)	91.45	8.55
			91.43	8.80
<i>XIId</i>	272–274	$C_{43}H_{48}$ (564.86)	91.45	8.55
			91.36	8.40

^a Mixture of positional *o*- and *p*-isomers; ^b the mixture could be separated cleanly by column chromatography: *o*, *o*-isomer (5%), m.p. 110–112°C; *o*, *p*-isomer (33%), m.p. 52–54°C; *p*, *p*-isomer (62%), m.p. 49–50°C. The structures were assigned from the ¹H-NMR spectra (Table III); ^c m.p. of the *all-p*-isomer (Table III).

Disproportionation by perchloric acid, generated in the course of alkylation, affords a very plausible explanation (Scheme 3, pathway *a*) for the anomalous result. Reverse protonization of *VIIIb* which may be formed transiently* in the reaction by perchloric acid would lead to the adduct *A* (Ar = mesityl) decomposing to give bis(mesitylmethyl)mesitylene (*Xa*) and mesitylmethyl carbenium ion *B*. *Xa* is then cleaved further, *via* intermediate *C*, under formation of dimesitylmethane (*XIa* ≡ *IXa*), whereas the carbenium ions *B* give the same final product by reaction with mesitylene nuclei.

However, another explanation which does not involve perchloric acid may be also proposed for the disproportionation (Scheme 3, pathway *b*). The intermediate *D*

* Eventually, disproportionation occurs already in earlier stages of alkylation.

TABLE III

Selected $^1\text{H-NMR}$ Spectra

Recorded on a Varian HA-100 spectrometer in CDCl_3 solution; chemical shifts (δ) are given in p.p.m. downfield from tetramethylsilane as an internal standard.

<i>VIIb</i>	CH_3 : 2.16 s (12 H); 2.24 s (6 H); CH_2 : 3.92 s (4 H) arom. protons: 6.82 s (4 H), 6.84 s (4 H)
<i>VIIc</i>	OCH_3 : 3.73 s (12 H), 3.76 s (6 H); CH_2 : 3.84 s (4 H); arom. protons: 6.11 s (4 H), 7.03 s (4 H)
<i>VIIb</i>	CH_3 : 2.18 s (12 H), 2.30 s (6 H); CH_2 : 4.01 s (4 H) arom. protons: 6.60 s (2 H), 6.86 s (4 H), 6.90 s (2 H)
<i>o, o'-VIIc</i>	OCH_3 : 3.77 s (6 H); CH_2 : 3.96 s (4 H); arom. protons: 6.70–7.25 cm (12 H)
<i>p, p'-VIIc</i>	OCH_3 : 3.75 s (6 H); CH_2 : 3.87 s (4 H); arom. protons: AA'BB' system centered at 6.77 and 6.97 (8 H), 7.12 cm (4 H)
<i>VIIId</i>	OCH_3 : 3.73 s (12 H), 3.81 s (6 H); CH_2 : 4.08 s (4 H); arom. protons: 6.19 s (4 H), 6.60–7.00 cm (4 H)
<i>VIIIb</i>	CH_3 : 2.01 s (9 H); 2.05 s (18 H), 2.21 s (9 H); 4.02 s (6 H) arom protons: 6.72 s (6 H)
<i>all-p-VIIIc</i>	CH_3 : 2.14 s (9 H); OCH_3 : 3.72 s (9 H); CH_2 : 4.06 s (6 H); arom. protons: AA'BB' system centered at 6.76 and 6.95 (12 H)
<i>XIIa</i>	OCH_3 : 3.73 s (18 H), 3.78 s (6 H), 3.41 s (3 H); CH_2 : 3.84 s (4 H), 3.89 s (4 H); arom. protons: 6.12 s (4 H), 6.29 s (1 H), 7.02 s (8 H)
<i>XIIb</i>	OCH_3 : 3.35 s (3 H), 3.73 s (12 H), 3.79 s (6 H), 3.83 s (6 H); CH_2 : 4.08 s (4 H), 4.15 s (4 H); arom. protons: 6.19 s (4 H), 6.60–7.10 cm (8 H), 7.34 s (1 H)

(X = Br or mesityl) arising in course of the alkylation, instead of deprotonation, rearranges prototropically to the adduct *E*. The carbenium ion *B* is then expelled from the latter adduct and reacts again with mesitylene to give dimesitylmethane ($\text{IXa} \equiv \text{XIa}$).

While interception of the non-catalyzed pathway *b* might be difficult, addition of a suitable base to the reaction mixture should suppress the process catalyzed by perchloric acid. (Deprotonation of the adduct *D* by an external (heterogeneous) base might also cause suppression of the pathway *b*. This, however, seems rather improbable owing to intramolecularity of the process).

Of agents capable of neutralizing the mineral acid without affecting the silver cation, precipitated calcium carbonate was found to be the most convenient base. The reaction of the bromide *IV* with mesitylene performed in the presence of the base gave the expected triarylated derivative *VIIIb* (together with higher alkylated compounds) as the major product; the products of disproportionation *IXa* and *Xa* were

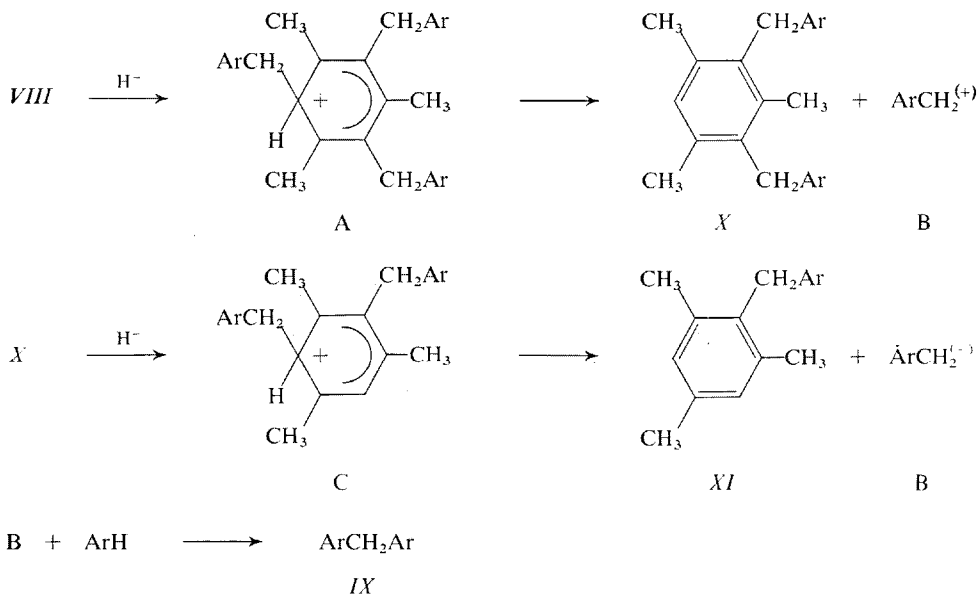
presented only in minor amounts (2% and 8%, respectively). Interestingly, practically identical results (according to thin-layer chromatography) were obtained from a parallel run securing a higher speed stirring and a gradual addition of the bromide *IV* suggesting thus that the acid-catalyzed pathway *a*) is the predominant but not the exclusive contributor to the disproportionation.

Polar as well as steric effects might be invoked to account for the disproportionation. To appreciate whether the former or the latter factors play the major role we examined next methoxybenzene as a sterically unbiased aromatic substrate, convertible however into an electronically highly stabilized methoxybenzyl carbenium ion in course of the reaction (Scheme 3). No disproportionation has been found in the alkylation by the bromides *I–III*; irrespective of the carbonate base, the corresponding methoxyphenyl derivatives (*Vc–VIIc*, respectively) accompanied by higher alkylated compounds were isolated as the sole product of the reaction. In the alkylation by the bromide *IV*, on the other hand, the expected methoxyphenyl derivative *VIIIc* could be obtained only from the reaction performed in presence of the carbonate base: in absence of the base, bis(methoxyphenyl)methane (*IXb*) and mesityl-methoxyphenylmethane (*XIb*) resulted (Scheme 3) as the principal products of the reaction. In accord with expectation, the methoxyphenyl derivatives *Vc–VIIIc*, *IXb* and *XIb* were mixtures of positional isomers (presumably *ortho*- and *para*-), as evidenced by thin-layer chromatography and vapour-phase chromatography. The *all-para*-isomer of *VIIIc*, was however, greatly predominating in the reaction of the bromide *IV* and could be easily isolated by crystallization, m.p. 142–143°C. Its structure was assigned from the NMR spectra (*A, A', B, B'* system).

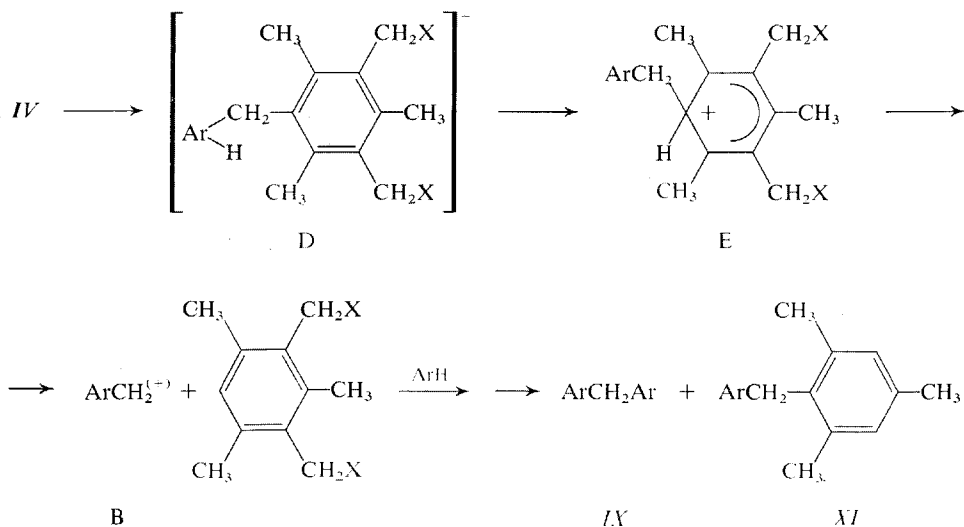
A very similar pattern of disproportionational behaviour is thus found for mesitylene and methoxybenzene indicating that steric factors are not of decisive importance in the reaction: electronic stabilization by adjacent substituents (available both in mesitylene and methoxybenzene) obviously may afford a sufficient driving force in the incipient carbenium ion (*B* in the Scheme 3) formation. (Steric effects cannot be dismissed entirely from consideration on such grounds. Absence of disproportionation in the sterically less encumbered derivatives *V–VII* suggests, in actual fact, that relief of strain may also be involved in the reaction. However, the derivatives *V–VII* possess undoubtedly a lower electron density than *VIII* on the site of protonation and they will therefore be less prone to the disproportionation).

An extreme propensity towards disproportionation would be expected in the alkylation of 1,3,5-trimethoxybenzene. Despite this, normal alkylation course (formation of *Vd–VIIId*) has been found in the reaction with the bromides *I–III*. Disproportionation occurred of course completely in the reaction with the tribromide *IV*. Strikingly, however, the carbonate base failed to suppress the disproportionation in this particular case, dealkylated compounds *Xc* and *XIc* together with *IXc* (Scheme 3) being again the sole products of the reaction. Traces of perchloric acid unscavenged by the heterogeneous base may account reasonably for the failure, by catalyzing

Pathway (a):



Pathway (b):



Ar in IX–XI: (a) mesityl, (b) methoxyphenyl, (c) 2,4,6-trimethoxyphenyl

X = Br or Ar

SCHEME 3

efficiently the pathway *a*. However, disproportionation by the non-catalyzed pathway (*b*) cannot be excluded in this extreme case. The observation that the product ratios ($IXc : Xc : XIc$) are very similar in the runs performed in presence and in absence of the base lends some support to the latter possibility.

On the Role of Perchloric Acid in the Alkylation Step

One might be tempted to conclude from these results that perchloric acid enters the reaction scheme merely as a subsequent complication suppressible in most cases easily by a suitable base. Indeed, a smooth formation of alkylated products (followed eventually by disproportionation) has been observed in majority of the reactions regardless of the acid buffering, suggesting thus that the acid is not involved in the alkylation step. However, three of the sixteen alkyl bromide–aromatic combinations examined in this study (Table I) have been found in this respect exceptional. Namely, while in absence of calcium carbonate the reactions of the bromides *I–III* with benzene afforded cleanly the corresponding alkylated products, arylmethyl perchlorates (*cf.* Scheme 1) persisted in the parallel runs buffered by the carbonate. A gradual decomposition occurred in course of the work-up of these reactions (evolution of perchloric acid) yielding darkly coloured residues which contained only minor amounts of the expected alkylated compounds.

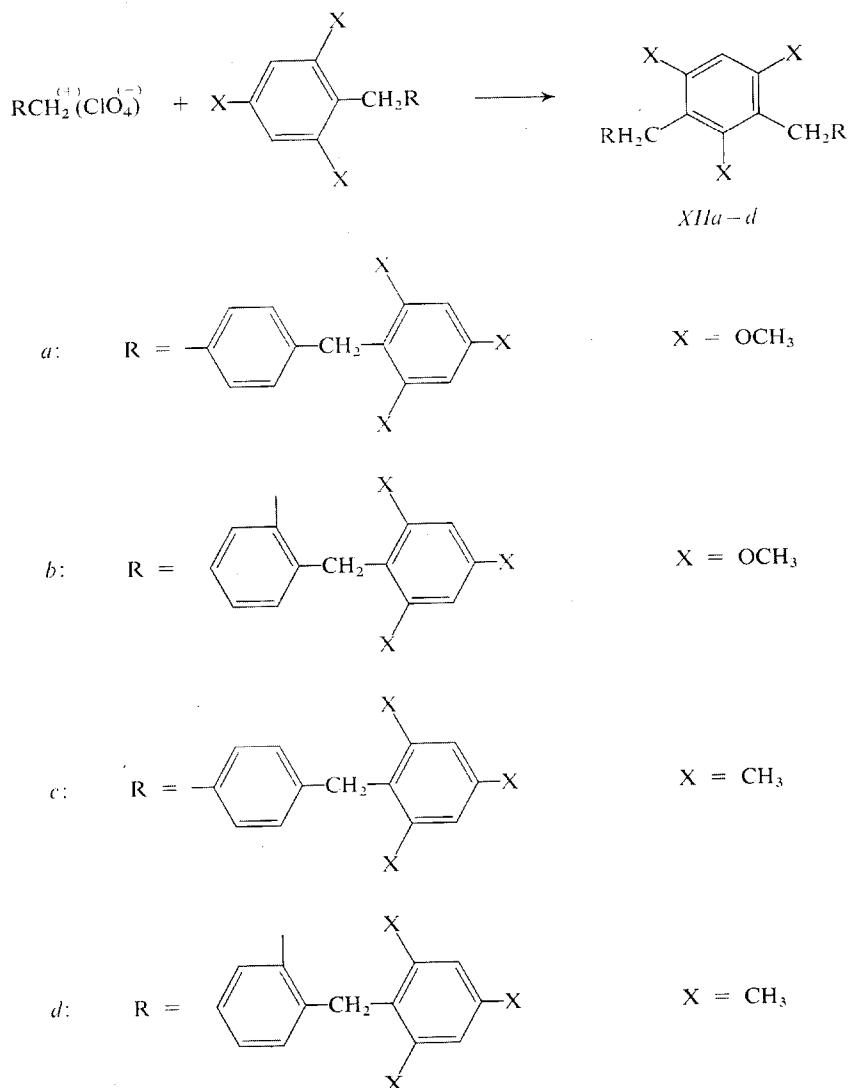
Unequal aptitude of alkyl perchlorates to ionization (Scheme 1) may account plausibly for these differences. In reactions of the tribromide *IV*, ionization of the perchlorate is assumed to be electronically (I-effect of the adjacent alkyl groups) as well as sterically (relief of strain) greatly favoured affording thus easily a high equilibrium concentration of the reactive ionized form. On the other hand, in reactions of the less disposed bromides *I–III* ionization of perchlorates will proceed more reluctantly leading eventually to a lower concentration of the ionized form. While this may suffice to satisfy aromatic nuclei of a very high electron density (such as in mesitylene or methoxybenzene), acid catalysis (autocatalysis) of the ionization is obviously required by less nucleophilic aromatic partners (such as benzene).

Formation of Higher Alkylated Products

Aside from the products discussed in the preceding sections, compound with higher molecular weights have been formed in the alkylation, amounting in some cases (Table I) up to 30% of the total reaction. In most cases, their separation could be achieved conveniently by column chromatography, the heavier products being eluted by more polar solvent mixtures.

Complex mixtures of these products resulted from the reactions of the tribromide *IV*. (From the runs performed in presence of calcium carbonate: the higher alkylated products were practically absent in the unbuffered reactions of *IV*, being presumably also subjected to disproportionation). Individual products could, however, be ob-

tained from the reaction of dibromides *II* and *III* with 1,3,5-trimethoxybenzene (m.p. 192–193°C and 225–227°C, respectively) both in agreement with the formula $C_{43}H_{48}O_9$. Structures *XIIa* and *XIIb* were assigned respectively to these products on the basis of their 1H -NMR spectra. Similarly, uniform products have been isolated from the reaction of *II* and *III* with mesitylene corresponding both to the formula $C_{43}H_{48}$ (m.p. 226°C and 273–274°C, respectively). By analogy, structures *XIIc* and *XIId* were assigned to these compounds. The reaction scheme (Scheme 4) is proposed for their formation.



SCHEME 4

Comparison with the Friedel–Crafts Catalysts

Within the framework of the present study, a cursory examination of the Friedel–Crafts alkylation catalyzed by aluminium chloride was performed for comparison. The reaction of the bromides *I–III* with benzene under standard conditions afforded the corresponding arylated derivatives in very satisfactory yields (according to thin-layer chromatography). On the other hand, reactions of the same bromides (*I–III*) with mesitylene and methoxybenzene have already been accompanied by disproportionation, insuppressible by the carbonate base. The reaction of the tribromide *IV* with any of the aromatic substrate examined did not yield either traces of the corresponding arylated products *VIIIa–c*: these, as it was established in separate experiments, are subject to an immediate destruction by aluminium chloride.

Nonetheless, some of the labile compounds (*Vib*, *VIIIa* and *VIIIb*) could be obtained^{5,6,21} in Friedel–Crafts alkylation by employing milder catalysts and under carefully controlled conditions; however, in very low²² or unspecified^{5,6} yields. Moreover, the reported values of melting points for these products were considerably lower (Table II) than those found in the present study.

Silver perchlorate offers therefore a valuable alternative to the customary Friedel–Crafts catalysts. Particularly for the synthesis of elaborated systems, labile as a rule towards Lewis acids, silver perchlorate buffered by calcium carbonate is expected to be a superior tool.

We wish to express our thanks to Dr A. Trka for the numerous mass-spectrometric analyses and Drs Z. Samek and M. Synáčeková for evaluation of the NMR spectra.

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