Solid-state reaction of a lead tetraacetate—metal halide system with naphthalene under mechanical activation

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A mechanically activated solid-state reaction of halogenation of naphthalene with a $Pb(OAc)_4$—alkaline or alkaline-earth metal halide system was carried out to yield 1-halonaphthalene as the main reaction product and 1,4-dihalonaphthalene. The solid-state halogenation of naphthalene is more selective than a liquid-phase reaction.

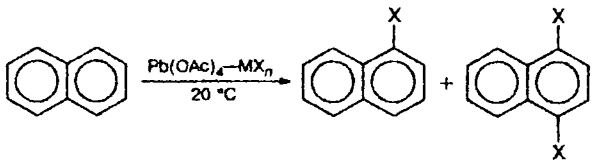
Key words: solid-state reaction, halogenation of naphthalene, lead tetraacetate, mechanical activation.

Reactions of organic compounds in the solid state have recently found wider use in organic synthesis. The increasing interest in these reactions is explained by a number of reasons. First of all, they need no solvent, often occur with higher regio- and stereoselectivity, and afford higher yields of target products compared to similar processes in the liquid phase.[1] Since the reaction rate of solids depends on the size of particles (the smaller the size, the higher the rate), it appears promising to use the mechanical activation of reaction mixtures with degradation of solids to accelerate solid-state reactions. Special devices, *e.g.*, ball, planetary, and vibration mills, disintegrators, *etc.*, have been designed to carry out such processes.[2] Grinding results in a mixture of reagents where the molecules are so close to one another that they can interact chemically.

In the present work, we first involved lead tetraacetate ($Pb(OAc)_4$), one of the oxidants most widely used in organic chemistry, in a solid-state reaction. Naphthalene was chosen as a substrate oxidized under the action of $Pb(OAc)_4$. Reaction mixtures were mechanically activated on vibration ball mills in closed steel reactors. Earlier, all known oxidation reactions of organic compounds with $Pb(OAc)_4$ or $Pb(OAc)_4$—metal halide systems have been carried out in the liquid phase. Most often benzene, less often acetic acid and trifluoroacetic acid, have been used as a solvent in whose absence the reagents could not interact chemically. In many cases, the reaction has been promoted by pyridine.[3]

The $Pb(OAc)_4$—metal halide system have been used earlier for oxidative halodecarboxylation of alkanoic acids into haloalkanes[4] and for halogenation of aliphatic[5] and alicyclic[6] alcohols. Its application to aromatic compounds has not been studied.

We established that a solid-state interaction of naphthalene with a $Pb(OAc)_4$—MX_n system results in two products: 1-halo- and 1,4-dihalonaphthalene.



M = Li, Na, K, Mg, Ca, Ba; X = Cl, Br (n = 1, 2)

The position of the halogen atom in the aromatic ring was determined by NMR spectroscopy. Thus, four doublets with δ 8.24, 7.83, 7.80, and 7.78 corresponding to the protons in positions 2, 4, 5, and 8 and three triplets with δ 7.59, 7.52, and 7.31 corresponding to the protons in positions 3, 6, and 7 were observed in the ^1H NMR spectrum of monobromosubstituted naphthalene. The spin-spin coupling constant of the doublets and triplets $^3J = 8.3$ Hz. This spectrum unambiguously corresponds to 1-bromonaphthalene. In the case of 2-bromonaphthalene, the signal of the proton in position 1 would be a singlet. The ^{13}C NMR spectrum of 1-bromonaphthalene obtained correlates with data published earlier.[7] The ^1H NMR spectrum of 1,4-dibromonaphthalene exhibits a typical AA′BB′ system of four protons in positions 5, 6, 7, and 8 with the centers of mirror-symmetrical multiplets at δ 8.24 and δ 7.63 and a singlet with δ 7.62. A singlet with an intensity of 2H is absent in the spectra of all other possible isomeric dibromonaphthalenes. In the ^{13}C NMR spectrum of 1,4-dibromonaphthalene, whose molecule has a plane of symmetry, five signals are observed: 132.9

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Table 1. Dependence of the conversion of naphthalene and the yield of reaction products on the reaction conditions

Entry	Ratio naphthalene : $Pb(OAc)_4$: MgO : LiX, X	Time /h	Frequency /Hz	Naphthalene conversion (%)	Product yield (%)	Product ratio (%) $1-X-C_{10}H_7$	$1,4-X_2-C_{10}H_6$
1	1 :1.2 :1.2 :3, Cl	4	12	3	73	71	29
2	1 :1.2 :1.2 :5, Cl	4	12	64	77	80	20
3	1 :1.2 :1.2 :5, Cl	3	12	39	59	74	26
4	1 :1.2 :— :3, Cl	4	12	44	57	69	31
5	1 :1.2 :— :5, Cl	4	12	52	67	71	29
6	1 :2 :2 :5, Cl	4	12	92	66	77	23
7	1 :2 :2 :2, Cl	4	12	43	88	79	21
8	1 :1.2 :1.2 :3, Cl	4	19	40	63	68	32
9	1 :1.2 :1.2 :5, Cl	4	19	49	63	68	32
10	1 :1.2 :— :3, Br	4	12	58	72	76	24
11	1 :1.2 :— :5, Br	4	12	68	96	67	33
12	1 :1.2 :1.2 :3, Br	4	12	53	70	81	19
13	1 :1.2 :1.2 :5, Br	4	12	71	96	91	9

Note. Reaction conditions: 20 °C; the amount of naphthalene is 0.005 mol; and the $Pb(OAc)_4$ conversion is 100%.

(C(9) and C(10)), 130.0 (C(2) and C(3)), 128.1 (C(5) and C(8)), 127.7 (C(6) and C(7)), and 122.5 (C(1) and C(4)). In the proton undecoupled ${}^{13}C$ NMR spectrum of this compound, the signal of C(2) and C(3) is a doublet with ${}^{1}J$ = 169.0 Hz, that of C(5) and C(8) is a doublet of doublets with ${}^{1}J$ = 161.6 and ${}^{2}J$ = 8.6 Hz, and that of C(6) and C(7) is a doublet of triplets with ${}^{1}J$ = 161.2 and ${}^{2}J$ = 4.5 Hz. The signals of C(9), C(10) and C(1), C(2) do not have direct spin-spin coupling constant ${}^{1}J$.

Results of the oxidative halogenation of naphthalene are given below. At 20 °C and with the molar ratio of naphthalene : $Pb(OAc)_4$: MX_n varying in the range 1 : (1.2—2) : (2—5), monohalonaphthalene always substantially prevails over dihalonaphthalene (by a factor of ~2—10) in the reaction products (see Table 1). Under these conditions, the conversion of naphthalene can attain 80%, the overall yield can run to 90%, and $Pb(OAc)_4$ is consumed almost completely. It was established for the halogenation of naphthalene with the $Pb(OAc)_4$—LiCl and $Pb(OAc)_4$—LiBr systems as examples that introduction of an equimolar (relative to $Pb(OAc)_4$) amount of magnesium oxide into the reaction mixture changes the ratio of mono- and dihalonaphthalenes formed, the content of the monosubstituted product increasing (see Table 1, entries *1, 4*; *2, 5*; *10, 12*; and *11, 13*). This effect is probably due to the fact that the polar molecules of monohalonaphthalene are insulated by the MgO molecules, which prevent monohalonaphthalene from interacting with the oxidative system, to a larger extent than the naphthalene ones. Another possible reason of why the formation of 1-monohalonaphthalene in the presence of MgO becomes more selective is that the acetic acid liberated during the reduction of $Pb(OAc)_4$ is transformed into magnesium acetate, which changes the parameters of the reaction mixtures, thus affecting the composition of the products.

Among halides used as a source of halogen, lithium chloride, calcium chloride, lithium bromide, and potassium bromide are the most effective with regard to the conversion of naphthalene and the yield of products. The highest selectivity of monohalogenation (>80—90%) was also attained with these salts (Table 2). All other factors being equal, the conversion of naphthalene increases with increasing amount of the taken halide (*e.g.*, see Table 1, entries *1, 2*; *6, 7*; and *12, 13*), whereas an increase in the working frequency of the vibration mill from 12 to 19 Hz somewhat reduces the selectivity of monochlorination of naphthalene with the $Pb(OAc)_4$—LiCl system (see Table 1, entries *1, 8* and *3, 9*).

To compare solid-state reactions with liquid-state ones, naphthalene was chlorinated and brominated in a traditional way with $Pb(OAc)_4$ and LiCl or LiBr in benzene at 80 °C. The reagents were taken in the same ratio as this was in the solid-state reaction. As follows from Table 3, a mixture of 1-mono- and 1,4-dihalonaphthalene is formed in the liquid-state process as well, but both the conversion of naphthalene and the selectivity of formation of 1-halonaphthalene decreases.

Thus, the mechanically activated solid-state halogenation of naphthalene with a $Pb(OAc)_4$—alkaline or alkaline-earth metal halide system is more selective than the liquid-state process.

Table 2. Solid-state halogenation of naphthalene with a $Pb(OAc)_4$—MX_n system

MX_n	Naphthalene conversion (%)	Product yield (%)	Product ratio (%) $1-X-C_{10}H_7$	$1,4-X_2-C_{10}H_6$
NaCl	3	75	50	50
KCl	9	67	58	42
LiCl	64	77	80	20
$CaCl_2$	80	89	87	13
$BaCl_2$	46	78	77	23
NaBr	45	74	93	7
KBr	54	86	70	30
LiBr	71	96	91	9
$MgBr_2$	34	66	73	27

Note. Reaction conditions: 20 °C; reaction duration 4 h; frequency 12 Hz; molar ratio of naphthalene : $Pb(OAc)_4$: MX_n : MgO = 1 : 1.2 : 5 : 1.2; amount of naphthalene 0.005 mol; $Pb(OAc)_4$ conversion 100%.

Table 3. Liquid-state and solid-state halogenation of naphthalene

Ratio naphthalene : $Pb(OAc)_4$: MgO : LiX,X	Reaction conditions[a]	Naphthalene conversion (%)	Product yield (%)	Product ratio (%)	
				$1\text{-}X\text{-}C_{10}H_7$	$1,4\text{-}X_2\text{-}C_{10}H_6$
1 : 1.2 : 1.2 : 3, Cl	A	44	53	47	53
1 : 1.2 : 1.2 : 3, Cl	B	37	73	71	29
1 : 2 : 2 : 5, Cl	A	51	63	63	37
1 : 2 : 2 : 5, Cl	B	92	66	77	23
1 : 2 : 2 : 5, Br	A	70	85	81	19
1 : 1.2 : 1.2 : 5, Br	B	71	96	91	9

Note. Reaction conditions: amount of naphthalene 0.005 mol; $Pb(OAc)_4$ conversion 100%. A, benzene, 80 °C; B, frequency of 12 Hz, 20 °C.

Experimental

GLC analysis was performed on an LKhM-80 chromatograph with a flame ionization detector, an analytical glass column (3000×3 mm), and 5% SE-30 on Chromaton N-AW-HMDS (0.16—0.20 mm). A 2000×10 mm copper column with 10% SE-30 on chromosorb W (0.20—0.25 mm) was used for preparative separation of reaction products. ^{1}H and ^{13}C NMR spectra were recorded on Bruker DRX-500 and Bruker AC-200P spectrometers under the standard conditions. Mass spectra were obtained with a Varian MAT-311A instrument (EI, 70 eV). Naphthalene (commercial of the "pure" grade) was used without additional purification. Lead tetraacetate (commercial of the "pure" grade) was washed with glacial AcOH and dried over NaOH *in vacuo*. Commercial purity reagents LiCl, NaCl, KCl, $CaCl_2$, $BaCl_2$, LiBr, NaBr, KBr, and $MgBr_2$ were dried before use.

General procedure of the solid-state halogenation of naphthalene with the $Pb(OAc)_4$—MX_n system. Reaction mixtures (of 1—2 g overall weight) were mechanically activated at ~20 °C using a vibration mill with a frequency of 12 or 19 Hz and an amplitude of 11 mm in a hermetically sealed steel reactor (~80 cm^3 volume) packed with steel balls 12.3 mm in diameter with an overall weight of ~150 g. On mechanical treatment for 3—4 h the reaction mixture (a gray sintered mass) was removed from the reactor and extracted with ether and chloroform. The conversion of the initial naphthalene and the yields and the ratio of products were determined by GLC with the internal standard. The solvent was removed, and the reaction products were isolated from the residue by preparative chromatography. The structures of compounds synthesized were determined by ^{1}H and ^{13}C NMR spectroscopy and GLC/MS spectrometry.

Naphthalene interacts with a $Pb(OAc)_4$—metal chloride system to give a mixture of 1-chloronaphthalene and 1,4-dichloronaphthalene.

1-Chloronaphthalene. MS, *m/z* (I_{rel} (%)): 162 (100) $[M]^+$, 127 (45), 101 (6), 81 (8), 63 (15), 50 (8), 28 (20). ^{1}H NMR ($CDCl_3$), δ: 7.32 (t, 1 H); 7.47 (t, 1 H); 7.50 (t, 1 H); 7.56 (d, 1 H); 7.70 (d, 1 H); 7.78 (d, 1 H); 8.20 (d, 1 H). The ^{13}C NMR spectrum coincides with data in Ref. 7 within the limits of the measurement error.

1,4-Dichloronaphthalene, m.p. 65 °C. MS, *m/z* (I_{rel} (%)): 197 (65) $[M]^+$, 196 (100), 161 (20), 126 (30), 98 (14), 74 (8), 50 (6), 28 (45). ^{1}H NMR ($CDCl_3$), δ: 7.19 (s, 2 H); 7.54 (m, 2 H); 8.19 (dd, 2 H). ^{13}C NMR ($CDCl_3$), δ: 125.00, 125.91, 127.82, 130.93, 131.65.

Naphthalene interacts with a $Pb(OAc)_4$—metal bromide system to give a mixture of 1-bromonaphthalene and 1,4-dibromonaphthalene.

1-Bromonaphthalene. MS, *m/z* (I_{rel} (%)(: 207 (90) $[M]^+$, 206 (95), 127 (97), 101 (10), 63 (25), 32 (22), 28 (100). ^{1}H NMR ($CDCl_3$), δ: 7.31 (t, 1 H); 7.52 (t, 1 H); 7.59 (t, 1 H); 7.78 (d, 1 H); 7.80 (d, 1 H); 7.83 (d, 1 H); 8.24 (d, 1 H). The spin-spin coupling constant of doublets and triplets ^3J = 8.3 Hz. The ^{13}C NMR spectrum coincides with published data.[7]

1,4-Dibromonaphthalene, m.p. 68 °C. MS, *m/z* (I_{rel} (%)): 286 (42) $[M]^+$, 205 (20), 143 (16), 126 (100), 99 (17), 87 (15), 74 (30), 63 (70), 50 (27), 39 (8). ^{1}H NMR ($CDCl_3$), δ: 7.62 (s, 2 H); 7.63 (m, 2 H); 8.24 (m, 2 H). ^{13}C NMR ($CDCl_3$), δ: 122.5 (C(1) and C(4)); 127.7 (C(6) and C(7)); 128.1 (C(5) and C(8)); 130.0 (C(2) and C(3)); 132.9 (C(9) and C(10)).

Halogenation of naphthalene with the $Pb(OAc)_4$—LiX system in benzene. A mixture of naphthalene, $Pb(OAc)_4$, and LiX in 20 mL of benzene was vigorously stirred at 80 °C for 4 h until the oxidant was consumed completely (a color reaction with KI for $Pb(OAc)_4$). The conversion of naphthalene, the yield of products, and their ratio were then determined by GLC (see Table 3).

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