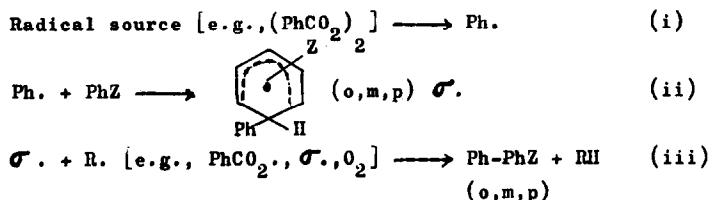VAPOUR-PHASE PHENYLATION OF SOME ARENES

R. Louw and J.W. Rothuizen

Laboratory of Organic Chemistry, The University of Leiden, Netherlands

Thus far, homolytic arylation of arenes has been studied exclusively in the liquid phase. Data on phenylation of substituted benzenes $(PhZ)^{x)}$, obtained under these conditions, show that $f_o \geqslant f_p \geqslant f_m \simeq 1$, irrespective of the polar properties of Z [provided Z is not a very bulky group, e.g. t-butyl](1). Mechanism (i-iii) has been generally accepted, isomer distributions being determined by (ii).

$$\text{Radical source } [e.g., (PhCO_2)_2] \longrightarrow Ph\cdot \qquad (i)$$

$$Ph\cdot + PhZ \longrightarrow \quad (o,m,p) \quad \sigma\cdot \qquad (ii)$$

$$\sigma\cdot + R\cdot [e.g., PhCO_2\cdot, \sigma\cdot, O_2] \longrightarrow Ph\text{-}PhZ + RH \qquad (iii)$$
$$(o,m,p)$$

It was found that with $Z=CH_3$, (ii) is faster than hydrogen abstraction from the side chain to give PhH and $PhCH_2\cdot$ (1,2). However, in the <u>gaseous</u> phase ($>500°C$) Ph. and $PhCH_3$ produce bibenzyl rather than methylbiphenyls, side chain abstraction apparently strongly predominating over nuclear addition(3). On the basis of the latter observation and on photolysis of Ph_2Hg in PhCl vapour, Fielding and Pritchard(4) concluded that radical additions to aromatic nuclei in the gas phase are unimportant.

We wish to communicate some of the first results we obtained on vapour phase reactions of phenyl radicals with $PhZ(Z=Cl,CN)$ leading to biaryls, Ph-PhZ. In Table I data on isomer distributions and relative rates of PhPhCl and PhPhCN formation with various Ph. sources are given, together with results obtained in the liquid phase.

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x) Ph is used interchangeably to denote C_6H_5 and C_6H_4 moieties.

TABLE I

Phenylation of Substituted Benzenes PhZ

|	Temp(^{o}C)	Phase	Radical source[x]	Isomer distribution of Ph-PhZ (%)			Rel.rate,k_{PhH}^{PhZ} calc.[+]	obs.	Analytical method
				o	m	p			
Z= Cl	70	l	BPO(6)	54	31	15	1.08	-	i.r.
	80	l	BPO(7)	50	32	18	1.04	1.06	i.r.
	105	l	BPO	55	30	15	1.11	-	
	420	g	AB+AP[a]	22	52	26	0.64	0.7	
	490	g	AB[a]	24	50	26	0.67	-	g.l.c. (i)
	500	g	PhN$_2$Ph	21	51	28	0.65	0.7	
	490	g	PhH+CCl$_4$ [b]	19	55	26	0.61	-	
Z= CN	80	l	BPO(8)	60	10	30	3.3	3.7	i.r.
	80	l	BPO	52	18	30	1.85	-	
	105	l	BPO	51	18	31	1.85	1.8	
	190	l	BPO	50	22	28	1.51	-	
	190	l	PhSO$_2$Cl	56	19	25	1.75	-	g.l.c.(ii)
	420	g	AB+AP[a]	33	36	31	0.93	0.9	
	490	g	AB[a]	32	36	32	0.95	0.8	
	500	g	PhN$_2$Ph	35	36	29	0.92	0.9	
	490	g	PhH+CCl$_4$ [b]	28	42	30	0.78	-	

x) BPO=dibenzoylperoxide; AB=allyl benzoate; AP=allyl pyruvate

+) according to (1), from the isomer distributions observed, on the basis of $f_m \equiv 1$

i) column: 5% Bentone 34 and 5% SE-30, succesively applied on Embacel (2 m, 180°C)

ii) column: 10% terephtalate-terminated Carbowax 20M on Embacel (4 m, 210°C)

a) Allyl benzoate has been shown (9) te decompose into C_3H_5·, CO_2 and Ph., analogously to benzyl benzoate (3,10). Phenyl radicals can also be generated via radical addition:

R.(e.g. Ph.,CH$_3$·) + CH$_2$=CH-CH$_2$-O-CO-Ph $\longrightarrow$ R-C$_3$H$_5$ + CO$_2$ + Ph.   (iv)
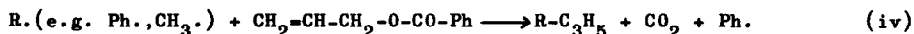
Allyl pyruvate homolysis is much faster than that of the acetate or benzoate (11), giving C_3H_5·,CO_2, CO and CH$_3$·; therefore, it can be employed to effect the decomposition of allyl benzoate at lower temperatures according to (iv).

b) Thermolysis of CCl$_4$ in an excess of ArH, currently under investigation in this laboratory (with Mr. W. Dorrepaal), produces both ArAr (about 1 mole/mole of CCl$_4$ decomposed) and (smaller amounts of) ArCl. It is believed that Cl. from the desintegration of CCl$_4$ gives rise to aryl radicals which in turn react with arene to lead to biaryl and with CCl$_4$ to give ArCl.

Gas phase runs were performed in a flow system as described (5). Products were iden-

tified and analysed by g.l.c., on two different columns, with the aid of pure reference

materials; in addition, Ph-PhZ was isolated by distillation and/or column chromatography

over neutral alumina and characterized by infrared spectrometry.

A representative example of an <u>allyl benzoate</u> run is given in Table II.

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TABLE II

Thermolysis of Allyl Benzoate in PhCl/PhCN at $490^{\circ}C$

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| Conditions	Ester conversion : 35.4% (g.l.c.)
Intake flow rates:	Products : (% on converted benzoate):
ester : 20.1 mmole.h^{-1}	CO_2 : 78
PhCl : 82.2 mmole.h^{-1}	Ph-PhCl : 13.5
PhCN : 56.1 mmole.h^{-1}	Ph-PhCN : 10.8
N_2 :285 mmole.h^{-1}	Ph-PhH : 2-3
av.residence time: 82 s.	

With PhCN as a substrate, biphenyl is less than 4% on PhPhCN. With PhCl, the Ph-Ph/

Ph-PhCl ratio is ~0.10(420°C) and ~0.17(490°C); the amount of ClPh-PhCl is much smaller

than that of biphenyl.

At 500°C, in a large excess of either PhH,PhCl or PhCN, <u>azobenzene</u> decomposes for about

one-half in 120 s, giving rise to approximately one mole of Ph-PhZ per mole of converted

PhN$_2$Ph. Biphenyl/Ph-PhZ ratios are $\simeq 0.05$ for Z=CN and $\simeq 0.15$ for Z=Cl.

These results demonstrate that, under our conditions, phenyl radicals add to benzene

nuclei in preference to dimerization, or to hydrogen abstraction (metathesis) according

to (v):

$$Ph. + Z\ PhH \longrightarrow PhH + Z\ Ph. \qquad (v)$$
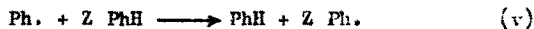
The larger proportion of biphenyl when PhCl is the substrate rather than PhCN is thought
to be due to the contribution of (vi):

$$Ph. + Ph-Cl \longrightarrow \text{[benzene ring structure]} \longrightarrow Ph-Ph + Cl. \qquad (vi)$$
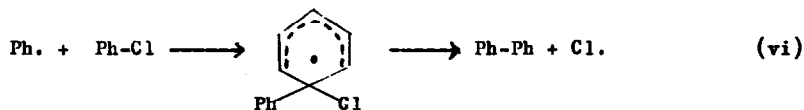
From runs with allyl benzoate it is inferred that the net rate of arylation of PhCl and
PhCN (R_n) is about 0.03 times the rate (R_s) of reaction iv $(R.=Ph.)$. This is in line
with observations on $PHCH_3$ (3), for which side chain abstraction highly predominates at
500^oC, assuming that the rate of addition to C=C double bonds and the rate of
abstraction of α-methylenic hydrogens are of a comparable magnitude, for methyl (12)
as well as phenyl radicals. The large difference between these results $(i.e., R_n/R_s \approx 0.03)$
and the predominating nuclear phenylation of $PhCH_3$ in the liquid Phase $(R_n/R_s \gg 5)(1)$ can
hardly be explained by differences in activation parameters alone, because in general,
temperature coefficients of addition-to-abstraction ratios are quite small, cf.(12,13).
A more satisfactory interpretation, in our opinion, is provided by assuming step(ii)
to be <u>reversible</u>, both under Szwarc's(3) and under our conditions.[*])
The <u>isomer distributions</u> observed in the vapour phase also seem plausible on this basis.
Available data on liquid phase phenylation [e.g. of PhCN, Table I, anisole (19) and
biphenyl (20)] suggest that the ortho-percentage does not decrease with increasing
temperature. In the gas phase at $400-500^oC$, however, again an invariant, but much
lower ortho content is observed.

[*)] On the basis of ΔH_f^o (Ph-Ph)g = 43.5 kcal (14), the heat of addition of H. to a benzene
nucleus (27 kcal)(15), and ΔH_f^o (Ph.)g = 80(16), ΔH_f^o (Ph-PhH.)g $\approx$ 69 and the heat of
addition of Ph. to benzene is about 31 kcal $mole^{-1}$; thus, the thermal stability of
Ph-PhH. is intermediate between that of n-propyl(17) and ethyl(18), eliminating CH_3.
and H., respectively. It should also be noted, that the acceptance of the "new"(16)
value for ΔH_f^o (Ph.)g implies that dissociation of Ph-PhH. into biaryl and H. may
well compete with the proposed reversibility in step (ii).

Neglecting possible small differences in relative rates of (iii) for o,m, and p-σ.,
this may be caused by thermodynamic factors operative in (ii,-ii) e.g. through steric
hindrance in o-σ.. In this connection it is relevant that the thermodynamic equilibrium
of Ph-PhCl has been found to be o/m/p = 3/64/33 at 160°C(21); some of the structural
factors responsible for this ratio may also be operative in o,m,p-σ. (Z=Cl, eq.ii)
and thus lead to an o/m/p-equilibrium ratio for these adduct radicals resembling the
isomeric composition observed for Ph-PhCl in the gas-phase phenylation of PhCl.

Isomer distributions and relative rates obtained with PhH+I_4(Table I) as well
as with PhH+Cl_2(22) as sources of aryl radicals are difficult to interpret due to the
fact that Ph-PhZ may arise from the reaction of Ph. with PhZ an from a ZPh. + PhH
interaction. A detailed study of these and analogous systems, also incorporating the
reactions of independently generated ZPh. fragments,—currently under investigation in
this laboratory—is expected to lead to more quantitative information on the mechanisms
involved in aromatic substitutions in the vapour phase.

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