Aryl Radical Formation during the Thermal Decomposition of Aryldiazo Alkyl Ethers

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Summary Measurements of the isomer ratios of the biaryl products and studies using CIDNP and e.s.r. spin trapping techniques indicate the presence of aryl radicals as intermediates during the thermolysis of aryldiazo alkyl ethers in aromatic solvents.

ARYLDIAZO ALKYL ETHERS (**1**) have been known[1] for more than 80 years to yield biaryls on heating in aromatic solvents, and more recently they have also been invoked[2] as intermediates in other arylation reactions, particularly those involving the *in situ* diazotisation of anilines by alkyl nitrites. While a homolytic pathway has been proposed[3] for the decomposition of (**1**) in alcoholic solvents, the free radical nature of the corresponding reaction in aromatic media has yet to be firmly established. We have reinvestigated this reaction and now present evidence, based on the isomer ratios of the biaryl products and on the results of studies using CIDNP and e.s.r. spin trapping techniques, which clearly demonstrates the participation of aryl radicals as intermediates.

The early reports[1] of biaryl formation were confirmed by heating under reflux solutions of (**1a**—**c**) in benzene (*ca.* 0·12 M) in a nitrogen atmosphere, the respective products formed being biphenyl (22%) and 4-nitrobiphenyl (75 and 55%). In the case of 4-nitrophenyldiazo pentyl ether (**1c**) the yields of the co-products, pentanol (60%) and nitrogen (54%) were also determined.

$$\underset{(\mathbf{1})}{\mathrm{Ar^1{-}N{=}N{-}O{-}R}} \xrightarrow{\mathrm{Ar^2H}} \mathrm{Ar^1\,Ar^2 + N_2 + ROH}$$

a; $\mathrm{Ar^1 = Ph,\ R = Me}$
b; $\mathrm{Ar^1 = 4\text{-}O_2NC_6H_4,\ R = Me}$
c; $\mathrm{Ar^1 = 4\text{-}O_2NC_6H_4,\ R = [CH_2]_4Me}$

Convincing evidence for the intermediate role of aryl radicals in the product forming sequence was provided by analysis of the mixture of biaryls produced from (**1a**) and (**1b**) in t-butylbenzene, anisole, and nitrobenzene. The results, listed in the Table, show that the *ortho*:*meta*:*para* ratios obtained were similar to those found for the authentic aryl radical sources dibenzoyl peroxide[4] and aniline–pentyl nitrite[5] and comparable to the values reported in the literature.[6–8]

$\mathrm{Bu^tNO}$ (**2**)

$\mathrm{PhCH{=}\overset{+}{N}(Bu^t)O^-}$ (**3**)

$\mathrm{Bu^tN(Ar)O\cdot}$ (**4**)

$\mathrm{PhCH(Ar)N(Bu^t)O\cdot}$ (**5**)

TABLE. Composition of the biaryl products for aromatic arylation using aryldiazo alkyl ethers and authentic aryl radical sources.

Radical	Source	Solvent	Biaryl product[a] % *ortho*	% *meta*	% *para*
Ph	PhN:NOMe	$PhBu^t$	22	52	25
Ph	$(PhCO_2)_2$[b]	$PhBu^t$	24	49	27
Ph	PhN:NOMe	$PhNO_2$	56	14	30
Ph	$(PhCO_2)_2$	$PhNO_2$	55	15	30
Ph	$(PhCO_2)_2$[c]	$PhNO_2$	56	16	28
Ph	PhN:NOMe	PhOMe	66	16	18
Ph	$(PhCO_2)_2$	PhOMe	66	15	19
Ph	$(PhCO_2)_2$[d]	PhOMe	70	14	16
$4\text{-}O_2NC_6H_4$	$4\text{-}O_2NC_6H_4N{:}NOMe$	$PhBu^t$	18	48	34
$4\text{-}O_2NC_6H_4$	$\left\{\begin{matrix}4\text{-}O_2NC_6H_4NH_2\\ C_5H_{11}ONO\end{matrix}\right\}$	$PhBu^t$	17	47	36

[a] Proportions (±1%) determined by g.l.c. [b] Ref. 6. [c] Ref. 7. [d] Ref. 8.

A complementary demonstration of the presence of aryl radicals was obtained from an e.s.r. examination of the decomposition in the presence of the spin traps (**2**) and (**3**), both of which are known[9] to scavenge aryl radicals to yield the long-lived nitroxyls (**4**) and (**5**). Thus (**1a**) and (**2**) in *m*-dichlorobenzene (1·18 M and 0·007 M) at ambient temperature gave a persistent e.s.r. signal with spectral parameters [a_N 1·270, a_H 0·185 (3H) and 0·088 (2H) mT and g 2·0060], indicating coupling of the unpaired electron to the nitrogen of a nitroxyl group and the five protons of a phenyl ring, the values being close to those reported[9] for (**4**) (Ar = Ph). In this way the identity of the trapped radical is firmly established. Likewise the corresponding spectrum from (**1b**) [a_N 1·048, 0·060, a_H 0·217 (2H) and 0·090 (2H) mT and g 2·0062] was similar to that recorded for (**4**) (Ar = $4\text{-}O_2NC_6H_4$) generated from 4-nitroaniline and pentyl nitrite.

The use of (**3**) as spin trap does not permit such definitive identification of the trapped radical,[10] its presence in the adduct (**5**) rarely leading to distinctive hyperfine structure and its influence usually being confined to small but characteristic changes in the α-proton splitting. However, the spectra obtained from (**1a**) (a_N 1·448, a_H 0·246 mT and g 2·0059) and (**1b**) (a_N 1·439, a_H 0·226 mT and g 2·0060) are, within experimental error, the same as those found for (**5**) produced from the appropriate aniline and pentyl nitrite, and thus provide supporting evidence for the presence of aryl radicals.

Further verification of a free radical pathway was achieved by following the reaction by ^1H n.m.r. spectroscopy. Thus when a solution of (**1a**) in dioxan (0·46 M) was heated at 80 °C emission signals were observed for the protons of the benzene produced by hydrogen abstraction from the solvent. The appearance of such CIDNP effects[11] proved the occurrence of at least one radical pair intermediate in the formation of the decomposition products. Although the identity of this radical pair remains uncertain, the application of Kaptein's rules and comparison with the analogues decomposition of aryldiazo alkyl sulphides[12] suggest pairs $\overline{ArN_2\cdot\cdot OR}$ and $\overline{Ar\cdot\cdot OR}$ as likely candidates. Alternatively, if in common with closely related dediazoniation processes[13,14] the reaction proceeds *via* a diazoanhydride ArN_2ON_2Ar, then pairs $\overline{ArN_2\cdot\cdot ON_2Ar}$ and $\overline{Ar\cdot\cdot ON_2Ar}$ may also be invoked.[14] In either case phenyl radicals escaping into the bulk solution are transformed into benzene with negative polarisation, in agreement with the observed emission signals. Likewise, CIDNP effects were also detected for a solution of (**1a**) in C_6D_6 at 100 °C, although in this case the observed emission signals have not been fully interpreted.

These polarisation effects, taken together with the e.s.r. and biaryl product isomer ratio evidence strongly support the hypothesis that aryl radicals are produced in the reaction. The thermolysis of aryldiazo alkyl ethers thus provides an effective method for the generation of aryl radicals at moderate temperatures.

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