# Vapour Phase Chemistry of Arenes. Part 6.† Arylation and Transcyanation in the Pyrolysis of Benzonitrile

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Pyrolysis of benzonitrile (1) above 650 °C leads not only to biphenyldicarbonitriles (2) but also to similar proportions of biphenylmonocarbonitriles (3) and benzenedicarbonitriles (4). With added free radical sources such as formaldehyde or hexachloroethane the process can be made to occur below 500 °C. A homolytic mechanism is advanced involving aryl radicals and hydrogen atoms as intermediates. Isomer distributions of the products (2)—(4) are in full accord with this interpretation. The ' mobility ' of cyano-groups is explained in terms of a transcyanation route ($Ar\cdot + Ar'CN \longrightarrow ArCN + Ar'\cdot$) competing with arylation (biaryl formation). Differences between the pyrolysis of benzonitrile (1) and that of chlorobenzene [lower rate and/or shorter chain length for (1)] are due to the greater stability of adduct radicals, such as $\cdot C_6H_6CN$ from (1) and $H\cdot$, in comparison with $\cdot C_6H_7$ from benzene and $H\cdot$.

UPON pyrolysis at ⩾500 °C, benzene forms biphenyl[1] and chlorobenzene gives dichlorobiphenyls.[2] These processes were rationalized as free-radical chain reactions involving aryl radicals, proceeding *via* homolytic arylation.[1,2]

Little is known in this respect of the behaviour of other (mono)substituted benzene derivatives which, by analogy, could lead to (di)substituted biaryls. We have now studied the pyrolysis of benzonitrile (1). The biaryls (2), the expected products, are of synthetic utility, as these dinitriles can be converted into macromolecular substances such as polyamides,[3] *s*-triazines,[4] and other materials of high thermal stability.[5]

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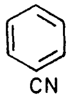
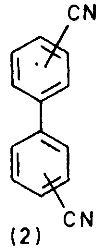
## RESULTS

(a) *Pyrolysis of Benzonitrile* (1).—Benzonitrile is markedly more stable than benzene or chlorobenzene; at *ca.* 500 °C, and with residence times of 1—2 min, negligible amounts of biaryls were formed ($<0.005\%$). Measurable degrees of conversion were observed only at temperatures above *ca.* 625 °C (Table 1). The reaction not only gives the dicyanobiphenyls (2) but also considerable proportions of monocyanobiphenyls (3) and dicyanobenzenes (4); despite the very high C–CN bond dissociation energy in benzonitrile of 126 kcal mol$^{-1}$,[6] the CN group appears to be 'mobile.' Work-up showed that little higher-boiling material is formed below *ca.* 800 °C.



(1)



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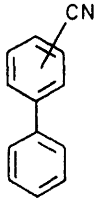

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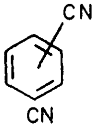

(4)

(b) *Effect of Additives*.—As with (chloro)benzene, the pyrolysis of benzonitrile could be made to occur at lower temperatures (400—500 °C) by using small proportions of free-radical forming agents, such as formaldehyde or hexachloroethane.

Table 1

Pyrolysis of benzonitrile

| $t$/°C | Av. res. time (s) | Product molar ratio (2) : (3) : (4) : $(C_6H_5)_2$ | Conversion of (1) into [(2) + (3) + (4)] (mole %) † |
|---|---|---|---|
| 628 | 25 | | (0.4) |
| 680 | 25 | 1 : 2.0 : 0.9 : 0.1 | 2.2 |
| 732 | 25 | 1 : 1.8 : 1.0 : — | 3.7 |
| 772 | 23 | 1 : 1.9 : 0.9 : 0.3 | 9.2 |
| 772 | 41 | 1 : 2.3 : 1.1 : 0.2 | 14 |
| 782 | 0.2 ‡ | | (0.1) |
| 870 § | 0.2 ‡ | 1 : 4 : 2.5 : 0.6 | (0.5) |
| 948 § | 0.2 ‡ | 1 : 3 : 2.7 : 0.6 | 6.0 |

† Benzene and hydrogen cyanide were also formed but not determined quantitatively. ‡ Flash vacuum pyrolysis at *ca.* 3 mmHg rather than at atmospheric pressure. § Tar and soot are also formed.

(i) Formaldehyde, introduced as *s*-trioxan,[2] decomposes to give hydrogen atoms.[2,7] By use of a few mol percent of trioxan, fair degrees of conversion into benzene and compounds (2)—(4) were obtained and traces of biphenyl were found (see Figure 1). Hydrogen cyanide was also observed, but not analysed quantitatively. In comparison with benzene–formaldehyde systems,[1] both the (maximum) effect obtained (in terms of moles of biaryl produced per mole of formaldehyde converted) and the scavenging effect of larger proportions of formaldehyde are much less pronounced. The ratio of products (3) : (2) tends to increase with increasing formaldehyde : benzonitrile intake ratios (see also Table 2); with 24% of formaldehyde this ratio is $>10:1$.

(ii) Hexachloroethane, decomposing thermally into tetrachloroethylene and chlorine *via* a free-radical chain process,[8,*] also accelerates the conversion of benzonitrile into biaryls. In comparison with formaldehyde-catalysed conversions, dicyanobiphenyls (2) are formed in larger proportions. Chlorinated biaryls were produced in trace amounts only.

(iii) Allyl benzoate is known to decompose above *ca.* 450 °C giving phenyl radicals;[10] in a large excess of benzene, the selectivity in formation of biphenyl is *ca.* 30%.[11] With benzonitrile, monocyanobiphenyl is the main product, the more so with increasing proportions of allyl benzoate (see Table 2).

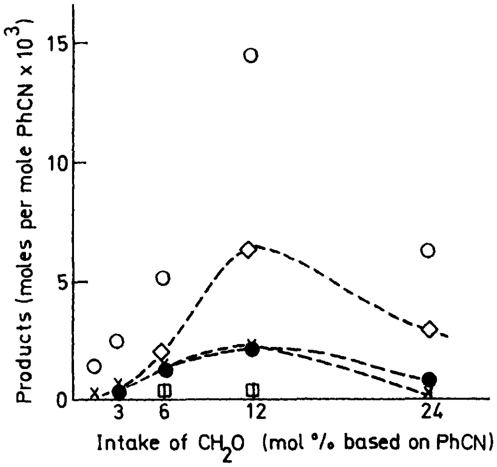

FIGURE 1 Pyrolysis of benzonitrile: effect of added formaldehyde (480 °C; residence time 90 s); (○) benzene, (×) dicyanobiphenyl, (◇) monocyanobiphenyl, (●) dicyanobenzene, (□) biphenyl

(c) *Reactions involving Mixtures of Benzonitrile and Hexadeuteriobenzene*.—With hexachloroethane (2% based on arene) as initiating agent, runs were performed with benzonitrile–benzene mixtures (up to 20 mole % of benzene) at *ca.* 490 °C. Relative amounts of monocyanobiphenyls (3) and biphenyl increased with increasing benzene–benzonitrile ratios (Table 3). Replacement of benzene by hexadeuteriobenzene revealed that H–D exchange is an important competitive reaction (*cf.* benzene pyrolysis).[1] Moreover, about one-half of the monocyanobiphenyl is formed from phenyl groups derived from benzonitrile (see Figure 2). Analogously, biphenyl appears to arise *via* phenylation of hexadeuteriobenzene with [$^2H_5$]- and [$^2H_0$]-phenyl radicals derived from hexadeuteriobenzene and benzonitrile, again in roughly equal amounts. Table 3 also

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[*] In our system, chlorine (atoms) are expected to abstract hydrogen from benzonitrile; *cf.* gas phase chlorination.[9] Maximal amounts of 2 mol of hydrogen chloride per mol of hexachloroethane converted can be expected. In the following series (2.5 mole % of hexachloroethane; average residence time 90 s) the following yields of hydrogen chloride based on hexachloroethane were observed: 430 °C, 30%; 455 °C, 80%; 500 °C, 150%. Table 2 shows that hexachloroethane conversions were *ca.* 65% at 480 °C. This supports the stoicheiometry of 2 mol of hydrogen chloride per mole of hexachloroethane converted.

[6] T. Fueno, K. Tabayashi, and O. Kajimoto, *J. Phys. Chem.*, 1973, **77**, 575.

[7] C. J. Chen and D. J. McKenney, *Canad. J. Chem.*, 1972, **50**, 992.

[8] M. L. White and R. R. Kuntz, *Internat. J. Chem. Kinetics*, 1973, **5**, 187.

[9] W. Dorrepaal and R. Louw, *Internat. J. Chem. Kinetics*, in the press.

[10] R. Louw and E. C. Kooyman, *Rec. Trav. chim.*, 1967, **86**, 147.

[11] R. Louw and J. W. Rothuizen, *Tetrahedron Letters*, 1967, 3807.

reveals a primary H–D isotope effect. Biphenyl : monocyanobiphenyl (3) and monocyanobiphenyl (3) : dicyanobiphenyl (2) ratios show that the production of $C_6H_5$-aryl is faster than that of $C_6D_5$-aryl by a factor of *ca.* 1.8.

(d) *Isomer Distributions.*—The isomer pattern for monocyanobiphenyls (3) obtained from induced pyrolysis of benzonitrile is similar to that for phenylation of benzonitrile with allyl benzoate as a source of phenyl radicals (Table 4). The dicyanobenzene (4) isomer distribution, markedly different from that of (3), is surprisingly close to that for vapour-phase chlorination of benzonitrile.[9]

TABLE 2

Benzonitrile pyrolysis; effect of additives on product composition

| Conditions (temp.) | | Molar ratio (2) : (3) : (4) | (2) (mole % based on converted additive) |
|---|---|---|---|
| Neat (700 ± 70 °C) | | 1 : 2 : 1 | |
| Formaldehyde: | 6% | 1 : 1.1 : 1 | *a* |
| (480 °C) | 12% | 1 : 2.6 : 1 | *a* |
| Hexachloroethane:[b] | 1% | 1 : 0.4 : 0.3 | 178 |
| (480 °C) | 2% | 1 : 0.3 : 0.3 | 136 |
| | 4% | 1 : 0.2 : 0.3 | 77 |
| Allyl benzoate:[c] | 1% | 1 : 3.1 : trace | 8 |
| (480 °C) | 2% | 1 : 3.8 : trace | 9 |
| | 4% | 1 : 5.0 : trace | 5 |

[a] Not determined. [b] Conversion 60—65%. [c] Conversion 35—40%.

## DISCUSSION

Our results provide convincing evidence for the free-radical nature of the thermolytic reactions of benzonitrile, and can be rationalized in terms of the homolytic mechanism given in the Scheme. The mode of initiation in neat pyrolysis is not known, but a bimolecular process, $2ArH \longrightarrow Ar\cdot + ArH_2\cdot$, may be important.[1] In enhanced pyrolysis, the initiating agent produces reactive free radicals, R· (such as H· or Cl·), capable of interacting with benzonitrile in several ways. Hydrogen abstraction (i) leads to cyanophenyl radicals, which give dicyanobiphenyls (2) *via* homolytic arylation (ii). Note that the addition step is reversible under the present conditions.[11] The overall reaction (ii), unlike the situation in liquid-phase arylation,[12] should then be associated with a kinetic H–D isotope effect, as is actually found [see section (c)]. Alternatively, $\cdot C_6H_4CN$ may add to the CN group of (1) [reaction (iii)] to give an intermediate iminyl radical,[13] which may revert or lead to the transcyanation product (4) and $\cdot C_6H_5$. Hence, the mobility of CN is not associated with direct Ar–CN bond breaking, *i.e.* there is no free ·CN involved.

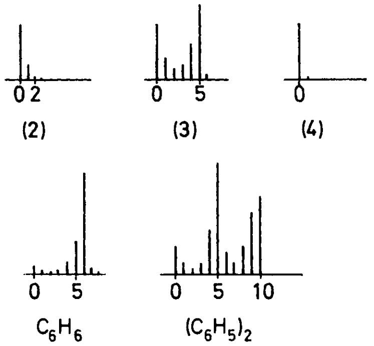

FIGURE 2 Deuterium distributions for products from the benzonitrile–hexadeuteriobenzene co-pyrolysis

Phenyl radicals, in turn, will produce (3) [reaction (iv)], transcyanation with (1) being an identity reaction. Hydrogen atoms add reversibly to (1) [equation (v)]. This process explains the (relatively rapid) H–D exchange[1] [section (c)]. Reactions (vi) (H abstraction) and (vii), transcyanation to give HCN, are straightforward.

TABLE 3

Arylation products from benzene–benzonitrile mixtures at 490 °C (res. time 90 s, 2% mole of $C_2Cl_6$ as initiator)

| Benzene (mole %) | Product molar ratio (2) : (3) : (4) : $(C_6H_5)_2$ | (2) (mole % based on $C_2Cl_6$ † converted) |
|---|---|---|
| 0 | 1 : 0.3 : 0.3 : (0.02) | 94 |
| 5 | 1 : 0.7 : 0.3 : 0.06 | 80 |
| 10 | 1 : 1.3 : 0.5 : 0.2 | 54 |
| 20 | 1 : 2.1 : 0.6 : $0.4_5$ | 58 |
| 15 * | 1 : 1.0 : 0.3 : $0.1_0$ | 110 |

* Hexadeuteriobenzene. † $C_2Cl_6$ conversion 70 ± 5%.

The main differences between chlorobenzene pyrolysis and that of benzonitrile are the low rate and the shorter (or even non-) chain character of the latter reaction. This is rationalized by considering equilibrium (v) and comparing it with the analogous situation for benzene, where $\Delta H$ is *ca.* 29 kcal $mol^{-1}$, and $\Delta S^\circ \approx -22$ cal $mol^{-1}$ $K^{-1}$.[14] This leads to $\log[C_6H_7\cdot]/[H\cdot] = 2$—3 at 500 °C.[1] Thus, there are few free hydrogen atoms in equilibria involving arene vapours. In comparison with $C_6H_7\cdot$ (and with $ClC_6H_6\cdot$), the adduct of H· and benzonitrile [reaction (v)] constitutes a CN-stabilized cyclohexadienyl radical. Note that the stabilization energy of $\cdot CH_2CN$ is *ca.* 6 kcal $mol^{-1}$.[15] Such a difference in heat of addition implies a 50-fold increase in $K_v$ compared with $K$ for the analogous reaction $H\cdot + C_6H_6 \rightleftarrows C_6H_7\cdot$. Hence the concentration of H· is much lower in gaseous benzonitrile than in benzene. This lowers the rate of the

TABLE 4

Isomer distributions for vapour-phase substitutions of benzonitrile at *ca.* 500 °C

| | Product | *o-* : *m-* : *p-* (%) |
|---|---|---|
| Pyrolysis | (3) | 28 : 38 : 34 |
| Phenylation [11] | (3) | 32 : 36 : 32 |
| Pyrolysis | (4) | 19 : 52 : 29 |
| Chlorination [9] | $ClC_6H_4CN$ | 18 : 52 : 30 |

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[12] M. J. Perkins, in ' Free Radicals,' vol. II, ed. J. K. Kochi, Wiley, New York, 1973, p. 231.

[13] D. D. Tanner and N. J. Bunce, *J. Amer. Chem. Soc.*, 1969, **91**, 3028.

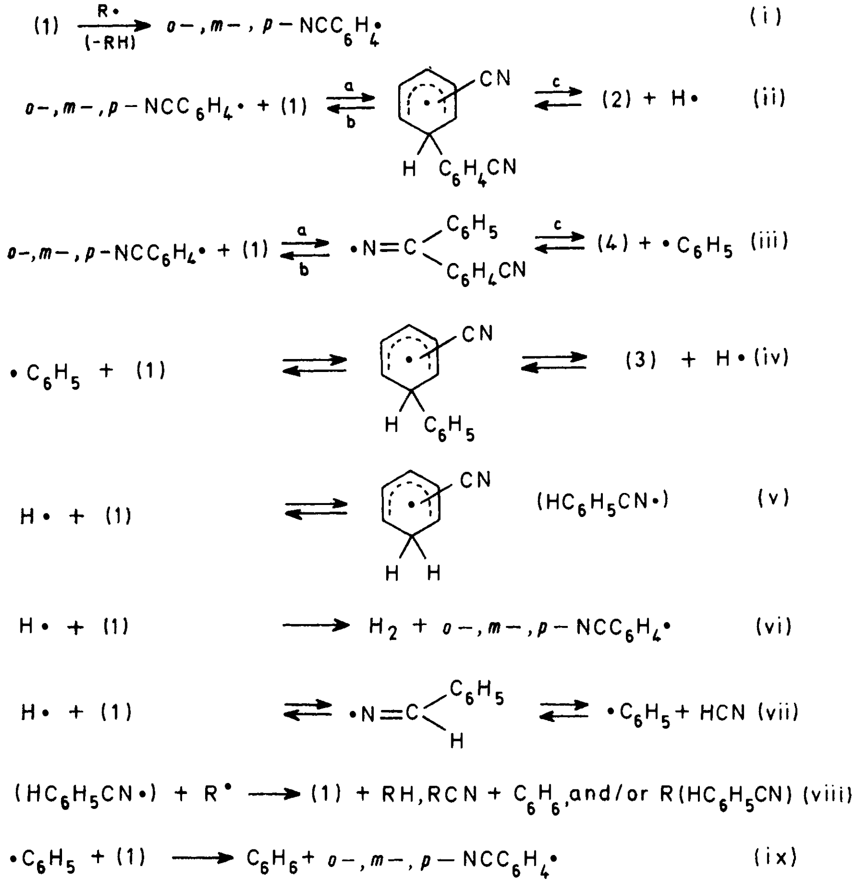
[14] S. W. Benson, ' Thermochemical Kinetics,' Wiley, New York, 1968.

[15] K. D. King and R. D. Goddard, *Internat. J. Chem. Kinetics*, 1975, **7**, 109.

propagation step (vi). Of course, analogous situations hold for equilibria of addition of aryl radicals to benzonitrile.

Adduct radicals such as $HC_6H_5CN\cdot$ [see reactions (v)] and $ArC_6H_5CN\cdot$ [reaction (ii)] will be important in terminations, generalized in reaction (viii). Products therefrom may contribute significantly to the overall reaction. Ratios of products (2) : (3) : (4) are thus expected to vary with experimental conditions, especially the type and amount of ' initiating ' agent (Table 2).

In the system with added allylbenzoate, introducing $\cdot C_6H_5$ radicals (and a scavenging agent), only trace amounts of (4) were observed. Apparently little or no $\cdot C_6H_4CN$ is formed, demonstrating that metathesis [reaction (ix)] is slow in comparison with reactions (ii)—(iv).



SCHEME

Product ratios indicate that reactions (ii) and (iii) proceed with similar overall rates. As (ii) involves a pre-equilibrium, ($k_{\text{iib}} > k_{\text{iic}}$) whereas in (iii) $k_{\text{iiib}} \approx k_{\text{iiic}}$, it is likely that $k_{\text{iia}}$ is at least ten times larger than $k_{\text{iiia}}$. This is in line with the normal character of the (kinetically controlled) liquid-phase arylation giving cyanobiaryls.

The similarity of isomer patterns for monocyanobiphenyls (3) obtained from pyrolysis and by phenylation [see section (d) and Table 4] is in line with the homolytic mechanism, the product determining step(s) in both cases being given by reaction (iv).

That chlorination and pyrolysis of benzonitrile lead to the same isomer distribution for chlorobenzonitriles and dicyanobenzenes (4), respectively, can be explained as follows. Hydrogen abstraction from benzonitrile by $Cl\cdot$ is markedly endothermal,[9] and is therefore associated with a ' late ' (aryl-radical like) transition state. The isomer distribution for $\cdot C_6H_4CN$ is therefore governed by differences in thermodynamic stabilities of the isomers; in other words, by differences in C–H bond strengths in benzonitrile.[9] As aryl radicals subsequently form chlorobenzonitriles by reaction with $Cl_2$, this pattern is transferred to the final product. Reaction (vi) is of equal endothermicity to abstraction by $Cl\cdot$. The nature of the abstracting species then is of minor importance. By way of reaction (iii) a corresponding isomer distribution for dicyanobenzenes (4) is expected.

The isomer pattern reported for dicyanobiphenyls (2) [see section (d)] may be compared with a calculated value, based on the assumption that (2) arises *via* arylation of benzonitrile [reaction (ii)] with the same rate constant for each $\cdot C_6H_4CN$ radical. Multiplication of the radical pattern (19 : 52 : 29; Table 3) by the substitution pattern for $\cdot C_6H_5$ + (1) (*ca.* 30 : 37 : 33; Table 3, first two entries) leads to a computed ratio of

5.7 : 37.6 : 56.6. The agreement with experiment (5 : 39 : 56) leaves little doubt that (2) is also produced by homolytic arylation. There is no need, therefore, to assume the operation of molecular processes, such as Diels–Alder type additions.[16]

## EXPERIMENTAL

Runs at *ca.* 500 °C were performed in our Pyrex flow reactor system[1] operating at atmospheric pressure with nitrogen as carrier gas. Benzonitrile pyrolysis at $\geqslant 650$ °C was performed in a quartz flow reactor (50 ml); residence times were *ca.* 20 s.

Analyses were performed by g.l.c. [2 m column of XE 5% on Chromosorb bW-AW (80—100 mesh); 90—240 °C] or by mass spectrometry (A.E.I. MS902 instrument).

The six isomeric dicyanobiphenyls (2) were identified, three at a time, through thermolysis of the allyl esters of the isomeric cyanobenzoic acids in an excess of benzonitrile at *ca.* 490 °C. The corresponding cyanophenyl radicals were thus generated to the exclusion of other isomers.[2] Mass spectral analysis of (deuteriated) materials from the benzonitrile–hexadeuteriobenzene experiments were performed at an ionizing voltage of 6 eV; the biphenyl fraction was collected by preparative g.l.c. after distilling off the major part of benzene and benzonitrile. High-grade benzonitrile was redistilled, its purity being checked before use. Hexachloroethane (Fluka) and *s*-trioxan (Fluka) were recrystallized, resulting in pure compounds (g.l.c.). Individual isomer of (3) and (4), *pp'*-bibenzonitrile, and the allyl esters of *o*-, *m*-, and *p*-cyanobenzoic acid were prepared by standard routes. Hexadeuteriobenzene (Merck Uvasol; min. 99% D) was used as such.

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[16] R. A. Firestone and J. S. Amato, *Tetrahedron*, 1970, 5195.