Transposition of the Cyano Group on a Benzene Ring in a Gaseous Plasma

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Transposition of the cyano group in dicyanobenzene in a radiofrequency plasma occurred predominantly *via* the prismane-type structure.

The non-equilibrium plasma generated by a glow discharge provides a unique medium for chemical reactions, and a number of intriguing organic reactions brought about in this way have been exploited.[1] These reactions are initiated by electron impact, which may bring about ionization or excitation.

In this paper, we describe the intramolecular transposition of the cyano group on a benzene ring. There have been few reports of the transposition of substituents in plasmolyses of substituted aromatic compounds; elimination or α-fission of the substituents themselves has usually prevailed. We chose dicyanobenzene as reactant, since the cyano group is exceptionally stable under these conditions.

The inductively coupled 13.56 MHz plasma apparatus used and the procedure are similar to those reported,[2] except that the reactor was set up in a thermostatic chamber to promote the vaporization of less volatile dicyanobenzenes and to prevent the starting materials from condensing on the reactor wall. The glow discharge was generated in a 40 × 4.5 cm (internal diam.) Pyrex reactor tube wound with five turns of copper coil. The starting dicyanobenzene was distilled through the plasma zone at a pressure of 1—100 Pa. The flow rate was determined by weighing the reactant reservoir before and after the run and measuring the elapsed time. The pressure varied with the flow rate. Products and unchanged starting material were collected in a cold trap at liquid nitrogen temperature and analysed by g.l.c. For separation of the three dicyanobenzene isomers, KG-02 was used as stationary phase. The products were identified by comparison with authentic samples; identification was confirmed by g.l.c.–mass spectrometry.

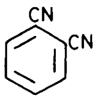
Table 1 summarizes typical results from the plasmolyses of the three isomeric dicyanobenzenes (**1**)—(**3**). In each case, transposition of the cyano group predominated and cyanobenzene (**4**) was obtained as a by-product. Small amounts of benzene and tricyanobenzenes were also found. Polymeric products were deposited on the reactor wall, but these were not quantified. On the whole, the yields of cyano transposition products were greatest at low conversions. However, the proportion of cyano transposition was substantially unchanged.

Two possible pathways for migration of the cyano group on benzene were considered. One was an intermolecular scheme involving the cyano radical. However, this seems unlikely, because a radical site in substituted phenyl radicals does not migrate;[3] consequently, recombination between phenyl and cyano radicals would lead only to starting material. Addition of a cyano radical to (**4**) is also improbable, because the product isomer ratio in the present study is distinctly different from that found in the reaction of (**4**) with the cyano radical generated from $(CN)_2$ in the plasma.[4] The other possible mechanism involves intramolecular transposition of the cyano group via a valence isomer resulting from rearrangement of the skeletal carbon atoms. It is well known that benzene has four typical valence isomers: benzvalene (**5**), fulvene (**6**), Dewar benzene (**7**), and prismane (**8**). Of these, only (**5**) and (**8**) could be involved in the present reaction. However, in view of the data in Table 1, an intermediary of type (**5**) can be ruled out; otherwise, (**1**) should not isomerize to (**3**), nor (**3**) to (**1**). In fact, production of (**3**) from (**1**) was significant, and *vice versa.* Consequently, we propose an intramolecular mechanism *via* an intermediary of type (**8**), as illustrated in Scheme 1. There, the prismane structure (**1a**) may be formed in two ways from the reactant. The intermediate (**1a**) may then give the benzene structure in three ways, two of them affording the starting compound (**1**), but the other leading to an isomeric product (**2**). Likewise, (**1b**) may give (**1**) and (**3**). Thus, one

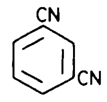
Table 1. Plasmolysis of dicyanobenzenes.

Conditions[a]	Conv.[b] (%)	Yields (%)[c] (1)	(2)	(3)	(4)
(1)					
A	66.4		10.4	4.5	1.6
B	33.6		19.7	7.9	1.7
C	14.8		25.5	10.0	2.7
(2)					
A	60.3	12.2		12.5	1.8
B	33.3	18.3		18.3	2.7
C	17.9	18.2		19.3	2.2
(3)					
A	73.9	6.1	14.5		1.2
B	38.2	12.0	25.5		2.3
C	13.0	18.2	41.7		3.2

[a] Plasma conditions: A, r.f. power (P) = 30 W, flow rate of reactant (r) = 0.35 ± 0.03 mmol min^{-1}; B, P = 30 W, r = 1.00 ± 0.01 mmol min^{-1}; C, P = 10 W, r = 0.91 ± 0.03 mmol min^{-1}. Each run continued for 10 min. [b] Conversion of reactant. [c] Yields based on moles of reactant converted.

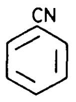


(**1**)

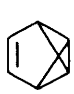


(**2**)

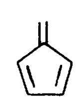
(**3**)



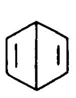
(**4**)



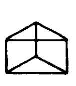
(**5**)



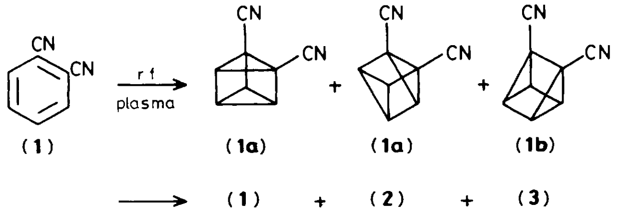
(**6**)



(**7**)



(**8**)



Scheme 1

Table 2. Estimated isomer ratios from dicyanobenzenes.[a]

	Products[b]		
Reactant	**(1)**	**(2)**	**(3)**
(1)	6	2	1
	[—]	[2.4]	[1.0]
(2)	2	5	2
	[2.3]	[—]	[2.4]
(3)	2	4	3
	[1.6]	[3.6]	[—]

[a] Transposition *via* the prismane structure assumed. [b] Values in square brackets show the averaged ratios of product moles [(conversion) × (yield) × (flow rate of reactant) × (reaction time)] obtained under the same conditions as Table 1.

can statistically derive the ratios of isomeric products from dicyanobenzenes on the basis of the assumption that the effects of cyano groups on the valence isomerization are not crucial. As seen in Table 2, the estimated ratios are in fair agreement with the experimental values in (square) brackets. This strongly suggests that dicyanoprismanes are the intermediates in the migration of the cyano group on a benzene nucleus.

It is well known the prismane (**8**) is produced in the gas-phase photolysis of benzene, where the excited singlet state ($^1B_{1u}$) is considered to be a precursor,[5] but the quantum yield is extremely low. From this point of view, it is especially interesting that dicyanoprismanes can be formed so effectively in the present reactions. It appears that excitation through collision with energetic electrons in the plasma is much more effective than through irradiation.

Further study is in progress to clarify the overall mechanism of transposition of substituents and to develop related synthetic reactions.

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References

1 H. Suhr, *Plasma Chem. Plasma Process.*, 1983, **3**, 1; L. L. Miller, *Acc. Chem. Res.*, 1983, **16**, 194.
2 M. Tezuka and L. L. Miller, *J. Am. Chem. Soc.*, 1978, **100**, 4201.
3 J. K. Kochi, 'Free Radicals,' vol. II, Wiley, New York, 1973, p. 126; J. F. Bunnett and C. C. Wamser, *J. Am. Chem. Soc.*, 1966, **88**, 5534; D. L. Brydon and J. I. G. Cadogan, *J. Chem. Soc. C*, 1968, 819.
4 Y. H. So and L. L. Miller, *J. Am. Chem. Soc.*, 1981, **103**, 4204.
5 J. A. Bartlop and J. D. Coyle, 'Excited States in Organic Chemistry,' Wiley, New York, 1975.