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Benzyne Formation and the Stepwise Decomposition of Benzenediazonium-2-carboxylate: A Re-Investigation

P. Christopher Buxton, Mark Fensome, Harry Heaney,* and Kenneth G. Mason

Department of Chemistry, The University of Technology, Loughborough, Leicestershire LE11 3TU

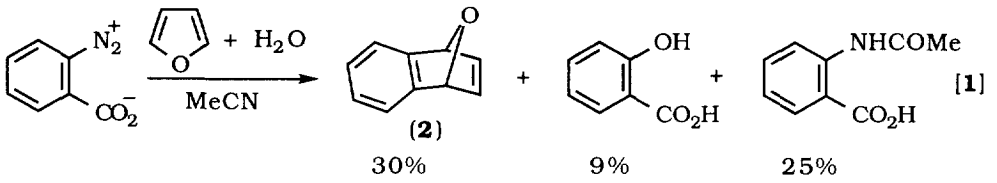
Abstract: *A study of the decomposition reactions of benzenediazonium-2-carboxylate, carried out in a number of mixed nucleophilic solvents, shows that a number of mechanistic pathways can operate simultaneously and can afford, in addition to products derived from benzyne, products derived from the 2-carboxyphenyl cation and the 2-carboxyphenyl radical: benzyne formation is favoured in halogenated solvents and occurs by the concerted loss of nitrogen and carbon dioxide.*

Introduction

The diazotisation of anthranilic acid and its derivatives is a frequently used method for the generation of benzyne and substituted benzynes after the loss of nitrogen and carbon dioxide from the neutral diazonium salt.[1] Benzenediazonium-2-carboxylate may be generated *in situ* from anthranilic acid by diazotisation in an aprotic medium,[2] or by the removal of the elements of hydrogen chloride from 2-carboxybenzenediazonium chloride.[3] 1,1-Dimethyl-3-(*o*-carboxyphenyl)triazene is another and more stable masked source of benzenediazonium-2-carboxylate that is often used.[4] Benzenediazonium-2-carboxylate, a violently explosive benzyne precursor, has been isolated and used on a number of occasions,[5] and several mechanistic pathways have been considered to account for the various products that are formed when it is allowed to decompose in the presence of a range of nucleophilic reagents.[6] A detailed study of the decomposition of benzenediazonium-2-carboxylate in the competitive presence of nucleophiles has been reported.[7] Interest in benzyne chemistry continues to stimulate new research.[8] Recent work has included studies where the modes of decomposition of a number of other benzyne precursors have been discussed.[9] Our interest in using substituted anthranilic acid derivatives as a route, particularly to the tetrahalogenobenzynes,[10] led us to re-investigate the modes by which benzenediazonium-2-carboxylate fragments, mainly because we had no evidence that suggested that tetrabromo- and tetrachloro- benzenediazonium-2-carboxylate gave the arynes by the stepwise loss of nitrogen and carbon dioxide and in addition we did not understand the absence of the product derived from acetonitrile when the decomposition of benzenediazonium-2-carboxylate was carried out in that solvent.

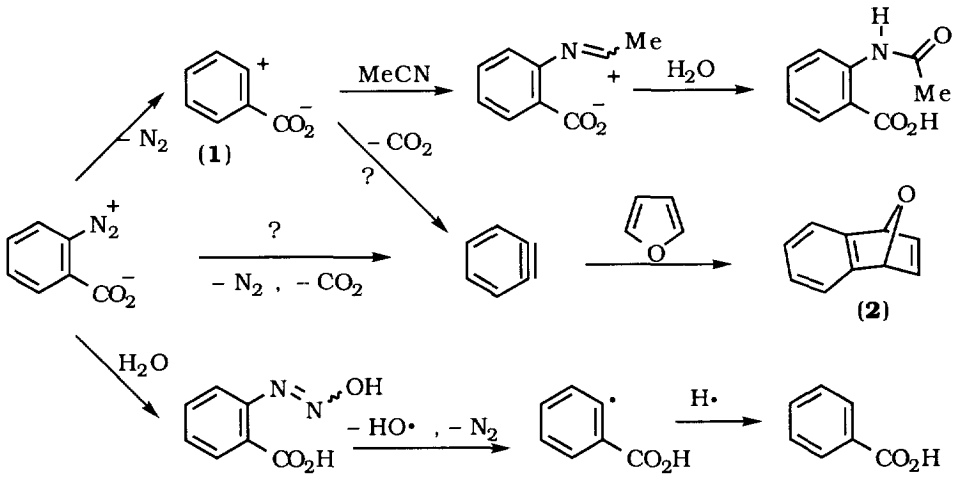
Discussion

In order to obtain a comparison with earlier results we decided to repeat some reactions of benzenediazonium-2-carboxylate involving water, methanol and mixtures of these with furan in acetonitrile on a preparative scale. The reaction with water proceeded as described previously and gave salicylic acid in 72% yield, presumably by way of the 2-carboxyphenyl cation (**1**).[5(a),(b),11] The decomposition in methanol was more complicated; the major products were identified as benzoic acid (59%) and *o*-methoxybenzoic acid (17%), together with small amounts of anisole, methyl salicylate, methyl *o*-methoxybenzoate, and methyl benzoate which were identified by gas chromatographic comparison with authentic samples. In a duplicate series of experiments the amount of the anisole was observed to vary widely, but the other three minor components were present in similar amounts: methyl salicylate (1.0% ± 0.15%), methyl *o*-methoxybenzoate (3.0% ± 0.3%), and methyl benzoate (1.0% ± 0.15%). Thus in the latter reaction the main process can be ascribed to the reduction of the diazonium function, or the 2-carboxyphenyl cation, to the 2-carboxyphenyl radical. Other workers have reported reactions with alcohols. The diazotisation of anthranilic acid in ethanol has been reported to afford ethyl benzoate,[12] and the alcoholysis of the diazonium function has been recorded in reactions with simple alcohols.[5b] When we allowed benzenediazonium-2-carboxylate to decompose in aqueous or methanolic acetonitrile containing furan we obtained unexpected results. Using water to trap the 2-carboxyphenyl cation (**1**) we obtained salicylic acid (9%), *N*-acetylanthranilic acid (25%), and 1,4-epoxy-1,4-dihydronaphthalene (**2**) (30%) (Equation [1]). The two carboxylic acids were isolated and identified as their methyl esters. Gas chromatography showed that phenol was produced in less than 1% yield. In a similar reaction we used methanol in place of water together with furan in acetonitrile under conditions identical to those used in the earlier reaction. After treatment of the acidic fraction with diazomethane we isolated methyl 2-methoxybenzoate (8%), and methyl *N*-acetylanthranilate (10%), together with 1,4-epoxy-1,4-dihydronaphthalene (32%) from the neutral fraction. Only a trace amount of methyl salicylate was detected by gas chromatography in the neutral fraction.



Since it was possible that silver nitrate had been used in the preparation of the benzenediazonium-2-carboxylate used in the earlier investigation we repeated the reaction where water was used as the trapping agent for the 2-carboxyphenyl cation. The only effect that the silver ion had on the reaction was to increase dramatically the amount of phenol produced. The yields of products in the latter reaction, in addition to phenol (6%), were salicylic acid (24%), N-acetylanthranilic acid (16%), and 1,4-epoxy-1,4-dihydronaphthalene (6%). The silver ion effect has been noted previously and ascribed to the formation of a cationic silver adduct.[13] Reactions in which benzenediazonium-2-carboxylate was allowed to decompose in acetonitrile or benzonitrile produced tarry products and were relatively uninformative. In the case of acetonitrile the acidic components were benzoic acid and N-acetylanthranilic acid which were isolated in 15% and 6% yields respectively. In the benzonitrile reaction

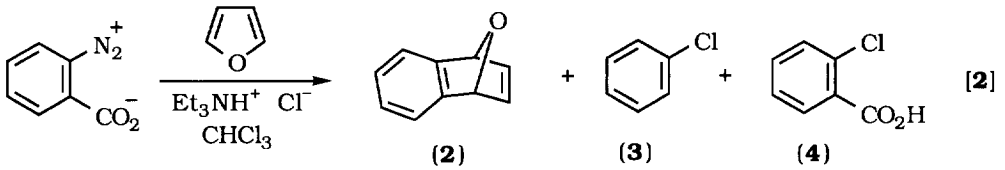
the only material isolated was a mixture of isomeric 2-carboxyphenylbenzonitriles. Our results clearly show that benzenediazonium-2-carboxylate decomposes by a number of processes (***Scheme 1***) and that the betaine (**1**) derived by the initial loss of nitrogen can be trapped, both by hydroxylic reagents and by acetonitrile.



Scheme 1

The formation of methyl salicylate in the earlier study is also confusing because we only detected small amounts in our reactions. In our opinion the reactions carried out previously and repeated at different concentrations by us, are subject to too many side reactions for us to be able to define the mechanism of formation of benzyne from benzenediazonium-2-carboxylate in any precise way, even though the arguments previously adduced are essentially sound. Furan is an effective trapping agent for benzyne but water is not an ideal trapping agent for the betaine for two reasons. Firstly, it limits the solvents that can be used to those that are miscible with water and which invariably promote side reactions. Secondly, the basic carboxylate moiety may induce the formation of the diazohydroxide and hence lead to side reactions that result from the formation of radicals. A similar argument should be considered in connection with the use of methanol as a trapping agent since it is known that arylazo ethers fragment to aryl radicals easily.[14] It is known, for example, that treatment of the *p*-nitrobenzenediazonium ion with sodium methoxide in methanol affords nitrobenzene in high yield.[15]

We decided to investigate the reactions further by using furan to trap benzyne and chloride ion to intercept the cation. Further, by using triethylamine hydrochloride as the source of chloride ion we could use chloroform as the solvent, as has frequently been the case in benzyne chemistry. A series of experiments was carried out using equimolar quantities of benzenediazonium-2-carboxylate and furan and variable amounts, up to one mol equivalent of triethylamine hydrochloride. Two sets of experiments were performed at room temperature and also at the reflux temperature of the mixtures. The results of the experiments and the yields of 1,4-epoxy-1,4-dihydronaphthalene (**2**), chlorobenzene (**3**), *o*-chlorobenzoic acid (**4**) (Equation [**2**]) are shown in the **Table**.



[2]

Table

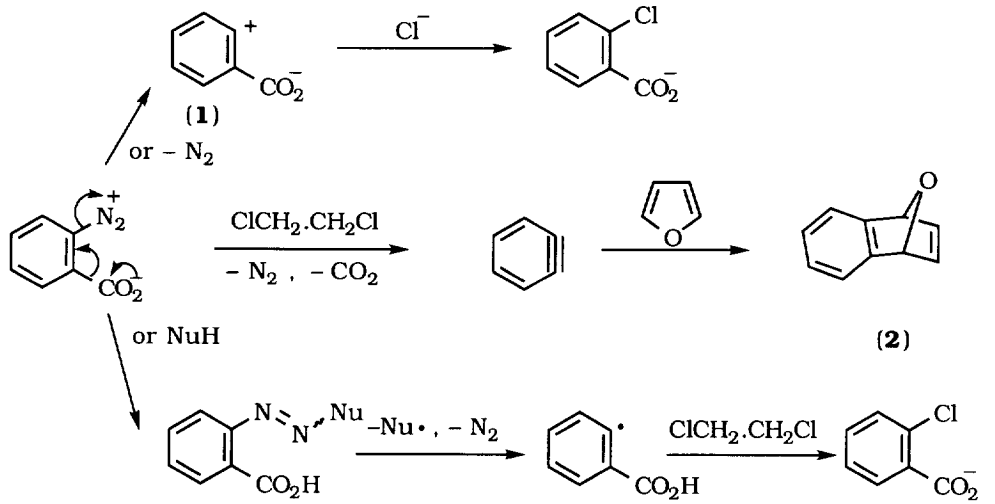
The decomposition of benzenediazonium-2-carboxylate in the presence of furan and triethylamine hydrochloride

entry	Et_3NH^+ Cl^-	temperature	% (**2**)	% (**3**)	total benzyne	% (**4**)
1	1.0 mol equiv.	25 °C	56	8	64	23
2	0.8 mol equiv.	25 °C	56	7	63	26
3	0.6 mol equiv.	25 °C	57	7	64	26
4	0.4 mol equiv.	25 °C	68	3	71	23
5	0.2 mol equiv.	25 °C	65	2	67	14
6	0.0 mol equiv.	25 °C				12
7	0.8 mol equiv.	60 °C	55	20	75	14
8	0.6 mol equiv.	60 °C	56	12	68	16
9	0.4 mol equiv.	60 °C	75	7	82	19
10	0.2 mol equiv.	60 °C	85	6	91	15
11	0.0 mol equiv.	60 °C				14

A control experiment using benzenediazonium-2-carboxylate and triethylamine hydrobromide in chloroform at 25 °C showed that the acidic fraction consisted of mainly *o*-chlorobenzoic acid. Two important conclusions may be drawn from these results. The yields of the benzyne products are virtually constant which is in accord with a concerted loss of nitrogen and carbon dioxide together with a small competitive side reaction that leads to the formation of *o*-chlorobenzoic acid (**3**). But equally important, it is clear that this side reaction is not entirely due to the intervention of the betaine (**1**) since even in the absence of triethylamine hydrochloride (entries six and eleven) there is still a significant amount of *o*-chlorobenzoic acid in the products of the reactions. This is presumed to be due to a radical displacement of chlorine from the solvent and accounts for almost all of the acid that is formed at 60 °C. The proportion of *o*-chlorobenzoic acid formed from the chloroform in the room temperature reaction is slightly lower which indicates that the the 2-carboxyphenyl cation (**1**) probably participates to a small extent. The abstraction of hydrogen chloride from chloroform was ruled out by the

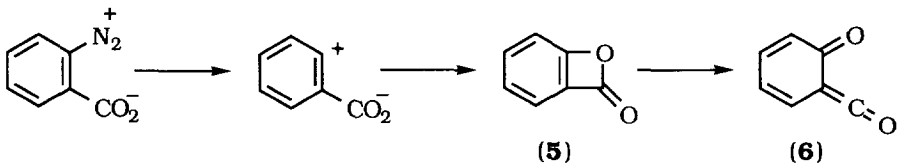
absence of chlorobenzene in the reactions carried out when triethylamine hydrochloride was not present. The acidic products that were formed in a reaction using a 1:1:1 molar ratio of benzenediazonium-2-carboxylate and triethylamine hydrobromide and furan at 60 °C in chloroform were shown to be *o*-bromobenzoic and *o*-chlorobenzoic acids in the ratio 1:23. Thus at 60 °C the involvement of the betaine is negligible. Similar results were obtained using other halogenated solvents that are commonly used in benzyne chemistry, for example 1,2-dichloroethane.[5c] In 1,2-dichloroethane the generation of benzyne was very efficient and the radical displacement process correspondingly small. The total acidic fraction, mainly *o*-chlorobenzoic acid, was always less than 5% and there was no evidence for the involvement of the betaine (**1**). We may note that the reaction of benzenediazonium-2-carboxylate with tetrakis(triphenylphosphine)platinum in benzene affords a product that may arise by interaction of the betaine (**1**) with the platinum complex.[16] However, in view of the fact that a bis(triphenylphosphine)platinum complex which contains the benzenediazonium-2-carboxylate fragment has been isolated and that that complex affords the former complex on being heated,[17] suggests that the betaine (**1**) may not be involved in either of these last two cases. There are reports of other reactions that may be rationalised initially as involving the betaine (**1**) but which then have been discounted as a result of a careful study.[3c]

The evidence of other studies and the results presented in the present paper lead us to conclude that the decomposition of benzenediazonium-2-carboxylate, like diazonium salts in general, is best accounted for by a partition between a number of different mechanisms. Benzyne is formed, in preparative scale experiments, by a concerted process which competes with the formation of the 2-carboxyphenyl radical and the 2-carboxyphenyl cation. The 2-carboxyphenyl cation (**1**) does not continue to give benzyne by the loss of carbon dioxide (***Scheme 2***).



Scheme 2

The important factors that are involved in affecting the balance between the various processes include the nature of the solvent and the substitution on the benzene ring. The cation appears to be formed as a major species in the more polar solvents where it is immediately scavenged by solvent molecules and other nucleophiles. When the diazonium ion is stabilised by the presence of electron withdrawing groups the cation would be at a higher energy than the 2-carboxyphenyl cation and the energy of the transition state involving the concerted loss of carbon dioxide and nitrogen would be lowered by the stabilisation due to the anionic contribution to the decarboxylation process. The published data and the results obtained in the present study indicate that the ideal solvent for benzyne formation involving benzenediazonium-2-carboxylate is 1,2-dichloroethane. In our experiments we observed little evidence for the intervention of the benzoxetanone (**5**) or the cumulenone (**6**) (equation[**3**]) which give rise to methyl salicylate on reaction with methanol.



(**5**) (**6**) [**3**]

The major difference between our preparative scale reactions and those reported in the earlier study[7] relate to the concentrations of the various reagents. In the earlier investigation the benzenediazonium-2-carboxylate was decomposed in a much more dilute solution and in the presence of a large excess of each of the potential trapping agents. We presume that these differences account for our detection and isolation of *N*-acetylanthranilic acid and also in the different distribution of the reaction products.

Experimental

Analytical gas chromatography was carried out using hydrogen flame ionisation detection and the detector response was calibrated by using solutions of known concentration at the appropriate levels. Analytical tlc and preparative layer chromatography was carried out using silica gel (PF_{254} according to Stahl).

Benzenediazonium-2-carboxylate

Prepared from anthranilic acid by the method reported.[5c]

Decomposition of Benzenediazonium-2-carboxylate in water

Benzenediazonium-2-carboxylate (1.1g) was dissolved in water (30 ml), warmed at 60 °C for 2h and left at room temperature for 15h. The crystalline solid that formed was shown to be salicylic acid (720 mg, 63%), mp 156-158 °C (lit.[18] mp 159 °C), infrared spectrum identical to that of an authentic sample.

Decomposition of Benzenediazonium-2-carboxylate in methanol

Benzenediazonium-2-carboxylate (1.0g) was added to methanol (30 ml) and kept at room temperature for 48h. The solvent was removed, replaced with ether and extracted with an aqueous solution of sodium carbonate (10%). Analysis of the neutral fraction by gas chromatography on a column of apiezon L on chromosorb W showed the presence of anisole, methyl benzoate, methyl salicylate, and methyl *o*-methoxybenzoate. The acidic fraction was shown to consist of benzoic acid (59%) and *o*-methoxybenzoic acid (17%) after methylation with diazomethane.

Decomposition of Benzenediazonium-2-carboxylate in acetonitrile containing water and furan

Benzenediazonium-2-carboxylate (1.3g) was dissolved in a solution of furan (5.0g, 73 mmol), and water (8.0g, 440 mmol) in acetonitrile (150 ml). After 30h at room temperature the solvents were carefully removed and the residual oil was redissolved in ether (100 ml) and extracted with an aqueous solution of sodium carbonate (10%). After acidification and extraction into ether a crude acid fraction (668 mg) showed a resonance at $\delta_H \approx 2.25$ ppm. The acid extract was methylated with ethereal diazomethane and the products separated by preparative layer chromatography to give: (i) R_f 0.7, methyl salicylate (124 mg, 9%), identified by comparison with an authentic sample by gc, and ir and ^{1}H nmr spectroscopy; (ii) Rf 0.2, methyl *N*-acetylanthranilate (379 mg, 25%), mp 99-101 °C (lit.[19] mp 98-99 °C) identified by comparison with an authentic sample by gc, and ir and ^{1}H nmr spectroscopy. The solvent from the neutral fraction was carefully evaporated to afford a yellow oil (438 mg) that was shown to be almost pure 1,4-epoxy-1,4-dihydronaphthalene (**2**)[20] (30%), contaminated by less than 1% of phenol.

Decomposition of Benzenediazonium-2-carboxylate in acetonitrile containing methanol and furan

Benzenediazonium-2-carboxylate (0.7g) was dissolved in a solution of furan (5.0g, 73 mmol) and methanol (12.5g, 390 mmol) in acetonitrile (150 ml). After 48h at room temperature the solvent was carefully removed from the mixture. The residual oil was dissolved in ether and extracted with an aqueous solution of sodium carbonate (10%). After acidification and extraction into ether a crude acid fraction (241 mg) was methylated with ethereal diazomethane and the products separated by preparative layer chromatography to give: (i) methyl *o*-methoxybenzoate (55 mg, 8%), (ii) methyl *N*-acetylanthranilate (80 mg, 10%). Minor amounts of methyl benzoate, methyl salicylate, and methyl anthranilate were isolated and identified by comparison with the infrared spectra of authentic samples.

Decomposition of Benzenediazonium-2-carboxylate in chloroform containing furan and triethylamine hydrochloride

In a series of experiments benzenediazonium-2-carboxylate (1.0g) was allowed to decompose at room temperature in chloroform (20 ml) containing furan (0.5g, 1 equiv.) and triethylamine hydrochloride (0.2, 0.4, 0.6, 0.8, and 1.0 equiv.) over a period of 48h. A second series of experiments was carried out in which benzenediazonium-2-carboxylate (1.0g) was allowed to decompose at room temperature in chloroform (20 ml) containing furan (1 equiv.) and triethylamine hydrochloride (0.2, 0.4, 0.6, and 0.8 equiv.) at 60 °C over a period of 1h. In each experiment the solvent was carefully removed from the mixture and the residual oil was dissolved in ether and extracted with an aqueous solution of sodium carbonate (10%). After acidification and

extraction into ether a crude acid fraction was weighed (to establish the yield of product) and then methylated with ethereal diazomethane and the product analysed by gas chromatography and shown to be predominantly methyl o-chlorobenzoate (>98%). The neutral fractions were examined by gas chromatography (an average of at least three injections using columns with PEG.A 10% and Apiezon L 10%) using calibration curves for chlorobenzene and 1,4-epoxy-1,4-dihydronaphthalene (**2**). The results obtained are tabulated in the discussion section.

Decomposition of Benzenediazonium-2-carboxylate in chloroform containing furan and triethylamine hydrobromide

Benzenediazonium-2-carboxylate (1.0g) was allowed to decompose in chloroform (20 ml) containing furan (0.5g, 1 equiv.) and triethylamine hydrobromide (1.25g, 1.0 equiv.) at 60 °C. The solution was extracted with an aqueous solution of sodium carbonate (10%) and, after acidification and extraction into ether, the crude acid fraction (220 mg) was methylated with ethereal diazomethane. The mixture was analysed by gas chromatography and shown to be a mixture of methyl *o*-chlorobenzoate and methyl *o*-bromobenzoate (ratio 23:1) together with a trace amount of methyl benzoate.

Decomposition of Benzenediazonium-2-carboxylate in 1,2-dichloroethane in the presence of furan

Benzenediazonium-2-carboxylate (1.0g) was heated in 1,2-dichloroethane (20 ml) containing furan (0.5g, 1 mol equiv.) at 80 °C during 2h. The solution was extracted with an aqueous solution of sodium carbonate (10%) and after acidification and extraction into ether a crude acid fraction (60 mg) was methylated with ethereal diazomethane and the product analysed by gas chromatography and shown to be a mixture of methyl *o*-chlorobenzoate and methyl salicylate. The neutral fraction was shown by gas chromatography (using columns with PEG.A 10% and Apiezon L 10%) to be 1,4-epoxy-1,4-dihydronaphthalene (**2**) (88%). Similar reactions in which triethylamine hydrochloride (1 equiv.) or triethylamine hydrobromide (1 equiv.) were added gave chlorobenzene (37%) and 1,4-epoxy-1,4-dihydronaphthalene (**2**) (29%) or bromobenzene (18%), chlorobenzene (4%) and 1,4-epoxy-1,4-dihydronaphthalene (**2**) (34%) respectively.

Decomposition of Benzenediazonium-2-carboxylate in acetonitrile

Benzenediazonium-2-carboxylate (1.0g) was allowed to decompose in acetonitrile (30 ml) over 48h. The solvent was removed, replaced with ether and extracted with an aqueous solution of sodium carbonate (10%) and after acidification and extraction into ether a crude acid fraction (214 mg) was obtained and shown to be a mixture of benzoic and *N*-acetylanthranilic acid (ratio 3:1) giving overall yields of 15% and 6% respectively. The neutral layer on evaporation gave a tar which yielded no identifiable material.

Decomposition of Benzenediazonium-2-carboxylate in benzonitrile

Benzenediazonium-2-carboxylate (1.0g) was allowed to decompose in benzonitrile (30 ml) over 48h. The solvent was removed, replaced with ether and extracted with an aqueous solution of sodium carbonate (10%) and after acidification and extraction into ether a crude acid fraction (242 mg) was obtained and which was methylated with diazomethane. The infrared spectrum of the mixture showed the presence of band at 2240 cm^{-1} assigned to an aromatic nitrile and molecular ions were observed in the mass spectrum at m/z 237. Gas

chromatography using a 20% SE30 stationary phase showed it to be a mixture tentatively identified as 2-methoxycarbonyl-3'-cyanobiphenyl and 2-methoxycarbonyl-4'-cyanobiphenyl. The neutral layer gave a brown oil which yielded no identifiable material other than residual benzonitrile.

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