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ipso SUBSTITUTION BY CYANIDE ANION IN PHOTOLYSIS OF 1-(p-METHOXYPHENYL)VINYL BROMIDES

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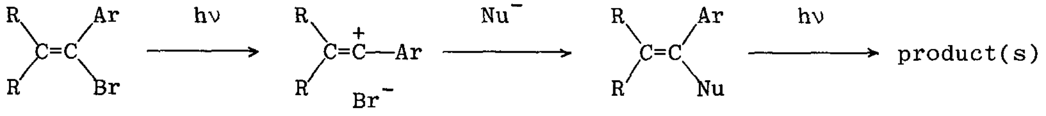
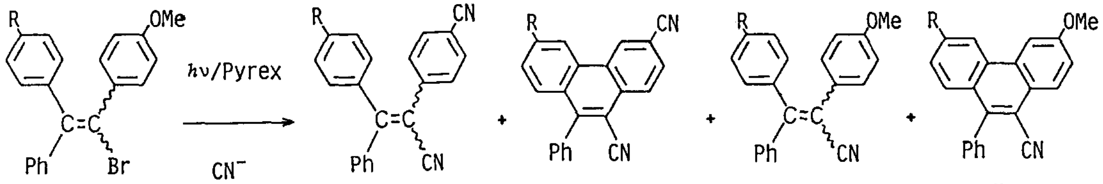
Summary: Photolysis of 1-(p-methoxyphenyl)vinyl bromides 1 in the presence of cyanide anion provided 1-cyano-1-(p-cyanophenyl)ethylenes 4 and 3,10-dicyanophenanthrenes 5. These were proven to be formed via a vinyl cation.

Studies on vinyl cations have been accumulated in an excellent book.1) However, few works concerning photochemical formation of vinyl cations are appeared.2) Recently we have reported that photogenerated vinyl cations react with typical nucleophiles, i.e., azide, cyanate, and thiocyanate anions, and the reactions are useful for nucleophilic substitution of vinyl halides.3) In these reactions, nucleophiles attack only on the sp carbon of the vinyl cations. In the course of studies on the photochemical nucleophilic substitution, we found novel behavior of 1-(p-methoxyphenyl)vinyl cations toward cyanide anion, i.e., double cyanation of 1-(p-methoxyphenyl)vinyl bromides by photolysis.



Irradiation of 1-(p-methoxyphenyl)-2,2-diphenylvinyl bromide (1a) (1 mmol) in acetonitrile (100 ml) in the presence of potassium cyanide (1 mmol) and 18-crown-6 (1 mmol) was carried out by use of a Pyrex-filtered high-pressure Hg lamp (100 W) at 10 °C under a N_2 atmosphere for 2 h. After evaporation of the solvent, the products extracted with ether-benzene were submitted to column chromatography on silica gel. The identified products were 1-cyano-1-(p-cyanophenyl)-2,2-diphenylethylene (4a)4) (trace), 3,10-dicyano-9-phenylphenanthrene (5a)4) (40%), 1-cyano-1-(p-methoxyphenyl)-2,2-diphenylethylene (6a)4) (19%), and 10-cyano-3-methoxy-9-phenylphenanthrene (7a)4) (trace) (conversion 90%). Photoreaction of 6a under the similar photochemical conditions employed above, however, resulted in a very low conversion into 7a. Therefore, monocyano-compounds and dicyano-compounds are produced, respectively, by different pathways.

Irradiation of 1,2-bis(p-methoxyphenyl)-2-phenylvinyl bromide (1b) (2 mmol) in acetonitrile (100 ml) in the presence of potassium cyanide (4 mmol) and 18-crown-6 (4 mmol) for 3 h gave 3,10-dicyano-6-methoxy-9-phenylphenanthrene (5b)$^{4)}$ (35%) and 1-cyano-1,2-bis(p-methoxyphenyl)-2-phenylethylene (6b)$^{4)}$ (28%) in 74% conversion.$^{5)}$ Dicyanophenanthrene 5b should be derived from photocyclization of 1-cyano-1-(p-cyanophenyl)-2-(p-methoxyphenyl)-2-phenylethylene (4b). The result indicates that the methoxyl group in the α anisyl group is displaced by cyanide anion.

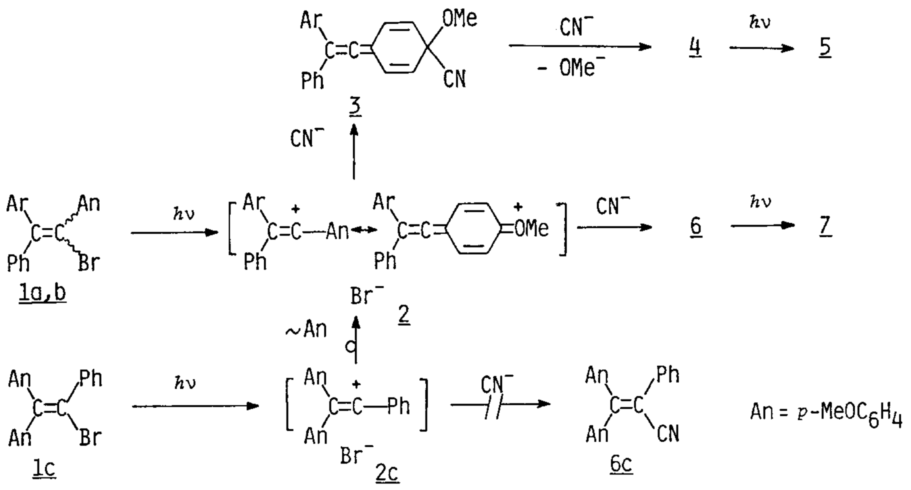


1 4 5 6 7

a : R = H
b : R = OMe

Formation of dicyano-compounds 4 and 5, apparently, reveals that cyanide anion displaces both the vinylic bromine and the methoxyl group in the α anisyl group. This observation is the first case of ipso substitution in vinylic systems. Then, we examined the presence of β-anisyl rearrangement in the photochemical cyanation in order to prove that substitution by cyanide anion takes place in photogenerated vinyl cations.

Irradiation of 2,2-bis(p-methoxyphenyl)-1-phenylvinyl bromide (1c) was carried out in a similar manner to that of 1b for 3 h. The identified products were 5b (48%) and 6b (28%) in 77% conversion.$^{5)}$ In the case of 2h-irradiation (55% conversion), 4b$^{4)}$ was formed in 35% yield together with 5b (13%) and 6b (49%). All the products obtained here bear a β-anisyl rearranged skeletone, indicating that rearrangement of β-anisyl group across the double bond should occur before cyanide anion attacks. This 1,2-anisyl rearrangement across the double bond is evidence for intermediacy of a vinyl cation in the photochemical cyanation because such a 1,2-aryl rearrangement takes place only in a vinyl cation.$^{6)}$ Accordingly, the pathway for the formation of dicyano-compounds begins with attack of cyanide anion on the photogenerated vinyl cation 2. Cyanide anion attacks on the ipso position of the methoxyl group in the anisyl group where positive charge is highly populated. The resulting allene derivative 3 undergoes nucleophilic attack of cyanide anion and expulsion of methoxide anion, to produce dicyanoethylene 4, which is easily photocyclized into phenanthrene derivative 5.



To confirm the existence of the allene intermediate 3, photolysis was conducted in a two-phase of dichloromethane and water using a phase transfer catalyst, in which system detection of 3 is expected owing to a low concentration of a nucleophile in the organic phase and a low polarity of the organic solvent. When irradiation of 1a (1 mmol) was carried out for 6 h in the presence of potassium cyanide (10 mmol) and tetrabutylammonium bromide (1 mmol) in dichloromethane (85 ml) and water (15 ml), the ^{1}H-NMR spectrum of the crude reaction mixture in $CDCl_3$ showed the presence of new signals at 3.3 (s, OMe), 5.8 (AA'BB', CH=CH), and 6.6 (AA'BB', CH=CH), as shown in Figure, which were assignable to those of 3-cyano-3-methoxy-6-(diphenylvinylidene)cyclohexa-1,4-diene (3a). This observation supports the reaction pathway described above.

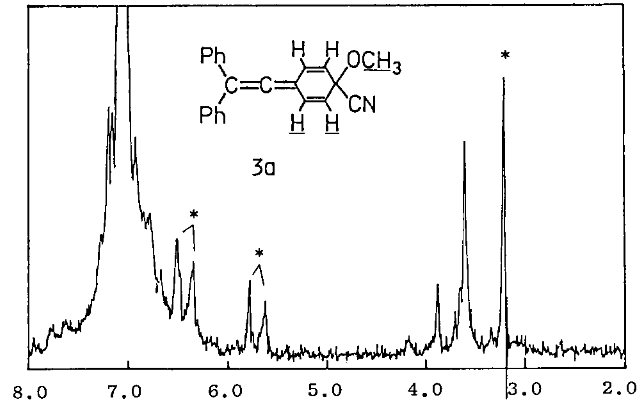


Fig. ^{1}H-NMR spectrum of the products from photolysis of 1a in CH_2Cl_2-H_2O.

In summary, it was found that the novel double cyanation of p-methoxyphenylvinyl bromides 1 occurs under photochemical conditions and proceeds with via a vinyl cation. Further details and application to other nucleophiles are now in progress.

References

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4) Yields in parentheses are isolated ones. 4a: mp 151-153 °C; NMR (CDCl$_3$) δ 6.74-7.45 (m, ArH); IR (nujol) 2230 and 2210 cm^{-1} (CN). 4b: mp 161-163 °C; NMR (CDCl$_3$) δ 3.86 (s, OMe), and 6.59-7.48 (m, ArH); IR (nujol) 2220 and 2200 cm^{-1} (CN). 5a: mp 304-306 °C; NMR (CDCl$_3$) δ 7.14-8.99 (m, ArH); IR (nujol) 2220 cm^{-1} (CN). 5b: mp 251-253 °C; NMR (CDCl$_3$) δ 4.08 (s, OMe) and 7.11-8.96 (m, ArH); IR (nujol) 2240 and 2220 cm^{-1} (CN). 6a: mp 147-149 °C; NMR (CDCl$_3$) δ 3.70 (s, OMe) and 6.62-7.38 (m, ArH); IR (nujol) 2200 cm^{-1} (CN). 6b: mp 162-164 °C; NMR (CDCl$_3$) δ 3.74 (s, OMe), 3.82 (s, OMe), and 6.59-7.42 (m, ArH); IR (nujol) 2200 cm^{-1} (CN). 7a: mp 180-183 °C; NMR (CDCl$_3$) δ 4.06 (s, OMe) and 7.30-8.82 (m, ArH); IR (nujol) 2260 cm^{-1} (CN). 7b: mp 160-163 °C; NMR (CDCl$_3$) δ 4.02 (s, OMe), 4.04 (s, OMe), and 7.03-8.34 (m, ArH); IR (nujol) 2200 cm^{-1} (CN). Stereochemistry of 4b and 6b was not determined. These products were confirmed by comparison with the samples prepared by cyanation of the corresponding bromides by use of cuprous cyanide.

5) Traces of 4b and 7b in some fractions were detected by ^{1}H-NMR.

6) Reference 1, p. 395. Lack of β-aryl rearrangements in 2-arylvinyl radicals has been studied. See, J. K. Haynes, Jr., and J. A. Kampmeier, J. Org. Chem., 37, 4167 (1972).

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