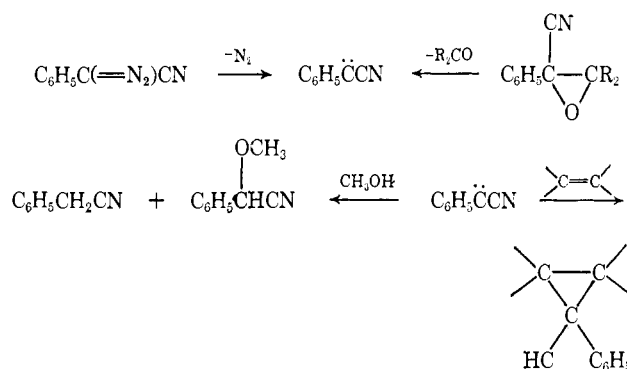# α,β-Dicyanostilbene from Phenylethynyl Azide and from Phenylethynyl Isocyanate[1]

## J. H. Boyer and R. Selvarajan

*Contribution from the Chemistry Department, University of Illinois,
Chicago Circle Campus, Chicago, Illinois 60680. Received April 28, 1969*

Abstract: The formation of dicyanostilbene **12** from an adduct **1** composed of equimolar amounts of phenylethynyl bromide and iodine azide, from 2-phenyl-3-bromotriazole **13**, and from phenylpropiolyl azide **15** is accounted for by photodimerization with loss of nitrogen or carbon monoxide from phenylethynyl azide **9** or phenylethynyl isocyanate **16**, as appropriate. Both **9** and **16** are assumed intermediates and **12** is transformed into 9,10-dicyanophenanthrene **14**. Intermolecular abstraction and insertion products for phenylcyanocarbene were photolytically obtained from both **13** and **15** but not from **1**. Accordingly interaction between the carbene and its precursors **9** and **16** provides an alternative mechanism, indistinguishable from dimerization of either **9** or **16**, to account for **12** from both **13** and **15** but not from **1**. A minor product, methyl benzoate, from the photolysis of **1** in methanol apparently is derived from 2-bromo-2-iodo-3-phenylazirine **11**. In dark reactions several reagents including alumina, magnesium, zinc, and thiourea, transformed **1** into **12**, with **9** as an assumed intermediate. There was no evidence for the intermediacy of either phenylcyanocarbene or phenylethynylnitrene.

Cyanocarbenes, generated by eliminating diazonitrogen[2] and by fragmenting cyanooxiranes,[3] gave typical carbene reactions by inserting into CH and OH bonds and adding to CC multiple bonds. Since both a cyanocarbene and an ethynylnitrene are available

$$C_6H_5C(=N_2)CN \xrightarrow{-N_2} C_6H_5\ddot{C}CN \xleftarrow{-R_2CO} C_6H_5\overset{\displaystyle CN}{\underset{\displaystyle O}{C}}-CR_2$$

$$C_6H_5CH_2CN + C_6H_5\overset{\displaystyle OCH_3}{\underset{}{C}}HCN \xleftarrow{CH_3OH} C_6H_5\ddot{C}CN \longrightarrow$$

from either the resonance hybrid, $R\ddot{C}CN \leftrightarrow RC\equiv C\ddot{N}$, by appropriate electron localization or the equilibrium, $RC\equiv C\ddot{N} \rightleftarrows R\ddot{C}C\equiv N$, a search for products derived from the nitrene was undertaken;[4] none have been

$$^3HC\equiv C-\ddot{C}-H \leftrightarrow {}^3H-C-C\equiv CH$$

$$^1HC\equiv C-\ddot{C}\diagdown_H \rightleftarrows {}^1H\diagdown_{\ddot{C}-C\equiv CH}$$
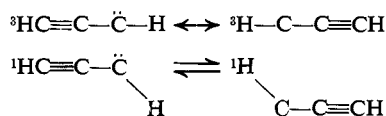
found.

To generate phenylethynylnitrene, $C_6H_5C\equiv C\ddot{N}$, by α elimination from nitrogen, the deoxygenation of 1-nitro- or 1-nitroso-2-phenylacetylene, $C_6H_5C\equiv CNO_2$-(NO), the elimination of molecular nitrogen from

phenylethynyl azide **9** and the elimination of carbon monoxide from phenylethynyl isocyanate **16**, were selected for investigation. After unsuccessful attempts to prepare starting materials[5] for deoxygenation, this approach was abandoned. After discouraging results were obtained on treating a phenylethynyl halide with a metal azide,[6,7] elimination of iodine bromide from an adduct **1** derived from phenylethynyl bromide and iodine azide[8a] as a possible route to the azide **9** was explored. A similar adduct[8b] was not obtained upon treatment of phenylethynyl bromide with iodine isocyanate. Phenylethynyl isocyanate was prepared but not isolated from the Curtius reaction on phenylpropiolyl azide.[9]

The adduct **1**, sensitive to both light and heat, reacted with cyclopentadiene to give a thermally unstable solid product, assumed to be a triazoline, but failed to react with diphenylacetylene. Although nitrogen and halogen are spontaneously lost even on storage in the refrigerator, the adduct **1** is more efficiently transformed into *cis*- and *trans*-dicyanostilbene **12** by treatment with alumina, magnesium in dioxane, zinc in benzene or cyclohexene, or thiourea in ethanol.[10] The best yield of the combined geometrical isomers of **12**

(1) Financial support was received from NASA Grant No. NGR-14-012-004.

(2) R. Breslow and C. Juan, *J. Am. Chem. Soc.*, **80**, 5991 (1958).

(3) P. C. Petrellis, H. Dietrich, E. Meyer, and G. W. Griffin, *ibid.*, **89**, 1967 (1967).

(4) R. A. Bernheim, R. J. Kempf, J. V. Gramas, and P. S. Skell [*J. Chem. Phys.*, **43**, 196 (1965)] report that triplet propargylene shows equal reactivity with olefins at C_1 and C_3, whereas singlet propargylene reacts only at C_1, the position vacated by N_2 in the photolysis of diazopropyne. G. L. Closs [in "Topics in Stereochemistry," Vol. 3, E. L. Eliel and N. L. Allinger, Ed., Interscience Publishers, New York, N. Y., 1968, p 226] describes triplet propargylene as a resonance hybrid and gives the possible interpretation for the singlet to be a bent structure with a significant barrier for configurational interchange of positions C_1 and C_3.

(5) (a) J. Loevinich and H. Gerber [*Chem. Ber.*, **63**, 1707 (1930)] reported a preparation of 1-nitro-2-phenylethyne by dehydrobromination of 1-nitro-1,2-dibromo-2-phenylethane, $C_6H_5CHBrCHBrNO_2 \rightarrow C_6H_5C\equiv CNO_2$. (b) E. Robson, J. M. Tedder, and D. J. Woodcock [*J. Chem. Soc.*, 1324 (1968)] were also unsuccessful in attempts to prepare 1-nitroso-2-phenylacetylene from diphenylethynylmercury and nitrosyl chloride.

(6) J. H. Boyer, C. H. Mack, N. Goebel, and L. R. Morgan, Jr., *J. Org. Chem.*, **23**, 1051 (1958).

(7) S. I. Miller [private communication] reports work with H. Taniguchi in which azide ion and phenylethynyl bromide gave an unidentified liquid azide, a solid azide tentatively assigned the structure $C_6H_5CH=C(Br)N_3$, and dicyanostilbene, **12**, mp 162°.
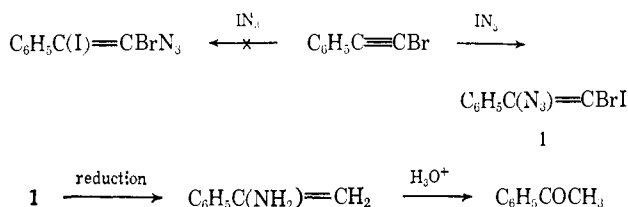
(8) According to general procedures reported by (a) A. Hassner and F. W. Fowler, *J. Org. Chem.*, **28**, 2686 (1968); (b) A. Hassner, M. E. Lorber, and C. Heathcock [*ibid.*, **32**, 540 (1967)] reported the adduct, $C_6H_5C(NCO)=CHI$, from phenylacetylene and iodine isocyanate in tetrahydrofuran.

(9) Th. Curtius and E. Kenngott [*J. Prakt. Chem.*, **112**, 314 (1926)] obtained phenylpropiolyl azide, mp 54°, by treating the hydrazide of phenylpropiolic acid with nitrous acid.

(10) The reaction with alumina was observed during column chromatography. No effort was made to establish formation of an organometallic compound by reaction with alumina, magnesium, or zinc, or of an alkylation of thiourea prior to loss of halogen.

was 67% obtained from the reaction with zinc in cyclohexene. The *trans* product predominated over its *cis* isomer, apparently not produced in reactions with either alumina, magnesium, or zinc in benzene. In addition to **12**, the adduct **1** was also transformed into α,β-diiodo-β-bromostyrene and an intractable viscous liquid or tar by alumina, trace amounts of an unknown colorless solid, mp 205–208°, by zinc in cyclohexene, and a yellow polymeric liquid by magnesium in dioxane. Very careful inspection of each reaction mixture revealed no other products. In particular, products diagnostic of a nitrene or a carbene intermediate were not found.

In either of its geometrically isomeric forms, dicyanostilbene **12** represents a formal dimer of phenylcyanocarbene. This appeared to support the conclusion, later proved to be incorrect, that the adduct was 1-azido-1-bromo-2-iodo-2-phenylethene[11a] from which the unstable intermediate, phenylethynyl azide, was derived by an elimination of iodine bromide. That the correct assignment is 1-iodo-1-bromo-2-azido-2-phenylethene[11b] is supported by catalytic reduction over platinum and chemical reductions employing tin and hydrochloric acid, zinc and acetic acid, hydriodic acid, and lithium aluminum hydride. The formation of acetophenone in each reduction, with the best yield of 64% from the reaction with hydriodic acid, reveals the attachment of azido and phenyl groups to the same carbon atom. From the isomer in which phenyl and azido groups are attached to different carbon atoms, reduction and hydrolysis would have produced either phenylacetaldehyde or β-phenylethanol, neither of which was detected. The assignment agrees with the prediction[11b] that the addition would proceed by an electrophilic attack of the iodonium cation at the acetylenic carbon bearing bromine rather than phenyl. Unexpectedly diborane failed to reduce the adduct **1**, which was recovered.

$$C_6H_5C(I)\!=\!CBrN_3 \xleftarrow{\text{IN}_3}{\times} C_6H_5C\!\equiv\!CBr \xrightarrow{\text{IN}_3}$$

$$C_6H_5C(N_3)\!=\!CBrI$$
$$\mathbf{1}$$

$$\mathbf{1} \xrightarrow{\text{reduction}} C_6H_5C(NH_2)\!=\!CH_2 \xrightarrow{H_3O^+} C_6H_5COCH_3$$

For the adduct **1** to be transformed into dicyanostilbene, either the phenyl group or a nitrogen function must migrate from carbon to carbon. While preserving the opportunity for migration to be either simultaneous or sequential with an elimination, the reaction may be initiated by (1) loss of a halogen atom, (2) concerted elimination of iodine bromide, or (3) elimination of nitrogen from either the azide **1** or its ring tautomer, an isotriazole, **2**. Conceivably *cis*- and *trans*-dicyanostilbene **12** would then be produced by (1) a dimerization from **4** or **5** with stepwise or concerted evolution of a halogen atom and nitrogen, not necessarily in that order, (2) a dimerization from **7**, **8**, or **9** with stepwise or concerted evolution of nitrogen, and/or (3) a dimerization from **11** with stepwise or concerted evolution of iodine bromide (X = Br or I as required).
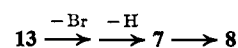
(11) (a) Preliminary observations have been described in *Chem. Eng. News*, **45**, No. 41, 52 (1967). (b) By private communication A. Hassner, Sept 1967, corrected our original structural assignment for the adduct and confirmed that thermolysis of the adduct gave *trans*-dicyanostilbene, **12**.

To test the hypothesis that the formation of dicyanostilbene could proceed directly or stepwise from **4** and/or **7**, the photolysis of 2-phenyl-3-bromotriazole **13** was investigated after it was found that attempted dehydrobromination by triethylamine at 90° or quinoline at 120° (extensive charring above 120°) was unsuccessful and permitted recovery of starting material. As previously reported,[12] phenylacetonitrile, α-methoxyphenylacetonitrile, methyl benzoate, and acetophenone are produced by the photolysis of **13** in methanol.
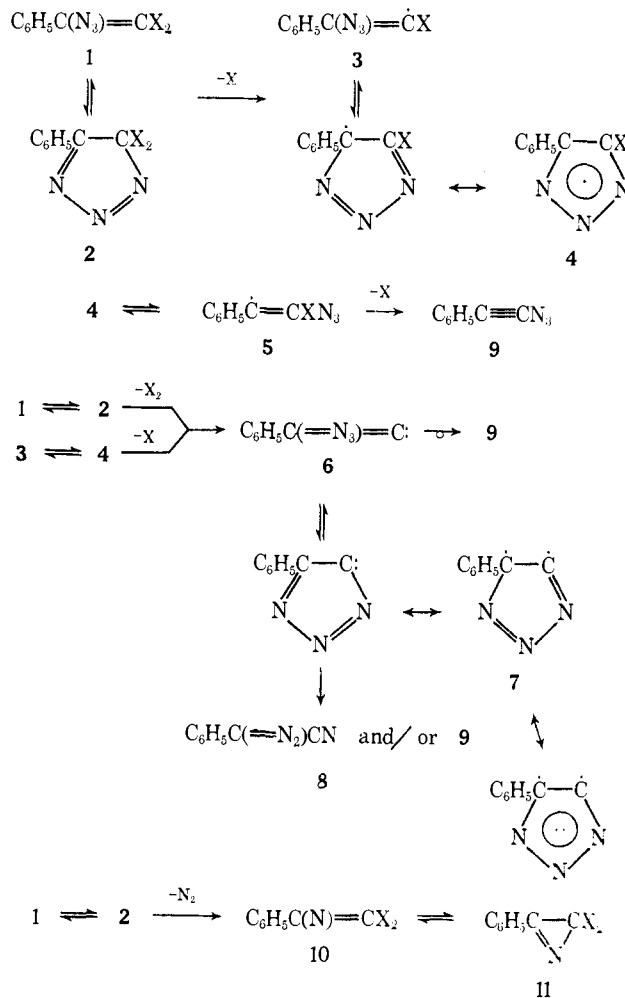
Photolysis in methylene chloride, however, affords 9,10-dicyanophenanthrene **14** and phenylacetonitrile. α-Cyano-β-chlorostyrene, previously unknown, characterized by ir, nmr, and mass spectra, is also obtained and is apparently produced by phenylcyanocarbene insertion into either a CH or CCl bond of methylene chloride followed by elimination of hydrogen chloride. Dicyanostilbene **12** is an assumed intermediate from which the formation of **14** proceeds by a known photocyclization and dehydrogenation.[13] It was not unexpected that **14** was also produced from **1** by photolysis. In addition to **14** irradiation of **1** in methanol

(12) J. H. Boyer and R. Selvarajan [*Tetrahedron Lett.*, 47 (1969) presented the mechanism

$$\mathbf{13} \xrightarrow{-Br} \xrightarrow{-H} \mathbf{7} \longrightarrow \mathbf{8}$$

and/or

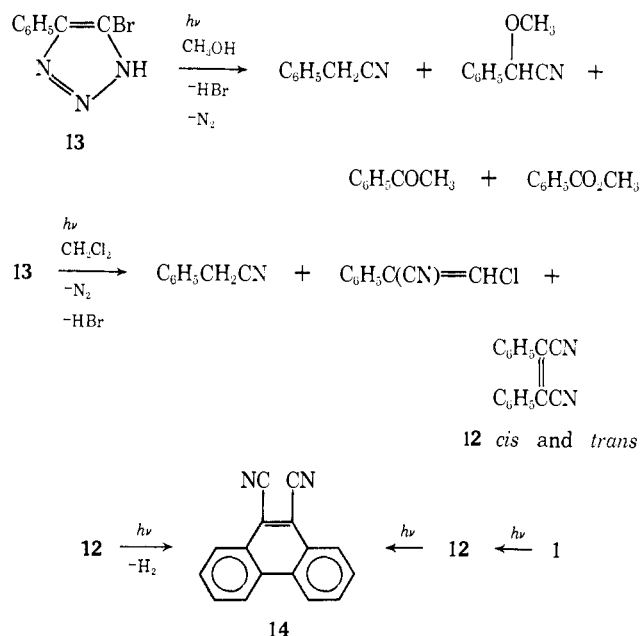$$\mathbf{9} \longrightarrow C_6H_5\dot{C}CN \longleftrightarrow C_6H_5C\!\equiv\!C\ddot{N}$$
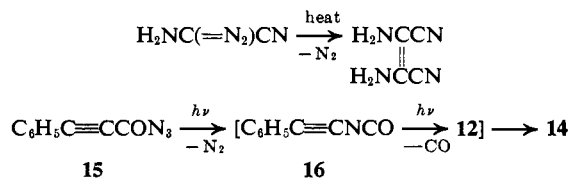
(13) M. V. Sargent and C. J. Timmons, *J. Am. Chem. Soc.*, **85**, 2186 (1963).

produces acetophenone and methyl benzoate and in benzene it gives **14** and α,α'-diiodostilbene. Apparently acetophenone is formed by a photoreduction of **1** by methanol. Methyl benzoate may also be accounted for (see below) but an explanation for the formation of diiodostilbene is not offered at this time.

$$C_6H_5C=CBr$$

13

13 $\xrightarrow[\substack{-N_2 \\ -HBr}]{\substack{hv \\ CH_2Cl_2}}$ $C_6H_5CH_2CN$ + $C_6H_5C(CN)=CHCl$ +

$$\begin{matrix} C_6H_5CCN \\ \| \\ C_6H_5CCN \end{matrix}$$

12 *cis* and *trans*

12 $\xrightarrow[-H_2]{hv}$ $\xleftarrow{hv}$ **12** $\xleftarrow{hv}$ **1**

14

Next it was necessary to evaluate **8** and/or **9**[14] as precursors for dicyanostilbene **12**. Although detection of **12** was not reported for the pyrolysis of α-diazophenylacetonitrile in the presence of diphenylacetylene,[2] it must nevertheless be considered here, since the formation of diaminomaleic nitrile has more recently been obtained from the pyrolysis of α-diazo-α-aminoacetonitrile.[15] From the generality that "dimeric" olefin formation from a diazo compound proceeds by interaction between the latter and the corresponding carbene, the transformation of **8** into **12** would require the intermediacy of phenylcyanocarbene. Apparently both photolytic and dark transformations of **1** into **12** bypass carbene and nitrene intermediates, since attempts to capture them by diagnostic abstraction, insertion, and addition reactions were unsuccessful.

Failure to isolate phenylethynyl azide **9** precluded a direct observation of its assumed transformation into dicyanostilbene, but support has been found in the similar photolytic transformation of the isosteric and isoelectronic phenylethynyl isocyanate **15** into dicyanostilbene. The latter without isolation is photolytically transformed into 9,10-dicyanophenanthrene **14**.[13]

$$H_2NC(=N_2)CN \xrightarrow[-N_2]{heat} \begin{matrix} H_2NCCN \\ \| \\ H_2NCCN \end{matrix}$$

$$C_6H_5C\equiv CCON_3 \xrightarrow[-N_2]{hv} [C_6H_5C\equiv CNCO \xrightarrow[-CO]{hv} 12] \longrightarrow 14$$
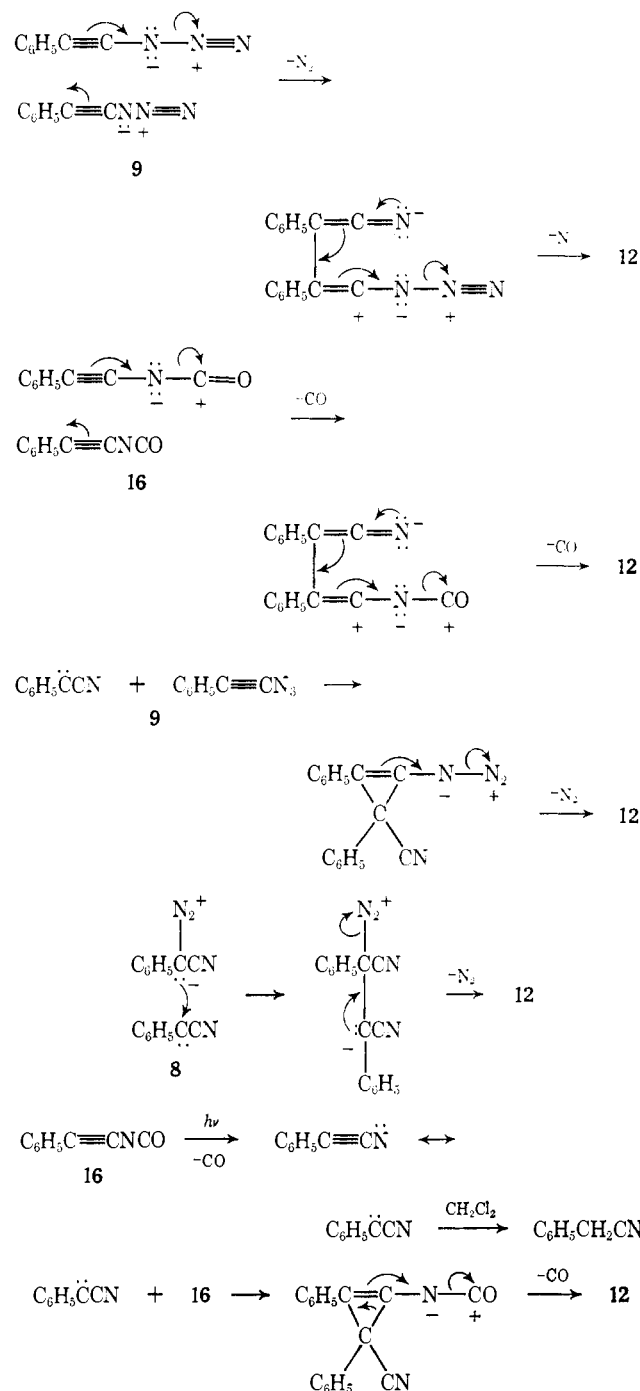$$\quad\quad\quad\quad\quad 15 \quad\quad\quad\quad\quad\quad 16$$

To account for abstraction and insertion products, phenylcyanocarbene appears to be a required intermediate in the photolysis of **13** in either methanol or

methylene chloride; however, dicyanostilbene **12** is also produced in the latter solvent only. In this instance there is no basis for a differentiation between dimerization of **9** with elimination of nitrogen and interaction between phenylcyanocarbene and its precursor, either **8** or **9**,[12] for the formation of **12**. Similarly the intermediacy of phenylcyanocarbene in the photolysis of phenylpropiolyl azide **15** in methylene chloride is revealed in the formation of phenylacetonitrile, the abstraction product. As before a dual mechanism for the formation of **12** must be recognized; dimerization of **16** with elimination of carbon monoxide[16] cannot be differentiated from an interaction between the carbene and **16** with evolution of carbon monoxide.

9

16

$$C_6H_5\ddot{C}CN + C_6H_5C\equiv CN_3 \longrightarrow$$
$$\quad\quad\quad\quad 9$$

8

$$C_6H_5C\equiv CNCO \xrightarrow[-CO]{hv} C_6H_5C\equiv C\ddot{N} \longleftrightarrow$$
$$\quad 16$$

$$C_6H_5\ddot{C}CN \xrightarrow{CH_2Cl_2} C_6H_5CH_2CN$$

$$C_6H_5\ddot{C}CN + 16 \longrightarrow$$ $\xrightarrow{-CO}$ **12**

(14) The rearrangement of **6** directly to **9** cannot be differentiated from the sequence, **6** → **7** → **9**.

(15) R. E. Moser, J. M. Fritsch, T. L. Westman, R. M. Kliss, and C. N. Matthews, *J. Am. Chem. Soc.*, **89**, 5673 (1967).

(16) J. H. Boyer, W. Kruger, and G. J. Mikol [*J. Am. Chem. Soc.*, **89**, 5504 (1967)] reported the probable generation of β-styrylnitrene from both β-styrylazide and β-styryl isocyanate.

Apparently the azirine **11** is not a precursor for dicyanostilbene **12** in these investigations on the adduct **1**; however, azirine formation would be expected whenever nitrogen elimination precedes halogen elimination from the vinyl azide **1**. Its facile transformation into benzoyl cyanide by water is an expected extension of azirine ring opening in the Neber rearrangement[17] and conceivably accounts for the small amount of methyl benzoate obtained from the photolysis of **1** in methanol. Benzoyl cyanide is known to be transformed by methanol under mild conditions into methyl benzoate.[18] That dimerization of an azirine generally does not successfully compete with hydrolytic ring

$$1 \rightleftharpoons 2 \xrightarrow[\substack{h\nu \\ -N_2}]{ROH} 11 \xrightarrow{ROH} C_6H_5COCN \xrightarrow{CH_3OH} C_6H_5CO_2CH_3$$
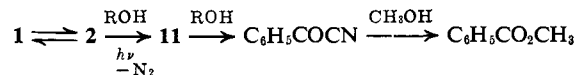
opening[17] greatly reduces the opportunity for **11** in a protic solvent to be a precursor for **12**. Since the phototransformation **1** → **12** in methanol requires halogen to be eliminated before nitrogen, in the absence of compelling evidence to the contrary, it is assumed that the same phototransformation in benzene proceeds by the same mechanism. There was no evidence for the intermediacy of **11** in the thermal transformation, **1** → **12**.

Experimental Section

Photolytic reactions were carried out at 35° under nitrogen in quartz vessels placed in a Rayonet chamber reactor equipped with 16 low-pressure mercury lamps. Each charge was degassed by flushing with nitrogen for 8–10 hr (unless stated otherwise) prior to irradiation.

1-Iodo-1-bromo-2-azido-2-phenylethene (1). To a well-stirred and cooled (0–5°) slurry of sodium azide (13.0 g, 0.2 mole) in acetonitrile (100 ml), iodine monochloride (16.14 g, 0.1 mole) was added dropwise for 30 min. After 15 min bromophenylacetylene (18.1 g, 0.1 mole) was added dropwise. The reaction mixture was kept stirred at 5° for 3 hr and at 25° for 12 hr. The brown slurry was dissolved in ether (200 ml) and washed with water repeatedly. The ether layer was dried (MgSO$_4$) and the solvent was removed below 35° to obtain a dark brown viscous liquid (32 g). Upon chromatography over alumina, elution with 9:1 hexane–benzene mixture gave **1**, a pale yellow liquid (16.0 g, 23%), sensitive to light and heat; n^{23}D 1.6805; ν_{max} (CHCl$_3$) 2120 (vs, doublet, −N$_3$ and 1620 cm^{-1} (s, aromatic); λ_{max} (MeOH) 206 mμ (ϵ 13,180) and 264 (6454). It has been reported[11b] to solidify on cooling to about −10°.

Elutions with 8:2 hexane–benzene mixture gave colorless crystals of α,β-diiodo-β-bromostyrene (1.6 g, 7.5%), mp 62–62.5° dec, mixture melting point with the authentic sample, obtained quantitatively by shaking phenylethynyl bromide and iodine in carbon tetrachloride, showed no depression; ν_{max} (CHCl$_3$) 1620 (s, broad, aromatic), 1500 (m), and 1450 cm^{-1} (s); nmr (CCl$_4$) multiplet centered at δ 7.28 (phenyl protons).

Anal. Calcd: C, 22.07; H, 1.15; halogen, 76.77. Found: C, 22.60; H, 1.39; halogen, 76.10.

Elutions with a 1:1 mixture of ethanol–diethyl ether gave colorless crystals of *trans*-dicyanostilbene (300 mg, 5.3%), mp and mmp with authentic sample 160.5–161.5.[19] Ethanol elutions gave an intractable viscous liquid.

Dehalogenation of 1-Iodo-1-bromo-2-azido-2-phenylethene (1). A solution of **1** (4.6 g, 13 mmole) in cyclohexene (20 ml) mixed with activated zinc dust (0.65 g, 10 mg-atom) was stirred for 12 hr at 35–45°, 24 hr at 55–65°, and 12 hr at 65–75°. The reaction mixture was filtered, the solvent removed under vacuum, and the residue was chromatographed over alumina.

The elutions with a 4:1 hexane–benzene mixture gave colorless crystals (600 mg, 40%), mp and mmp with *trans*-dicyanostilbene

160.5–161.5°. The elutions with a 2:1 hexane–benzene mixture afforded colorless crystals of *cis*-dicyanostilbene[20] (400 mg, 27%): mp 132–133°; ν_{max} (CHCl$_3$) 2230 cm^{-1} (m, -C≡N); λ_{max} (CHCl$_3$) 284 (ϵ 11,220); nmr (CCl$_4$) δ 7.33 (s, C$_6$H$_5$) and by mass spectra, M 230. Pale yellow crystals eluted in trace amounts by a 2:1 benzene–ether mixture, mp 160–161°, and a colorless solid eluted by ethanol, mp 205–208°[20] were obtained in insufficient amounts for further characterization.

A similar reaction employed zinc in benzene and gave *trans*-dicyanostilbene in 42% yield. Dehalogenation of **1** by thiourea gave both *cis*- (2.7%) and *trans*-dicyanostilbene (26%) and by magnesium in dioxane gave *trans*-dicyanostilbene, 42%.

Reduction of 1. By following standard procedures, acetophenone was obtained in 16% yield from reduction over platinum, 48% yield using either tin and hydrochloric acid or zinc and acetic acid, 64% using hydriodic acid, and 2.5% using lithium aluminum hydride.

Photolysis of 1 in Benzene. A solution of **1** (2.7 g, 8 mmole) in benzene (400 ml), previously degassed for 1 hr by flushing with nitrogen, was irradiated for 20 hr using 2537-Å lamps and the reaction was monitored by ir. Solvent was partially removed under vacuum and the solid was collected and recrystallized from a mixture of chloroform–dimethyl sulfoxide to give pale yellow crystals of 9,10-dicyanophenanthrene (210 mg, 23%), mp 289–290°.[13]

The benzene filtrate was diluted, washed successively with sodium thiosulfate solution and water, dried and concentrated. The residual product was triturated with methylene chloride and the colorless crystals of α,α'-diiodostilbene (230 mg, 7%) were collected, mp with decomposition 206–207°.[21] The filtrate upon concentration yielded a tarry residue.

Photolysis of 1 in Methanol. Into methanol (400 ml), previously degassed for 8 hr by flushing nitrogen, **1** (3.49 g, 10 mmole) was added, the solution was irradiated at 2537 Å for 14 hr as the reaction was monitored by ir. Solvent was removed under suction, the residue was dissolved in chloroform (50 ml) and washed successively with sodium thiosulfate and water. Chloroform was removed after drying and the residue was chromatographed over silica gel. A 1:1 mixture of hexane–benzene eluted a colorless liquid which, by gc and mass spectra, was identified as a mixture of acetophenone (72 mg, 6%) and methyl benzoate (136 mg, 10%). Chloroform eluted an unidentified yellow polymeric oil (160 mg) and chloroform–ethanol (9:1) eluted pale yellow crystals of 9,10-dicyanophenanthrene (190 mg, 17%), mp and mmp 288–289°.

Photolysis of 4-Phenyl-5-bromo-1,2,3-triazole in Methylene Chloride. A solution of the triazole[12] (1 g, 4.46 mmole) in anhydrous methylene chloride (700 ml) was irradiated at 2537 Å for 16 hr. The solution was concentrated and the residue was chromatographed over silica gel. Benzene–petroleum ether (bp 30–60°) mixtures, 2:3 and 1:1, eluted a pale yellow liquid which was further fractionated by preparative gc (silicone GE XE-60 column). Of the three volatile components the first one found in trace amounts could not be identified. The second one was characterized by ir and nmr spectra to be phenylacetonitrile (21 mg, 4%), and the third was identified as α-cyano-β-chlorostyrene (4 mg, 1.8%), an oil which solidified in the refrigerator; ν_{max} (CCl$_4$) 2215 cm^{-1} (m, C≡N); nmr (CCl$_4$) δ 7.16 (s, 1, >C=C(ClH) and 7.38 (broad, s, 5, phenyl); mass spectrum M$^+$ 165 and 163 (intensity ratio 1:3, respectively, due to chlorine isotopes), m/e 128 (M − Cl), m/e 127 (M − HCl) and m/e 87 and 85 (M$^+$ − C$_6$H$_6$).

The latter elutions with a 1:1 mixture of benzene–petroleum ether and pure benzene gave pale yellow crystals of 9,10-dicyanophenanthrene (17 mg, 3.4%), mp and mmp 287–288°.

Phenylpropiolyl Azide. Following Curtius and Kenngott[9] a condensation between ethyl phenylpropiolate and hydrazine was carried out. In our hands 3-phenyl-5-pyrazolone, mp 236°,[9] was repeatedly obtained in nearly quantitative yield rather than the hydrazide of phenylpropiolic acid. The following alternative preparation was then developed.

A solution of phenylpropiolyl chloride[22] (4.39 g, 30 mmole) in acetonitrile (10 ml) was added dropwise, through 30 min, to a cooled (−10°) and stirred slurry of sodium azide (2.6 g, 40 mmole) in 1:1

(17) (a) A. Hassner and W. Fowler, *J. Am. Chem. Soc.,* **90,** 2869 (1968); (b) J. A. Deyrup and R. B. Greenwald, *ibid.,* **87,** 4538 (1965).

(18) G. Griffin, private communication.

(19) D. G. Coe, M. M. Gale, R. P. Linstead, and C. J. Timmons, *J. Chem. Soc.,* 123 (1957).

(20) M. V. Sargent and C. J. Timmons [*ibid.,* 2222 (1964)] report mp 132–133° for *cis*-dicyanostilbene and mp 199–204° (dependent on rate of heating) for *trans*-9,10-dicyano-9,10-dihydrophenanthrene.

(21) 1,2-Diiodostilbene, mp 206–207° dec, was prepared according to E. Fisher, *Ann.,* **211,** 233 (1882).

(22) G. I. Poos, J. Kleis, R. R. Wittekind, and J. D. Rosenan, *J. Org. Chem.,* **26,** 4898 (1961).

mixture of diethyl ether–acetonitrile (100 ml). The mixture was kept stirred for 2 hr at −10° and for 3 hr at 10–20°. It was then mixed with ether (100 ml), successively washed with water, sodium bicarbonate solution, and water, dried, and concentrated under vacuum (35°). The brown residual solid was chromatographed over silica gel. Ether–petroleum ether (30–60°) mixtures (1:1 and 2:1) eluted pale yellow glistening crystals of phenylpropiolyl azide (1.6 g, 30.8%): mp 51–52°;[9] ν_{max} (CCl$_4$) 2210 (s, –C≡C–), 2130 (s, –N$_3$), and 1680 cm^{-1} (s, C≡CC=O); nmr (CCl$_4$) multiplet centered at δ 7.42 (C$_6$H$_5$).

Elutions with benzene and chloroform gave an unidentified polymeric liquid.

Photolysis of Phenylpropiolyl Azide. A solution of the azide (1.03 g, 6 mmole) in methylene chloride (400 ml) was irradiated at 3000° for 10 hr as the reaction was monitored by ir. The solution was concentrated and the brown residue was chromatographed over silica gel. Elutions with 1:1 and 2:1 benzene–hexane mixtures gave a pale yellow liquid (50 mg) which upon gc analysis was found to contain phenylacetonitrile (3%) and two other unidentified components. Further elutions with 3:1 benzene–hexane mixture and

pure benzene gave pale yellow glistening crystals of 9,10-dicyanophenanthrene (22 mg, 3.2%), mp and mmp 288–289°. Chloroform elution gave intractable tarry material.

Addition of Iodine Isocyanate to Phenylethynyl Bromide. Iodine (5.08 g, 20 mmole) was added to a well-stirred slurry of silver cyanate (4.05 g, 27 mmole) in tetrahydrofuran (80 ml) cooled to −30°. The temperature was maintained for 90 min as nitrogen was flushed through the reaction mixture. Then phenylethynyl bromide (3.6 g, 20 mmole) was added and the mixture was stirred for 5 hr at room temperature. The reaction mixture was filtered and the filtrate was concentrated. The concentrate having ir absorption at 2260 cm^{-1} (N=C=O) was dissolved in methanol (20 ml) and left overnight. Methanol was then removed under vacuum, the residue was extracted in ether (100 ml), washed with sodium thiosulfate solution and water, dried, and concentrated. The concentrate was chromatographed over alumina. Mixtures of hexane–benzene eluted colorless crystals of α,β-diiodo-β-bromostyrene (2.8 g, 33%), mp 62–62.5°. Chloroform eluted an intractable resinous liquid (0.45 g). A yellow polymeric material on top of the column was not eluted by ethanol.

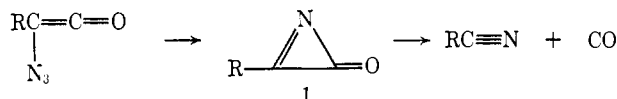# Additions to Bromophenylethyne[1]

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Abstract: Addition of IN$_3$ to bromophenylethyne (**2**) led to an unstable adduct **3**, whose structure was indicated as 1-azido-2-bromo-2-iodo-1-phenylethyne by conversion to acetophenone. Hydration of **2** was also shown to proceed regiospecifically leading to phenacyl bromide, thus suggesting the intermediacy of an α-phenylvinylcarbonium ion. Pyrolysis of IN$_3$ adduct **3** produced *trans*-dicyanostilbene (**5**) in 60% yield. Attempts to trap phenylcyanocarbene, a likely intermediate in this reaction, were unsuccessful. Reaction of **3** with aniline produced N,N'-diphenylbenzamidine (**11**) as the major product. The BrN$_3$ adduct of **2** also reacts with aniline to form **11**. The likelihood of azirine intermediates in the above reactions is suggested.

Azirinones **1** (azacyclopropenones) represent a ring system of theoretical and synthetic interest.[2] Attempts to prepare this small ring heterocycle have led so far only to isolation of nitriles and CO suggesting the possible instability of **1** with respect to these products.[2]

$$RC=C=O \;\;\rightarrow\;\; \underset{1}{\text{(azirinone)}} \;\;\rightarrow\;\; RC\equiv N \;+\; CO$$

An alternate entry into this system could be provided by the hydrolysis of a dihaloazirine, analogous to formation of cyclopropenones.[3] Addition of iodine azide to bromophenylethyne (**2**) should produce the required intermediate **4** since photolysis or pyrolysis of vinyl azides is known to furnish azirines.[4] Dihaloazirines (*e.g.*, **4**) would also be expected to lead to the theoretically interesting[3] 2 π-electron azirinium ion **7**.

Bromophenylethyne (**2**) gave an IN$_3$ adduct but pyrolysis of the latter in dry refluxing diglyme produced *trans*-dicyanostilbene (**5**) as the only insoluble product

(1) Stereochemistry. XLV. For the previous paper in this series, see A. Hassner and Foboerwinkle, *Tetrahedron Lett.*, in press.

(2) A. Hassner, R. J. Isbister, R. B. Greenwald, J. T. Klug, and E. C. Taylor, *Tetrahedron*, 25, 1637 (1969).

(3) (a) R. Breslow, L. J. Altman, A. Krebs, E. Mohacsi, I. Murata, R. A. Peterson, and J. Posner, *J. Am. Chem. Soc.*, 87, 1326 (1965); (b) S. W. Tobey and R. West, *ibid.*, 86, 4215 (1964).

(4) (a) G. Smolinsky, *J. Org. Chem.*, 27, 3557 (1962); (b) A. Hassner and F. W. Fowler, *J. Amer. Chem. Soc.*, 90, 2869 (1968).

$$C_6H_5C\equiv CBr \;+\; IN_3 \;\longrightarrow\; \underset{3}{C_6H_5\overset{|}{\underset{N_3}{C}}=CBrI} \;\longrightarrow$$
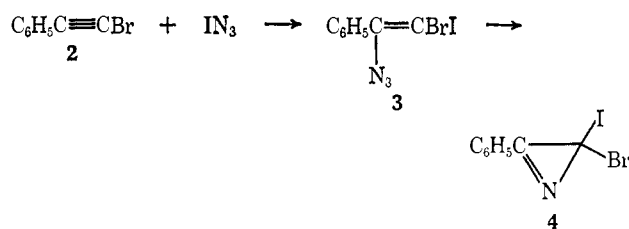
in 60% yield. The structure of **5** was confirmed by its hydrolysis to diphenylmaleic anhydride. At the same time, Boyer and coworkers[5] independently prepared the IN$_3$ adduct of **2** and observed its transformation to **5** on heating with zinc. They first interpreted these results to indicate the regioisomeric[6a] structure **6** for the IN$_3$ adduct from which IBr elimination with zinc produced azidophenylethylene (**10**). Loss of nitrogen from the latter was assumed to give phenylcyanocarbene (**9**) which on reaction with **10** would lead to **5**.

Since little is known about the regiochemistry of electrophilic additions[6b] to haloalkynes, we decided to provide a structure proof (**3** or **6**) for the IN$_3$ adduct of **2**. By studying the mercuric ion catalyzed hydration of bromophenylethyne (**2**) which yielded exclusively

(5) J. H. Boyer, *Chem. Eng. News*, 45, No. 41, 52 (1967). Subsequently, J. H. Boyer and R. Selvarajan [*J. Am. Chem. Soc.*, 91, 6122 (1969)] also found evidence that the IN$_3$ adduct possessed structure **3**.

(6) Regio is used to denote direction: A. Hassner, *J. Org. Chem.*, 33, 2684 (1968). (b) See A. Hassner, R. J. Isbister, and A. Friederang, *Tetrahedron Lett.*, 2939 (1969).