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, $-C{\equiv}C-$), 2130 (s, $-N_3$), and 1680 cm^{-1} (s, $C{\equiv}CC{=}O$); nmr (CCl_4) multiplet centered at δ 7.42 (C_6H_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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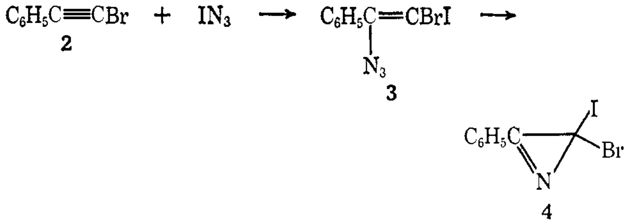
Contribution from the Department of Chemistry, University of Colorado, Boulder, Colorado. *Received May 12, 1969*

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]

1

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 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 azidophenylethyne (**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

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(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).

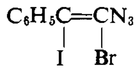
(3) (a) R. Breslow, L. J. Altman, A. Krebs, E. Mohacsi, I. Murata, R. A. Peterson, and J. Posner, *J. Am. Chem. Soc.*, **87**, 1326 (1965); (b) S. W. Tobey and R. West, *ibid.*, **86**, 4215 (1964).

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

(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) (a) 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).

phenacyl bromide we obtained the first indication that electronically the vinyl carbonium ion is preferred next



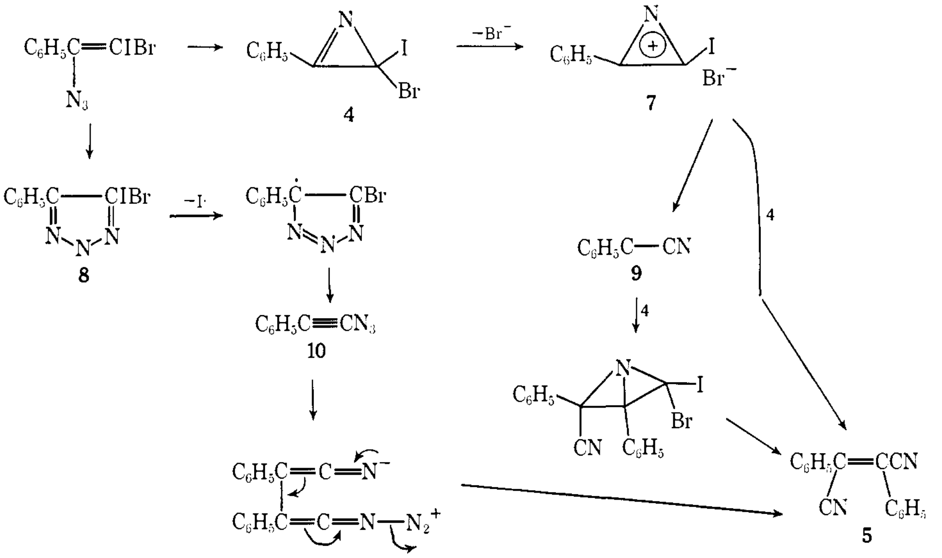
$$\underset{\text{I}}{C_6H_5C}{=}\underset{\text{Br}}{CN_3}$$

6

to phenyl rather than next to bromine. Furthermore, treatment of the IN_3 adduct of **2** with zinc in acetic acid–ether or in methanol produced acetophenone and unreacted adduct. Careful examination of the zinc reduction product by tlc and comparison with authentic phenyl acetic acid showed the absence of the latter acid, a product expected from reduction of **6**. We were able to show that reductive hydrolysis of vinyl azides as well as β-halovinyl azides with zinc provides conclusive proof for the location of the azide function.[6b]

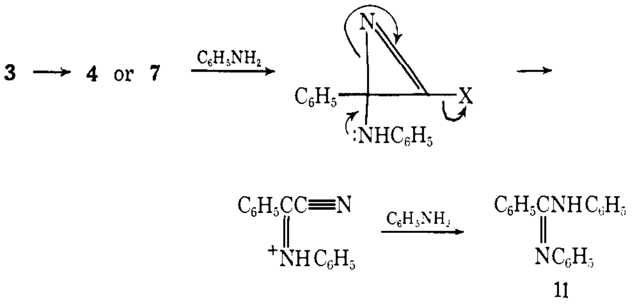
Possible pathways for the conversion of **3** to *trans*-dicyanostilbene (**5**) are shown in Scheme I. Since phenylcyanocarbene (**9**) is a likely intermediate in the formation of **5**, we attempted to trap it either with tolane or methanol. This carbene has been successfully trapped before using these reagents.[7,8] Pyrolysis of **3** in the presence of tolane led only to the isolation of **5** and the IBr adduct of tolane in 50% yield, indicating that IBr was formed in the decomposition of **3**. Treatment of **3** with zinc in methanol lead to formation of acetophenone in 74% yield. No methoxyphenylacetonitrile, which is known to result in good yield by trapping of carbene **9** with methanol,[8] was detected.

Scheme I

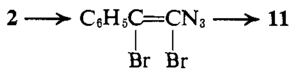


These results suggest that the intermediacy of **9** is unlikely or that **9** if formed is efficiently trapped, possibly by a molecule such as azirine **4**. Our experiments further indicate that zinc is not necessary for the conversion of the adduct **3** to dicyanostilbene **5**, thus suggesting a primary pyrolytic ring closure to **4** or **8**.[9]

Reaction of **3** with aniline at 40° produced N,N′-diphenylbenzamidine (**11**) as the major product and a small amount of benzanilide. By contrast, the reaction of β,β-dicyanovinylazides with aniline proceeds through rearrangement to a ketenimine.[10] Since cyanoimines are known to undergo substitution with aniline to yield amidines[11] the following pathway is suggested.



Free-radical addition of BrN_3 to **2** led to an adduct which detonated at 25° on concentration under vacuum. When the addition was carried out in the cold, followed by solvent evaporation at 0° and treatment with aniline, benzamidine **11** was isolated in 78% over-all yield. A mechanism similar to that shown for **3** → **11** is probably applicable, except that the starting adduct is expected to have structure **12** in view of the known regiochemistry of free-radical additions of BrN_3 to multiple bonds.[12] The conversion of both **3** and **12** to benzamidine **11** on treatment with aniline also suggests the formation of an azirinium ion intermediate **7**.



$$\mathbf{2} \longrightarrow \underset{\text{Br}}{C_6H_5C}{=}\underset{\text{Br}}{CN_3} \longrightarrow \mathbf{11}$$

12

Experimental Section[13]

1-Azido-2-bromo-2-iodo-1-phenylethene (3). Sodium azide (7.5 g) in 40 ml of CH_3CN was cooled to −15° and 9.15 g of ICl was

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(7) R. Breslow and C. Yuan, *J. Amer. Chem. Soc.*, 80, 5991 (1958).

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

(9) J. H. Boyer and R. Selvarajan, University of Illinois, Chicago Circle Campus (private communication), were able to trap **9** as methoxyphenylacetonitrile from the photolysis of 3-bromo-2-phenyltriazole or of phenylpropiolyl azide but not from the photolysis of **3** in methanol. Hence, we assume a different pathway for these reactions and favor conversion of **3** to **4**.

(10) I. Lengyel and J. C. Sheehan, *Angew. Chem. Intern. Ed. Engl.*, 7, 25 (1968).

(11) F. Koehnke and H. H. Stenernagel, *Chem. Ber.*, **96**, 486 (1963).

(12) A. Hassner and F. Boerwinkle, *J. Amer. Chem. Soc.*, **90**, 216 (1968).

(13) All melting points were determined on a Fisher-Johns melting point block and are uncorrected. Infrared spectra were recorded with a Beckman IR-5 spectrometer. Nuclear magnetic resonance spectra were recorded with a Varian A-60A spectrometer. Microanalyses were performed by A. Bernhardt, Mulheim, Germany.

added dropwise in 10 ml of CH_3CN. The mixture was allowed to stir in the cold for 30 min and the bromophenylethyne[14] (9.05 g, bp 54–55° (113 mm) was added in one portion and the flask wrapped in aluminum foil. The mixture was allowed to come to room temperature over a 14-hr period, poured into 100 ml of sodium thiosulfate (5%), and then extracted into 125 ml of ether in three portions. After washing four times with 2% of sodium thiosulfate, drying over $MgSO_4$, and evaporation of the bright yellow solution *in vacuo* without heating, an orange oil was obtained. This oil was chromatographed on 400 g of silica gel, eluting with pentane. The first few fractions contain unreacted starting material followed by 12.77 g (88%) of a clear yellow oil that solidified at *ca.* −10°; ir 2123, 1626, 1585, 1295 cm^{-1}. The product darkens rapidly on standing.

Pyrolysis of 3. A. In Diglyme. Adduct **3** (7 g) was added dropwise to 75 ml of stirred refluxing dry diglyme while the solution turned blood red. Immediately following addition, the solution was poured into 600 ml of ice cold 2% sodium thiosulfate solution. The decolorized mixture was extracted with CH_2Cl_2. The dried extract was evaporated *in vacuo* to give an amber oil which solidified. Crystallization from acetone–pentane yielded 1.37 g (60%) of *trans*-dicyanostilbene, mp 156° (lit.[15] mp 161°). It was converted by basic hydrolysis ($NaOH/MeOH/H_2O$) to diphenylmaleic anhydride, mp 143–145° (lit.[16] mp 156°), identical by ir with authentic material.

Similar results were obtained on heating **3** with zinc dust in refluxing benzene or ethanol.

B. In Tolane. Tolane (10 g) was melted on a steam cone and 5 g of IN_3 adduct **3** was added dropwise to the hot melt. The reaction was exothermic and the flask was removed from the heat. The residue was extracted with ether leaving 2.73 g of material: mp 230°, identified as *1-bromo-2-iodostilbene* (50% yield); ir 768, 692, 645 cm^{-1}; crystallized from $CHCl_3$, mp 232°.

Anal. Calcd for $C_{14}H_{10}BrI$: C, 43.66; H, 2.62. Found: C, 43.74; H, 2.56.

The ether solution was washed with 5% sodium thiosulfate solution, dried over $MgSO_4$, and the solvent removed *in vacuo*. The residue was then chromatographed on aluminum oxide. Skellysolve A–benzene (1:1) eluted unreacted tolane, 8.45 g; benzene–CH_2Cl_2 (3:1) eluted *trans*-dicyanostilbene, 0.71 g; mp 155–160°, 45% yield based on IN_3 adduct **3**.

Reductive Hydrolysis of 3. A. Using Zn–HOAc. To 100 ml of ether and 25 ml of HOAc cooled to −15° was added 1 g of zinc dust followed by dropwise addition of 5 g of **3** to the stirred solution. The reaction mixture was kept cold for 3 hr and then allowed to equilibrate to room temperature. Water (300 ml) was added and after additional stirring the mixture was extracted with ether. The ether solution was washed with saturated $NaHCO_3$ and dried ($MgSO_4$). Removal of the solvent *in vacuo* yielded 1.97 g of a brown oil. This oil (1 g) was chromatographed on 80 g of silica gel, yielding phenylbromoethyne (17 mg), starting material (770 mg), and acetophenone (88 mg), identified by ir comparison with an authentic sample.

Adduct **3** was recovered unchanged (90%) upon treatment with H_2SO_4–H_2O–ether (4:1:25) for 45 min at 25°.

B. Using Zn–Methanol. Stirring of 0.5 g of **3** with 1 g of zinc dust, 14 ml of methanol, and 1 ml of water for 3 days at 25° gave after work-up 210 mg of an oil containing acetophenone (74% by nmr) which was isolated by thick layer chromatography on buffered (pH 7) silica gel (elution with CH_2Cl_2). Tlc of the crude product showed no indication of phenylacetic acid by comparison with tlc of known material.

Hg-Catalyzed Hydration of Bromophenylethyne (2). To 2.5 g of the alkyne **2** in 5 ml of (95%) of EtOH was added 1 g of HgO and then 4 ml of concentrated H_2SO_4 was added dropwise with stirring. Work-up with water yielded 2.34 g of pale green solid, mp 37–44° (86%). Crystallization from MeOH furnished pure phenacyl bromide, mp 44–46° (lit.[17] mp 50°).

Reaction of Bromophenylethyne (2) with BrN_3 Followed by Aniline. Bromophenylethyne (4.52 g), dissolved in 50 ml of pentane and purged with N_2, was added to a solution of BrN_3, which was prepared by adding 4 g of bromine to a stirred slurry of 16 g of NaN_3, 13 ml of H_2O, and 50 ml of pentane purged with nitrogen and then decanted. The reaction mixture was kept cold (0°) and irradiated with a 150-W incandescent lamp. After 90 min, the color of the solution had changed from brown to cloudy yellow. The solution was filtered through a glass wool plug. Attempts to obtain the BrN_3 adduct **12** by evaporation led to an explosion. The above solution was added to 15 ml of reagent aniline and the pentane removed *in vacuo* at 0°. The aniline solution was then warmed to 40° for *ca.* 1 hr, *in vacuo*, and the resulting residue was extracted with pentane. The pentane insoluble residue yielded 1.424 g of diphenylbenzamidine (**11**): mp 143–145° (lit.[11] mp 145–146°); ir 3311, 1621, 1585, 1531 cm^{-1}; nmr τ 2.6–3.1. Addition of D_2O changes the splitting pattern.

Mass spectral analysis of the benzamidine salt gave a benzamidine molecular ion peak at *m/e* 272. The pentane extracts were evaporated to yield 1.15 g of aniline identified by ir comparison with an authentic sample.

The ethereal filtrate was saturated with HCl and the solids were filtered. Following evaporation of the ether and clarification with Woelm neutral alumina, 3.19 g of bromophenylethyne was obtained. The yield of the benzamidine **11**, based on alkyne consumed, was 78%. On exposure to aniline under the same conditions bromophenylethyne was recovered unchanged.

Reaction of 3 with Aniline. Treatment of 1.0 g of **3** with 1.86 g of aniline at 40° for 75 min and work-up as described above led to isolation of pentane insoluble diphenylbenzamidine (**11**, 65 mg, mp 143–145°) and 650 mg of unreacted **3**. Further treatment of this material with 2 ml of aniline for 20 hr at 40° produced 250 mg of **11** and 80 mg of benzanilide, recrystallized from $CHCl_3$–pentane, mp 161–163° identical with authentic material.

Acknowledgment. We are grateful to the National Science Foundation for support of this work through Grant GP-8675.

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(14) Prepared by a modification of the procedure of S. Miller, G. R. Ziegler, and R. Wieleseck, *Org. Syn.*, **45**, 86 (1965), using a Morton flask with efficient stirring instead of a mechanical shaker.

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

(16) A. T. Blomquist and E. A. LaLancette, *J. Amer. Chem. Soc.*, **83**, 1387 (1961).

(17) "Handbook of Chemistry and Physics," 47th ed, The Chemical Rubber Publishing Co., Cleveland, Ohio, 1966.