2-Methyl-1,2,3,4-tetrahydroisoquinoline (3).11 2-Methylisoquinolinium iodide (5.4 g; 0.020 mol) was reduced with sodium borohydride (5.0 g; 0.13 mol) in 500 ml of methanol plus 10 ml of water essentially as described in the literature.<sup>11</sup> 2-Methyl-1,2,3,4-tetrahydroisoquinoline (2.5 g; 86%) was obtained as a colorless oil, bp 55-58° (0.5 mm). The hydrochloride melted at 226-228° [lit.14 228°]

Iodimetric Analysis for Dihydroisoquinoline. Freshly distilled material was used routinely for the assay, which was done under nitrogen. A carefully weighed sample (50-100 mg) of the reduced isoquinoline was dissolved in 10 ml of absolute alcohol and was transferred quantitatively with the help of several 2-ml volumes of solvent to 20.0 ml of a standardized solution of iodine (0.5-1.0 g) in absolute ethanol. The mixture in a stoppered flask was stirred magnetically for 40 min at room temperature. Solid potassium iodide (1.0 g) and sodium bicarbonate (0.5 g) were then introduced followed by 100 ml of water and an excess of standard 0.1 N sodium thiosulfate. After 10 min of stirring, the colorless solution was back-titrated with standard iodine to a pale-blue starch end point.

When pure 2-methyl-1,2,3,4-tetrahydroisoquinoline was analyzed with this procedure, it required  $2.02 \pm 0.01$  mol of iodine per mole of substrate. Pure 2-methyl-1,2-dihydroisoquinoline, if available, would consume 1.00 mol of iodine per mole. One exceptional batch of dihydroisoquinoline required  $1.02 \pm 0.03$  mol and so was practically homogeneous. All other samples absorbed between 1 and 2 mole of iodine per mole, from which result the composition could be directly obtained.

2,2-Dimethyl-1,2-dihydroisoquinolinium Iodide (4). Methyl iodide (3.0 g; 0.02 mol) was added slowly to a stirred solution of 2methyl-1,2-dihydroisoquinoline (1.5 g) in 5 ml of acetonitrile. The mixture was stirred under nitrogen at room temperature for 1 day. The yellow precipitate was collected, washed with a little alcohol, and dried to give the 2,2-dimethyl compound 4 (1.0 g), mp 158.5-159.5°. Crystallization from ethanol did not change the melting point.

Anal. Calcd for C11H14IN: C, 46.01; H, 4.91; I, 44.19; N, 4.88; (CH<sub>3</sub>)<sub>2</sub>N, 10.45. Found: C, 46.00; H, 5.00; I, 44.35; N, 5.00; N-methyl, 10.43.

2,2-Dimethyl-1,2,3,4-tetrahydroisoquinolinium Iodide (5) from Tetrahydroisoquinolinium Iodide (3). A solution of 2methyltetrahydroisoquinoline (0.3 g) and methyl iodide (0.35 g) in benzene (5 ml) was refluxed for 5 min. The solid deposited from the cooled mixture was crystallized from alcohol to give yellow crystals of 2,2-dimethyltetrahydroisoquinolinium iodide (5), mp 188–189° (sinter 183°) [lit.<sup>15</sup> mp 189°]. Anal. Calcd for  $C_{11}H_{16}IN$ : C, 45.69; H, 5.58. Found: C, 45.77; H,

5.58

2,2-Dimethyl-1,2,3,4-tetrahydroisoquinolinium Iodide (5) from Dihydroisoquinolinium Iodide 4. A solution of dihydro compound 4 (71 mg; 0.25 mmol) in 15 ml of 1:1 water-alcohol was stirred under hydrogen at room temperature with the catalyst prereduced from 60 mg of platinum oxide. After 4 hr, 0.25 mmol of hydrogen had been absorbed; continued stirring resulted in no further uptake. Removal of catalyst and solvent left 70 mg of 2,2-dimethyl-1,2,3,4-tetrahydroisoquinolinium iodide (5), mp 179-180°. Crystallization from alcohol gave material with mp 186-187° (sinter 174°). The mixture melting point with the same material prepared from the tetrahydroisoquinoline was 186-187° (sinter 175°); the infrared absorption spectra of the two iodides were identical.

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Registry No.-1, 3947-77-1; 2, 14990-40-0; 3, 1612-65-3; 3 HCl, 53112-33-7; 4, 53112-34-8; 5, 1637-45-2.

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- Starting material. We did not ry what appears to be an attractive preparation utilizing disobutylaluminum hydride.<sup>4</sup>
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cyclohexane 240 and 330 nm.<sup>4</sup> 2-Butyl-1,2-dihydroisoquinoline in alcohol shows  $\lambda_{max}$  235, 282, and 330 nm.<sup>1</sup>. The unsubstituted 1,2-dihydroisoquinoline has been reported with  $\lambda_{max}$  (CHCl<sub>3</sub>) 265, 280, and 320 nm; no 230 nm maximum appears in alcohol solvent.<sup>8</sup> 2,4-Dimethyl-1,2-dihydroisoquinoline shows  $\lambda_{max}$  (C2H<sub>2</sub>OH) 202, 241, and 334.<sup>9</sup> Since in protic solvent the immonium form of the dihydroisoquinolines could be created it would be desirable to study the effect of solvent on the ultrapresent, it would be desirable to study the effect of solvent on the ultra-

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# **Chemistry of Azoethenes and Azoethynes. I. Synthesis** of Phenylazoethynylbenzene and Its Derivatives

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1-(2-Hydroxynaphthylazo)hexyne was suggested as a reaction intermediate by Robson and Tedder.<sup>1</sup> Later Sladkov and coworkers reported the synthesis of electron-withdrawing-group-bearing arylazoethynylbenzenes by the reaction of arenediazonium chlorides in aqueous solution with silver acetylides.<sup>2</sup> Their procedure gave only poor to fair yields of the azoethynes among difficult-to-separate reaction product mixtures. The simplest compound of the series, phenylazoethynylbenzene (1) and the electron-dop-methoxyphenylazoethynylbennating-group-bearing zene (2) cannot be obtained by their method. We have now successfully synthesized 1, 2, and other arylazoethynylbenzenes (3-10) in fair to good yields (Table I) by a new procedure.

Our method involved the reaction of purified arenediazonium salts (chlorides or bromides) with silver phenylacetylide in alcohol-chloroform (eq 1). Compounds 1-10 thus obtained were easily purified by column chromatography.

$$\operatorname{ArN}_{2}^{*}X^{*} + \operatorname{AgC} \equiv \operatorname{CPh} \longrightarrow \operatorname{ArN} = \operatorname{NC} \equiv \operatorname{CPh} + \operatorname{AgX} (1)$$
  
1-10

Compounds 1-10 exhibit ir signals in the range 2160-2165 cm<sup>-1</sup> and nmr signals expected for the structures.<sup>3</sup> The mass spectra of these compounds all show a common fragmenation pattern (Scheme I), in agreement with the assigned structures.<sup>3</sup>

The uv spectra of 1-10 (Table I) show absorption in ethanol  $\lambda_{\text{max}}$  360-384 nm (with log  $\epsilon \sim 4$ ) attributed to the  $-N = NC = C - \text{group}^2$  The insertion of the -C = C - group



<sup>a</sup> Satisfactory analytical data ( $\pm 0.4\%$ ) for C, H, and N were obtained for all compounds listed in this table. <sup>b</sup> In ethanol. <sup>c</sup> By mass spectrometry. <sup>d</sup> 2 decomposes rapidly. <sup>e</sup> Sladkov and coworkers prepared 3 in 39%, 4 in 24%, and 6 in 26% yield.<sup>2</sup>

### Scheme I

$$(Ar - N = N - C \equiv C - Ph)^{+} \xrightarrow{-Ar^{+}} Ph - C \equiv C - N_{2}^{+} \xrightarrow{-N_{2}^{+}} \int_{\text{major path}} Ph - C \equiv C - N_{2}^{+} \xrightarrow{-N_{2}^{+}} \int_{\text{minor path}} Ph - C \equiv C^{+}$$

$$Ar - N_{2}^{+} \xrightarrow{-N_{2}^{-}} Ar^{+}$$

into the arylazobenzene structure produces a strong bathochromic shift (trans-azobenzene has  $\lambda_{\max}$  318 in ethanol<sup>4</sup>). The introduction of a group with +M effect produces a bathochromic shift whereas the introduction of a group with -M effect produces little change on the  $\lambda_{max}$  of 1. Qualitatively one expects the polarization of the -N=NC=Cgroup in the direction represented by structure la rather than by structure 1b for 1. The Hammett  $\sigma_p$  constants for the PhN=N group and the Ph group are 0.64 and  $-0.01 \pm$ 0.05, respectively;<sup>5</sup> the PhN=N group is stronger electronwithdrawing (stabilizes a negative charge better) than the Ph group. This should result in a higher electron density at  $C_1$  (the carbon on which the PhN=N group is attached) than at  $C_2$  (the carbon on which the Ph group is attached). Also, the Shoolery's effective nmr shielding constants for the Ph group and the PhC=C group are 1.82 and 1.65, respectively; the Ph group is stronger electron withdrawing than the PhC=C group. This should result in higher elec-



tron density at  $N_{2'}$  (the nitrogen on which the Ph group is attached) than  $N_{1'}$  (the nitrogen on which the PhC=C group is attached). Whether this extended conjugation results in a linear structure for the -N=NC=C- group or not is not certain at the present time.

Compounds 1-9 show a tendency to undergo thermal dimerization to give 2,5-diaryl-3,5-diphenyl-1,2,4,5-tetraazapentalenes, D1-D9, as reported by Simamura and coworkers.<sup>6</sup> A mechanism has been proposed by Grundman and coworkers for the dimerizations of arylazoethynylbenzenes and bis(arylazo)acetylenes, as shown in eq 2 for the dimerization of 1-9 to D1-D9.<sup>7</sup> Attempts to obtain dimer from the highly hindered 10 failed.



The reduction of 1-10 to any lazoethenylbenzenes will be reported in a separate article.<sup>8</sup>

## **Experimental Section**

Melting points were taken on a Köfler hot-stage apparatus and were corrected. The ir spectra were measured on a Perkin-Elmer Infrachord 137 spectrophotometer. The nmr spectra were determined using a Varian A-60 spectrometer. The uv spectra were determined using a Beckman DB spectrophotometer. Mass spectra were obtained on an AEI MS-9 mass spectrometer. Analyses were performed by Baron Consulting Co., Orange, Conn. Thin-layer chromatography was performed on 0.25-mm layers using silica gel GF 254 and PF 254 (Merck), Darmstadt, Germany. The silica gel used for column chromatography was obtained from Gerbrüder Herman, Köln, Germany. All solvents and reagents were purified according to standard procedures before use.

Compounds 1-10 were prepared and purified according to the general procedure described below.

Arylazoethynylbenzenes (1-10). To a solution of 10 mmol of silver nitrate in 250 ml of aqueous ethanol (75% by volume) at room temperature was added slowly with vigorous stirring a solution of 10 mmol of phenylacetylene in 25 ml of ethanol. The white silver phenylacetylide precipitated out was filtered, washed with water, and dried in vacuo. Meanwhile the arenediazonium halide (chloride or bromide) was prepared by slowly adding 12 mmol of n-butyl nitrite into a solution of 10 mmol of the corresponding aniline hydrohalide in 20 ml of ethanol at 0 to  $-5^{\circ}$  with vigorous stirring. The mixture was stirred for 15 min and was diluted with ether. The arenediazonium halide that crystallized out was filtered and washed with ether and then redissolved in 25 ml of ethanol. The dried silver phenylacetylide was suspended in 100 ml of chloroform at room temperature with vigorous stirring and the ethanolic arenediazonium halide was added dropwise. The orange mixture was stirred for 30 min and was filtered with the aid of a filter cell. The filtrate (tlc of which generally showed a major yellow-orange spot for 1-10 followed by a more polar fluorescent spot for D1-D9) was evaporated in vacuo and separated on a 300-g silica gel or Florisil column eluted with benzene and chloroform. The major yellow-orange fraction was collected and evaporated to give the arylazoethynylbenzenes 1-10. The melting point, molecular weight, and spectroscopic data are listed in Table I.<sup>3</sup>

A more polar fraction eluted from the column generally gave small amounts of D1-D9. Long time lag between preparation and separation resulted in the increased yields of D1-D9 at the expense of the yields of 1-9.

**Dimers D1-D9.** Solutions of 1-9 in cyclohexane were heated to reflux and the reactions were followed by tlc at regular time intervals. At the end of 24 hr, evaporation of solvent and separation on

a silica gel column gave pure D1-D9.3,6 The yields of D1-D9 ranged from 15% for D2 to 60% for D1. No dimer could be obtained by heating 10 under the same conditions.

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Registry No.-1, 53198-79-1; 2, 53198-80-4; 3, 5076-51-7; 4, 5076-52-8; 5, 53198-81-5; 6, 5076-53-9; 7, 53198-82-6; 8, 53198-83-7; 9, 53198-84-8; 10, 53198-85-9; phenylacetylene, 536-74-3.

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# A Convenient, High-Yield Conversion of Aldehydes to Nitriles

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We wish to report a new method for accomplishing the conversion of aldehydes to nitriles. There have been a number of methods reported for this transformation;<sup>1-6</sup> ours differs from these in the fact that the experimentalist need not isolate and purify the intermediate oxime or related aldehyde derivative, although he may do so if he wishes; the method therefore saves one step in the aldehyde-to-nitrile conversion. The method additionally features relatively mild reaction conditions as well as a convenient internal indicator for the extent of reaction.

The development of efficient amino protecting groups has facilitated the synthesis of a variety of sensitive com-

pounds, including O-substituted hydroxylamines.7 Although a number of these are highly unstable,<sup>8</sup> others have significant synthetic utility. Their electrophilic character has been exploited in their increasing use as aminating agents.<sup>9,10</sup> Their nucleophilicity has been demonstrated by their reaction with ketones to form substituted oximes which undergo facile Beckmann and Neber rearrange $ments.^{11}$ 

Our method makes use of one of these reagents, O-2,4dinitrophenylhydroxylamine (1), and proceeds according to eq 1 and 2.



The O-2,4-dinitrophenyloxime is formed by simply warming an alcoholic suspension of equivalent amounts of the aldehyde and 1 until the solution becomes homogeneous, followed by the addition of a few drops of mineral acid. The O-2,4-dinitrophenyloximes of aromatic aldehydes immediately precipitate from the reaction mixture and can be isolated by filtration after cooling. High yields of these materials have been obtained; their sharp melting points indicate that only one isomer is probably formed. Others have reported similar observations, and have presented evidence that the isomer formed is the Z isomer (syn isomer) about the C=N bond.<sup>12</sup> Higher yields of 2 can often be obtained by the addition of 1 vol of water to the reaction mixture before cooling. Elimination to form the nitrile is accomplished by warming a suspension of the Osubstituted oxime in alcohol with excess base until the mixture becomes homogeneous (method A). The development of a deep, yellow-to-red color of the 2,4-dinitrophenolate ion indicates the extent of completion of the reaction.

The aliphatic oxime derivatives in our hands do not precipitate from the reaction mixture; however, subsequent

| Table I |
|---------|
|---------|

| Results of Synthesis of O-2,4-Dinitrophenyloximes of Variou | us Aldehydes and Their Conversion to Nitriles |
|---|---|
|---|---|

| Aldehyde<br>(method)                   |                      |              |           |                             |             |                 |              | Nitrile |                             |             |                 |
|--|----------------------|--------------|-----------|-----------------------------|-------------|-----------------|--------------|---------|-----------------------------|-------------|-----------------|
|  | Registry<br>No.      | Sol-<br>vent | Mp,<br>°C | Lit.<br>mp, <sup>a</sup> °C | Yield,<br>% | Registry<br>No. | Sol-<br>vent | Mp, °C  | Lit.<br>mp, <sup>a</sup> °C | Yield,<br>% | Registry<br>No. |
| Benzaldehyde (A)                       | 100-52-7             | EtOH         | 143-145   | 145                         | 93          | 53188-15-1      | MeOH         |         |                             | 84          | 100-47-0        |
| <i>p</i> -Methoxybenz-<br>aldehyde (A) | 123-11-5             | EtOH         | 185-187   | 187                         | 91          | 53188-16-2      | MeOH         | 61-62   | 60-62                       | 91          | 874-90-8        |
| <i>p</i> -Bromobenz-<br>aldehyde (A)   | 1122-91-4            | EtOH         | 213-214   | 207                         | 85          | 53188-17-3      | MeOH         | 110–113 | 113                         | 89          | 623-00-7        |
| p-Nitrobenz-<br>aldehyde (A)           | 555-16-8             | EtOH         | 215-216   | 216                         | 91          | 53188-18-4      | EtOH         | 147-150 | 147-148                     | 94          | 619-72-7        |
| Piperonal (A)<br>Heptaldehyde (B)      | 120-57-0<br>111-71-7 | EtOH<br>MeOH | 194-195   | 196                         | .98         | 53188-19-5      | EtOH<br>MeOH | 92-93   | 92-93                       | $91^{b}$    | 629-08-3        |
| Undecylenic<br>aldehyde (B)            | 112-45-8             | EtOH         |           |                             |             |                 | EtOH         |         |                             | 93          | 53179-04-7      |

<sup>a</sup> For oximes, the melting point data are from ref 12a; for nitriles, the data are from Beilstein.<sup>b</sup> The product contained a trace of the starting aldehyde, as shown by infrared and by the diagnostic reaction with 4-amino-3-hydrazino-5-mercapto-1,2,4-triazole.12