in ΔJC_3 and ΔTNT_3^- is to refer to the displacement from the fast equilibrium, reaction 3, only. With the mass balance, eq 26, one arrives at eq 27. When eq 24, 26, 27, and 28 are inserted into eq 20, one obtains eq 9.

$$\Delta JC_3 = -\Delta TNT_3^- \tag{26}$$

$$\Delta TNT_3^- = -\frac{\Delta K_3[TNT][TNT^-]}{1 + K_3[TNT]} \tag{27}$$

$$[JC] = K_3[TNT][TNT^-] \tag{28}$$

$$\frac{\Delta OD}{OD} = \frac{\Delta K_3[TNT](\epsilon_{JC} - \epsilon_{TNT^-})}{(1 + K_3[TNT])(\epsilon_{TNT^-} + \epsilon_{JC}K_3[TNT])} \tag{9}$$

C. Amplitude of τ_2 when [TNT] $\gg$ [RO$^-$].—In this situation ΔTNT_2^- and ΔJC_2 which refer to the equilibration of the slow reaction 2 are given by eq 29 and 30 where ΔTNT_{2+3}^- and ΔJC_{2+3} are the total displacement of the concentrations from the final equilibrium state. Note that

$$\Delta TNT_2^- = \Delta TNT_{2+3}^- + \Delta TNT_3^- \tag{29}$$

$$\Delta JC_2 = \Delta JC_{2+3} - \Delta JC_3 \tag{30}$$

$$\Delta JC_2 = K_3[TNT]\Delta TNT_2^- \tag{31}$$

because with respect to reaction 2 equilibrium 3 is always established. This simplifies eq 20 to eq 32.

$$\frac{\Delta OD}{OD} = \frac{\Delta TNT_2^-}{[TNT^-]} \tag{32}$$

ΔTNT_{2+3}^- and ΔJC_{2+3} are given by eq 33 and 34, whereas eq 35 holds for the mass balance. Combining eq 33, 34, and 35, one gets eq 36. Thus by inserting eq 27 and 36 into eq 29 and dividing by [TNT$^-$], eq 32 becomes eq 8.

$$\Delta TNT_{2+3}^- = K_2[TNT]\Delta RO_{2+3}^- + \Delta K_2[TNT][RO^-] \tag{33}$$

$$\Delta JC_{2+3} = K_3[TNT]\Delta TNT_{2+3}^- + \Delta K_3[TNT][TNT^-] \tag{34}$$

$$\Delta TNT_{2+3}^- + \Delta RO_{2+3}^- + \Delta JC_{2+3} = 0 \tag{35}$$

$$\Delta TNT_{2+3}^- = \frac{\Delta K_2[TNT][RO^-] - K_2\Delta K_3[TNT]^2[TNT^-]}{1 + K_2[TNT] + K_2K_3[TNT]^2} \tag{36}$$

$$\frac{\Delta OD}{OD} = \frac{\Delta K_2}{K_2(1 + K_2[TNT] + K_2K_3[TNT]^2)} + \frac{\Delta K_3[TNT]}{(1 + K_3[TNT])(1 + K_2[TNT] + K_2K_3[TNT]^2)} \tag{8}$$

The Intermediacy of Phenylpropargylene and Phenylethynylnitrene[1]

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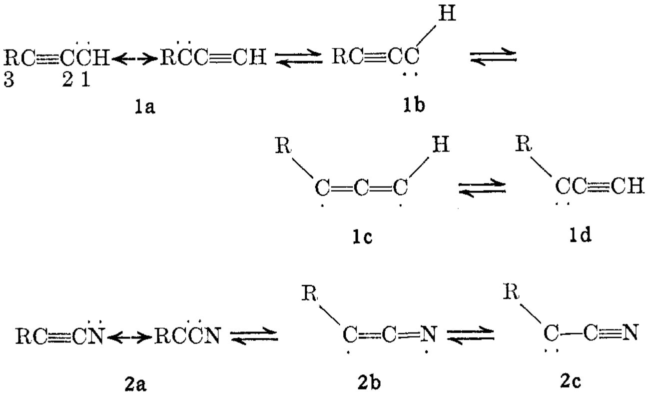
Diazomethane combines with phenylpropiolyl chloride to give 4-phenyl-1-diazo-3-butyn-2-one (**3**) and 3-chloroacetyl-4-phenylpyrazole (**4**). Phenylpropargylene (**1a**, R = C_6H_5), generated by irradiating the ketone **3**, abstracted hydrogen to produce benzylacetylene (**8**), phenylallene (**9**), and 1-methyl-2-phenylacetylene (**10**). Irradiation isomerized the allene **9** into the acetylene **8** but did not isomerize either of the acetylenes **8** and **10**. Phenylpropiolylcarbene (**5**) gave 4-phenyl-3-butyn-2-one (**7**) by hydrogen abstraction. A thermal Curtius reaction in different solvents transformed phenylpropiolyl azide (**11**) into phenylacetonitrile (**13**), but when the intermediate phenylethynyl isocyanate **12** was formed in aqueous ethanol it gave ethyl *N*-phenylacetylcarbamate (**15**) and *N*,*N*′-bisphenylethynylurea (**16**). A formal adduct between phenylpropiolylnitrene (**18**) and the isocyanate **12**, combined with ethanol, and subsequent isomerization gave 2-phenylethynyl-4- (or 5-) phenyl-5- (or 4-) carbethoxyaminooxazole (**17**) (tentative assignment). Irradiation of the azide **11** in methanol generated phenylethynylnitrene (**2a**, R = C_6H_5), which then reacted as phenylcyanocarbene (**2a**) to give α-methoxyphenylacetonitrile (**19**) by insertion and **13** by abstraction.

Centers of reactivity for propargylene (**1**, R = H) and ethynylnitrene (**2**, R = H) are displayed in formulas for respective resonance hybrids **1a** and **2a** and tautomers **1b–d** and **2b,c**; however, certain centers have such a low order of reactivity that they have not been detected. Propargylene and its methyl and phenyl derivatives, obtained by the photolysis of the appropriate diazopropyne, each showed electron paramagnetic resonance.[2] Triplet propargylene gave equal reactivity with olefins at C_1 and C_3. On the other hand, singlet propargylene reacted with olefins only at C_1, the position vacated by nitrogen.[2] Although phenylethynylnitrene (**2a**, R = C_6H_5) was presumed to have been initially formed from the irradiation of either phenylethynyl azide or phenylethynyl isocyanate, it reacted exclusively as phenylcyanocarbene (**2a**, R = C_6H_5).[3]

This report describes additional chemical properties pertaining to phenylpropargylene (**1a**, R = C_6H_5) and phenylethynylnitrene (**2a**, R = C_6H_5).



Diazomethane reacted with phenylpropiolyl chloride to give 4-phenyl-1-diazo-3-butyn-2-one (**3**) along with

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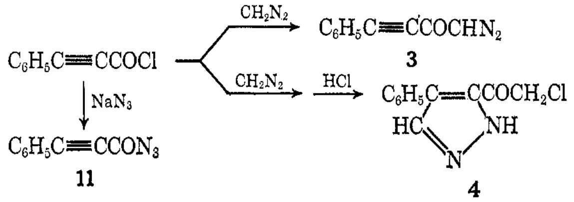
[1] Financial support was received from NASA Grant No. NGR-14-012-004.

[2] R. A. Bernheim, R. J. Kempf, J. V. Gramas, and P. S. Skell, *J. Chem. Phys.*, **43**, 196 (1965).

[3] J. H. Boyer and R. Selvarajan, *J. Amer. Chem. Soc.*, **91**, 6122 (1969).

4-phenyl-5(3)-chloroacetylpyrazole (**4**).[4] Attempts to find optimum conditions for the formation of the ketone **3** were not made; however, to minimize the reaction between hydrogen chloride and the diazoacetyl function, an excess of diazomethane was present.



Irradiation of the diazo ketone **3** in cyclohexane brought about the elimination of nitrogen and left the residue both as unrearranged phenylpropiolylcarbene **5** and as the rearranged phenylethynylketene **6**. Isolation of phenylethynyl methyl ketone **7** offers diagnostic evidence for the intermediacy of the carbene **5** and its abstraction of hydrogen. Differentiation between a rearrangement of the carbene **5** and a rearrangement simultaneous with the release of nitrogen from **3** was not attempted. To account for the generation of phenylpropargylene (**1a**, R = C_6H_5), it is assumed that the undetected ketene underwent photoelimination of carbon monoxide. Again products of hydrogen abstraction confirmed the intermediacy of a carbene. Benzylacetylene (**8**) was generated from **1a** and/or **1d** (R = C_6H_5), while phenylallene (**9**) and methyl-2-phenylacetylene (**10**) were similarly generated from **1a** and/or **1c** and from **1a** and/or **1b** (R = C_6H_5), respectively. It was considered unlikely that either acetylene **8** or **10** could be the photo precursor of the other since independent irradiation of each did not bring about isomerization to a detectable extent. While photoisomerization of the allene **9** did afford benzylacetylene (**8**), not a trace of 1-methyl-2-phenylacetylene (**10**) could be found.[5] It is therefore concluded that the allene **9** could not be a required photo precursor of the acetylenes. It is of interest that products of carbene insertion into cyclohexane CH bonds were not found for either carbene **5** or **1** (R = C_6H_5); however, several minor products detected by gc have remained unidentified.

$$\mathbf{3} \xrightarrow[-N_2]{h\nu} \underset{\mathbf{5}}{C_6H_5C{\equiv}CCO\ddot{C}H} + \underset{\mathbf{6}}{C_6H_5C{\equiv}CCH{=}C{=}O}$$

$$\mathbf{5} \xrightarrow{C_6H_{12}} \underset{\mathbf{7}}{C_6H_5C{\equiv}CCOCH_3}$$

$$\mathbf{6} \xrightarrow[-CO]{h\nu} \mathbf{1}\ (R = C_6H_5)$$

$$\mathbf{1a}\text{ and/or }\mathbf{1d} \xrightarrow{H} \underset{\mathbf{8}}{C_6H_5CH_2C{\equiv}CH}$$

$$\mathbf{1a}\text{ and/or }\mathbf{1c} \xrightarrow{H} \underset{\mathbf{9}}{C_6H_5CH{=}C{=}CH_2}$$

$$\mathbf{1a}\text{ and/or }\mathbf{1b} \xrightarrow{H} \underset{\mathbf{10}}{C_6H_5C{\equiv}CCH_3}$$

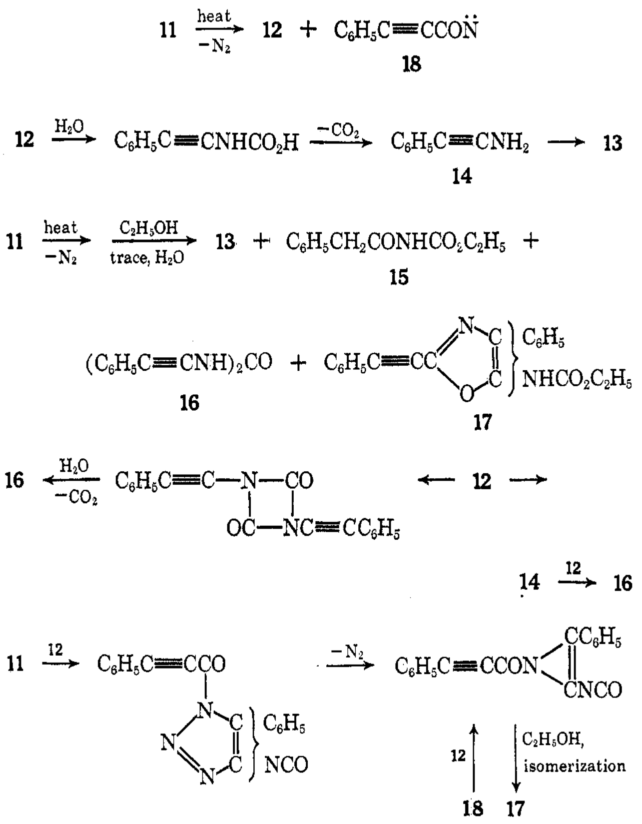
The photolysis of phenylpropiolyl azide (**11**) parallels the photolysis of the diazo ketone **3** insofar as the intermediacy of phenylethynyl isocyanate (**12**) and the ketene **6**, respectively, are required. Furthermore both intermediates apparently underwent photoelimination of carbon monoxide; however, the nitrene, produced from the isocyanate **12**, apparently reacted only as its isomer, phenylcyanocarbene (**2a,c**, R = C_6H_5).[3]

$$\mathbf{11} \xrightarrow[-N_2]{h\nu} \underset{\mathbf{12}}{C_6H_5C{\equiv}CNCO} \xrightarrow[-CO]{h\nu} \mathbf{2}\ (R = C_6H_5) \xrightarrow{H} \underset{\mathbf{13}}{C_6H_5CH_2CN}$$

Further comparison between the diazo ketone **4** and the azide **11** was attempted by an investigation of their thermal reactions. When copper-catalyzed pyrolysis of the diazo ketone **3** gave only intractable material, this portion was dropped and the dark chemistry of the azide was reinvestigated.

Curtius and Kenngott obtained phenylacetonitrile (**13**) in unspecified low yield on pyrolysis of phenylpropiolyl azide in either dry ether, benzene, or carbon tetrachloride.[6] Without establishing the source of methylene hydrogen, they recognized that hydrolysis of isocyanate **12** followed by decarboxylation and tautomerization of phenylethynylamine (**14**) (Scheme I) could account for the product and, accordingly assumed the presence of trace amounts of water. In a similar reaction brought about by irradiation of phenylpropiolyl azide in anhydrous methylene chloride, the formation of phenylacetonitrile was attributed to hydrogen abstraction by phenylcyanocarbene.[3] Without

SCHEME I



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[4] A. Nabeya, F. B. Culp, and J. A. Moore, *J. Org. Chem.*, **35**, 2015 (1970), reported **4**, mp 185° (darkening). An ir spectrum (private communication) proved to be identical with the spectrum obtained in this work. See also A. Nabeya and J. A. Moore, *ibid.*, **35**, 2022 (1970).

[5] Photoisomerization of an allene had not been previously observed. D. R. Taylor, *Chem. Rev.*, **67**, 317 (1967), discussed base-catalyzed and thermal (catalytic) isomerization of allenes into internal (disubstituted) acetylenes.

[6] Th. Curtius and E. Kenngott, *J. Prakt. Chem.*, **112**, 314 (1926).

invoking an unprecedented facile thermal elimination of carbon monoxide from an isocyanate, the present work supports the dark formation of phenylacetonitrile by the sequence of reactions initiated by hydrolysis of the isocyanate; however, the source of trace amounts of water was not established. Following pyrolysis of a 1% solution of the azide in anhydrous benzene and removal of excess solvent *in vacuo,* gc separation of the residue isolated the nitrile in 2.45% yield. A marked increase to 21.5% was established for the reaction of a 10% solution of the azide in benzene subsequently treated with ethanol after nitrogen evolution had ceased. A confirmation of the intermediacy of the isocyanate was found in the latter experiment in the formation of ethyl *N*-phenylacetylcarbamate (**15**) which required both hydration of the acetylenic function and addition of ethanol to the isocyanate function. Furthermore hydration of the isocyanate **12**, perhaps in the form of its uretidinedione dimer, is apparently required for the formation of *N,N′*-bisphenylethynylurea (**16**).[7]

Pyrolysis of phenylpropiolyl azide also gave a product tentatively assigned the structure of 2-phenylethynyl-4-(or 5-) phenyl-5- (or 4-) carbethoxyaminooxazole (**17**), which is supported by elemental analysis and nmr, ir, and mass spectra. Addition of either the azide **11** or the nitrene **18** to an acetylenic bond followed by nitrogen evolution if necessary and ring expansion through valence isomerization would account for its formation.

Failure to find either the carbamate **15**, or urea **16**, or oxazole **17** in the reaction mixture obtained by irradiation of phenylpropiolyl azide in methylene chloride[3] indicates that phenylethynylamine (**14**) was not formed. On the other hand, an unambiguous diagnostic test for intermediacy of phenylcyanocarbene is based on the formation of an insertion product. Photolysis of the azide **11** in methanol produced a mixture which contained α-methoxy-α-phenylacetonitrile (**19**), the result of carbene insertion into the methanolic hydroxyl bond. Methyl phenylpropiolate (**20**), produced by solvolysis of the azide **11**,[8] as well as phenylacetonitrile (**13**) and methyl phenylacetylcarbamate (**21**) were also found.

$$\mathbf{11} \xrightarrow[\mathrm{CH_3OH}]{h\nu} \mathbf{13} + \underset{\mathbf{19}}{\mathrm{C_6H_5CH(CN)OCH_3}} + \underset{\mathbf{20}}{\mathrm{C_6H_5C{\equiv}CCO_2CH_3}} + \underset{\mathbf{21}}{\mathrm{C_6H_5CH_2CONHCO_2CH_3}}$$

Experimental Section[9]

4-Phenyl-1-diazo-3-butyn-2-one.—A solution of phenylpropiolyl chloride[10] (8.2 g, 50 mmol) in diethyl ether (50 ml) was added dropwise to a stirred and cooled (5°) solution of diazomethane (6.0 g, 140 mmol) in ether (600 ml). After the solution was left overnight at room temperature, a clear yellow solution was separated from an unknown red resinous material by decantation and the solvent was removed under vacuum at 20°. A pale yellow residue (10.2 g) was purified by chromatography over a column of silica gel. A mixture, diethyl ether–petroleum ether, bp 30–60° (1:2, 1.2 l.), eluted pale yellow crystals of 4-phenyl-1-diazo-3-butyn-2-one (3.6 g, 42.5%): mp 54–54.5° (diethyl ether–petroleum ether, bp 30–60°); ν max (CCl_4) 2200 (s, C≡C), 2100 (vs, N_2), and 1615 cm^{-1} (vs, >C=O); λ max (MeOH) 218 nm (ε 14,290), 285 (16,630), and 307.5 (21,330); nmr ($CDCl_3$) δ 5.50 (s, broad, 1 H, $O{=}CCHN_2$) and 7.48 (m, 5 H, phenyl). *Anal.* Calcd for $C_{10}H_6N_2O$: C, 70.59; H, 3.53; N, 16.47. Found: C, 70.58; H, 3.63; N, 16.67.

Elution with a 1:1 mixture of diethyl ether–petroleum ether, bp 30–60° (1.2 l.), afforded colorless crystals of 3(5)-chloroacetyl-4-phenylpyrazole (1.25 g, 11.4%): mp 202–203° dec (ethyl acetate–hexane); ν max (KBr) 3230 (vs, broad, >NH), and 1680 cm^{-1} (vs, α,β-unsaturated carbonyl); nmr [$(CD_3)_2SO$] δ 5.12 (s, 2 H, $O{=}CCH_2Cl$), 7.50 (m, 5 H, phenyl), and 8.20 (s, 1 H, H-3(5)); mass spectrum *m/e* 222 and 220 (intensity ratio 1:3, M^+), 185 $(M - Cl)^+$, 171 $(M - CH_2Cl)^+$, 144, 143 $(M - COCH_2Cl)^+$, and 143 $(M - C_6H_5)^+$. *Anal.* Calcd for $C_{11}H_9N_2OCl$: C, 60.01; H, 4.09; N, 12.73. Found: C, 59.87, 59.86; H, 4.10, 4.15; N, 12.73.

Further elution with different solvents gave only an intractable resinous mixture.

Photolysis of 4-Phenyl-1-diazo-3-butyn-2-one in Cyclohexane.—A solution of the diazo ketone (0.68 g, 4 mmol) in anhydrous cyclohexane (200 ml) was irradiated at 300 nm while the reaction was monitored by ir. After 53 hr of irradiation the solution had turned dark brown and a coating had deposited on the walls of the reaction vessel. A weak ir absorption characteristic of the diazo function still persisted. The solution was concentrated under vacuum (45°) and the dark brown residue (0.43 g) was analyzed by gc (5% poly-*m*-phenyl ether, 6 ring, 6 ft by 0.25 in., 105°). Of the six volatile components three were identified, by comparison with their authentic gc retention times, to be benzylacetylene (trace), phenylallene (trace), and 1-methyl-2-phenylacetylene (3.66 mg, 0.95%, based on the recovered starting material).[11] Analysis by gc (Apiezon L, 10%) and mass spectra combination enabled identification of four components: 4-phenyl-3-butyn-2-one (**3**) (M^+ 144), benzylacetylene (**8**) (M^+ 116), phenylallene (**9**) (M^+ 116), and 1-methyl-2-phenylacetylene (**10**) (M^+ 116). The mass spectra of **8**, **9**, and **10** were identical.[12] Purification was attempted by chromatography over silica gel (12 in. × 1 in.). Elutions with a 1:1 mixture of hexane–benzene (1 l.) gave a pale yellow viscous liquid (21 mg): ν max (CCl_4) 2200 (s, C≡C), 1950 (m, >C=C=C<), 1750 (vs, >C=O), and 1680 cm^{-1} (s, >C=O); the presence of benzylacetylene, phenylallene, and 1-methyl-2-phenylacetylene was detected by gc.

Further elutions with benzene (400 ml) gave the unreacted 4-phenyl-1-diazo-3-butyn-2-one (110 mg, 16.2%). Elutions with different solvents afforded a dark brown resinous material which was not characterized further.

Photolyses of 1-Methyl-2-phenylacetylene, Phenylallene, and Benzylacetylene.—In quartz test tubes, solutions of 1-methyl-2-phenylacetylene[11] (80 mg, 0.69 mmol), phenylallene[11] (32.5 mg, 0.28 mmol), and benzylacetylene[11] (75 mg, 0.65 mmol) in anhydrous cyclohexane (18 ml) were separately irradiated at 300 nm under nitrogen while the reactions were monitored by gc. After 96 hr of irradiation the solutions were analyzed by gc (5% poly-*m*-phenyl ether, 6 ring, 6 ft × 0.25 in., 105°); unreacted 1-methyl-2-phenylacetylene (28 mg, 35%) and benzylacetylene (61 mg, 80%) but no isomerization of either was detected. The reaction mixture from phenylallene contained benzylacetylene (2.3 mg, 7.4%), unreacted phenylallene (4.6 mg, 1.47%), and an unidentified oil, apparently polymeric, which was the major component. Intractable material was found de-

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[7] This appears to be the first example of a CNH atom sequence in which C is acetylenic. This assignment is based on ir, uv, nmr, and mass spectra and elemental analysis data (see Experimental Section). Tautomers, which require the presence of a ketenimine function, and nitrile isomers conceivably produced by rearrangement of ketenimines are not allowed by the data.

[8] Upon standing overnight cinnamoyl azide in ethanol gave ethyl cinnamate in a similar solvolysis.

[9] By flushing nitrogen for 12 hr the solvent was degassed in each case and photolyses were carried out at 35° under nitrogen in quartz vessels placed in Rayonet chamber reactor equipped with 16 low-pressure mercury lamps. Instrumental data were obtained from a Perkin-Elmer 237-B infrared spectrophotometer, a Cary-14 ultraviolet spectrometer, a Varian A-60A nmr spectrometer, and a Varian-Aerograph 1800 gas chromatograph. All yields are based on recovered starting material.

[10] Phenylpropiolyl chloride was obtained from Columbia Organic Chemicals Co., Inc., Columbia, S. C.

[11] Synthesis of benzyl acetylene following the procedure of J. R. Johnson and W. L. McEwen, *J. Amer. Chem. Soc.*, **48**, 469 (1926), led to a mixture of benzylacetylene, phenylallene, and trace quantities of two unidentified compounds. Preparative gc (30% SE-30, 20 ft × 0.37 in., 165°) gave pure samples of benzylacetylene (34%) and phenylallene (3.5%). 1-Methyl-2-phenylacetylene was commercially available.

[12] K. B. Wiberg, W. J. Bartley, and F. P. Lossing, *ibid.*, **84**, 3980 (1962). Propyne, allene, and cyclopropene gave identical mass spectra due to one common cation, $C_3H_3^+$, the structure of which is believed to be the cyclic and symmetrical cyclopropenylium cation.

posited on the walls of the reaction vessel in each of the three photolytic reactions.

Pyrolysis of a 1% Solution of Phenylpropiolyl Azide (11) in Benzene.—The pale yellow solution of the azide (1.02 g, 6 mmol) in anhydrous benzene (100 ml) was heated with stirring for 4 hr at 65°. The dark brown solution was evaporated to dryness under vacuum and the brown residue (0.99 g) was analyzed by gc over Apiezon L (15%) and Carbowax (15%) columns. Two volatile components in trace amounts and phenylacetonitrile (17.1 mg, 2.45%) were detected. The above residue was dissolved in 50 ml of ethanol (unknown water content) and refluxed for 2 hr and left standing overnight. The solvent was removed and the residue was chromatographed over silica gel (12 in. × 1 in.).

Benzene–chloroform mixtures (4:1 and 3:1, 200 ml each) eluted colorless crystals of *N*,*N′*-bisphenylethynylurea (**16**) (32 mg, 4.1%): mp 240–241°; ν max (KBr) 3480 and 3380 (s, >NH), 2200 (s, C≡C), 1625 (s, amide I), 1575 (s, amide II), and 1300 cm^{-1} (m, amide III); λ max (CH_3OH) 250 nm (ε 50,320) 297 (11,610), 310 (10,480), and 350 (11,290); nmr [$(CD_3)_2SO$] δ 7.35 (m, phenyl); mass spectrum *m/e* 260 (M^+), 259, 242 $(M - H_2O)^+$, 232 $(M - CO)^+$, 204 $(M - CO - N_2)^+$, 130 $(M)^{2+}$, 102 $(M - CO - N_2)^{2+}$, 78, and 77 $(C_6H_5)^+$. *Anal.* Calcd for $C_{17}H_{12}N_2O$: C, 78.47; H, 4.61; N, 10.77. Found: C, 78.42; H, 4.84; N, 10.53.

A benzene–chloroform mixture (1:1, 600 ml) eluted colorless crystals of 2-phenylethynyl-4(5)-carbethoxyamino-5(4)-phenyloxazole (**17**) (22 mg, 2.2%): mp 186–187°; ν max (KBr) 3500 (m, >NH), 2220 (m, C≡C), 1700 (s, amide I), 1575 (m, amide II), 1389, and 1314 cm^{-1}; λ max (CH_3OH) 228 nm (ε 37,390), 245 (44,230), 320 (10,030), 332 (10,030); nmr ($CDCl_3$) δ 1.15 (t, 3 H, $CH_2\mathbf{CH_3}$), 4.00 (q, 2 H, $O\mathbf{CH_2}CH_3$), 6.15 (broad, >NH), and 7.55 (m, 10 H, phenyl); mass spectrum *m/e* 332 (M^+), 288 $(M - CO_2)^+$, 287 $(M - OC_2H_5)^+$, 286 $(M - C_2H_5OH)^+$, 273 $(M - CO_2 - CH_3)^+$, 260 $(M - CO_2 - C_2H_4 - CO)^+$, 258 $(M - C_2H_5OH - CO)^+$, 243, 242, 241, 232, 230 $(M - C_2H_5OH - 2CO)^+$, 205, 204, 189 $(C_6H_5C{\equiv}CNHCO_2C_2H_5)^+$, 188, 127 $(C_6H_5C{\equiv}CCN)^+$, 102 $(C_6H_5C{\equiv}CH)^+$, 101 $(C_6H_5C{\equiv}C)^+$, 88 $(NHCO_2C_2H_5)^+$, and 77 $(C_6H_5)^+$. *Anal.* Calcd for $C_{20}H_{16}N_2O_3$: C, 72.28; H, 4.82; N, 8.43. Found: C, 72.12; H, 4.85; N, 9.53.

Elutions with pure chloroform, ethyl acetate, and ethanol afforded a brown polymeric oil and a brown polymeric solid (220 mg) decomposing above 190°.

Pyrolysis of a 10% Solution of 11 in Benzene.—A solution of the azide (0.55 g, 3.21 mmol) in benzene (5 ml) was heated with stirring at 65–68° for 1 hr or until the evolution of nitrogen had ceased. After cooling to 25°, the reaction mixture was treated with absolute ethanol (10 ml) and refluxed for 2 hr. The solvent was removed and the black resinous residue was analyzed by gc (Apiezon L, 6 ft × 0.25 in., 180°). Phenylacetonitrile (81 mg, 21.5%) and an unidentified component were detected. Tlc (silica plates) with different eluents (benzene, chloroform, and ethyl acetate) established the presence of the oxazole **17**, the urea **16**, and two unidentified components. The above residue was chromatographed over silica gel (12 in. × 1 in.). Elutions with 4:1 and 3:1 mixtures of benzene–chloroform (800 ml) gave a mixture of two solids (56 mg) which upon sublimation [95–100° (0.2 mm)] gave colorless crystals of ethyl *N*-phenylacetylcarbamate (**15**) (24 mg, 3.8%) collected on the cold finger: mp 110–111°;[13] ν max (KBr) 3247 and 3175 (s, >NH), 1754 (s), and 1701 cm^{-1} (m, imide carbonyl); λ max (CH_3OH) 247 nm (ε 644), 252 (632), 258 (575), and 264 (433); nmr ($CDCl_3$) δ 1.28 (t, 3 H, $CH_2\mathbf{CH_3}$), 4.06 (s, 2 H, $C_6H_5\mathbf{CH_2}CO$), 4.22 (q, 2 H, $CH_3\mathbf{CH_2}CO_2$), and 7.31 (s, 5 H, phenyl); mass spectrum *m/e* 207 $(M)^+$, 179 $(M - C_2H_4)^+$, 162 $(M - OC_2H_5)^+$, 161 $(M - C_2H_5OH)^+$, 135 $(M - C_2H_4 - CO_2)^+$, 117 $(M - C_2H_4 - CO_2 - H_2O)^+$, 116 $(C_6H_5CHCN)^+$, and 91 $(\text{tropylium})^+$.

The residual solid left behind in the sublimation apparatus was crystallized twice from the chloroform–hexane mixture to give the oxazole **17** (26 mg, 4.8%), mp 186–187°. Further chromatographic elutions with pure chloroform and ethyl acetate gave a polymeric oil.

Photolysis of Phenylpropiolyl Azide 11 in Methanol.—Into anhydrous methanol (250 ml), degassed for 16 hr by flushing with nitrogen, the azide (1.02 g, 6 mmol) was added and the solution was irradiated at 300 nm under nitrogen for 7 hr with ir monitoring. The solvent was removed under vacuum and the brown residual viscous liquid (1.03 g) was analyzed by gc and gc–mass spectrum combination over SE-30 column (2.5%, 6 ft × 0.12 in., 100°). Of the four volatile components three were identified as phenylacetonitrile (4.98 mg, 0.71%, M^+ 117), α-methoxy-α-phenylacetonitrile (1.2 mg, 0.14%, M^+ 147), and methyl phenylpropiolate (M^+ 160). The residual product was chromatographed over silica gel (12 in. × 1 in.). A mixture of hexane–benzene (1:1, 400 ml) eluted a colorless liquid (160 mg) which upon fractionation by preparative gc (SE-30, 30%, 20 ft × 0.37 in., 225°) afforded methyl phenylpropiolate (60 mg, 6.3%): mp 25–26°; ν max (CCl_4) 2250 (vs, C≡C) and 1710 cm^{-1} (vs, >C=O); nmr (CCl_4) δ 3.80 (s, 3 H, CO_2CH_3) and 7.50 (m, 5 H, phenyl); mass spectrum *m/e* 160 (M^+).

A benzene–chloroform mixture (3:1, 1 l.) eluted colorless crystalline methyl phenylacetylcarbamate (**21**) (170 mg, 14.7%): mp 154–155°; ν max (KBr) 3247 and 3185 (m, >NH), 1754 (s), and 1684 cm^{-1} (m, imide carbonyl); λ max (CH_3OH) 247 nm (ε 448), 252 (434), 258 (388), and 263 (275); nmr (acetone-d_6) δ 3.73 (s, 3 H, CO_2CH_3), 4.00 (s, 2 H, $C_6H_5\mathbf{CH_2}CO$), and 7.33 (s, 5 H, phenyl); mass spectrum *m/e* 193 (M^+), 161 $(M - CH_3OH)^+$, 118 $(C_6H_5CH{=}CO)^+$, and 91 $(\text{tropylium})^+$. *Anal.* Calcd for $C_{10}H_{11}NO_3$: C, 62.17; H, 5.70; N, 7.25. Found: C, 62.80; H, 5.79; N, 7.25.

Registry No.—**1a** (R = Ph), 28850-17-1; **2a** (R = Ph), 28861-28-1; **3**, 28861-29-2; **4**, 28861-30-5; **12**, 28861-31-6; **15**, 4283-15-2; **17**, 28850-18-2; **20**, 4891-38-7; **21**, 28861-34-9.

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(13) S. Ruhemann and J. G. Priestly, *J. Chem. Soc.*, **95**, 449 (1909), reported mp 114–115°. Berger, F. Giagiu, Gh. Pollack, and C. Schonberger, *Lucr. P. Conf. Nat. Farm.*, 66 (1958) [*Chem. Abstr.*, **53**, 6213*d* (1959)], reported mp 106°.