solid was filtered. Partial melting occurred at about 140° and the semisolid resolidified. The latter crystals had mp 217–218°. The former crystals were dissolved in hot ethanol, and the first crop of crystals that separated out was shown to be a mixture by tlc. The second and third crops were shown to be pure by tlc. They were combined and dissolved in tetrahydrofuran to which Skellysolve B was added dropwise resulting in a precipitation of 0.5 g of a white solid (yield 71.4%). In a previously heated silicone oil bath a small sample of this solid in a capillary was introduced. It melted, then slowly resolidified, and melted at 217–218°: λ_{max} (95% ethanol) 275 mμ (ε 11,860); ir 2.87, 3.05, and 5.94 μ. A corresponding dark reaction produced only starting material.

Anal. Calcd for $C_8H_9N_3O$: C, 58.88; H, 5.82; N, 25.80. Found: C, 58.60; H, 5.69; N, 26.21.

The hydrolysis of the photoproduct of benzaldehyde semicarbazone with aqueous HCl to benzaldehyde and the isomerization of the initially prepared semicarbazone was accomplished in the same manner as described for acetophenone semicarbazone.

Preparation of the Two Semicarbazones of α-Methyldeoxybenzoin.—This was accomplished through the published procedures of Ramart-Lucas and Bruzau.[8]

Acetophenone Semicarbazone in Trifluoroacetic Acid.—Acetophenone semicarbazone (1.2 g) was dissolved in 10.4 g of trifluoroacetic acid. The solution was allowed to stand for 2 hr and then was poured into an ice–water mixture. The white precipitate was filtered immediately with a Büchner funnel, washed with an ice–sodium bicarbonate solution and later with water. The air-dried white solid melted at 194–197°. After recrystallization from 95% ethanol three times, it had the melting point of 201.5–202.0° and the mixture melting point with the starting material was undepressed.

Registry No.—Table I, **1**, 17539-52-5; Table I, **2**, 17539-53-6; Table I, **3**, 17539-54-7; Table I, **4**, 17539-55-8; Table I, **5**, 17539-56-9; Table I, **6**, 17539-57-0; Table I, **7**, 17539-58-1; Table I, **8**, 14066-73-0.

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Reactions of Ynamines

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Reactions of ynamines with acidic carbon compounds such as malononitrile and ethyl cyanoacetate gave cyanoenamines, whereas acidic nitrogen compounds such as arylsulfonamides gave saturated amidines. The condensation of several arylsulfonylimides with ynamines and electrocyclic opening of the adducts led to unsaturated amidines while 2-pyridal-*p*-toluenesulfonimide gave a pyrrocoline. Reactions of diphenylketene and dimethylketene with ynamines furnished aminocyclobutenone and four-membered cyclic enol ether products. Similarly, sulfenes and ynamines formed cyclic sulfones. Aryl isocyanates and ynamines gave 4-amino-2-quinolones and 2-amino-4-quinolones. An example of a 1,3 dipolar addition and a reaction with tetraphenylcyclopentadienone, which gave a pentaphenylaniline, are also described.

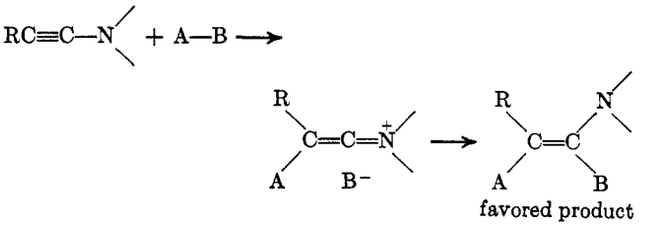
Ynamine chemistry has been investigated only in the last 4 years and remains largely unexplored. During the course of our studies in this area, preparative methods for this new class of compounds became available,[2-8] and some reactions of these compounds were described.[9-11] This report presents further aspects of ynamine chemistry.

Two of the ynamines used in this work have not been described previously. N,N-dipropylheptynylamine (**1**) was prepared by a displacement reaction from an acetylenic ether,[5] whereas N,N-diethylcarbomethoxyethynylamine (**2**) was obtained from N,N-diethyltrichlorovinylamine, butyllithium, and methyl chlorocarbonate.

$$CH_3(CH_2)_4C{\equiv}COC_2H_5 \xrightarrow{(C_3H_7)_2NLi} CH_3(CH_2)_4C{\equiv}CN(C_3H_7)_2$$
1

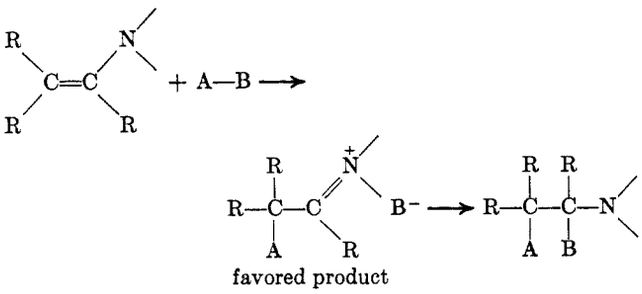
$$Cl_2C{=}CN(C_2H_5)_2 \xrightarrow[ClCO_2CH_3]{BuLi} CH_3O_2CC{\equiv}CN(C_2H_5)_2$$
2

Since electrophilic substitution adjacent to a carboxyl group often presents a serious synthetic obstacle, formal activating derivatives of carboxylic acids, such as ynamines, are of potential synthetic interest. However, ynamines do not parallel enamines in their broad utility for substitution reactions.[12] In contrast to the formation of aliphatic imonium salts, which one obtains on nucleophilic reactions of enamines, energetically less favorable allenic imonium functions are generated by electrophilic attack on ynamines. Thus one can expect ynamines to be less reactive toward monofunctional electrophiles than enamines and to undergo preferentially reactions in which addition takes place at positions α and β to the nitrogen. Ynamines should thus be good substrates for reactions with di-



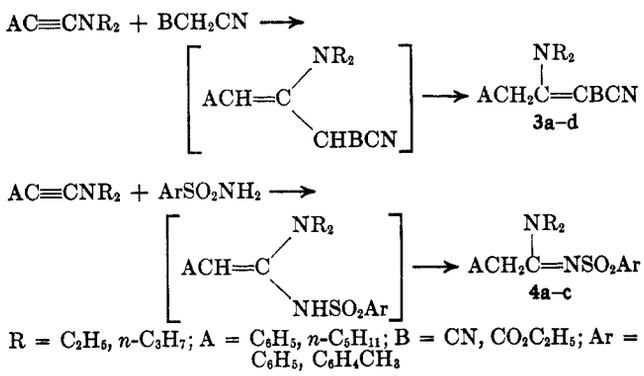
favored product

(1) Alfred P. Sloan Fellow.
(2) H. G. Viehe, *Angew. Chem.*, **75**, 638 (1963).
(3) J. Ficini and C. Barbara, *Bull. Soc. Chim. Fr.*, 871 (1964).
(4) J. Ficini and C. Barbara, *ibid.*, 2787 (1965).
(5) P. P. Montijin, E. Harryvan, and L. Brandsma, *Rec. Trav. Chim. Pays-Bas*, **83**, 1211 (1964).
(6) H. G. Viehe and M. Reinstein, *Angew. Chem.*, **76**, 537 (1964).
(7) R. Buijle, A. Halleux, and H. G. Viehe, *ibid.*, **78**, 593 (1966).
(8) J. Ficini, C. Barbara, S. Colodny, and A. Duréault, *Tetrahedron Lett.*, 943 (1968).
(9) For a summary, see H. G. Viehe, *Angew. Chem.*, **79**, 744 (1967).
(10) J. Ficini and A. Krief, *Tetrahedron Lett.*, 2497 (1967).
(11) J. Ficini and A. Krief, *ibid.*, 947 (1968).
(12) For a summary of enamine chemistry with 630 references, see M. E. Kuehne in "Enamines: Their Synthesis, Structure and Reactions," A. G. Cook, Ed., Marcel Dekker, Inc., New York, N. Y., 1968.



polar or electrically opposing bifunctional molecules, particularly if a concerted addition to the acetylenic system is possible.

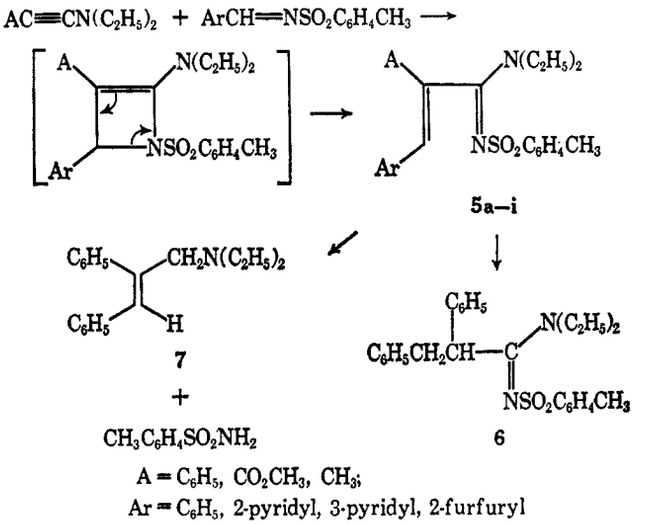
The hydration and addition of amines and alcohols to ynamines under acid catalysis has already been described.[9,13] We have found that acidic carbon and nitrogen species will add spontaneously to ynamines to give ketone-related enamines and amidine derivatives, respectively. Thus ethyl cyanoacetate and malononitrile added readily to phenyl- and pentyl-substituted ynamines to give vinylogous cyanamides, **3a–d**, through double-bond rearrangement of the initially formed enamines. Similarly, benzene and *p*-toluenesulfonamides gave adducts which rearranged to arylsulfonamidines, **4a–c**.



R = C_2H_5, *n*-C_3H_7; A = C_6H_5, *n*-C_5H_{11}; B = CN, $CO_2C_2H_5$; Ar = C_6H_5, $C_6H_4CH_3$

Ketones and imines have also been found to react with ynamines, particularly in the presence of Lewis acids such as boron trifluoride.[9] Substituted amides and amidines were thus obtained, presumably by rearrangement of initially formed four-membered-ring adducts. Arylsulfonylimines[14] showed an expected greater reactivity with ynamines and led to the corresponding unsaturated arylsulfonamidines **5a–i**. The structures of these products were established by catalytic and chemical reductions. While the phenylynamine-derived product **5a** was stable to refluxing acid or alkali and resistant to hydrogenation at atmospheric pressure, its stilbene double bond was reduced over a palladium catalyst at 850 psi, giving the saturated sulfonamidine **6**. Lithium aluminum hydride reduction of the sulfonamidine group in **5a** led to the aminomethyl-*cis*-stilbene **7** and *p*-toluenesulfonamide.

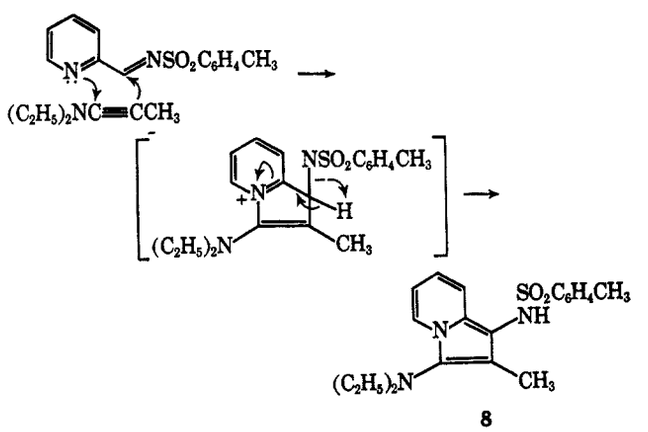
The formation of a *cis*-stilbene system in **5a** is especially interesting since it indicates that opening of



A = C_6H_5, CO_2CH_3, CH_3;
Ar = C_6H_5, 2-pyridyl, 3-pyridyl, 2-furfuryl

the initially formed four-membered-ring adduct may follow the Woodward–Hoffmann[15] selection rules for electrocyclic transformations. (The required *trans* arrangement of the aryl and sulfonyl substituents on the four-membered ring can be assumed.)

A remarkable departure from the reaction path followed by the other sulfonimides was found with the 2-pyridalsulfonimide in its reaction with the methyl-substituted ynamine. Here, formation of a pyrrocoline **8**

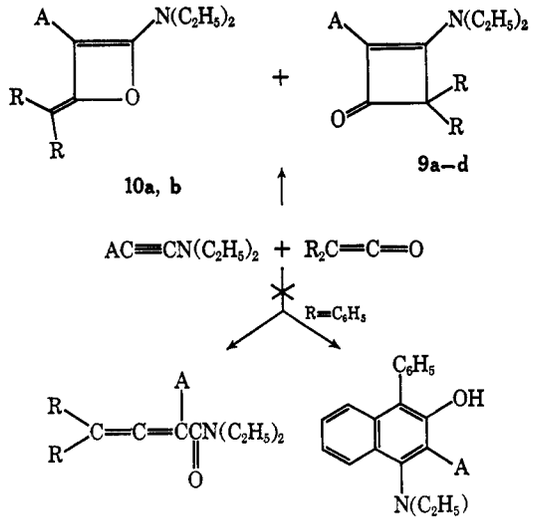


indicates that the relative nucleophilicities of the nitrogens in the pyridalsulfonimide, rather than in a zwitterionic cyclization precursor, may govern the course of the reaction. This result would then be a direct reflection of the preferred concerted addition reactions of ynamines. Formation of a pyrrocoline from the least polarized ynamine is consistent with this postulate.

The addition of diphenylketene to ynamines led to both of the possible four-membered-ring cyclization products, **9a–c** and **10a, b**. Allenic amide structures, which could have arisen from opening of the heterocyclic adducts **10** in analogy to the opening found with cyclic sulfonamides (above) were excluded by the absence of characteristic allenic absorption in the infrared. Ultraviolet, infrared, and nuclear magnetic resonance spectra also excluded aminophenol structures analo-

(13) J. Ficini and C. Barbara, *Tetrahedron Lett.*, 6425 (1966).
(14) G. Kresze and R. Albrecht, *Angew. Chem.*, **74**, 781 (1962).
(15) R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 395 (1965). Of two possible conrotatory cyclobutene openings one expects to favor the process which avoids eclipsing of initial *trans* substituents.

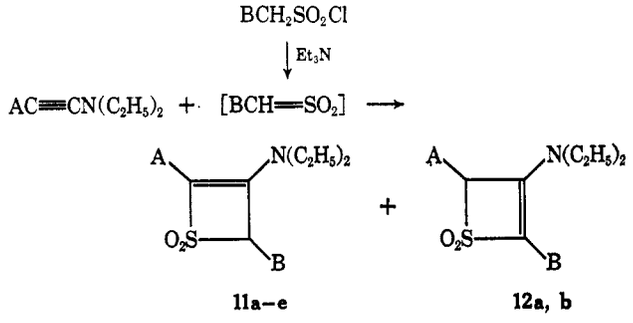
gous to the quinolones formed with aryl isocyanates (below). An aminocyclobutenone **9d** was also obtained with dimethylketene and N,N-diethylphenylethynylamine.



10a, b **9a–d**

A = C_6H_5, CO_2CH_3, CH_3; R = C_6H_5, CH_3

Analogous to the addition of ketenes, sulfenes were also found to give adducts with ynamines. The four-membered cyclic sulfonamide structures **11a–e** and **12a, b** were assigned on the basis of nmr spectra. Double-bond isomerization from type **11** to **12** was only observed in the products derived from the methyl-substituted ynamine.



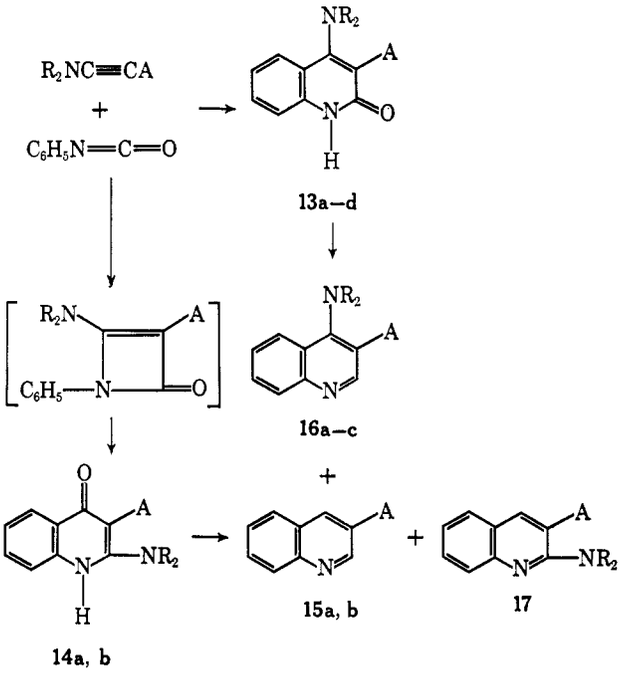
11a–e **12a, b**

A = C_6H_5, CO_2CH_3, CH_3; B = H, C_6H_5

In contrast to the preceding reactions, ynamines reacted with phenyl isocyanate to give 4-amino-2-quinolones **13a–d** by 1,4 addition as well as 2-amino-4-quinolones **14a, b** by initial 1,2 addition, subsequent opening of the four-membered-ring adduct, and cyclization to the 4-quinolone products. The relative extent of 1,4 *vs.* 1,2 addition was found to depend on solvent polarity. Thus 2-quinolone formation was favored in acetonitrile while more 4-quinolone isomer was produced in benzene.[16] Infrared absorption at 1755 cm^{-1}, which was seen in the course of the reactions, may be assigned to the intermediate unsaturated four-membered lactams.

Structural assignments for the aminoquinolones were based on complete reductions with lithium aluminum hydride to the quinolines **15a, b**, common to each isomer pair, as well as partial reductions to the respective aminoquinolines **16a–c** and **17**. The 4-amino-quinolines **16a–c** displayed an nmr singlet at δ 8.5–8.7 for the C-2 proton, downfield[17] from the other aromatic proton signals, while the isomeric 4 proton of the 2-aminoquinoline **17** was found at 7.6.[17] In the quinolines **15a, b** the C-2 proton was again seen downfield, but as a doublet.

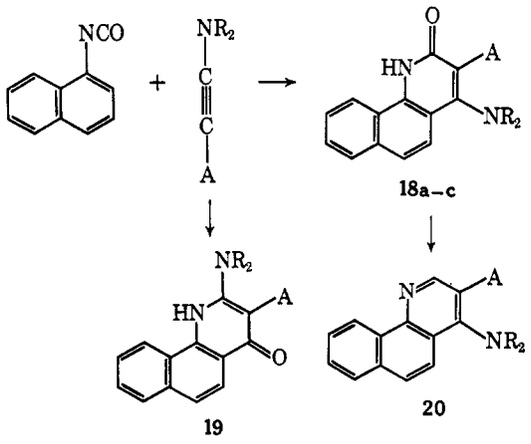
The isomeric aminoquinolones could also be differentiated by infrared spectra, which showed strong maxima at 1640, 1600, and 900 cm^{-1} for the 4-amino-2-quinolones **13a–c** *vs.* 1615 and 1570 cm^{-1} for the 2-amino-4-quinolones **14a, b**. The ultraviolet spectra of the isomeric compounds could be consistently distinguished by their general shapes but showed the same positions and relative intensities of maxima.



13a–d **16a–c** **14a, b** **15a, b** **17**

A = C_6H_5, C_5H_{11}, CO_2CH_3, CH_3; R = C_2H_5, C_3H_7

The reaction of 1-naphthyl isocyanate and ynamines also led to 1,4-addition products **18a–c** in acetonitrile, and a rearranged 1,2-addition product **19** could be isolated from a reaction in cyclohexane. Reduction of the benzo-2-quinolone **18a** with lithium aluminum hydride gave the desoxyproduct **20** with an nmr singlet at δ 8.56. The 1,4-addition products **18a–c** could again be cor-



18a–c **19** **20**

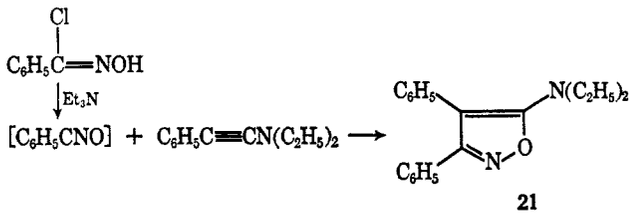
A = C_5H_{11}, CO_2CH_3, CH_3; R = C_2H_5, C_3H_7

(16) Recently,[11] the addition of phenyl isocyanate to two ynamines was reported to give the 4-amino-2-quinolones **13a** and **d**. However, the products obtained correspond in physical properties to our 2-amino-4-quinolones **14a** and **b**.

(17) R. F. M. White in "Physical Methods in Heterocyclic Chemistry," A. R. Katritzky, Ed., Academic Press, New York, N. Y., 1963, p 143.

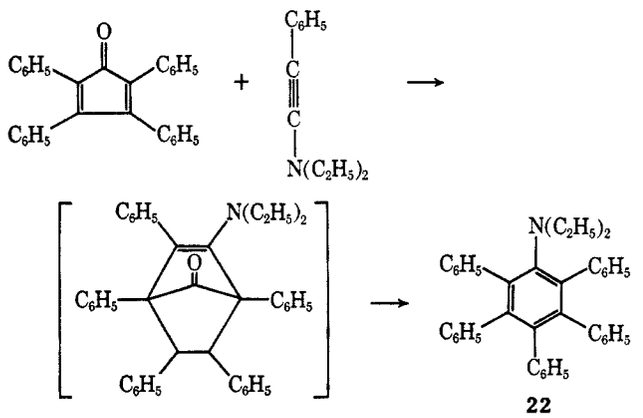
related by infrared spectra (1625, 1600, and 850 cm^{-1}) and differentiated from the isomer **19** (1600 and 1545 cm^{-1}).

Additions of 1,3 dipolar species to ynamines were described during the course of our work.[18] A further example, leading to compound **21**, is found in the reaction of benzonitrile oxide with the phenyl-substituted ynamine.



21

The phenyl-substituted ynamine was also found to undergo a Diels–Alder addition to tetraphenylcyclopentadienone. The corresponding decarbonylation product **22** was isolated in low yield.



22

Experimental Section

The proton magnetic resonance (pmr) spectra were recorded on a Varian Associates Model A-60 spectrometer as 10% solutions in carbon tetrachloride or deuterated chloroform. Chemical shifts for the compounds are reported as δ (parts per million) relative to tetramethylsilane (TMS), internal or external. Infrared (ir) spectra were recorded on a Perkin-Elmer Model 237B infrared spectrometer. Solids were recorded as potassium bromide discs and liquids as films on sodium chloride plates. Ultraviolet (uv) spectra were recorded on a Perkin-Elmer Model 202 spectrometer, and extinction coefficients were determined on a Cary 14 spectrometer. All reported melting points are corrected, but boiling points are uncorrected. All reactions were carried out in a nitrogen atmosphere.

Preparation of Ynamines.—The N,N-diethylphenylethynylamine used in the following reactions was prepared by the method of Ficini.[3]

The N,N-dipropylpentylethynylamine, **1**, previously unreported, and the N,N-dipropylethylethynylamine were prepared from the corresponding acetylenic ethyl ethers by the method of Montijin.[5] The N,N-dipropylpentylethynylamine had the following physical constants: bp 93–94° (4.7 mm); ir 2240 cm^{-1}. This amine could be hydrolyzed to the N,N-dipropylamide of heptanoic acid by dilute aqueous acid. The amide was compared with an authentic sample by matching ir spectra.

Preparation of N,N-Diethylcarbomethoxyethynylamine (2).—N,N-diethyl-1,2,2-trichlorovinylamine,[19] 5.0 g (23 mmol), was cooled to −15° under a nitrogen atmosphere, and *n*-butyllithium (50 mmol) in hexane (diluted with one-third volume of dry ether) was added dropwise at −10°. The mixture was left at room temperature for 45 min, then cooled to −10°, and methyl chloroformate, 2.16 g, in 5 ml of dry ether was added dropwise while the temperature of the reaction mixture was kept at −10°. After addition of methyl chloroformate, the mixture was left at room temperature for 45 min. Centrifugation and distillation of the centrifugate gave 2.5 g (70% yield) of the ynamine: bp 91° (2.5 mm); ir 2200, 1695 cm^{-1}; nmr (neat with external TMS) δ 1.20 (t, 6 H), 2.97 (q, 4 H), 4.35 (s, 3 H).

Reaction of N,N-Diethylphenylethynylamine with Malononitrile.—A solution of 0.51 g (3.0 mmol) of the ynamine in 2 ml of dry acetonitrile was added dropwise to a stirred solution of 0.2 g (3.0 mmol) of malononitrile in 10 ml of dry acetonitrile, and the mixture was stirred for 22 hr. The solvent was removed under vacuum, and recrystallization of the residue from ethyl acetate–petroleum ether (bp 30–60°) gave 0.3 g (51% yield) of adduct **3a**, mp 110–111°. A reaction in dry benzene gave a 10% yield: ir 1575, 2175, 2200 cm^{-1}; λ_{max}^{EtOH} 208, 293 mμ; nmr (in $CDCl_3$ with internal TMS) δ 1.23 (t, 6 H), 3.60 (q, 4 H), 4.00 (s, 2 H), 7.33 (m, 5 H).

Anal. Calcd for $C_{15}H_{17}N_3$: C, 74.07; H, 7.55; N, 18.51. Found: C, 73.98; H, 7.32; N, 18.25.

Reaction of N,N-Dipropylpentylethynylamine with Malononitrile.—This reaction was carried out under the conditions of the previous reaction, except that benzene was used as a solvent. Distillation of the reaction mixture gave a light brown oil, bp 110° (0.005 mm). This compound, **3b**, 3.35 g (84% yield), was homogeneous by thin layer chromatography (tlc) on Eastman silica gel plates in dichloromethane and also in benzene: ir 2200, 2210, 1565 cm^{-1}; λ_{max}^{EtOH} 210, 295 mμ; nmr (in $CDCl_3$ with internal TMS at sweep width of 250 cps) δ 0.75–2.50 (m, 21 H), 2.50 (m, 2 H), 3.47 (t, 4 H).

Anal. Calcd for $C_{16}H_{27}N_3$: C, 73.51; H, 10.41. Found: C, 73.44; H, 10.66.

Reaction of N,N-Diethylphenylethynylamine with Ethyl Cyanoacetate.—This reaction was carried out in acetonitrile and gave a 42% yield of the product **3c** which crystallized from ethyl acetate–petroleum ether (bp 30–60°): mp 74–75°; ir 1690, 1560, 2205 cm^{-1}; λ_{max}^{EtOH} 210, 307 mμ; nmr (in $CDCl_3$ with internal TMS) δ 1.2 (m, 9 H), 3.55 (q, 4 H), 4.2 (q, 2 H), 4.4 (s, 2 H), 7.3 (m, 5 H).

Anal. Calcd for $C_{17}H_{22}N_2O_2$: C, 71.39; H, 7.75; N, 9.80. Found: C, 71.54; H, 7.79; N, 9.60.

Reaction of N,N-Dipropylpentylethynylamine with Ethyl Cyanoacetate.—This reaction was carried out in dry benzene to give a 51% yield of product **3d**: bp 105° (0.005 mm); ir 1695, 1535, 2205 cm^{-1}; λ_{max}^{EtOH} 220, 311 mμ; nmr (in $CDCl_3$ with external TMS) δ 0.8–1.6 (m, 24 H), 2.78 (m, 2 H), 3.43 (t, 4 H), 4.11 (q, 2 H).

Anal. Calcd for $C_{18}H_{32}N_2O_2$: C, 70.09; H, 10.46; N, 9.08. Found: 70.31; H, 10.54; N, 8.95.

Reaction of N,N-Diethylphenylethynylamine with *p*-Toluenesulfonamide.—A solution of 0.5 g (3.0 mmol) of the ynamine in 5 ml of dry acetonitrile was added dropwise to a solution of 0.5 g of *p*-toluenesulfonamide in 20 ml of dry acetonitrile. The mixture was stirred for 72 hr, and the solvent taken off under a vacuum. Recrystallization of the residue from ethyl acetate–petroleum ether (bp 30–60°) afforded 0.82 g (80% yield) of N-*p*-toluenesulfonyl-N′,N′-diethylphenylacetamidine (**4a**): mp 134–135°; ir 1555, 1280, 1145 cm^{-1}; λ_{max}^{EtOH} 250 mμ; nmr (in $CDCl_3$ with internal TMS) δ 1.00 (pentet, 6 H), 2.35 (s, 3 H), 3.35 (m, 4 H), 4.40 (s, 2 H), 7.0–7.5 (m, 7 H), 7.83 (d, 2 H).

Anal. Calcd for $C_{19}H_{24}N_2O_2S$: C, 66.33; H, 7.03; N, 8.14; S, 9.32. Found: C, 66.11; H, 6.95; N, 7.90; S, 9.26.

Attempts to reduce this N-*p*-toluenesulfonyl-N′,N′-diethylphenylacetamidine in dry dioxane with palladium on charcoal and hydrogen at atmospheric pressure or with platinum dioxide in dry ethanol failed.

Reaction of N,N-Dipropylpentylethynylamine with *p*-Toluenesulfonamide.—This reaction was carried out in dichloromethane and gave a 79% yield of the N-*p*-toluenesulfonyl-N′,N′-dipropylheptamidine (**4b**): bp 190° (0.001 mm); ir 1550, 1275 (SO_2 *as*), 1150 cm^{-1} (SO_2 *s*); λ_{max}^{EtOH} 248 mμ; nmr (in $CDCl_3$ with internal TMS) δ 0.90 (t, 9 H), 1.35 (m, 12 H), 2.39 (s, 3 H), 2.88 (t, 2 H), 3.30 (q, 4 H), 7.25 (d, 2 H), 7.90 (d, 2 H).

Anal. Calcd for $C_{20}H_{34}N_2O_2S$: C, 65.53; H, 9.35; N, 7.64; S, 8.73. Found: C, 65.37; H, 9.52; N, 8.16; S, 8.91.

Reaction of N,N-Diethylphenylethynylamine with Benzenesulfonamide.—This reaction, carried out in dry acetonitrile, gave a 67% yield of the N-benzenesulfonyl-N′,N′-diethylphenylacetamidine (**4c**), mp 68–69°, after recrystallization from cyclohexane–ethyl acetate: ir 1550, 1270 (SO_2 *as*), 1145 cm^{-1} (SO_2 *s*);

(18) R. Fuks, R. Buijle, and H. G. Viehe, *Angew. Chem.*, **78**, 594 (1966).
(19) A. J. Speziale and L. R. Smith, *J. Amer. Chem. Soc.*, **84**, 1868 (1962).

λ_{max}^{EtOH} 247 mμ; nmr (in $CDCl_3$ with internal TMS) δ 1.00 (pentet, 6 H), 3.35 (m, 4 H), 4.42 (s, 2 H), 7.30 (m, 8 H), 7.90 (m, 2 H).

Anal. Calcd for $C_{18}H_{22}N_2O_2S$: C, 65.51; H, 6.72; N, 8.49; S, 9.72. Found: C, 65.74; H, 6.56; N, 8.28; S, 9.72.

Reaction of N,N-Diethylphenylethynylamine with Benzal p-Toluenesulfonimide.[14]—A solution of 0.50 g (3.0 mmol) of the ynamine in 5 ml of dry benzene was added dropwise to a stirred solution of the benzal *p*-toluenesulfonimide, 0.78 g (3.0 mmol) in 20 ml of dry benzene. The mixture was stirred for 20 hr. Evaporation of the solvent under a vacuum and recrystallization of the solid from ethyl acetate gave 0.93 g (75% yield) of product **5a**, mp 163–164°. With acetonitrile as a solvent a yield of 70% was obtained: ir 1540, 1280, 1145 cm^{-1}; λ_{max}^{EtOH} 247 mμ; nmr (in $CDCl_3$ with external TMS) δ 0.72 (t, 3 H), 1.16 (t, 3 H), 2.35 (s, 3 H), 3.33 (q, 4 H), 6.63 (s, 1 H), 7.1–7.3 (m, 12 H), 7.71 (d, 2 H).

Anal. Calcd for $C_{26}H_{28}N_2O_2S$: C, 72.20; H, 6.53; N, 6.48; S, 7.40. Found: C, 72.18; H, 6.74; N, 6.37; S, 7.48.

Reaction of N,N-Diethylcarbomethoxyethynylamine with Benzal p-Toluenesulfonimide.[14]—This reaction was carried out in benzene to give a 60% yield of product **5b**, mp 113–114°, which was recrystallized from ethyl acetate. With acetonitrile as the reaction medium an 18% yield was obtained: ir 1725, 1610, 1525, 1140 cm^{-1}; λ_{max}^{EtOH} 253 mμ; nmr (in $CDCl_3$ with internal TMS) δ 1.16 (m, 6 H), 2.36 (s, 3 H), 3.2–3.7 (q and s, 7 H), 6.78 (s, 1 H), 7.1–7.85 (m, 9 H).

Anal. Calcd for $C_{22}H_{26}N_2O_4S$: C, 63.74; H, 6.32; N, 6.76; S, 7.74. Found: C, 64.00; H, 6.28; N, 7.00; S, 7.82.

Reaction of N,N-Diethylmethylethynylamine with Benzal p-Toluenesulfonimide.[14]—This reaction was carried out in benzene and gave a 95% yield of product **5c**, mp 142–143°, which was recrystallized from ethyl acetate: ir 1535, 1275, 1150 cm^{-1}; λ_{max}^{EtOH} 252 mμ; nmr (in $CDCl_3$ with internal TMS) δ 1.18 (t, 6 H) 2.11 (s, 3 H), 2.33 (s, 3 H), 3.45 (m, 4 H), 6.21 (s, 1 H), 7.0–7.9 (m, 9 H).

Anal. Calcd for $C_{21}H_{26}N_2O_2S$: C, 68.27; H, 6.82; N, 7.58; S, 8.68. Found: C, 68.25; H, 7.01; N, 7.69; S, 8.69.

Reaction of N,N-Diethylphenylethynylamine with 2-Pyridal p-Toluenesulfonimide.[14]—This reaction was carried out in dry benzene and gave a 54% yield of product **5d**, mp 145–146°, after recrystallization from ethyl acetate–petroleum ether (bp 30–60°): ir 1530, 1280, 1145 cm^{-1}; λ_{max}^{EtOH} 235, 295 mμ; nmr (in $CDCl_3$ with internal TMS) δ 0.68 (t, 3 H), 1.16 (t, 3 H), 2.35 (s, 3 H), 3.40 (m, 4 H), 6.70 (s, 1 H), 7.25 (m, 11 H), 7.83 (d, 2 H).

Anal. Calcd for $C_{25}H_{27}N_3O_2S$: C, 69.26; H, 6.28; N, 9.69; S, 7.38. Found: C, 68.98; H, 6.15; N, 9.47; S, 7.40.

Reaction of N,N-Diethylcarbomethoxyethynylamine with 2-Pyridal p-Toluenesulfonimide.[14]—This reaction was carried out in dry benzene to give a 41% yield of product **5e**, mp 132–133°, after recrystallization from ethyl acetate: ir 1735, 1620, 1550, 1280, 1150 cm^{-1}; λ_{max}^{EtOH} 215, 250 mμ; nmr (in $CDCl_3$ with internal TMS) δ 1.18 (t, 6 H), 2.35 (s, 3 H), 3.58 (m, 4 H), 3.65 (s, 3 H), 6.88 (s, 1 H), 7.16 (m, 4 H), 7.73 (m, 4 H).

Anal. Calcd for $C_{21}H_{23}N_3O_4S$: C, 60.71; H, 6.07; N, 10.12; S, 7.70. Found: C, 60.69; H, 6.26; N, 9.92; S, 7.58.

Reaction of N,N-Diethylmethylethynylamine with 3-Pyridal p-Toluenesulfonimide.—This reaction was carried out in dry benzene to give a 72% yield of product **5f**, mp 168–169°, after recrystallization from ethyl acetate: ir 1540, 1275, 1145 cm^{-1}; λ_{max}^{EtOH} 247 mμ; nmr (in $CDCl_3$ with internal TMS) δ 1.16 (t, 6 H), 2.13 (s, 3 H), 2.33 (s, 3 H), 3.41 (m, 4 H), 6.21 (s, 1 H), 7.23 (m, 3 H), 7.66 (m, 3 H), 8.50 (s, 2 H).

Anal. Calcd for $C_{20}H_{25}N_3O_2S$: C, 64.67; H, 6.78; N, 11.31; S, 8.61. Found: C, 64.79; H, 6.53; N, 11.04; S, 8.38.

Reaction of N,N-Diethylmethylethynylamine with 2-Pyridal p-Toluenesulfonimide.[14]—A solution of 0.33 g (3.0 mmol) of the ynamine in 5 ml of dry acetonitrile was added dropwise to a stirred solution of 0.78 g (3.0 mmol) of 2-pyridal-*p*-toluenesulfonimide in 20 ml of dry acetonitrile, cooled to 5°. The ynamine was added dropwise over a 30-min period, and the mixture stirred another 2 hr at 5° and 16 hr at room temperature. The solvent was removed under a vacuum, and the black-green oil was treated with Florisil and dichloromethane to give, after recrystallization from ethyl acetate–petroleum ether (bp 30–60°), 0.5 g (45% yield) of product **8**: mp 120–121°; ir 3300, 1345, 1150 cm^{-1}; λ_{max}^{EtOH} 235 mμ; nmr (in $CDCl_3$ with internal TMS) δ 0.86 (t, 6 H), 1.73 (s, 3 H), 3.06 (q, 4 H), 6.4–6.6 (m, 3 H), 7.3–7.7 (m, 3 H), 7.16 (d, 3 H), 7.60 (d, 2 H), 8.00 (m, 1H).

Anal. Calcd for $C_{20}H_{25}N_3O_2S$: C, 64.67; H, 6.78; N, 11.31; S, 8.62. Found: C, 64.57; H, 6.93; N, 11.03; S, 8.80.

The singlet at δ 6.58 disappeared when the solvent was CH_3OD, indicating exchange of the N–H hydrogen of the sulfonamide.

Reaction of N,N-Diethylmethylethynylamine with 2-Furfural p-Toluenesulfonimide.[14]—This reaction was carried out in dry benzene and gave a 65% yield of product **5g**, mp 127–128°, after recrystallization from ethyl acetate: ir 1530, 1280, 1150 cm^{-1}; λ_{max}^{EtOH} 257 mμ; nmr (in $CDCl_3$ with internal TMS) δ 1.16 (t, 6 H), 2.18 (s, 3 H), 2.36 (s, 3 H), 3.36 (m, 4 H), 6.00 (s, 1 H), 6.40 (m, 2 H), 7.16 (d, 2 H), 7.45 (s, 1 H), 7.75 (d, 2 H).

Anal. Calcd for $C_{19}H_{24}N_2O_3S$: C, 63.32; H, 6.71; N, 7.77; S, 8.88. Found: C, 63.03; H, 6.86; N, 7.74; S, 8.62.

Reaction of N,N-Diethylcarbomethoxyethynylamine with 2-Furfural p-Toluenesulfonimide.[14]—This reaction was carried out in dry benzene and gave a 57% yield of the adduct **5h**, mp 146–147°, after recrystallization from ethyl acetate: ir 1550, 1620, 1720 cm^{-1}; λ_{max}^{EtOH} 222, 245, 325 mμ; nmr (in $CDCl_3$ with external TMS) δ 1.20 (m, 6 H), 2.38 (s, 3 H), 3.50 (m, 4 H), 3.73 (s, 3 H), 6.46 (s, 1 H), 6.63 (m, 1 H), 7.1–8.0 (m, 6 H).

Anal. Calcd for $C_{20}H_{24}N_2O_5S$: C, 59.40; H, 5.98; N, 6.93; S, 7.91. Found: C, 59.14; H, 5.93; N, 6.72; S, 8.02.

Reaction of N,N-Diethylmethylethynylamine with 2-Naphthal p-Toluenesulfonimide.—This reaction was carried out in dry benzene and gave a 94% yield of product **5i**: mp 137–138°; ir 1535, 1275, 1145 cm^{-1}; λ_{max}^{EtOH} 213, 248, 294 mμ; nmr (in $CDCl_3$ with internal TMS) δ 1.20 (t, 6 H), 2.20 (s, 3 H), 2.31 (s, 3 H), 3.43 (m, 4 H), 6.36 (s, 1 H), 7.1–7.9 (m, 11 H).

Anal. Calcd for $C_{25}H_{28}N_2O_2S$: C, 71.41; H, 6.71; N, 6.66; S, 7.61. Found: C, 71.24; H, 6.80; N, 6.84; S, 7.63.

Catalytic Reduction of the N-p-Toluenesulfonyl-N′,N′-diethylstilbylformamidine (5a).—A solution of 0.1 g (0.22 mmol) of the formamidine in 20 ml of dry ethanol was shaken with 15 mg of 10% palladium on charcoal under 850 psi of hydrogen for 24 hr. The catalyst was filtered, and the solvent taken off under vacuum. Recrystallization of the residue from ethyl acetate–petroleum ether (bp 30–60°) gave 30 mg of the dihydro compound **6**: mp 125–126°; ir 1550, 1260, 1135 cm^{-1}; λ_{max}^{EtOH} 210, 252 mμ; nmr (in $CDCl_3$ with internal TMS) δ 0.78 (m, 6 H), 2.35 (s, 3 H), 3.33 (m, 6 H), 5.95 (t, 1 H), 7.1–7.9 (m, 14 H).

Attempts to reduce the formamidine at atmospheric pressure failed. The starting material was recovered in all cases.

The compound was also stable to refluxing 10% aqueous hydrochloric acid and 10% sodium hydroxide.

Anal. Calcd for $C_{26}H_{30}N_2O_2S$: C, 71.85; H, 6.96; N, 6.45; S, 7.38. Found: C, 72.01; H, 7.22; N, 6.33; S, 7.43.

Lithium Aluminum Hydride Reduction of N-p-Toluenesulfonyl-N′,N′-diethylstilbylformamidine (5a).—A solution of 0.1 g (0.22 mmol) of the formamidine in 20 ml of dry dioxane was refluxed for 48 hr with 60 mg of lithium aluminum hydride. The excess lithium aluminum hydride was hydrolyzed with a few drops of 50% sulfuric acid. The mixture was then made basic and extracted with three 20-ml portions of dichloromethane. The extract was dried over magnesium sulfate, and the solvent was removed under vacuum. Distillation of the remaining oil gave 50 mg (83% yield) of the amine **7**, bp 83–88° (block temperature) at 0.005 mm. The hydrobromide salt was crystallized from isopropyl alcohol: mp 176–177°; ir spectrum (hydrobromide salt) 2475–2560 cm^{-1}; λ_{max}^{EtOH} 225 mμ (ε 22,000), 270 (13,000);[20] nmr (in CCl_4 with external TMS) (free amine) δ 1.06 (t, 6 H), 2.30 (q, 4 H), 3.20 (s, 2 H), 6.51 (s, 1 H), 6.8–7.2 (m, 10 H).

Anal. Calcd for $C_{19}H_{24}BrN$: C, 65.89; H, 6.98; N, 4.05; Br, 23.08. Found: C, 66.12; H, 6.94; N, 4.07; Br, 23.30.

The solution was then made acidic and extracted with three 20-ml portions of chloroform. This extract was dried over magnesium sulfate, and after removal of the solvent gave 23 mg of *p*-toluenesulfonamide, mp 134–137°, identical with the known compound by mixture melting point and ir spectrum.

Reaction of N,N-Diethylphenylethynylamine with Diphenylketene.—A solution of 0.51 g (3.0 mmol) of the ynamine in 2 ml of dry benzene was added dropwise to a stirred solution of 0.58 g (3.0 mmol) of diphenylketene in 15 ml of dry benzene. The mixture was stirred for 24 hr. Evaporation of the solvent and crystallization of the residue from ethyl acetate gave 0.7 g (64% yield) of 2,2-diphenyl-3-N,N-diethyl-4-phenylcyclobutenone **9a**, mp 192–193°. With acetonitrile as a solvent the same yield was obtained: ir 1743, 1608, 1585 cm^{-1}; λ_{max}^{EtOH} 272 mμ;

(20) For a comparable uv absorption of *cis*-stilbene see M. Calvin and H. W. Alter, *J. Chem. Phys.*, **19**, 765 (1951).

nmr (in $CDCl_3$ with internal TMS) δ 0.44 (t, 3 H), 1.01 (t, 3 H), 3.35 (m, 4 H), 7.43 (m, 15 H).

Anal. Calcd for $C_{26}H_{25}NO$: C, 84.98; H, 6.86; N, 3.81. Found: C, 85.06; H, 6.68; N, 3.84.

Attempts to isomerize this cyclobutenone to the aminonaphthol with BF_3 etherate, *p*-toluenesulfonic acid, or methanolic hydrochloric acid failed. The starting cyclobutenone was recovered in all cases.

Reaction of N,N-Diethylcarbomethoxyethynylamine with Diphenylketene.—This reaction was carried out in dry benzene for 2 hr and gave a 15% yield of the cyclobutenone **9b**, mp 216–217° (turned blue at the melting point), after recrystallization from ethyl acetate: ir 1755, 1685, 1612 cm^{-1}; λ_{max}^{EtOH} 247, 275 mμ; nmr (in $CDCl_3$ with internal TMS) δ 0.45 (t, 3 H), 1.38 (t, 3 H), 3.39 (q, 2 H), 3.68 (s, 3 H), 4.14 (q, 2 H), 7.36 (s, 10 H).

Anal. Calcd for $C_{22}H_{23}NO_3$: C, 75.66; H, 6.64; N, 4.01. Found: C, 75.80; H, 6.51; N, 4.01.

Crystallization of the ethyl acetate soluble material from carbon tetrachloride–petroleum ether (bp 30–60°) gave a 53% yield of the cyclic ether **10a**: mp 114–115°; ir 1720, 1625 cm^{-1}; λ_{max}^{EtOH} 265 mμ; nmr (in $CDCl_3$ with internal TMS) δ 0.90 (t, 3 H), 1.17 (t, 3 H), 3.37 (m, 4 H), 3.82 (s, 3 H), 7.43 (s, 10 H).

Anal. Calcd for $C_{22}H_{23}NO_3$: C, 75.66; H, 6.64; N, 4.01. Found: C, 75.29; H, 6.41; N, 4.04.

Reaction of N,N-Diethylmethylethynylamine with Diphenylketene.—This reaction gave an 11% yield of the substituted cyclobutenone **9c**, mp 116–117°, which was crystallized from ethyl acetate–petroleum ether (bp 30–60°): ir 1740 cm^{-1}; λ_{max}^{EtOH} 228, 287 mμ; nmr (in $CDCl_3$ with internal TMS) δ 0.48 (t, 3 H), 1.31 (t, 3 H), 1.85 (s, 3 H), 3.33 (m, 4 H), 7.30 (s, 10 H).

Anal. Calcd for $C_{21}H_{23}NO$: C, 82.58; H, 7.59; N, 4.59. Found: C, 82.39; H, 7.74; N, 4.67.

Recrystallization of the ethyl acetate–petroleum ether (bp 30–60°) soluble material from ligroin (bp 90–120°) gave a 27% yield of the cyclic ether **10b**: mp 88–89°; ir 1620 cm^{-1}; λ_{max}^{EtOH} 215, 271 mμ; nmr (in $CDCl_3$ with internal TMS) δ 0.98 (t, 6 H), 2.11 (s, 3 H), 3.30 (q, 4 H), 7.33 (s, 10 H).

When this reaction was carried out in dry acetonitrile at −27° only the cyclic ether was obtained in 48% yield.

Anal. Calcd for $C_{21}H_{23}NO$: C, 82.58; H, 7.59; N, 4.59. Found: C, 82.75; H, 7.32; N, 4.51.

Reaction of N,N-Diethylphenylethynylamine with Dimethylketene.—Dimethylketene was generated by pyrolysis of tetramethylcyclobutanedione and trapped in dry tetrahydrofuran at −75°. The ynamine, 0.5 g (3.0 mmol), was added dropwise to the stirred solution of the dimethylketene at 0°. The mixture was then warmed to room temperature and stirred for an additional 2 hr. The solvent was removed under vacuum, and the mixture was chromatographed on 35 g of neutral alumina with these solvents: (1) benzene; (2) benzene–30% dichloromethane; and (3) benzene–40% dichloromethane. The 30% fraction gave 0.12 g (17% yield) of substituted cyclobutenone **9d**: bp 103° (0.05 mm); mp 51–52°; ir 1725 cm^{-1}; λ_{max}^{EtOH} 210, 280 mμ; nmr (in $CDCl_3$ with external TMS) δ 1.06 (t, 6 H), 1.30 (s, 6 H), 3.33 (q, 4 H), 7.20 (s, 5 H).

Anal. Calcd for $C_{16}H_{21}NO$: C, 78.97; H, 8.70; N, 5.76. Found: C, 79.23; H, 8.95; N, 5.53.

Reaction of N,N-Diethylphenylethynylamine with Phenylsulfene.—A solution of benzylsulfonyl chloride, 0.57 g (3.0 mmol), in 5 ml of dry tetrahydrofuran was added dropwise to a stirred solution of triethylamine, 0.39 g, and the ynamine, 0.51 g (3.0 mmol), in 20 ml of dry tetrahydrofuran. The mixture was stirred for 20 hr, and the triethylamine hydrochloride was filtered. Evaporation of the solvent under vacuum and crystallization of the residue from ethyl acetate afforded 0.40 g (42% yield) of product **11a**: mp 143–144°; ir 1620, 1275, 1100 cm^{-1}; λ_{max}^{EtOH} 227, 272 mμ; nmr (in $CDCl_3$ with internal TMS) δ 0.88 (t, 6 H), 3.06 (q, 4 H), 5.72 (s, 1 H), 7.44 (m, 10 H).

Anal. Calcd for $C_{19}H_{21}NO_2S$: C, 69.70; H, 6.47; N, 4.28; S, 9.77. Found: C, 69.96; H, 6.49; N, 4.09; S, 9.48.

Reaction of N,N-Diethylcarbomethoxyethynylamine with Phenylsulfene.—This reaction was carried out in benzene to give a 32% yield of product **11b**, mp 185–186°, after recrystallization from ethyl acetate. With tetrahydrofuran as a solvent the reaction gave a 16% yield of the product: ir 1615, 1710, 1283, 1170 cm^{-1}; λ_{max}^{EtOH} 222, 279 mμ; nmr (in $CDCl_3$ with internal TMS) δ 0.86 (t, 3 H), 1.26 (t, 3 H), 3.08 (q, 2 H), 3.82 (s, 3 H), 4.00 (q, 2 H), 5.65 (s, 1 H), 7.43 (m, 5 H).

Anal. Calcd for $C_{15}H_{19}NO_4S$: C, 58.24; H, 6.19; N, 4.54; S, 10.37. Found: C, 58.08; H, 6.19; N, 4.60; S, 10.24.

Reaction of N,N-Diethylmethylethynylamine with Phenylsulfene.—This reaction was carried out in dry benzene and gave a 54% yield of product **12a**, mp 108–109°, after recrystallization from isopropyl alcohol: ir 1635, 1255, 1085 cm^{-1}; λ_{max}^{EtOH} 236, 247 mμ; nmr (in $CDCl_3$ with internal TMS) δ 1.03 (t, 6 H), 1.66 (d, 3 H); 3.16 (q, 4 H), 4.63 (q, 1 H), 7.35 (s, 5 H).

Anal. Calcd for $C_{14}H_{19}NO_2S$: C, 63.38; H, 7.22; N, 5.28; S, 12.06. Found: C, 63.14; H, 7.21; N, 5.17; S, 11.98.

Reaction of N,N-Diethylcarbomethoxymethylethynylamine with Sulfene.—Methanesulfonyl chloride, 0.34 g (3.0 mmol), in 5 ml of dry benzene was added dropwise to a stirred solution of the ynamine, 0.46 g (3.0 mmol), and 0.3 g of triethylamine in 20 ml of dry benzene. The mixture was stirred for 20 hr, and the triethylamine hydrochloride was filtered. Evaporation of the solvent under vacuum and crystallization of the residue from ethyl acetate gave 0.21 g (30% yield) of product **11c**, mp 144–145°. With dioxane as the reaction solvent a yield of 23% was obtained: ir 1700, 1625, 1285, 1125 cm^{-1}; λ_{max}^{EtOH} 277 mμ; nmr (in $CDCl_3$ with internal TMS) δ 1.28 (t, 6 H), 3.43 (q, 2 H), 3.78 (s, 3 H), 3.98 (q, 2 H), 4.41 (s, 2 H).

Anal. Calcd for $C_9H_{15}NO_4S$: C, 46.35; H, 6.48; N, 6.01. Found: C, 46.51; H, 6.35; N, 5.86.

Reaction of N,N-Diethylphenylethynylamine with Sulfene.—This reaction was carried out in dry tetrahydrofuran and gave a 60% yield of product **11d**, mp 132–133°, after recrystallization from ethyl acetate: ir 1640, 1270, 1115 cm^{-1}; λ_{max}^{EtOH} 229, 284 mμ; nmr (in $CDCl_3$ with internal TMS) δ 1.00 (t, 6 H), 3.15 (q, 4 H), 4.43 (s, 2 H), 7.40 (s, 5 H).

Anal. Calcd for $C_{13}H_{17}NO_2S$: C, 62.14; H, 6.82; N, 5.57. Found: C, 62.39; H, 6.70; N, 5.73.

Reaction of N,N-Diethylmethylethynylamine with Sulfene.—This reaction was carried out in dry tetrahydrofuran and gave a 66% yield of an oil, bp 120–125° (block temperature) at 0.001 mm, which was a 1:1 mixture of double-bond isomers, **11e** and **12b** (the mixture was not formed by thermal rearrangement, since the nmr spectra before and after distillation showed the same 1:1 ratio): ir 1610, 1640, 1265, 1100 cm^{-1}; λ_{max}^{EtOH} 204, 240 mμ; nmr (in CCl_4 with external TMS) δ 1.18 (t, 6 H); 1.50 (d, 1.5 H), 1.83 (s, 1.5 H), 3.21 (q, 4 H), 4.18 (d, 1 H), 4.53 (q, 0.52 H), 5.08 (s, 0.53 H); mass spectrum, *m/e* 189 (molecular ion), 96, 68 (major ions).

Reaction of N,N-Diethylphenylethynylamine with Phenyl Isocyanate.—A solution of 0.50 g (3.0 mmol) of the ynamine in 2 ml of dry acetonitrile was added dropwise to a stirred solution of 0.36 g (3.0 mmol) of phenyl isocyanate in 10 ml of dry acetonitrile. The mixture was stirred for 19 hr, and the white precipitate was filtered. Recrystallization from isopropyl alcohol–ethyl acetate gave 0.15 g (17% yield) of the carbostyril **13a**: mp 238–239°; ir 1640, 3450 cm^{-1}; λ_{max}^{EtOH} 233, 275, 335 mμ; nmr (in $CDCl_3$ with internal TMS) δ 1.00 (t, 6 H), 2.90 (q, 4 H), 7.40–7.90 (m, 9 H), 12.00 (s, 1 H).

No additional carbostyril could be obtained even after chromatography on Florisil.

When the reaction was carried out in nitromethane and dichloromethane the yields of **13a** were 15 and 9%, respectively.

Anal. Calcd for $C_{19}H_{20}N_2O$: C, 78.15; H, 6.90; N, 9.59. Found: C, 77.72; H, 6.73; N, 9.57.

A solution of 0.51 g of the ynamine in 5 ml of dry benzene was added dropwise to a stirred solution of 0.36 g of phenyl isocyanate in 25 ml of dry benzene. The temperature of the reaction was kept at 45° during the addition, and the mixture was stirred at room temperature for 24 hr after the addition. The precipitated solid **14a** was filtered and recrystallized from ethanol: 0.25 g (28% yield); mp 258–259°; ir 1620, 1575 cm^{-1}; λ_{max}^{EtOH} 230, 267, 325 mμ.

Anal. Calcd for $C_{19}H_{20}N_2O$: C, 78.15; H, 6.90; N, 9.59. Found: C, 78.30; H, 6.94; N, 9.86.

Reaction of N,N-Dipropylpentylethynylamine with Phenyl Isocyanate.—This reaction was carried out for 96 hr in dry acetonitrile to give a 50% yield of the carbostyril **13b** which recrystallized from ethyl acetate–petroleum ether (bp 30–60°): mp 119–120°; ir 1650, 3450 cm^{-1}; λ_{max}^{EtOH} 223, 282, 355, 373 mμ; nmr (in $CDCl_3$ with internal TMS) δ 0.95 (t, 9 H), 1.67 (m, 10 H), 2.95 (s, 2 H), 3.30 (t, 4 H), 7.50–8.10 (m, 3 H), 9.50 (d, 1 H), 13.70 (s, 1 H).

Anal. Calcd for $C_{20}H_{30}N_2O$: C, 76.37; H, 9.62; N, 8.90. Found: C, 76.09; H, 9.80; N, 9.17.

Reaction of N,N-Diethylcarbomethoxyethynylamine with Phenyl Isocyanate.—This reaction was run in dry acetonitrile for 20 hr to give a 51% yield of the carbostyril **13c**, which crystallized from ethyl acetate: mp 191–192°; ir 1735, 1650, 1605 cm^{-1}; λ_{max}^{EtOH} 233, 330 mμ; nmr (in $CDCl_3$ with internal TMS) δ, 1.16 (t, 6 H), 3.35 (q, 4 H), 4.00 (s, 3 H), 7.0–7.50 (m, 3 H), 7.83 (d, 1 H), 12.95 (s, 1 H).

Anal. Calcd for $C_{15}H_{18}N_2O_3$: C, 65.82; H, 6.62; N, 10.22. Found: C, 65.71; H, 6.52; N, 10.13.

Reaction of N,N-Diethylmethylethynylamine with Phenyl Isocyanate.—This reaction was carried out under the same conditions and gave a 63% yield of carbostyril **13d**, which crystallized from ethyl acetate: mp 122–123°; ir 1640 cm^{-1}; λ_{max}^{EtOH} 215, 271 mμ; nmr (in $CDCl_3$ with internal TMS) δ 1.08 (t, 6 H), 2.30 (s, 3 H), 3.33 (q, 4 H), 7.0–8.0 (m, 4 H), 12.83 (s, 1 H); (in hexamethylphosphortriamide) δ 11.83 (sharp s) for NH.

Anal. Calcd for $C_{14}H_{18}N_2O$: C, 73.01; H, 7.88; N, 12.17. Found: C, 72.78; H, 7.83; N, 12.17.

The reaction of the N,N-diethylmethylethynylamine with phenyl isocyanate in benzene gave a 31% yield of the 2-N,N-diethylamino-3-methyl-4-quinolone **14b**: mp 294–295° (from ethanol); ir 1620, 1580 cm^{-1}; λ_{max}^{EtOH} 230, 263, 324 mμ; nmr in hexamethylphosphortriamide showed the N–H at δ 11.50 as a very broad singlet.

Anal. Calcd for $C_{14}H_{18}N_2O$: C, 73.01; H, 7.88; N, 12.17. Found: C, 73.06; H, 7.87; N, 12.25.

Recrystallization of the alcohol-soluble material gave a 20% yield of the 3-methyl-4-N,N-diethyl-2-quinolone **13d**, mp 122–123°, from ethyl acetate.

Reaction of N,N-Dipropylpentylethynylamine with α-Naphthyl Isocyanate.—This reaction was carried out in dry acetonitrile for 5 hr. A 66% yield of the addition product **18a** was obtained. The compound recrystallized from ethyl acetate: mp 199–201°; ir 1625, 3260 cm^{-1}; λ_{max}^{EtOH} 232, 282 355, 373 mμ; nmr (in $CDCl_3$ with internal TMS) δ 0.95 (t, 9 H), 1.67 (m, 10 H), 2.95 (s, 2 H), 3.30 (t, 4 H), 7.50–8.10 (m, 5 H), 9.50 (d, 1 H), 13.70 (s, 1 H).

Anal. Calcd for $C_{24}H_{32}N_2O$: C, 79.08; H, 8.86; N, 7.70. Found: C, 79.06; H, 8.60; N, 7.87.

Reaction of N,N-Diethylcarbomethoxyethynylamine with α-Naphthyl Isocyanate.—This reaction was carried out under the same conditions and gave a 92% yield of the adduct **18b**, mp 250–251°, which was recrystallized from dichloromethane–ethyl acetate: ir 1620, 1735 cm^{-1}; λ_{max}^{EtOH} 230, 283 mμ; nmr (in $CDCl_3$ with internal TMS) δ 1.20 (t, 6 H), 3.40 (q, 4 H), 4.08 (s, 3 H), 7.4–7.90 (m, 5 H), 9.06 (m, 1 H), 12.92 (s, 1 H).

Anal. Calcd for $C_{19}H_{20}N_2O_3$: C, 70.35; H, 6.22; N, 8.64. Found: C, 70.09; H, 6.32; N, 8.78.

Reaction of N,N-Diethylmethylethynylamine with α-Naphthyl Isocyanate.—This reaction was carried out in dry acetonitrile for 24 hr and gave a 73% yield of product **18c**, mp 199–200°, after recrystallization from ethyl acetate: ir 3140, 1625 cm^{-1}; λ_{max}^{EtOH} 240, 285, 355, 372 mμ; nmr (in $CDCl_3$ with internal TMS) δ 1.11 (t, 6 H), 2.41 (s, 3 H), 3.36 (q, 4 H), 7.4–8.0 (m, 5 H), 9.15 (d, 1 H), 12.90 (s, 1 H), (in hexamethylphosphortriamide with external TMS) δ 12.5 (broad singlet, 1 H).

Anal. Calcd for $C_{18}H_{20}N_2O$: C, 77.10; H, 7.19; N, 9.99. Found: C, 76.62; H, 7.65; N, 9.56.

Alternatively, this reaction was run in cyclohexane to give an immediate precipitate of the 3-methyl-4-N,N-diethylamino-7,8-benzo-2-quinolone (**18c**). Removal of the solvent under vacuum gave a yellow oil, which, on heating at 100° for 3 hr and cooling gave 0.12 g of 2-N,N-diethyl-3-methyl-7,8-benzo-4-quinolone (**19**) [mp 210–211°, ir 1600, 1545 cm^{-1}; λ_{max}^{EtOH} 225, 246, 275 mμ; nmr (in hexamethylphosphortriamide with external TMS) δ 11.0 (broad singlet, 1 H)] after recrystallization from ethanol. A mixture of compounds **19** and **18c** melted at 165–185°.

Anal. Calcd for $C_{18}H_{20}N_2O$: C, 77.10; H, 7.19; N, 9.99. Found: C, 77.21; H, 7.40; N, 9.86.

Reduction of 3-Methyl-4-N,N-diethyl-2-quinolone.—A solution of 2.0 g (8.7 mmol) of the 2-quinolone **13d** in 60 ml of dry dioxane was refluxed with 1 g of lithium aluminum hydride for 24 hr. The excess lithium aluminum hydride was hydrolyzed with a few drops of 50% sulfuric acid; the dioxane was taken off under vacuum and 15 ml of 10% NaOH solution was added. The basic solution was then extracted with three 20-ml portions of dichloromethane; the extract was dried over magnesium sulfate; and concentrated to an oil. Chromatography of this oil, 1.8 g, on 40 g of neutral alumina, activity I, with (1) petroleum ether–20% dichloromethane, (2) dichloromethane, and (3) dichloromethane–20% chloroform as solvents gave, in fraction 1, an oil that was a mixture of 3-methylquinoline **15a** and 3-methyl-4-N,N-diethylaminoquinoline **16a**. This oil was distilled to give 0.3 g of 3-methylquinoline **15a**, bp 74–76° (block temperature) at 1 mm. This quinoline formed a picrate, mp 186–187° (lit.[21] mp 187°), after recrystallization from ethanol: ir 2700, 1625, 1555, 1315 cm^{-1}; λ_{max}^{EtOH} (picrate) 210, 229, 233, 360 mμ; nmr (in CCl_4 with external TMS) (free amine) δ 2.11 (t, 3 H), 6.7–7.1 (m, 4 H), 7.91 (d, 1 H), 8.45 (d, 1 H).

Anal. Calcd for $C_{16}H_{12}N_4O_7$: C, 51.62; H, 3.25; N, 15.05. Found: C, 51.34; H, 3.67; N, 14.26.

The second fraction of 0.2 g, bp 57–61° (block temperature) at 0.005–0.001 mm, was 3-methyl-4-N,N-diethylaminoquinoline **16a**. It formed a perchlorate salt, which crystallized from ethanol: mp 237–240°; ir (perchlorate salt) 3250, 1115 cm^{-1}; λ_{max}^{EtOH} 208, 230, 265, 388 mμ; nmr (in CCl_4 with external TMS) (free amine) δ 0.90 (t, 6 H), 2.21 (s, 3 H), 3.18 (q, 4 H), 7.2–7.5 (m, 2 H), 7.8–8.1 (m, 2 H), 8.45 (s, 1 H).

Anal. Calcd for $C_{14}H_{19}ClN_2O_4$: C, 53.41; H, 6.09; N, 8.90; Cl, 11.27. Found: C, 53.27; H, 5.87; N, 8.78; Cl, 11.41.

Reduction of 3-Methyl-2-N,N-diethylamino-4-quinolone with Lithium Aluminum Hydride.—Reduction of quinoline **14b** with lithium aluminum hydride in refluxing N-ethylmorpholine for 6 hr gave 2-N,N-diethylamino-3-methylquinoline (**17**). This quinoline could be separated by tlc on silica gel with chloroform–ethanol (98:2) as the eluent. The 2-N,N-diethylamino-3-methylquinoline formed a perchlorate which was recrystallized from ethanol: mp 188–189°; ir (perchlorate salt) 3400, 1635, 1100 cm^{-1}; λ_{max}^{EtOH} 215, 253, 340 mμ; nmr (in CCl_4) (free amine) δ 1.15 (t, 6 H), 2.38 (s, 3 H), 3.33 (q, 4 H), 7.2–7.9 (m, 5 H).

Anal. Calcd for $C_{14}H_{19}ClN_2O_4$: C, 53.41; H, 6.09; N, 8.90. Found: C, 53.94; H, 6.22; N, 8.53.

Reduction of the quinolone **14b** in dioxane gave only 3-methylquinoline **15a**.

Reduction of 3-Phenyl-4-N,N-diethylamino-2-quinolone with Lithium Aluminum Hydride.—This reduction gave a mixture that could be separated by tlc on silica gel with dichloromethane–ethanol (49:1) as the eluent. The 3-phenyl-4-N,N-diethylaminoquinoline **16b** was recrystallized from petroleum ether (bp 30–60°): mp 117–118°; λ_{max}^{EtOH} 229, 276, 355 mμ; nmr (in $CDCl_3$ with internal TMS) δ 1.00 (t, 3 H), 3.00 (q, 4 H), 7.2–8.1 (m, 9 H), 8.66 (s, 1 H).

Anal. Calcd for $C_{19}H_{20}N_2$: C, 82.57; H, 7.29; N, 10.14. Found: C, 82.80; H, 7.13; N, 9.80.

Reduction of 3-Pentyl-4-N,N-dipropylamino-2-quinolone with Lithium Aluminum Hydride.—This reduction gave an oil that on distillation gave 3-pentylquinoline **15b**, bp 69–72° (block temperature) at 0.005–0.001 mm. This oil formed a picrate, which was recrystallized from ethanol: mp 155–156°; ir (picrate) 2550–2750 cm^{-1}; λ_{max}^{EtOH} 210, 230, 235, 362 mμ; nmr (in CCl_4) (free base) δ 0.8–1.8 (m, 9 H), 2.71 (t, 2 H), 7.4–8.1 (m, 5 H), 8.53 (d, 1 H).

Anal. Calcd for $C_{20}H_{20}N_4O_7$: C, 56.07; H, 4.71; N, 13.08. Found: C, 56.32; H, 4.95; N, 13.23.

Distillation of the remaining oil gave the 3-pentyl-4-N,N-dipropylaminoquinoline: bp 80–82° (block temperature) at 0.001 mm; λ_{max}^{EtOH} 229, 262 mμ; nmr (in CCl_4, external TMS) δ 0.83 (t, 9 H), 1.1–1.8 (m, 10 H), 2.75 (t, 2 H), 3.21 (t, 4 H), 7.3–8.1 (m, 4 H), 8.65 (s, 1 H). A hydrobromide formed in ethyl acetate: mp 133°.

Reduction of 3-Methyl-4-N,N-diethylamino-7,8-benzo-2-quinolone with Lithium Aluminum Hydride.—Reduction of this quinolone gave 3-methyl-4-N,N-diethylamino-7,8-benzoquinoline (**20**) in essentially quantitative yield. This quinoline formed a hydrobromide salt, which was recrystallized from isopropyl alcohol: mp 215–216°; ir (salt) 2700–2800 cm^{-1}; λ_{max}^{EtOH} 211, 233, 270 mμ; nmr (in CCl_4 with external TMS) (free base) δ 0.91 (t, 6 H), 2.30 (s, 3 H), 3.16 (q, 4 H), 7.4–8.0 (m, 5 H), 8.56 (s, 1 H), 9.16 (m, 1 H).

Anal. Calcd for $C_{18}H_{21}BrN_2$: C, 62.55; H, 6.13; N, 8.11; Br, 23.13. Found: C, 62.29; H, 6.03; N, 8.20; Br, 23.37.

Reaction of N,N-Diethylphenylethynylamine with Benzonitrile Oxide.—A solution of 1 ml of triethylamine in 10 ml of anhydrous ether was added dropwise to a stirred solution of 0.43 g of phenylchlorohydroxamic acid and 0.45 g of N,N-diethylphenylethynylamine in 20 ml of anhydrous ether. The triethylamine hydrochloride was filtered, and the residue on crystallization from petroleum ether (bp 30–60°) afforded 0.47 g (42% yield) of the

(21) W. P. Untermohlen, Jr., *J. Org. Chem.*, **18**, 544 (1953).

1,3 dipolar cycloaddition product **21**: mp 87–88°; ir 1615, 775 cm^{-1} (N–O); λ_{max}^{EtOH} 245, 293 mμ; nmr (in CCl_4 with external TMS) δ 1.1 (t, 6 H), 3.2 (q, 4 H), 7.23 (m, 10 H).

Anal. Calcd for $C_{19}H_{20}N_2O$: C, 78.15; H, 6.90; N, 9.59. Found: C, 77.93; H, 6.87; N, 9.35.

Reaction of N,N-Diethylphenylethynylamine with Tetraphenylcyclopentadienone.—Tetraphenylcyclopentadienone, 0.5 g (1.5 mmol), and the ynamine, 0.25 g (1.5 mmol), in 3 ml of dry diglyme were heated in a sealed tube at 180° for 12 hr. Filtration of the mixture and recrystallization of the solid from toluene gave 50 mg (7% yield) of pentaphenyl-N,N-diethylaniline (**22**): mp 326–328; nmr (in $CDCl_3$ with internal TMS) δ 0.55 (t, 6 H), 2.5 (q, 4 H), 6.80 (m, 15 H), 7.10 (10 H).

Anal. Calcd for $C_{40}H_{35}N$: C, 90.69; H, 6.66; N, 2.64. Found: C, 90.90; H, 6.55; N, 2.90.

2-Naphthal- and 3-Pyridalsulfonimides.—The 2-naphthal-*p*-toluenesulfonimide was prepared in 90% yield according to the method of Kresze.[14] This sulfonimide was recrystallized from ethyl acetate and had mp 114–115°.

Anal. Calcd for $C_{18}H_{15}NO_2S$: C, 69.89; H, 4.89; N, 4.53; S, 10.34. Found: C, 69.69; H, 5.04; N, 4.57; S, 10.33.

The 3-pyridal-*p*-toluenesulfonimide was prepared in the same manner in 40% yield and had mp 131–132° after recrystallization from ethyl acetate–petroleum ether (bp 30–60°).

Anal. Calcd for $C_{18}H_{12}N_2O_2S$: C, 59.99; H, 4.65; N, 10.77; S, 12.29. Found: C, 59.53; H, 4.78; N, 10.30; S, 11.99.

Registry No.—**1**, 17691-74-6; **2**, 17691-75-7; **3a**, 17691-76-8; **3b**, 17691-77-9; **3c**, 17691-78-0; **3d**, 17691-79-1; **4a**, 17691-80-4; **4b**, 17691-81-5; **4c**, 17691-82-6; **5a**, 17692-75-0; **5b**, 17692-86-3; **5c**, 17692-87-4; **5d**, 17692-88-5; **5e**, 17692-76-1; **5f**, 17693-46-8; **5g**, 17693-47-9; **5h**, 17693-48-0; **5i**, 17693-49-1; **6**, 17693-50-4; **7**, 17692-77-2; **7** HBr, 17692-78-3; **8**, 17691-83-7; **9a**, 17691-84-8; **9b**, 17691-85-9; **9c**, 17691-86-0; **9d**, 17691-87-1; **10a**, 17691-88-2; **10b**, 17691-89-3; **11a**, 17691-90-6; **11b**, 17691-91-7; **11c**, 17691-92-8; **11d**, 17691-93-9; **11e**, 17691-94-0; **12a**, 17691-95-1; **12b**, 17691-96-2; **13a**, 17691-97-3; **13b**, 17691-98-4; **13c**, 17691-99-5; **13d**, 17692-00-1; **14a**, 17692-01-2; **14b**, 17692-02-3; **15a**, 612-58-8; **15b**, 17692-04-5; **15b** picrate, 17692-05-6; **16a**, 17692-06-7; **16a** perchlorate, 17692-07-8; **16b**, 17692-08-9; **17** perchlorate, 17692-09-0; **18a**, 17692-10-3; **18b**, 17692-11-4; **18c**, 17692-12-5; **19**, 17692-79-4; **20** HBr, 17692-80-7; **21**, 17692-81-8; **22**, 17692-82-9; 3-pentyl-4-N,N-dipropylaminoquinoline, 17692-83-0; 3-pentyl-4-N,N-dipropylaminoquinoline HBr, 17743-99-6; 2-naphthal *p*-toluenesulfonimide, 17692-84-1; 3-pyridal *p*-toluenesulfonimide, 17692-85-2; **15a**, picrate, 17693-31-1.

Formation of Pyrazoles from 3,3-Disubstituted 2,4-Pentanediones. Evidence of a Novel Claisen–Cope Type of Rearrangement

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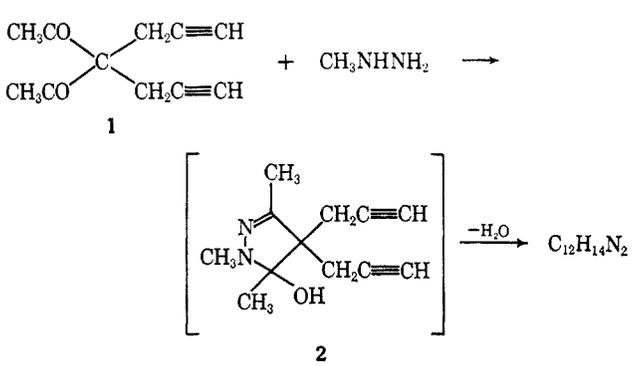
Reaction of monosubstituted hydrazines with 3,3-disubstituted 2,4-pentanediones having one or more allylic or propargylic groups at C-3 afforded high yields of pyrazoles bearing, respectively, 5-$CH_2CH(R)CH{=}CH_2$ or 5-$CH_2C(R){=}C{=}CH_2$ substituents. All evidence points to formation of an intermediate 5-methylene pyrazoline whose allylic or propargylic groups undergo a novel type of Claisen–Cope rearrangement, becoming attached to the enaminic methylene group with synchronous pyrazole formation. Treatment of 3-allyl-3-(2-propynyl)-2,4-pentanedione (**17**) with methylhydrazine leads to condensation and propargyl → allene rearrangement even at 0° and the relative rearrangement rates of allyl to propargyl were about 1.6:1 under the conditions studied. Similar reaction of methylhydrazine with 3-benzyl-3-methyl-2,4-pentanedione (**13**) produced the *exo*-methylene enamine **14** which was relatively stable under its conditions of formation. The enamine **14** underwent thermal rearrangement at 175° to 5-(2-phenylethyl)-1,3,4-trimethylpyrazole (**16**), evidently by a different type of process.

While the reaction of 3,3-disubstituted 2,4-pentanediones with hydrazine to give isopyrazoles is well known,[1,2] reaction of such substituted diketones with substituted hydrazines is imperfectly understood. Bis-2,4-dinitrophenylhydrazones[3–5] and bisphenylhydrazones[6] are usually formed, although 1:1 addition[7] and lack of reaction[8] have also been reported. Condensations with monoalkylhydrazines have apparently not been studied.

Reaction of 3,3-di(2-propynyl)-2,4-pentanedione (**1**) with methylhydrazine (*ca.* 1:1 mol ratio) in refluxing ethanol containing aqueous acetic acid gave a 72% yield of a crystalline base, $C_{12}H_{14}N_2$, corresponding to a loss of 1 mol of water from the hypothetical carbinolamine **2**.[9] The infrared (ir) spectrum of the product



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