TABLE I
DIETHYL β-KETOTHIOPHOSPHONATES 3[a]

Series	R	Bp, °C (mm)	Yield,[b] %
a	CH_3	70–71 (0.12)	85
b	n-C_3H_7	101 (0.50)	92
c	n-C_4H_9	96–97 (0.10)	93
d	n-C_6H_{13}	140 (0.76)	87
e	$C_6H_5CH_2CH_2$	157–158 (0.10)	71

[a] Satisfactory analytical values (±0.4% for C, H, P, S) were obtained for all compounds. [b] This is the per cent yield of the distilled material based on the starting alkynyl-1-thiophosphonates 1.

ethyl groups display two quartets (J_{PH} = 7.5, J_{PH} = 10.5 Hz) at δ ~4.15. However, at 100 MHz, further resolution into four quartets occurs. This splitting pattern is apparently due to the magnetic nonequivalence of these methylene protons.

Experimental Section

The nmr spectra were determined on a Varian A-60 spectrometer using deuteriochloroform as solvent and tetramethylsilane as an internal standard. The chemical analyses were performed by Geller Microanalytical Laboratories, Saddle River, N.J.

Preparation of Diethyl β-Ketothiophosphonates 3a–e. General Procedure.—The diethyl alkynyl-1-thiophosphonates 1 (0.025 mol) were refluxed with a 10–12 molar excess of n-butylamine. The reflux was continued for 2–3 days until the ir spectra of a test portion of the reaction mixture showed complete disappearance of the absorption band in the region of 4.52–4.56 μ (C≡C).[2] The excess amine was evaporated *in vacuo* at aspirator pressure. The resulting adduct was dissolved in ether (100 ml) and 100 ml of 1% aqueous solution of oxalic acid was added. The two-layer reaction mixture was stirred for 4–5 hr at room temperature and then transferred to a separatory funnel. The organic layer was separated and the aqueous layer was extracted twice with 25-ml portions of ether. The combined ether extracts were dried ($MgSO_4$) and filtered, and ether was distilled off. The resulting oil was short path distilled under reduced pressure.

Registry No.—**3a**, 1067-72-7; **3b**, 34281-17-9; **3c**, 34297-64-8; **3d**, 34281-18-0; **3e**, 34281-19-1.

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Preparation of *N*,*N*-Diethylcyanoynamine and Its Reactions with Phenyl Isocyanate and Phenylsulfene

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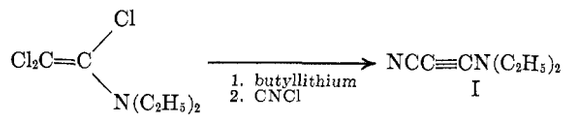
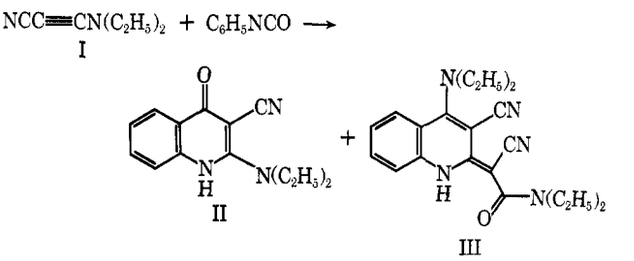
In a previous investigation of ynamine chemistry[1] we had prepared *N*,*N*-diethylcarbomethoxyethynylamine by a reaction of methyl chlorocarbonate with the lithium salt of *N*,*N*-diethylethynylamine. Similarly, the cyanoynamine I could be prepared in 63% yield from *N*,*N*-diethyltrichlorovinylamine, n-butyllithium, and cyanogen chloride.[2,3]



While our earlier study had shown that phenyl isocyanate adds to ynamines with methyl, phenyl, and carbomethoxy substituents to give 4-amino-2-quinolones and 2-amino-4-quinolones, we have now found that the cyanoynamine I reacts with phenyl isocyanate to produce a 2-amino-4-quinolone II and a 2:1 adduct of ynamine and phenyl isocyanate as the major product. Spectroscopic evidence indicated a conjugated dinitrile diethylamide with four aromatic protons and one NH proton [ir 3420, 2205, 2180, 1612 cm^{-1}; nmr δ 1.29 (t, 12 H), 3.6 and 3.8 (q, 8 H), 7.6 (m, 4 H), 15.0 (s, 1 H); m/e 363 (parent), 100 (100%, diethyl amide)]. A 4-amino-2-quinolone methine or a 2-amino-4-quinolone methine structure was thus possible for the 2:1 adduct. The first alternative, III, could be established by single-crystal X-ray analysis.[4]



The formation of the new product does not seem to be due to reaction of an initially formed 4-amino-2-quinolone with a second equivalent of ynamine, since attempts to add the cyanoynamine I to 3-phenyl or 3-carbomethoxy-4-amino-2-quinolones led only to recovered starting materials. Furthermore, very slow addition of the cyanoynamine to 2 equiv of phenyl isocyanate again gave only the initially observed products and unreacted phenyl isocyanate, but no 4-amino-2-quinolone.

These results demonstrate a third reaction pathway for the addition of phenyl isocyanate to an ynamine. In addition to the initially observed six-center reaction (path a, stepwise or concerted) leading directly to 4-amino-2-quinolones and the β-lactam formation (path b) as intermediate to 2-amino-4-quinolones, one now encounters addition of the ynamine to the carbonyl double bond of phenyl isocyanate (path c), followed by ring opening and addition of a second equivalent of ynamine to the keteneimine.[5,6] An alternative scheme, where the four-membered intermediate of path b is

(1) M. E. Kuehne and P. J. Sheeran, *J. Org. Chem.*, **33**, 4407 (1968).

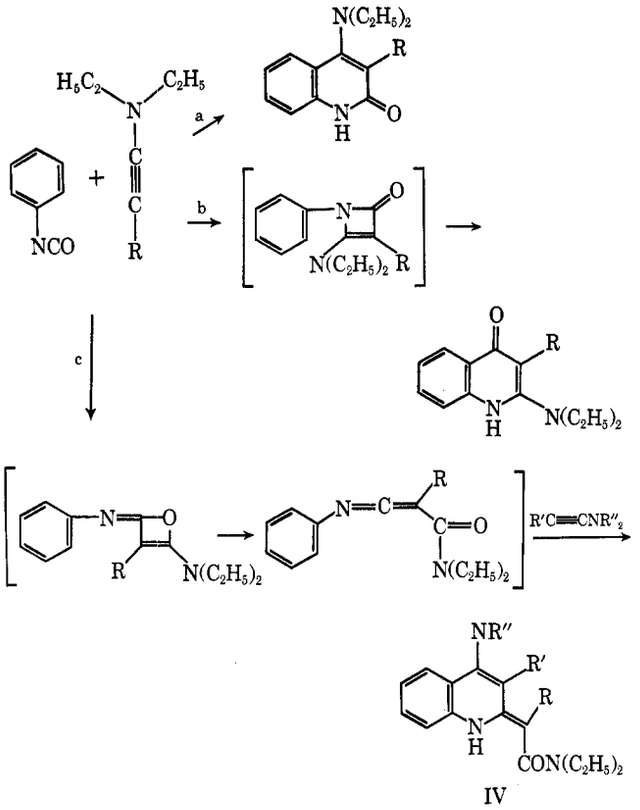
(2) The principle of this reaction was first described by J. Ficini and C. Barbara, *Bull. Soc. Chim. Fr.*, 2787 (1965).

(3) An alternative route to cyanoynamines from chlorocyanoacetylene and secondary amines has since been described: T. Sasaki and A. Kojina, *J. Chem. Soc. C*, 476 (1970).

(4) We thank Drs. J. A. Lerbscher and J. Trotter of the University of British Columbia, Vancouver, Canada, for the results of this study which will be published separately.

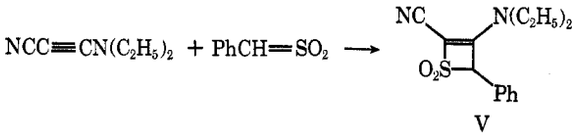
(5) Reactions of *N*-phenylketeneimines with ynamines have been found to produce 2-alkyl-4-aminoquinolines: L. Ghosez and P. de Perez, *Angew. Chem., Int. Ed. Engl.*, **10**, 184 (1971).

(6) Alkyl isocyanates and diethylamino-1-propyne gave keteneimines: J. U. Piper, M. B. Allard, and V. Lee, Abstracts, 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971, ORGN 103.



converted to all three product types, could not yet be ruled out rigorously.

The cyanoynamine I reacted with phenylsulfene to give a four-membered cyclic sulfone V in analogy to other ynamines reported[1] previously.



Experimental Section

Preparation of *N*,*N*-Diethylcyanoethynylamine (I).—A solution of 36.5 ml of 1.6 *M* *n*-butyllithium in hexane (58.5 mmol) diluted with 10 ml of dry ether was slowly added to 5.8 g (28.6 mmol) of *N*,*N*-diethyl-1,2,2-trichlorovinylamine at −20°. After stirring at room temperature for 45 min the mixture was cooled again to −20° and 1.75 g (28.6 mmol) of cyanogen chloride in 5 ml of dry ether was added slowly. The mixture was stirred for 45 min at room temperature and centrifuged. Evaporation of the supernatant and two ether washes of the precipitated lithium chloride gave a thick liquid which was distilled. The ynamine was collected in Dry Ice, bp 45–55° (0.04 mm). After two distillations 2.10 g (63%) of the ynamine was collected: bp 47° (0.05 mm); ν_{max}^{neat} 2945, 2210, 2135, 1432 cm^{-1}; nmr ($CDCl_3$ with TMS) δ 1.24 (t, 3 H), 3.13 (q, 2 H); uv λ_{max}^{hexane} 221, 232, 242 (ϵ 5.85 × 10^5), 254 mμ.

Anal. Calcd for $C_7H_{10}N_2$: C, 68.82; H, 8.25; N, 22.93. Found: C, 68.59; H, 8.27; N, 22.75.

Reaction of *N*,*N*-Diethylcyanoethynylamine with Phenylsulfene.—Benzylsulfonyl chloride, 0.932 g (4.91 mmol), suspended in 5 ml of benzene was added to a solution of 0.6 g (4.91 mmol) of the cyanoynamine and 0.6 g (5.95 mmol) of triethylamine in 15 ml of dry benzene. The solution was stirred for 18 hr and the precipitated triethylamine hydrochloride was filtered. The collected filtrate was vacuum evaporated to a thick oil which crystallized from ethyl acetate. Recrystallization from isopropyl alcohol gave 0.132 g (9.8%) of the 1:1 adduct V, mp 194–195°. Reactions in tetrahydrafuran and dichloromethane at −30° for 1 hr and subsequently at 0° for 48 hr did not give improved yields of the adduct, nor could other products be identified.

Spectral data follow: ν_{max}^{KBr} 2190, 1600, 1580, 1512, 1308, 1160, 1120 cm^{-1}; nmr (DMSO-d_6 with TMS) δ 1.12 (t, 6 H), 3.53 (q, 4 H), 4.61 (s, 1 H), 7.50 (s, 5 H); uv λ_{max}^{EtOH} 223, 283, 344 mμ.

Anal. Calcd for $C_{14}H_{16}N_2O_2S$: C, 60.86; H, 5.84; N, 10.14; S, 11.58. Found: C, 60.93; H, 5.68; N, 10.10; S, 11.69.

Reaction of *N*,*N*-Diethylcyanoethynylamine with Phenyl Isocyanate.—A solution of 0.840 g (7.85 mmol) of phenyl isocyanate in 5 ml of dry acetonitrile or benzene was added to 0.862 g (7.12 mmol) of the ynamine I at room temperature. The solution was stirred for 60 hr under nitrogen, and the precipitated 2-amino-4-quinolone was filtered and washed with ethanol, yielding 60 mg (7.1%) of white needles: mp 297–298° dec; ν_{max}^{KBr} 2940, 2200, 1627, 1613, 1580, 1333 cm^{-1}; nmr (HMPA) sharp NH singlet at δ 8.75; uv $\lambda_{max}^{Ethanol}$ 243, 260, 308 mμ.

Anal. Calcd for $C_{14}H_{15}N_3O$: C, 69.68; H, 6.27; N, 17.42. Found: C, 69.88; H, 6.36; N, 17.16.

Changing solvent from acetonitrile to benzene did not affect this reaction and no 4-amino-2-quinolone could be obtained even when a dilute solution of ynamine (0.5 g in 10 ml) was added to a twofold excess of phenyl isocyanate in benzene or acetonitrile over a period of 7 hr. Evaporation of the filtrate and chromatography on a column of Woelm silica gel (activity I) in methylene chloride and ethanol (0.5%) gave a yellow solid, 0.592 g (46%), which was recrystallized from ethyl acetate to mp 135–136° and distilled at block temperature 170° (0.001 mm). This product is the 2:1 adduct IV by the following data: ν_{max}^{KBr} 3420, 2950, 2910, 2205, 2180, 1612, 1600, 1562, 1552 cm^{-1}; nmr ($CDCl_3$ with TMS) δ 1.29 (t, 12 H), 3.6 (q), 3.8 (q) (total 8 H), 7.6 (m, 4 H), 15.0 (s, 1 H); uv ν_{max}^{EtOH} 230, 243, 264, 333 mμ; the 333-mμ absorption shifted to 353 mμ in base and returned to 333 mμ upon acidification; major mass spectrum peaks *m/e* (rel intensity) 363 (10), 348 (10), 334 (10), 266 (10), 239 (10), 100 (100), 72 (40), 44 (10), 29 (20).

Anal. Calcd for $C_{21}H_{25}N_3O$: C, 69.38; H, 6.93; N, 19.27. Found: C, 69.21; H, 7.04; N, 19.49.

A reaction in tetrahydrofuran at −30° for 1 hr and 0° for 48 hr gave a 17% yield of the 2:1 adduct. No other products or intermediates could be identified. Attempted reactions of 4-*N*,*N*-diethylamino-3-phenyl-2-quinolone with *N*,*N*-diethylcyanoethynylamine.

Addition of the cyanoynamine I to the 3-phenyl- (or 3-carbethoxy-) 4-amino-2-quinolone in either hexamethylphosphotriamide or acetonitrile for 36 hr yielded only starting materials by tlc and ir.

Registry No.—I, 26391-04-8; IV, 34281-05-5; V, 34281-06-6; phenyl isocyanate, 1122-85-6; phenylsulfene, 17346-42-8; 2-amino-4-quinolone, 34281-08-8.

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A Facile Method for N-Acylation of Ring Activated Phenylhydroxylamines

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During a study of methods for the preparation of structural analogs of 2,4-dihydroxy-1,4-benzoxazin-3-one,[2] it was found that the acylation of *o*-methoxy-

(1) Taken in part from the dissertation presented by M. D. Corbett, Nov 1970, to the Graduate School of the University of Kansas in partial fulfillment of the requirements for the Doctor of Philosophy Degree.

(2) E. E. Smissman and M. D. Corbett, *J. Org. Chem.*, **37**, 1704 (1972).