Addition of Secondary Amines to Diacetylenic Ketones

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Secondary amines add across the free ethynyl group of unsubstituted diacetylenic ketones. Reactions of piperidine with 1-phenylhexa-2,4-diyn-1-one (7), a methyl-substituted derivative, afford 1-phenyl-5-piperidinohex-4-en-2-yn-1-one (17), 3,5-dipiperidinobiphenyl (20), and a diadduct (21); in the presence of water 1-phenyl-3-piperidinohex-2-ene-1,5-dione (27) is also obtained. Strong solvent-induced shifts, of up to 40 nm, are observed in the u.v. spectra of the adducts. Some unstable alkyl diacetylenic ketones [(4)—(6)] have been obtained.

THE reactivity of the triple bond towards nucleophilic reagents is greatly increased by conjugation with a carbonyl or nitrile group. Addition of various nucleophiles to acetylenic acids and esters has been reviewed by Johnson, by Raphael,[1,2] and, more recently, by Winterfeldt.[3] Jones *et al.*[4] have studied the addition of of secondary amines to acetylenic and alkyl butenynyl ketones. In his search for chemical models for the biosynthesis of thiophens Bohlmann treated thiols with carbonyl-activated mono- and di-acetylene.[5] Results of recent studies by Vereshchagin [6] and by Kishida [7] on the reaction of amines with diacetylenic ketones parallel some of the findings described here.[8] The reactions of the aryl acetylenic ketones (1) and (2) and the aryl and alkyl diacetylenic ketones (3)—(8) with the secondary cyclic amines, piperidine and morpholine are now reported.

PhCO·C≡CR
(1) R = H
(2) R = Me

$R^2CO{\cdot}C{\equiv}C{\cdot}C{\equiv}CR^1$
(3) R^1 = H, R^2 = Ph
(4) R^1 = H, R^2 = Me
(5) R^1 = H, R^2 = Et
(6) R^1 = H, R^2 = Pr^i
(7) R^1 = Me, R^2 = Ph
(8) R^1 = R^2 = Me

The ketones were prepared from the corresponding carbinols with Jones reagent.[9,10] Although unstable, the alkyl diacetylenic ketones (4)—(6) and (8) were obtained fairly pure. In an attempt at distillation hexa-3,5-diyn-2-one (4) violently decomposed at 70°.

$PhCO{\cdot}CH{=}C(NC_5H_{10})R$
(9) R = H
(10) R = Me

$PhCO{\cdot}CH{=}C(NC_4H_8O)R$
(11) R = H
(12) R = Me

$R^2CO{\cdot}C{\equiv}C{\cdot}CH{=}C(NC_5H_{10})R^1$
(13) R^1 = H, R^2 = Ph
(14) R^1 = H, R^2 = Me
(15) R^1 = H, R^2 = Et
(16) R^1 = H, R^2 = Pr^i
(17) R^1 = Me, R^2 = Ph

$R^2CO{\cdot}C{\equiv}C{\cdot}CH{=}C(NC_4H_8O)R^1$
(18) R^1 = H, R^2 = Ph

The addition of piperidine and morpholine to compounds (1)—(3) gave the adducts (9)—(13) and (18). The coupling constant for the olefinic protons in compounds (9), (11), and (13) showed these protons to be *trans*-oriented, which is consistent with *cis*-addition. Huisgen [11] also observed predominant *cis*-addition of amines to acetylenic esters, the *cis–trans* ratio depending on solvent polarity. The ketones (4)—(6) likewise gave unstable piperidine adducts (14)—(16). The addition to compound (8) gave a mixture.

Capillin (7), on treatment with piperidine in ether, gave compounds (17) and (20), which correspond to the pyrrolidine derivatives obtained similarly by Kishida. With piperidine in dry ethanol, chloroform, methylene chloride, or acetonitrile the same compounds were formed along with compound (21); a fourth derivative (27) was obtained by treatment with piperidine in aqueous ethanol. The formation of compound (27) is in agreement with Vereshchagin's work [6] on the addition of secondary amines to 1,5-diphenylpenta-2,4-diyn-1-one; hydration of the triple bond directly linked to the original carbonyl group seems however to occur in the diaryl system. Highest yields (53%) of the diketone (27) were obtained when 4 equiv. of the amine were used. Analysis of compound (21) agreed with the formula $C_{34}H_{38}N_2O_2$, which

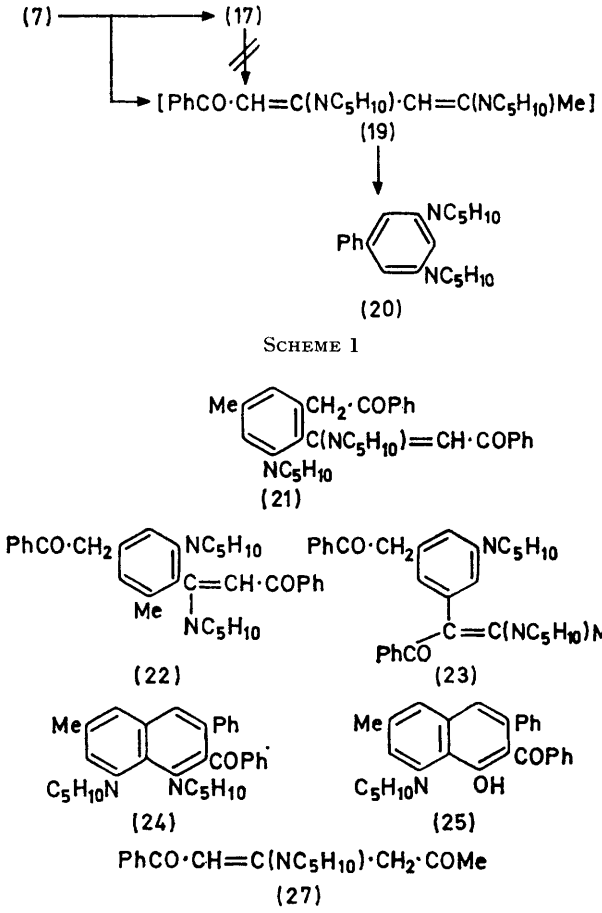
TABLE 1

Yields of derivatives obtained on addition of piperidine to capillin (0·06M) in various solvents

Compd.	Amine (equiv.)	$CHCl_3$	CH_2Cl_2	Et_2O	EtOH	MeCN
(17)	1	5	14	37	10	32
	2	0	10	20	5	31
	4	0	0	8	0	23
	10	0	0	0	0	16
21)	1	16	20	5	15	14
	2	36	25	7	22	16
	4	17	0	6	14	12
	10	0	0	0	14	6
(20)	1	5	0	5	0	0
	2	12	5	15	5	0
	4	21	30	16	16	5
	10	58	55	30	22	5

[1] A. W. Johnson, 'The Chemistry of Acetylenic Compounds,' Edward Arnold, London, 1950, vol. II, pp. 69, 106, 218.
[2] R. A. Raphael, 'Acetylenic Compounds in Organic Synthesis,' Butterworths, London, 1955, p. 40.
[3] E. Winterfeldt, *Angew. Chem. Internat. Edn.*, 1967, **6**, 423.
[4] K. Bowden, E. A. Braude, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 1946, 45.
[5] (*a*) F. Bohlmann, N. Bornowski, and D. Kramer, *Chem. Ber.*, 1963, **96**, 548; (*b*) F. Bohlmann and E. Bresinsky, *ibid.*, 1964, **97**, 2109; (*c*) F. Bohlmann, and E. Bresinsky *ibid.*, 1967, **100**, 107.
[6] L. I. Vereshchagin, R. L. Bol'shedvorskaya, and L. L. Okhapkina, *Zhur. org. Khim.*, 1970, **6**, 32 (*Chem. Abs.*, 1970, **72**, 78,800s).
[7] Y. Kishida, T. Hiraoka, and M. Yoshimoto, *Chem. and Pharm. Bull.* (*Japan*), 1969, **17**, 2126.
[8] R. Mestres, D.Phil. Thesis, Oxford, 1965.
[9] K. Bowden, E. A. Braude, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 1946, 39.
[10] (*a*) F. Bohlmann, P. Herbst, and I. Dohrmann, *Chem. Ber.*, 1963, **96**, 226; (*b*) J. B. Armitage, E. R. H. Jones, and M. C. Whiting, *J. Chem. Soc.*, 1952, 1993.
[11] R. Huisgen, K. Herbig, A. Siegl, and H. Huber, *Chem. Ber.*, 1966, **99**, 2526; R. Huisgen, B. Giese, and H. Huber, *Tetrahedron Letters*, 1967, 1883.

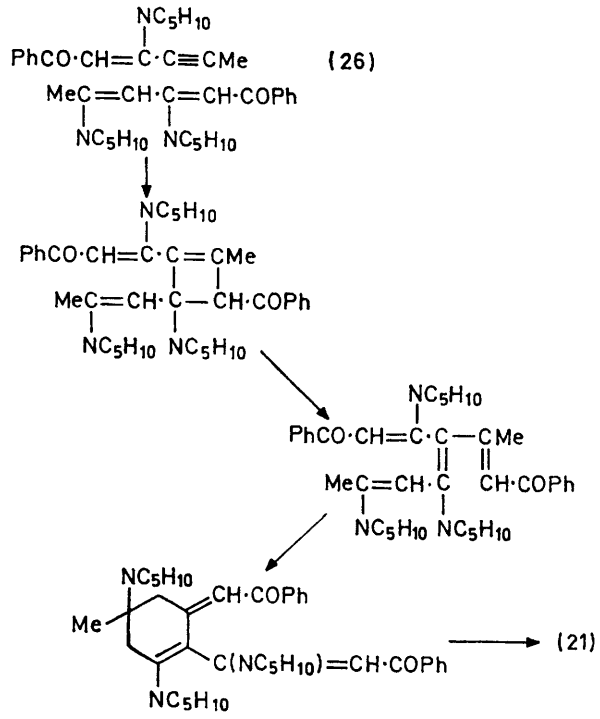
implies the addition of 2 equiv. of piperidine as well as the combination of two molecules of the substrate. Spectral data suggest the following features: a PhCO·CH=C(NC_5H_{10})·CH=C(NC_5H_{10})Me unit, a second piperidine group, a methyl group attached to an aromatic ring or to a double bond, a substituted aromatic ring, and a benzyl phenyl ketone group, and the absence of a triple bond, in agreement with structure (21). This identification is only tentative. The formation of compound (21) can be rationalised in terms of addition of piperidine, to produce the adduct (26) (not isolated), and subsequent reactions as shown in Scheme 2. Similar 1,2-cycloadditions of enamines to electrophilic triple bonds have been described.[3,12] Treatment of compound (21) with aqueous acid gave the naphthalenes (24) and (25).



Scheme 1

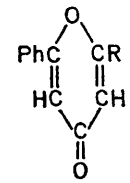
Treatment of the adducts (13) and (17) with acid in aqueous ethanol afforded the corresponding phenyl-substituted γ-pyrones (28) and (29). Kishida [7] has obtained the methyl-substituted pyrone (29) by mercuric-ion catalysed hydration of capillin.

Huisgen [11] found the velocity constants for amine additions to acetylenic esters to depend on the structure of the amine and on solvent polarity. We observed no significant differences in rough quantitative measurements of reaction rates of additions of amines to monoacetylenic ketones, except for the much slower addition of *N*-methylaniline. The reaction of piperidine with 1-phenylbut-2-yn-1-one (2) appeared to be much faster in ethanol than in ether, but no such difference was observed in the addition to 1-phenylpropyn-1-one (1).



Scheme 2

Jones *et al.* have studied the light absorption properties of the enamino-ketones resulting from the addition of amines to acetylenic ketones, and have recently discussed [4,13] possible values of the changes in absorption maxima wavelengths of natural acetylenic systems on addition of amines. Absorption maxima of the adducts (9)—(18), along with the maxima of the starting acetylenic ketones, are included in Table 2. The magnitude of the change in absorption maximum on addition of amine depends very much on the solvent. Bathochromic shifts of as much as 30—40 nm in the conjugation bands of the acetylenic enamino-ketones (13)—(18) on changing solvent from hexane to ethanol are observed.



(28) R = H
(29) R = Me

[12] C. F. Huebner, L. Dorfman, M. M. Robinson, E. M. Donoghue, W. C. Pierson, and P. L. Strachan, *J. Org. Chem.*, 1963, **28**, 3134.

[13] C. H. Fawcett, D. M. Spencer, R. L. Wain, A. G. Fallis, Sir Ewart R. H. Jones, M. Le Quan, C. B. Page, V. Thaller, D. C. Shubrook, and P. M. Whitham, *J. Chem. Soc.* (*C*), 1968, 2455.

TABLE 2

U.v. data of amino-derivatives and their parent acetylenic ketones

	Derivative				Parent ketone			
	Solvent	$\lambda_{max.}$/nm	ε		$\lambda_{max.}$/nm	ε	Δλ
(9)	C_6H_{14}	242	8100	(1)			
		324	13,400		258	12,000	66
	Et_2O	243	14,900				
		335	23,600		260	13,900	75
	EtOH	246	12,360				
		345·5	26,000		264·5	14,500	81
(11)	C_6H_{14}	241·5	12,200				
		320	19,400				62
	Et_2O	242	15,100				
		325·5	23,000				65·5
	EtOH	246	9600				
		343	20,500				78·5
(10)	C_6H_{14}	240·5	11,150	(2)			
		326·5	22,900		256	11,900	70·5
	Et_2O	240·5	12,450				
		330	27,100		256·5	13,800	73·5
	EtOH	244·5	11,000				
		344	29,200		259·5	8900	84·5
(12)	C_6H_{14}	243	8300				
		319·5	17,800				63·5
	Et_2O	241	15,000				
		324·5	25,000				68
	EtOH	246·5	6300				
		339·5	15,100				80
(13)	C_6H_{14}	258	11,800	(3)			
		361	24,400		272	17,000	89
	Et_2O	257	16,200				
		369·5	34,900		273·5	14,500	96
	EtOH	263·5	16,200				
[	(3H	397·5	34,900		273	13,800	124·5
(18)	C_6H_{14}	259	7500				
		353	23,600				81
	Et_2O	258·5	15,800				
		365·5	27,700				92
	EtOH	262·5	16,500				
		390·5	30·700				117·5
(17)	C_6H_{14}	256	9500	(7)			
		367	26,200		276	3,000	91
	Et_2O	258	17,700				
		380	29,800		278	14,000	102
	EtOH	261·5	21,600				
		407	49,600		274	22,400	133
(14)	Et_2O	336	30,500	(4)	260·5		85·5
(15)	Et_2O	339·5	22,300	(5)	260		79·5
(16)	Et_2O	345		(6)	260		85

The mass spectra of the acetylenic ketones described here and of their piperidine and morpholine derivatives have been discussed in a previous publication.[14]

EXPERIMENTAL

U.v. absorption spectra were measured with a Cary model 14M double-beam spectrophotometer; data quoted in Table 2 are not included in this section. I.r. spectra were recorded for solutions in carbon tetrachloride, unless otherwise stated, with Perkin-Elmer 237 and 257 spectrophotometers. N.m.r. spectra were obtained for deuteriochloroform solutions with Perkin-Elmer R10 and R14 spectrometers. Mass spectra were determined with an A.E.I. MS9 mass spectrometer, by use of a direct insertion probe.

M.p.s were determined with a Kofler hot-stage apparatus. Silica gel (Whatman SG 31) and neutral alumina (Woelm grade III) were used for column chromatography.

Chromic acid reagent was prepared by dissolving chromium trioxide (36 g) in water (100 ml) and sulphuric acid (30 ml). All evaporations were carried out at water-pump pressure with a rotary evaporator.

2-Methylhepta-4,6-diyn-3-ol.—Dichlorobutyne (40 g) was added dropwise during 0·5 h to a solution of sodium (24 g) in liquid ammonia (600 ml). Isobutyraldehyde (20 ml) in dry ether (70 ml) was added, and the mixture was stirred for 2 h. Ammonium chloride was then added and the solution was allowed to evaporate overnight. The residue was treated with water and ether; the ethereal layer was washed with 2N-hydrochloric acid and water, dried, and evaporated, and the residue was chromatographed on silica gel. Elution with light petroleum–ether (10 : 1) gave *2-methylhepta-4,6-diyn-3-ol* (11 g) as a pale yellow oil, b.p. 47—48° at 0·02 mmHg (Found: C, 79·0; H, 7·95%; M^+, 122. $C_8H_{10}O$ requires C, 78·65; H, 8·25%; M^+, 122); $\nu_{max.}$ 3625, 3480, 3320, 2980, 2940, 2915, 2892, 2070, and 1473 cm^{-1}; τ 8·98 (6H, d, *J* 6 Hz), 8·7 (1H, sept, *J* 6 Hz), 7·91 (1H, s), 7·35br (1H), and 5·83 (1H, d, *J* 6 Hz).

Hepta-3,5-diyn-2-ol.—1,4-Dichlorobutyne (20 g) was added dropwise during 45 min to a stirred suspension of sodamide [from sodium (12·0 g)] in liquid ammonia (300 ml). After 0·5 h, methyl iodide (10·2 ml) was added during 0·5 h. The mixture was stirred for 3·5 h, and more sodamide [from sodium (4·5 g)] in liquid ammonia was then added. Acetaldehyde (9·2 ml) in ether (15 ml) was added during 10 min, and the mixture was stirred for 1 h. Addition of ammonium chloride, work-up as usual, and distillation afforded hepta-3,5-diyn-2-ol, b.p. 45·5—46·5° at 0·2 mmHg, m.p. −5°, n_D^{22} 1·5191 (lit.,[15] b.p. 72—74° at 2 mmHg) (Found: C, 77·8; H, 7·55%; M^+, 108. Calc. for C_7H_8O: C, 77·75; H, 7·45%; M^+, 108); $\nu_{max.}$ (C_2Cl_4) 3610, 2980, 2920, 2255, 2035, and 1445 cm^{-1}; τ 8·57 (3H, d, *J* 6·9 Hz), 8·05 (3H, d, *J* 1·2 Hz), 7·4 (1H, s), and 5·5 (1H, dq, *J* 6·9 and 1·2 Hz).

Hexa-3,5-diyn-2-one (4).—Chromic acid reagent was added dropwise (until a yellow colour persisted) to a stirred solution of hexa-3,5-diyn-2-ol in acetone under nitrogen cooled with an ice–water bath. The mixture was diluted with water and treated with light petroleum; the light petroleum solution was washed with water and dried. Evaporation afforded hexa-3,5-diyn-2-one as an oil (rapidly darkening), which on cooling gave a white solid, m.p. 3—6° (Found: M^+ 92. Calc. for C_6H_4O: M^+, 92); $\nu_{max.}$ 3318, 2265, 2213, 2063, 1690, 1420, 1362, and 1232 cm^{-1}; τ 7·67 23,000, s) and 7·38 (1H, s).

Hepta-4,6-diyn-3-one (5).—This was obtained analogously from hepta-4,6-diyn-3-ol (1·8 g) as an *oil* (0·74 g) (Found: M^+, 106. C_7H_6O requires M^+, 106); $\nu_{max.}$ 3615vw, 3318, 2988, 2945, 2910, 2885, 2218, 2070, 1688, 1465, 1414, 1385, 1351, and 1175 cm^{-1}; τ 8·86 (3H, t, *J* 7·0 Hz) 7·42 (2H, q, *J* 7·0 Hz), and 7·33 (1H, s).

2-Methylhepta-4,6-diyn-3-one (6).—This was obtained by the same procedure from 2-methylhepta-4,6-diyn-3-ol; $\nu_{max.}$ 3320, 2983, 2940, 2860, 2217, 2070, 1685, 1470, 1390, 1370, and 1242 cm^{-1}; τ 8·80 (6H, d, *J* 7·0 Hz), 7·37 (1H, sept, *J* 7·0 Hz), and 7·35 (1H, s).

Hepta-3,5-diyn-2-one (8).—This *ketone* was obtained by the same method from hepta-3,5-diyn-2-ol; b.p. 75—76° at

[14] R. T. Aplin and R. Mestres, *Org. Mass Spectroscopy*, 1970, **3**, 1067.

[15] G.P. 1086–224/1960.

16 mmHg (lit.,[5c] 35° at 0·05 mmHg), n_D^{20} 1·5263 (Found: C, 79·6; H, 5·95%; M^+, 106. C_7H_6O requires C, 79·2; H, 5·7%; M^+, 106), $\lambda_{max.}$ (Et_2O) 240 (ε 3200), 252·5 (7200), 266 (11,100), and 281 nm (8500); $\nu_{max.}$ (C_2Cl_4) 2910, 2830, 2230, 2150, 1680, and 1420 cm^{-1}; τ 7·94 (s) and 7·71 (s).

Addition of Piperidine to 1-*Phenylpropyn*-1-*one*.—Piperidine (0·06 ml) was added to a solution of 1-phenylpropyn-1-one (78 mg) in dry ether (25 ml). Samples (1 ml) for determination of absorption spectra were taken immediately and again after 2 and 4 h, and the solvent was evaporated off after 5 h. Crystallisation of the residue (111 mg) from light petroleum–ether gave 1-phenyl-3-piperidinoprop-2-en-1-one (9) (98 mg), long needles, m.p. 88—90°; $\nu_{max.}$ (C_2Cl_4) 3030, 2935, 2850, 1657, 1605, 1565, and 1455 cm^{-1}; τ 8·38br (6H), 6·68br (4H), 4·25 (1H, d, *J* 14 Hz), 2·41 (1H, d, *J* 14 Hz), and *ca.* 2·6 and 2·2 (5H, m).

Similarly were obtained 1-phenyl-3-piperidinobut-2-en-1-one (10), cubes, m.p. 97—98° (lit.,[16] 99°); $\nu_{max.}$ 3050, 2930, 2850, 1625, 1595, 1530, and 1420 cm^{-1}; τ 8·35br (6H), 7·47 (3H, s), 6·6br (4H), 4·23 (1H, s), and *ca.* 2·7 and 2·2 (5H, m); 3-morpholino-1-phenylpropen-1-one (11), m.p. 76—78° (from light petroleum–ether) [lit.,[17] 90—93° (carbon tetrachloride)]; $\nu_{max.}$ 3060, 2975, 2900, 1657, 1605, 1590vs, 1565vs, 1450, and 1375 cm^{-1}; τ (CCl_4) 6·65 (4H, t, *J* 6 Hz), 6·25 (4H, t, *J* 6 Hz), 4·14 (1H, d, *J* 13 Hz), *ca.* 2·55 (3H, m), 2·3 (1H, d, *J* 13 Hz), and *ca.* 2·1 (2H, m); and 3-morpholino-1-phenylbut-2-en-1-one (12), m.p. 143·5—145° (lit.,[18] 143—144°); $\nu_{max.}$ 3060, 2970, 2900, 1640, 1600, 1450, 1430vs, and 1362 cm^{-1}; τ (CCl_4) 7·42 (3H, s), 6·64 (4H, t, *J* 6 Hz), 4·15 (1H, s), *ca.* 2·6 (3H, m), and 2·18 (2H, m).

Addition of Piperidine to 1-*Phenylpenta*-2,4-*diyn*-1-*one*.—(*a*) Piperidine (0·19 ml) was added to a solution of 1-phenylpenta-2,4-diyn-1-one (285 mg) in dry ether (45 ml), and the solution was set aside for 24 h. The solvent was evaporated off and the residue (422 mg) dissolved in ether. Dark red plates (106 mg) precipitated. Crystallisation from ether gave 1-*phenyl*-5-*piperidinopent*-4-*en*-2-*yn*-1-*one* (13) (70 mg), m.p. 107—109° (Found: C, 80·8; H, 7·25; N, 6·15%; M^+, 239. $C_{16}H_{17}NO$ requires C, 80·3; H, 7·15; N, 5·85%; M^+, 239); $\nu_{max.}$ (C_2Cl_4) 3060, 3020, 2940, 2850, 2150, 1640, 1600, 1560, 1450, and 1410 cm^{-1}; $\nu_{max.}$ (CS_2) 1270, 940, 750, and 690 cm^{-1}; τ 8·35br (6H), 6·78br (4H), 5·6 (1H, d, *J* 14 Hz), 3·03 (1H, d, *J* 14 Hz), and *ca.* 2·5 and 1·9 (5H, m).

Chromatography on alumina of the ether solution afforded more (204 mg) of the same compound.

(*b*) Addition of piperidine (0·20 ml) to 1-phenylpenta-2,4-diyn-1-one (315 mg) in ethanol (70 ml), evaporation of the solvent, and chromatography of the residue gave the same compound (211 mg).

Addition of Morpholine to 1-*Phenylpenta*-2,4-*diyn*-1-*one*.—1-Phenylpenta-2,4-diyn-1-one (156 mg) was dissolved in dry ether (10 ml) and morpholine (0·18 ml) was added. The solution was set aside for 24 h, then evaporated; the residue was chromatographed on alumina (20 g) and eluted with ether. Partial evaporation of the solvent from the eluate and addition of light petroleum afforded yellow needles of 5-*morpholino*-1-*phenylpent*-4-*en*-2-*yn*-1-*one* (18) (55 mg), m.p. 105—107°. From the mother liquors a little more product was obtained m.p. and mixed m.p. with the first crop 120—121° (Found: C, 74·65; H, 6·25; N, 5·7%; M^+, 241. $C_{15}H_{15}NO_2$ requires C, 74·65; H, 6·25; N, 5·8%; M^+, 241); $\nu_{max.}$ 3060, 2980, 2862, 2160, 1637, 1600, 1487, 1463, 1452, 1405, and 1270 cm^{-1}; τ 6·18 (4H, t, *J* 6 Hz), 6·30 (4H, t, *J* 6 Hz), 5·47 (1H, d, *J* 13 Hz), 2·89 (1H, d, *J* 13 Hz), and *ca.* 2·5 (3H, m) and 1·9 (2H, m).

Addition of Piperidine to 1-*Phenylhexa*-2,4-*diyn*-1-*one*.—(*a*) Piperidine (0·14 ml) was added to 1-phenylhexa-2,4-diyn-1-one (213 mg) in ether (15 ml). The solution was set aside for 50 h, then evaporated, and the residue was chromatographed on alumina (20 g). Elution with light petroleum–ether (1 : 1) afforded crude 3,5-*dipiperidinobiphenyl* (20) (73 mg) as an oil, which was purified by chromatography on alumina (11 g) [light petroleum–ether (3 : 1)] and crystallisation from light petroleum; m.p. 136—137·5° (Found: C, 82·35; H, 8·8; N, 8·95%; M^+, 320. $C_{22}H_{28}N_2$ requires C, 82·45; H, 8·8; N, 8·75%; M^+, 320); $\lambda_{max.}$ (Et_2O) 247 (ε 21,500) and 318·5 nm (2300); $\lambda_{max.}$ (EtOH) 247 (ε 25,100) and 314·5 nm (1600); $\nu_{max.}$ (C_2Cl_4) 3060, 3050, 3020, 2930, 2850, 2790, 1590, 1570, 1500, and 1450 cm^{-1}; $\nu_{max.}$ (CS_2) 1380, 1225, 1200, 1125, 990, 925, 830, 740, and 695 cm^{-1}; τ 8·35br (6H), 6·84br (4H), 3·63 (1H, t, *J* 1·7 Hz), 3·48 (2H, d, *J* 1·7 Hz), and *ca.* 2·65 (5H, m).

Further elution with light petroleum–ether (1 : 1) gave crude 1-*phenyl*-5-*piperidinohex*-4-*en*-2-*yn*-1-*one* (147 mg), which crystallised from light petroleum–ether as red plates (44 mg), m.p. 105—107° (Found: C, 81·0; H, 7·7; N, 5·45%; M^+, 253. $C_{17}H_{19}NO$ requires C, 80·55; H, 7·55; N, 5·55%; M^+, 253); $\nu_{max.}$ (C_2Cl_4) 3060, 2935, 2850, 2150, 1630, 1600, 1560, and 1440 cm^{-1}; $\nu_{max.}$ (CS_2) 1340, 1310, 1250, 985, 890, 750, and 695 cm^{-1}; τ 8·4br (6H), 7·73 (3H, s), 6·72br (4H), 5·48 (1H, s), and *ca.* 2·5 and 1·9 (5H, m).

(*b*) Piperidine (0·07 ml) was added to 1-phenylhexa-2,4-diyn-1-one (220 mg) in 96% ethanol (28 ml). The solution was set aside for 13 h then evaporated, and the residue (191 mg) was chromatographed on alumina (14 g). Elution with light petroleum–ether (1 : 1) afforded the *dimeric diadduct* (21) (45 mg), as prisms (18 mg), m.p. 184—187° (from light petroleum–ether) (Found: C, 80·55; H, 7·65; N, 5·75. $C_{34}H_{38}N_2O_2$ requires C, 80·55; H, 7·55; N, 5·55%); $\lambda_{max.}$ (C_6H_{14}) 233·5 (ε 23,600) and 334 nm (22,700); $\lambda_{max.}$ (Et_2O) 244 (ε 24,400) and 336 nm (20,300); $\lambda_{max.}$ (EtOH) 249 (ε 26,200) and 346 nm (22,400); $\nu_{max.}$ (C_2Cl_4) 3060, 3025, 2940, 2850, 2790, 1665, 1630, 1595, 1575, 1530, 1465, and 1450 cm^{-1}; $\nu_{max.}$ (CS_2) 1380, 1360, 1260, 1200, 950, 850, 765, and 705 cm^{-1}; τ 8·77br (6H), 8·48br (6H), 7·70 (3H, s), 7·26br (4H), 6·57br (4H), 5·42br (2H), 3·92 (1H, s), 3·18 and 3·11 (2H), and 2·6 and 2·2 (10H, m); *m/e* 506 (50%), 489 (75), 488 (87), 401 (100), 384 (42), 318 (19), 296 (25), 291 (42), and 105 (65).

Further elution with the same solvent gave 1-phenyl-5-piperidinohex-4-en-2-yn-1-one (21 mg), plates, from light petroleum–ether, m.p. and mixed m.p. 105—106·5°; and 1-*phenyl*-3-*piperidinohex*-2-*ene*-1,5-*dione* (27) (45·5 mg), prisms (from light petroleum–ether), m.p. 70—72° (Found: C, 74·9; H, 7·65; N, 5·35. $C_{17}H_{21}NO_2$ requires C, 75·25; H, 7·8; N, 5·15%); $\lambda_{max.}$ (C_6H_{14}) 242·5 (ε 11,800) and 311 nm (18,800), $\lambda_{max.}$ (Et_2O) 241·5 (ε 12,800) and 333·5 nm (21,600); $\lambda_{max.}$ (EtOH) 243·5 (ε 10,000) and 335 nm (17,000); $\nu_{max.}$ (C_2Cl_4) 3060, 3020, 2940, 2850, 1720, 1630, 1600, 1580, 1530, and 1450 cm^{-1}; $\nu_{max.}$ (CS_2) 1355, 1210, 1180, 1125, 1020, 960, 920, 765, and 700 cm^{-1}; τ 8·33br (6H), 7·9br (0·8H), 7·63 (2·2H, s), 6·58br (4H), 5·48 (1·3H, s), *ca.* 4·9br (0·5H), 3·95 (1H, s), and *ca.* 2·5 and 2·1 (5H, m); *m/e* 271 (24%), 254 (70), 228 (31), 166 (50), 105 (60), 84 (100), and 77 (55).

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Addition of Piperidine to Hexa-3,5-diyn-2-one.—Piperidine (0·38 ml) was added to a solution of hexa-3,5-diyn-2-one (0·17 g) in dry ether (34 ml), and the solution was set aside at room temperature for 6 h. A sample taken 1 h after addition of the amine showed the same u.v. absorption spectrum as the final product. The solvent was evaporated off and the residue was chromatographed on neutral alumina with ether as eluant to give crude 6-piperidinohex-5-en-3-yn-2-one (14) as a yellow oil which rapidly turned dark; $\nu_{max.}$ 3320w, 3060, 2950, 2865, 2155, 1655, 1605vs, 1457, 1360, 1250, 1090, and 967 cm^{-1}. Similarly were obtained 7-piperidinohept-6-en-4-yn-3-one (15), $\nu_{max.}$ 3320w, 3060, 2980, 2950, 2870, 2155, 1650, 1605, 1458, 1250, 1130, 1025, and 950 cm^{-1}; and 2-methyl-7-piperidinohept-6-en-4-yn-3-one (16), $\nu_{max.}$ 3100, 2950, 2865, 2155, 1648, 1610, 1518, 1470, 1456, 1393, 1380, 1250, 1123, and 970 cm^{-1}.

Hydrolysis of 1-Phenyl-5-piperidinopent-4-en-2-yn-1-one.—Hydrochloric acid (0·6N) in 96% ethanol (2 ml) was added to 1-phenyl-5-piperidino-pent-4-en-2-yn-1-one (64 mg) in 96% ethanol (20 ml), and the solution was set aside for 40 h. Anhydrous potassium carbonate was added and the solution was filtered and evaporated. The residue was treated with ether, and the resulting solution was chromatographed on alumina. Elution with ether afforded 2-phenyl-4*H*-pyran-4-one (28) (34 mg), which crystallised from light petroleum–ether as needles, m.p. 102—103° (lit.,[19] m.p. 104°) (Found: C, 76·6; H, 4·65. Calc. for $C_{11}H_8O_2$: C, 76·75; H, 4·7%); $\lambda_{max.}$ (EtOH) 257 nm (ε 21,200); $\nu_{max.}$ (C_2Cl_4) 3060, 1660, 1600, 1570, 1490, 1450, and 1400 cm^{-1}; τ 3·67 (1H, dd, *J* 6 and 2·5 Hz), 3·28 (1H, d, *J* 2·5 Hz), *ca.* 2·5 and 2·25 (5H, m), and 2·18 (1H, d, *J* 6 Hz).

Hydrolysis of 1-Phenyl-5-piperidinohex-4-en-2-yn-1-one.—Hydrochloric acid (0·6N) in 96% ethanol (1 ml) was added to the piperidino-ketone (100 mg) in ethanol (15 ml) and the solution was set aside for 40 h. Similar work-up afforded 2-methyl-5-phenyl-4*H*-pyran-4-one (29), needles (from light petroleum), m.p. 75—78°, changing into needles of m.p. 82—83° (lit.,[19] 77—78° and 87—88°; lit.,[20] 79·5 and 86—86·5°); $\lambda_{max.}$ (EtOH) 271 nm (ε 22,000); $\nu_{max.}$ (C_2Cl_4) 3050, 2950, 2910, 1665, 1532, 1495, and 1450 cm^{-1}; $\nu_{max.}$ (CS_2) 1387, 1370, 915, 850, 760, and 680 cm^{-1}; τ 7·63 (3H, s), 3·92 (1H, d, *J* 2 Hz), 3·4 (1H, d, *J* 2 Hz), and *ca.* 2·5 and 2·25 (5H, m).

Hydrolysis of the Dimeric Diadduct (21).—A mixture of the dimeric diadduct (208 mg), 65% aqueous ethanol (20 ml), and conc. hydrochloric acid (1 ml) was left at room temperature for 24 h; the solid went into solution in about 1 h. The solution was neutralised with sodium carbonate and filtered; evaporation afforded a yellow oil (161 mg). Yellow needles (42 mg) precipitated from light petroleum–benzene, recrystallisation of which gave 2-*benzoyl*-6-*methyl*-3-*phenyl*-8-*piperidino*-1-*naphthol* (25) (16 mg), m.p. 257—260° (decomp.) (Found: C, 82·3; H, 6·2; N, 3·35. $C_{29}H_{27}NO_2$ requires C, 82·65; H, 6·45; N, 3·3%); $\lambda_{max.}$ (C_7H_{16}) 236 (ε 47,500, 260sh (20,300), 277sh (15,400), and 350sh nm (3000); $\nu_{max.}$ 3570, 3060, 2940, 2860, 2800, 1640, 1620, 1600, 1490, 1450, 1290, 950, and 690 cm^{-1}; τ *ca.* 9·6—8·6 (complex), 7·9—7·1 (complex), 7·52br, 3·27br, and *ca.* 3·1—2·57 (complex); *m/e* 421 (100%), 344 (59), 171·5 (19), 105 (45), 85 (18), and 77 (35).

Chromatography of the mother liquors on silica gel [1 mm layer; light petroleum–ether (5 : 1)] gave an oil (R_F 0·4), which on addition of light petroleum afforded cubes of 2-*benzoyl*-6-*methyl*-3-*phenyl*-1,8-*dipiperidinonaphthalene* (16 mg), m.p. 198—200° (Found: C, 85·55; H, 7·2; N, 5·8. $C_{34}H_{36}N_2O$ requires C, 85·55; H, 7·45; N, 5·75%); $\lambda_{max.}$ (C_7H_{16}) 232 (ε 45,000), 254sh (30,000), 285sh (14,400), and 325sh nm (4200); $\nu_{max.}$ 3060, 3030, 2940, 2855, 2800, 2720, 2778, 1617, 1595, 1468, 1450, 1387, 1260, 1200, and 1030 cm^{-1}; τ 9·6—9·0 (complex), 8·63br, 7·50 (s), 7·22br, 6·8br, 3·1 (d), and *ca.* 2·92—2·4 (m); *m/e* 488 (100%), 411 (13), 244 (12), 105 (10), and 77 (9).

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