The Synthesis of Nitrogen Heterocycles *via* the Intramolecular Khand Reaction: Formation of Tetra- and Hexa-hydrocyclopenta[*c*]pyrrol-5(1*H*)-ones and Hexahydro-6*H*-2-pyrindin-6-ones

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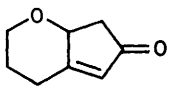
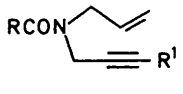
Azabicyclo[3.3.0]octenones and azabicyclo[4.3.0]nonenones have been obtained by cyclisation of hexacarbonyldicobalt complexes of aza-heptenynes and -octenynes respectively. An unusual feature of the cyclisation of *N*-acyl-4-azahept-1-en-6-ynes is the extensive formation of the reduced products, *N*-acyl-3-azabicyclo[3.3.0]octan-7-ones under most reaction conditions.

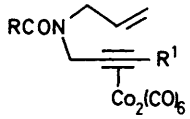
The first example of an intramolecular Khand reaction was the formation of the 2-oxabicylononenone (**1**) from the cobalt complex of pent-4-ynyl vinyl ether.[1] Numerous 3-oxabicyclo-[3.3.3]oct-5-en-7-ones [5-oxa-4,5,6,6a-tetrahydro-1*H*-pentalen-2-ones] have subsequently been efficiently synthesised in the same way from variously substituted allyl prop-2-ynyl ethers.[2–7]



(**1**)

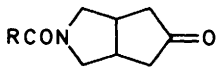


(**2**)

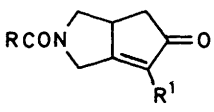


(**3**)

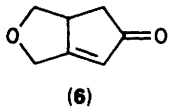
a; R = Me, R^1 = H
b; R = Me, R^1 = $SiMe_3$
c; R = Me, R^1 = Et
d; R = Ph, R^1 = H
e; R = Me, R^1 = D



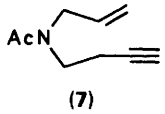
(**4**)
a; R = Me
b; R = Ph



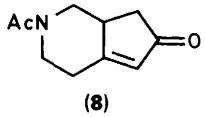
(**5**)
a; R = Me, R^1 = H
b; R = Me, R^1 = $SiMe_3$
c; R = Me, R^1 = Et
d; R = Ph, R^1 = H



(**6**)



(**7**)



(**8**)

Heterocycles with heteroatoms other than oxygen have not been obtained by this method so far as we are aware. We first attempted to obtain cyclic silicon compounds but have so far been unable to cyclise the hexacarbonyldicobalt complexes of allyldimethylprop-2-ynylsilane or of (allyloxy)dimethyl(prop-2-ynyloxy)silane. Our attention was then turned to nitrogen-containing ring systems and we here describe the intramolecular Khand reactions of *N*-acylhept- and *N*-acyloct-enynes.

We have recently reported[8] on the efficacy of ultrasound in accelerating the Khand reaction and our first attempts to cyclise *N*-acetyl-*N*-allyl-*N*-prop-2-ynylamine (**2a**) *via* its cobalt complex (**3a**) used this technique. A ketonic product was readily isolated, but its IR and ^{1}H NMR spectra clearly identified it as the cyclopentanone derivative (**4a**) instead of the expected cyclopentenone (**5a**). Although we have frequently encountered trace by-products with IR spectra suggesting cyclopentanone derivatives (ν_{CO} *ca.* 1 740 cm^{-1}) from Khand reactions, and Serratosa and co-workers[9,10] have isolated and identified more significant quantities of such products from reactions conducted at relatively high temperatures, we believe that the formation of compound (**4a**) is the first case where a cyclopentanone has been obtained as the sole or even major ketonic product.

The highly efficient solid phase method pioneered by Smit and co-workers[6,10–14] works better in air than under an inert atmosphere. In the hope that these conditions would be less likely to promote a reductive side reaction, complex (**3a**) was adsorbed on silica and warmed in air to 70 °C for 1.5 h. Again the saturated ketone (**4a**) was the only isolated product; it was indeed formed in much improved yield.

We have shown[10,15] that irradiation can be used as an alternative energy source for Khand reactions. When this method was tried with complex (**3a**) using hydrocarbon solvents the saturated ketone (**4a**) was again the only product, but on one occasion only, photolysis in tetrachloromethane produced pure cyclopentenone (**5a**). Repetition of this experiment on a larger scale produced mixtures, and ultrasonic conditions also yielded mixtures of the two ketones (**4a**) and (**5a**) when benzene replaced iso-octane as solvent. *N*-Allyl-*N*-benzoyl-*N*-prop-2-ynylamine (**2d**) behaved similarly, giving the saturated ketone (**4b**) except on photolysis of its complex (**3d**) in tetrachloromethane when the enone (**5d**) was obtained.

These results and the results for the Khand reactions of the trimethylsilyl (**3b**) and ethyl substituted complexes (**3c**) are collected in Table 1. The internal alkyne complex (**3c**) reacted smoothly to give exclusively the enone (**5c**) under all conditions tried. The highest yield was obtained by the solid-phase technique in agreement with the result of Smit's group[6,10–14] for the formation of related oxa- and carba-cyclic systems. However reaction of the silane (**3b**) proved surprisingly difficult. In the majority of reported cases trimethylsilyl-protected alkyne complexes react very smoothly[10,16–18] and may lead to higher yields and stereoselectivity than analogues with a CH or CMe terminus.[19,20] But cases of failure or low yields have also been reported,[9,21] possibly attributable to additional steric hindrance at the alkene terminus. It was, nevertheless, unexpected to find that the silyl-protected complex (**3b**) reacted only under relatively severe conditions and in poor yield to give the cyclopentenone (**5b**); its reaction using the solid-phase technique was accompanied by reductive removal of the protecting

Table 1. Cyclisation reactions

Expt. no.	$CH_2{=}CHCH_2N(CH_2)_nC{\equiv}CR'$ R	R'	n	No.	Method	Solvent	Reaction temp. (°C)	Time (h)	Products: Saturated Structure	%	Unsaturated Structure	%
1	CH_3	H	1	3a	Thermal	Iso-octane	100	24	(4a)	5	(5a)	0
2	CH_3	H	1	3a	Thermal	C_2Cl_4	110	24	(4a)	6	(5a)	3
3	CH_3	H	1	3a	UV	Iso-octane	50	20	(4a)	33	(5a)	0
4	CH_3	H	1	3a	UV	Benzene	50	20	(4a)	32	(5a)	0
5	CH_3	H	1	3a	UV	CCl_4	50	18	(4a)	0	(5a)	38[a]
6	CH_3	H	1	3a	Ultrasound	Iso-octane	60	5	(4a)	36	(5a)	0
7	CH_3	H	1	3a	Ultrasound	Benzene	60	4	(4a)	12	(5a)	22
8	CH_3	H	1	3a	SiO_2	—	70	1.5	(4a)	67	(5a)	0
9	CH_3	D	1	3e	SiO_2	—	90	1.5	(4e)	67	—	—
10	CH_3	D	1	3e	Ultrasound	Iso-octane	60	3.5	(4e)	32	—	—
11	C_6H_5	H	1	3d	Thermal	Iso-octane	110	6	(4d)	31	(5d)	0
12	C_6H_5	H	1	3d	UV	Iso-octane	50	20	(4d)	33	(5d)	0
13	C_6H_5	H	1	3d	UV	CCl_4	50	20	(4d)	0	(5d)	35
14	C_6H_5	H	1	3d	Ultrasound	Iso-octane	60	4.5	(4d)	32	(5d)	0
15	C_6H_5	H	1	3d	SiO_2	—	90	1.5	(4d)	45	(5d)	0
16	CH_3	$SiMe_3$	1	3b	Thermal	C_2Cl_4	110	20	—	—	(5b)	28
17	CH_3	$SiMe_3$	1	3b	SiO_2[b]	—	80	4	(4a)	46	(5b)	0
18	CH_3	Et	1	3c	Thermal	Iso-octane	100	3	—	—	(5c)	57
19	CH_3	Et	1	3c	UV	Iso-octane	50	20	—	—	(5c)	52
20	CH_3	Et	1	3c	Ultrasound	Iso-octane	60	3	—	—	(5c)	47
21	CH_3	Et	1	3c	SiO_2	—	70	1	—	—	(5c)	75
22	CH_3	H	2	7	Thermal	Iso-octane	100	6	—	—	(8)	30
23	CH_3	H	2	7	UV	Iso-octane	50	18	—	—	(8)	32
24	CH_3	H	2	7	Ultrasound	Iso-octane	60	5	—	—	(8)	43
25	CH_3	H	2	7	SiO_2	—	70	4	—	—	(8)	44

[a] Attempted repetition of this experiment on a larger scale did not yield compound (**5a**) free from (**4a**). [b] Al_2O_3 gave an identical result; this complex (**3b**) was substantially unchanged by irradiation in iso-octane for 5 days or ultrasound at 60 °C (iso-octane, 24 h).

group so that the unsubstituted saturated ketone (**4a**) was again the product.

The fact that only the terminal alkyne complexes showed this pronounced tendency to form cyclopentanones led us to examine whether the acetylenic proton is itself involved in the reduction process. To this end the precursor (**2a**) was deuteriated to yield the monodeuterio-amide (**2e**) and then converted into the cobalt complex (**3e**). However Khand cyclisation of the latter yielded the bicyclic ketone (**4a**) with appreciable loss of deuterium, indicating H/D exchange during the reaction. Di- (or poly-) deuterio derivatives of ketone (**4a**) were not present in significant quantities.

That the reduction depends not only on the presence of the free acetylenic hydrogen, the reaction conditions, and the presence of the *N*-acyl group [as mentioned in the introduction, allyl prop-2-ynyl ethers, in contrast to the amides (**2**), react 'normally' to yield oxabicyclo[3.3.0]octenones of type (**6**)[10]], but also on the size of ring being formed was evident from the behaviour of *N*-acetyl-*N*-allyl-*N*-but-3-ynylamine (**7**) which cyclises to the azabicyclo[4.3.0]nonenone derivative (**8**) under all conditions tried (Table 1). It is difficult to find a convincing mechanistic explanation which accounts for the importance of all these factors. The source of hydrogen must also remain speculative at present. It is tempting to invoke the solvents as a likely source and comparison of Experiments 3 and 5, 6 and 7, 12 and 13 (Table 1) lends some credence to this suggestion, but benzene is an unlikely source (*cf.* Experiment 4). In the highly efficient solvent-free solid state reactions hydroxy groups on silica (or alumina) would appear to be the only likely source with reduction, presumably at the expense of cobalt(0).

The enynes and their cobalt complexes were prepared using well-known general methods; full details are given in the Experimental section. In view of the low air-stability of the enynamines and even their acyl derivatives, only the cobalt complexes were subjected to microanalysis as well as spectral characterisation.

Experimental

Unless otherwise stated, all reactions were conducted under nitrogen. Evaporation of solutions was carried out by means of a rotary evaporator. Light petroleum refers to the fraction of b.p. 30–40 °C.

(N-*Acetyl*-N-*allyl*-N-*prop*-2-*ynylamine*)*hexacarbonyldicobalt* (**3a**).—Following the method of Vilenshchik *et al.*[22] *N*-allyl-*N*-prop-2-ynylamine was prepared from allylamine (41.1 g, 720 mmol) by warming with 2M aqueous sodium hydroxide (250 ml) to 40 °C and adding prop-2-ynyl chloride (23.8 g, 360 mmol) dropwise over 3 h with vigorous stirring which was maintained for a further 3 h. The reaction mixture was then cooled to room temperature and extracted with ether (4 × 100 ml). The combined extracts were then washed with brine (2 × 50 ml), dried (Na_2SO_4), and the ether distilled off at atmospheric pressure. *N*-Allyl-*N*-prop-2-ynylamine (11.7 g, 34%) then distilled off at 49–50 °C/37 Torr,* b.p. 123–125 °C/760 Torr (lit., b.p.[23] 38–40 °C/26 Torr; b.p.[24] 123 °C); δ($CDCl_3$) 1.50 (1 H, s, NH), 2.24 (1 H, m, ≡CH), 3.40 (4 H, m, CH_2), 5.10 and 5.25 (2 H, overlapping m, $=CH_2$), and 5.83 (1 H, v br m, –CH=). A further fraction comprising *N*-allyldiprop-2-ynylamine (5.72 g, 24%) distilled at 67–69 °C/16 Torr.

To obtain *N*-acetyl-*N*-allyl-*N*-propynylamine (*N*-allyl-*N*-prop-2-ynylacetamide) (**2a**) acetyl chloride (5.68 g, 72.5 mmol) was added dropwise over 5 min to a vigorously stirred solution of *N*-allyl-*N*-propynylamine (6.90 g, 72.5 mmol) in dry ether (50

* 1 Torr = 133.322 Pa.

ml) and stirring continued for 1 h. Sufficient 3M aqueous potassium hydroxide was then added to make the mixture basic; the ether layer was separated and the aqueous layer extracted with ether (3 × 50 ml). The combined ether solutions were dried (K_2CO_3) and the acetylation procedure repeated with a further quantity of acetyl chloride (2.35 g, 30 mmol). Evaporation of the resulting ether solution and distillation of the residue at 44–46 °C/0.22 Torr gave the product (**2a**) (8.55 g, 86%). A similar experiment using a single treatment with excess of acetyl chloride (7.06 g, 90 mmol) gave 7.36 g (74%) of this product; δ($CDCl_3$) 2.12 (3 H, s, CH_3), 2.20 (1 H, m, ≡CH), 4.05 and 4.17 (4 H, overlapping m, $-CH_2-$), 5.14 and 5.30 (2 H, overlapping m, $=CH_2$), and 5.75 (1 H, v br m, –CH=).

The product (**2a**) (4.37 g, 31.9 mmol) in ether (20 ml) was added dropwise over 20 min to a stirred solution of octacarbonyldicobalt (10.89 g, 31.9 mmol) in dry ether (40 ml). Stirring at room temperature was continued for 6 h. The solution was then filtered through Kieselguhr and evaporated, and the residue chromatographed on neutral alumina. The complex (**3a**) was eluted with ether (9.45 g, 70%), and crystallised from light petroleum, giving dark red crystals, m.p. 50–52 °C (capillary sealed under N_2); ν_{max}($CHCl_3$) 3 285, 2 970, 2 080–1 980 (several intense peaks, ν_{CO}), and 1 630 cm^{-1} (Found: C, 39.4; H, 2.5; N, 3.3%. $C_{14}H_{11}Co_2NO_7$ requires C, 39.7; H, 2.6; N, 3.3%).

To obtain the deuteriated derivative (**3e**), the amide (**2a**) (10.0 g, 73 mmol) in tetrahydrofuran (350 ml) was first treated at −78 °C with butyl-lithium solution (90 mmol) added over 15 min, followed by further stirring for 15 min. Excess of deuterium oxide (18 g) in tetrahydrofuran (20 ml) was then added dropwise at −78 °C over 25 min and stirring continued for 30 min before the mixture was allowed to warm to room temperature over 1 h. After filtration, evaporation, and distillation (90 °C/0.6 Torr) the product (7.2 g) was shown by ^1H NMR to contain 80% of the deuterio derivative (**2e**). This was converted into the complex, shown similarly to contain the same percentage of deuterio derivative (**3e**).

[N-*Acetyl*-N-*allyl*-N-(3-*trimethylsilylprop*-2-*ynyl*)*amine*]-*hexacarbonyldicobalt* (**3b**).—A solution of *N*-acetyl-*N*-allyl-*N*-prop-2-ynylamine (**2a**) (10 g, 73 mmol) in anhydrous ether (75 ml) was stirred and cooled to −50 °C while a solution of butyl-lithium (90 mmol) in hexane was added by syringe. After the mixture had been stirred for 15 min chlorotrimethylsilane (10.86 g, 100 mmol) in ether (40 ml) was added dropwise and stirring continued for 2 h at −25 °C; the mixture was then allowed to come to room temperature over 2 h and stirred for a further 2 h. The mixture was then poured into ice–water (250 ml), separated, and the aqueous layer extracted with ether (4 × 100 ml). The combined ether solutions were washed with brine, dried (K_2CO_3), and evaporated, and the residue distilled at 62–64 °C/0.2 Torr to give the product (**2b**) (8.25 g, 54%); δ($CDCl_3$) 0.05 (9 H, s, $SiMe_3$), 1.97 and 2.06 (3 H, 2 s corresponding to two conformers, CH_3CO), 3.92 and 4.00 (4 H, overlapping m, $-CH_2-$), 5.10 (2 H, br m, $=CH_2$) and 5.60 (1 H, br m, –CH=).

This alkyne (**2b**) (6.60 g, 31.5 mmol) was converted into the title compound (**3b**) (13.80 g, 88%) as described above for complex (**3a**). Ether–light petroleum (1:2) was used for elution from the alumina column and the product (**3b**) (after evaporation of the eluate) was obtained as a dark red oil, ν_{max}(film) 3 080, 2 960, 2 900, 2 095–1 980, and 1 670–1 660 cm^{-1}; δ($CDCl_3$) 0.17 (9 H, s, $SiMe_3$), 1.96 (3 H, s, CH_3CO), 3.94 (2 H, m, $CH_2C=$), 4.58 (2 H, br s, $CH_2C\equiv$), 5.10 (2 H, br m, $=CH_2$), and 5.63 (1 H, v br m, CH=) (Found: C, 41.1; H, 3.8; N, 3.0%. $C_{17}H_{18}Co_2NO_7Si$ requires C, 41.1; H, 4.1; N, 2.8%).

(N-*Acetyl*-N-*allyl*-N-*pent*-2-*ynylamine*)*hexacarbonyldicobalt* (**3c**).—1-Bromopent-2-yne[25] (29.0 g, 200 mmol) was added dropwise with stirring over 1 h to allylamine (33.6 g, 590 mmol) in water (25 ml). The solution was stirred at room temperature overnight after which sodium hydroxide (14 g) was added and the mixture extracted with ether (3 × 75 ml). The combined extracts were dried (K_2CO_3) and ether was distilled off through a 30 cm Vigreux column. The residual product, *N*-allyl-*N*-pent-2-ynylamine (10.1 g, 41%) distilled at 66–68 °C/20 Torr; δ($CDCl_3$) 1.14 (3 H, t, CH_3), 1.33 (1 H, s, NH), 2.20 (2 H, m, CH_2CH_3), 3.35 (4 H, m, CH_2NHCH_2), 5.08 and 5.22 (2 H, overlapping m, $=CH_2$), and 5.85 (1 H, br m, CH=). Although not fully resolved, an approx. 1 Hz coupling between the two CH_2 groups of the pentyne moiety is clearly discernible.

This amine (8.00 g, 65 mmol) was acetylated as described above for the preparation of the amide (**2a**). *N*-Allyl-*N*-pent-2-ynylacetamide (**2c**) (9.22 g, 86%) was obtained as an oil, b.p. 76–78 °C/0.7 Torr, δ($CDCl_3$) 1.13 (3 H, t, CH_3CH_2), 2.16 (5 H, m, CH_3CO and CH_2CH_3), 4.08 (4 H, m, CH_2NHCH_2), 5.11 and 5.28 (2 H, overlapping m, $=CH_2$), and 5.75 (1 H, v br m, –CH=).

Conversion of this alkyne (**2c**) (5.00 g, 30.3 mmol) into its cobalt complex (**3c**) (10.39 g, 76%) again followed the procedure described above for complex (**3a**). After elution of the alumina column with ether–light petroleum (1:2) and evaporation, the complex (**3c**) was obtained as a dark red oil, ν_{max}(film) 3 080, 2 980, 2 900, 2 095–1 980, and 1 660–1 640 cm^{-1} (Found: C, 43.0; H, 3.5; N, 3.1%. $C_{16}H_{15}Co_2NO_7$ requires C, 42.6; H, 3.4; N, 3.1%).

(N-*Allyl*-N-*benzoyl*-N-*prop*-2-*ynylamine*)*hexacarbonyldicobalt* (**3d**).—Benzoyl chloride (17.60 g, 140 mmol) and 2M aqueous sodium hydroxide (200 ml) were added to *N*-allylprop-2-ynylamine (12 g, 126 mmol) and the mixture was stirred at room temperature in a corked conical flask for 20 min, the cork being released occasionally, and then for a further 2 h. The mixture was extracted with ether (3 × 100 ml) and the dried (K_2CO_3) extract evaporated. Distillation of the residue at 108–110 °C/0.35 Torr gave *N*-allyl-*N*-benzoyl-*N*-prop-2-ynylamine [*N*-allyl-*N*-prop-2-ynylbenzamide] (**2d**) (22.6 g, 92%), δ($CDCl_3$) 2.32 (1 H, t, ≡CH), 4.14 (4 H, m, CH_2), 5.18 (1 H, m) and 5.33 (1 H, m, $=CH_2$), 5.8 (1 H, v br m, CH=), and 7.43 (5 H, m, Ph).

This amide (**2d**) (6.00 g, 30.1 mmol) was converted by the standard method [see (**2a**)] into its cobalt complex (**3d**) (11.90 g, 92%). After elution from the alumina column with ether and crystallisation from light petroleum it formed dark red crystals, m.p. 55–56 °C, ν_{max}($CHCl_3$) 3 285, 2 980, 2 920, 2 090–1 980, and 1 630 cm^{-1} (Found: C, 46.7; H, 2.4; N, 2.8%. $C_{19}H_{13}Co_2NO_7$ requires C, 47.0; H, 2.7; N, 2.9%).

(N-*Acetyl*-N-*allyl*-N-*but*-3-*ynylamine*)*hexacarbonyldicobalt*.—1-Bromobut-3-yne was prepared from but-3-yn-1-ol by the literature method[25] but without isolation of the intermediate toluene-*p*-sulphonate. This bromo compound (24.1 g, 180 mmol) was then added dropwise over 1 h to a stirred, ice-cooled solution of allylamine (31.0 g, 540 mmol) in water (20 ml). Stirring was then continued at room temperature overnight. Sodium hydroxide (15 g) was then added and the mixture extracted with ether (3 × 75 ml). From the combined, dried (K_2CO_3) ether extracts the solvent was distilled off through a 30 cm Vigreux column. Distillation at 66–68 °C/20 Torr then yielded *N*-allyl-*N*-but-3-ynylamine [*N*-prop-2-enyl-*N*-but-3-ynylamine] (8.84 g, 45%); δ($CDCl_3$) 1.39 (1 H, s, NH), 2.00 (1 H, t, ≡CH), 2.38 (2 H, dt, $CH_2C\equiv$), 2.89 (2 H, t, CH_2CH_2N), 3.27 (2 H, dt, $CH_2CH=$), 5.06 and 5.22 (2 H, overlapping m, $=CH_2$), and 5.88 (1 H, v br m, CH=).

Acetylation of this amine (8.00 g, 73 mmol) was carried out as described for the preparation of the amide (**2a**) and yielded *N*-allyl-*N*-but-3-ynylacetamide (**7**) (9.71 g, 88%), b.p. 76–78 °C/0.7 Torr; δ($CDCl_3$) 2.07 (3 H, s, CH_3CO), 2.18 (1 H, s, ≡CH), 2.46 (2 H, dt, $CH_2C\equiv$), 3.48 (2 H, t, CH_2CH_2N), 4.02 (2 H, m, $CH_2CH=$), 5.11 and 5.26 (2 H, overlapping m, $=CH_2$), and 5.79 (1 H, v br m, CH=).

Table 2. Properties and analyses of ketones.

Compd.	Formula	M.p. (or b.p.)/ (°C/Torr)	ν_{CO}/cm^{-1}		Analysis					
					Found (%)			Required (%)		
			Keto	*N*-Acyl	C	H	N	C	H	N
(4a)	$C_9H_{13}NO_2$	75–77	1 740	1 630	64.4	7.9	8.3	64.6	7.8	8.4
(4b)	$C_{14}H_{15}NO_2$	(120/0.005)	1 740	1 620	71.6	6.9	6.0	73.4	6.6	6.1
(5a)	$C_9H_{11}NO_2$		1 705	1 630						
(5b)	$C_{12}H_{19}NO_2Si$	103–105	1 695	1 650	60.6	8.1	5.8	60.7	8.1	5.9
(5c)	$C_{11}H_{15}NO_2$	(150/0.015)	1 710	1 650						
(5d)	$C_{14}H_{13}NO_2$	156–158	1 690	1 640	73.7	5.6	6.1	74.0	5.8	6.2
(8)	$C_{10}H_{13}NO_2$	127–129	1 700	1 640	67.6	7.6	7.8	67.0	7.3	7.8

Using the standard method [see complex (**3a**)], this alkyne (**7**) (5.00 g, 33.0 mmol) was converted into (*N*-acetyl-*N*-allyl-*N*-but-3-ynylamine)hexacarbonyldicobalt (9.65 g, 67%), a dark red oil, ν_{max}(film) 3 080, 2 980, 2 900, 2 095–1 980, and 1 660–1 640 cm^{-1}; δ($CDCl_3$) 2.10 and 2.16 (3 H, 2 s, CH_3), 3.10 (2 H, m, $CH_2C\equiv$), 3.50 (2 H, m, NCH_2CH_2), 3.98 (2 H, m, $CH_2C=$), 5.25 (2 H, m, $CH_2=$), 5.80 (1 H, br m, =CH–), and 6.03 (1 H, br s, CH≡) (Found: C, 40.9; H, 3.0; N, 3.1%. $C_{15}H_{13}Co_2NO_7$ requires C, 41.2; H, 3.0; N, 3.2%).

Khand Cyclisations.—The cyclisations summarised in Table 1 employ four standard methods; a representative example of each is described below. The ^1H NMR spectra of the ketonic products are unexpectedly complex, most probably because of the presence in solution of two relatively stable conformers involving the *N*-acyl groups. We have therefore only ascertained that the ratios of different types of protons are consistent with the structures assigned.

1. *'Thermal' (in solution): cyclisation of complex* (**3a**). A solution of complex (**3a**) (2.00 g, 4.73 mmol) in iso-octane (40 ml) was heated to 100 °C. After 24 h at this temperature no more starting material could be detected by TLC. The mixture was cooled, filtered through Kieselguhr, and the solvent evaporated. The residue was purified by flash chromatography eluting with methanol–light petroleum–dichloromethane (1:5:4). The ketone (**4a**) so obtained (40 mg, 5%) crystallised from ethyl acetate (charcoal), m.p. 75–77 °C (Table 2).

2. *Photochemical: cyclisation of the complex of alkyne* (**7**). A solution of this complex (2.10 g, 4.80 mmol) in iso-octane (50 ml) was placed in a 100 ml quartz tube and irradiated in a Rayonet Photochemical reactor using a 'sunlight' phosphor 300 nm/85 W light source. After 18 h no more starting material could be detected by TLC. The solution was filtered through Kieselguhr, evaporated, and the residue purified by flash chromatography as in (1). The product (**8**) (0.277 g, 32%) was recrystallised from toluene (charcoal), m.p. 127–129 °C.

3. *Ultrasonic: cyclisation of complex* (**3d**). A solution of complex (**3d**) (2.10 g, 4.33 mmol) in iso-octane (50 ml) was placed in an ultrasonic cleaning bath which maintained a temperature of 60 °C. After 4.5 h, no more starting material was detected and the mixture was worked up as in (1). The product (**4d**) (0.317 g, 32%) was purified by flash chromatography using methanol–light petroleum–dichloromethane (1:5:4) as eluant and by distillation, b.p. 120 °C/0.005 Torr.

4. *Solid-phase method: cyclisation of complex* (**3c**). Silica gel ('for chromatography,' 60–120 mesh; 10 g per mmol of complex) was covered with ether. Complex (**3c**) (2.20 g, 4.88 mmol) dissolved in ether (50 ml) was then added and the ether evaporated from the mixture using a rotary evaporator. A stream of air was then admitted and the temperature of the evaporator bath was raised to 70 °C. After 4 h at this temperature no more starting material could be detected by TLC. The silica gel adsorbent was now extracted with methanol and the extract evaporated. Distillation of the residue at 150 °C/0.015 Torr gave the cyclopentenone derivative (**5c**) (0.709 g, 75%).

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