Synthesis and Chemistry of Azolenines.† Part 16.[1] Preparation of both 3*H*- and 2*H*-Pyrroles from 2,2-Disubstituted 1,4-Diketones *via* the Paal–Knorr Reaction, and Isolation of Intermediate 2-Hydroxy-3,4-dihydro-2*H*-pyrroles[2]

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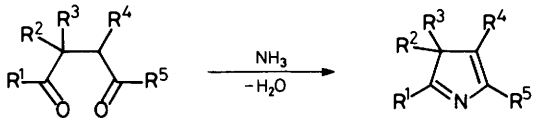
Treatment of 2,2-disubstituted 1,4-diketones (**1**) with liquid ammonia gives high yields of isolable isomeric 2-hydroxy-3,4-dihydro-2*H*-pyrroles (**10**) and (**11**), many of which may be dehydrated to 3*H*-pyrroles (**2**) together, in certain cases, with isomeric methylene-pyrrolines (**14**) and (**15**). When heated in acetic acid with ammonium acetate, the diketones (**1**) yield 2*H*-pyrroles (**18**), sometimes in admixture with 3*H*-pyrroles (**2**) from which they are formed by rearrangement. The diketones (**1**), including some novel examples, are prepared from nitro-ketones (**6**) by the Nef reaction, as well as other methods.

The 3*H*-pyrroles constitute a little-known ring system, with a potentially rich chemistry in terms of addition, cycloaddition, and rearrangement reactions. While a number of examples have been prepared having *N*- and other hetero-linked substituents at unsaturated ring carbon atoms,[3] no generally useful synthetic routes are available for preparing 3*H*-pyrroles bearing only *C*-linked substituents.[4]

A potentially general route to the latter compounds (**2**) is the Paal–Knorr reaction between 2,2-disubstituted 1,4-diketones (**1**) and ammonia (Scheme 1). In a recent exploration of this



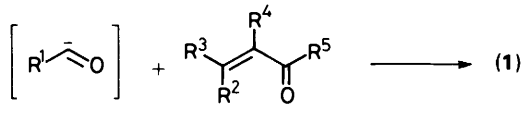
(**1**) (**2**)

Scheme 1.

approach, using the readily-accessible cyclic 2-(acylmethyl)-2-alkyl-1,3-diketones (**1**; $R^1R^2 = [CH_2]_{2-3}CO$), we obtained not the expected 3-acyl-3*H*-pyrroles (**2**; R^2 = acyl), but the isomeric 1-acyl-1*H*-pyrroles *via* rearrangement.[5] Of the four mechanisms considered for this rearrangement through a 2-hydroxy-3,4-dihydro-2*H*-pyrrole intermediate, each was mediated by the additional acyl substituent.[5] It thus seemed likely that 3*H*-pyrroles might be obtained from diketones (**1**) having both R^2 and R^3 as simple alkyl or aryl groups. We now describe the preparation of a number of such diketones, and their conversions into both 3*H*- and 2*H*-pyrroles.

Results and Discussion

Preparation of the 1,4-*Diketones* (**1**).—Diketones of the desired type have been prepared by many different methods,[6] some of which permit wide variation of the substituents R^1–R^5. A potentially general route, attractive on account of its simplicity, is the conjugate addition of acyl anion equivalents (**3**) to 3,3-disubstituted 2-enones (**4**) (Scheme 2). Competition



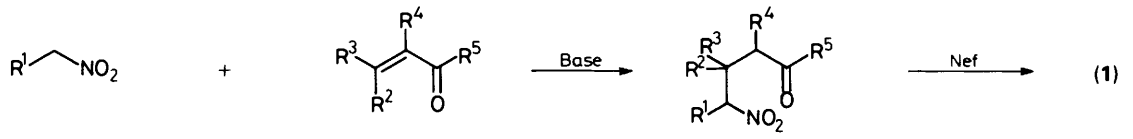
(**3**) (**4**)

Scheme 2.

between 1,2- and 1,4-addition has been reported to be a problem in certain cases,[7] and we found that the methodology developed by Stetter[8] fails with enones of this type. However, anions of nitroalkanes (**5**) have been added regiospecifically to enones of type (**4**) to give the nitroketones (**6**),[9] which have been further converted into the 1,4-diketones (**1**) by the Nef reaction[10] (Scheme 3). Conjugate additions of nitroalkane anions have been carried out under a wide variety of conditions.[11] We have found that for additions of (**5a–c**) and (**5e**) to the enones (**4**) optimum yields were obtained using Triton B (0.15 mol) as the base in dioxane[12] (method A), while sodium ethoxide (0.15 mol) in ethanol[13] (method B) was effective for additions of nitromethane (**5a**). In most cases, an excess of one of the two reactants was required. Additions of nitroethane (**5b**) to the ketone (**4c**), phenylnitromethane (**5d**) to the ketones (**4a–d**), and methyl nitroacetate (**5e**) to (**4c**) and (**4d**) were unsuccessful under these conditions, probably due to steric effects. However, the use of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (1 mol) in acetonitrile[11b] (method C) gave, on prolonged reaction with (**5d**) and (**4a**), the nitroketone (**6d**) together with *trans*-1,2-diphenylethene; under the same conditions, the reaction between (**5d**) and (**4b**) yielded not the expected product (**6h**), but rather a single diastereoisomer of the benzoylcyclopropane (**7**). The structure of (**7**) (assumed to be *trans*) was confirmed from analytical and spectroscopic data; it is possible that ring-closure may involve loss of the nitro group *via* an electron transfer mechanism. Yields and conditions for formation of the nitroketones (**6**) are given in Table 1.

The conditions for conversion of nitro compounds into ketones by the original Nef reaction[14] have been improved,[10,15] and also modified to include basic-oxidative,[16] neutral-oxidative,[16c,17] reductive,[18] and other[19] conditions. Of the many methods we investigated, the most generally useful for converting the nitroketones (**6**) into the diketones (**1**) were treatment with: (a) ethanolic sodium hydroxide, followed by hydrochloric acid[10,15] (method D); or (b) aqueous methanolic potassium carbonate, followed by hydrogen peroxide[16e] (method E). Exceptions were the ester (**6e**), which lost its ester group to give exclusively (**6a**) by methods D and E, and failed to give the diketoester (**1e**) by other methods, including electrolysis[19b] (method F); and also examples having R^1 = H. The latter were converted into keto aldehydes using aqueous methanolic potassium hydroxide, followed by potassium per-

† The term 'azolenines' refers to the non-aromatic isomers of the azoles.



(5)

	R^1
a;	H
b;	Me
c;	Et
d;	Ph

(4)

	R^2	R^3	R^4	R^5
a;	Me	Me	H	Me
b;	Me	Me	H	Ph
c;	Ph	Me	H	Ph
d;	Me	Me	$CH_2CH_2CH(Me)CH_2$	
e;	Me	Me	Me	Me

(6)

	R^1	R^2	R^3	R^4	R^5
a;	H	Me	Me	H	Me
b;	Me	Me	Me	H	Me
c;	Et	Me	Me	H	Me
d;	Ph	Me	Me	H	Me
e;	CO_2Me	Me	Me	H	Me
f;	H	Me	Me	H	Ph
g;	Me	Me	Me	H	Ph
h;	Ph	Me	Me	H	Ph
i;	H	Ph	Me	H	Ph
j;	Me	Ph	Me	H	Ph
k;	H	Me	Me	$CH_2CH_2CH(Me)CH_2$	

Scheme 3.

Table 1. Preparative details for nitroketones (6) and for their conversion into the diketones (1).

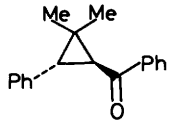
Substituents					Nitro-ketone	Method	Ratio (5):(4)	Conditions (°C; h)	Yield (%)	Diketone	Method	Yield[a] (%)
R^1	R^2	R^3	R^4	R^5								
H	Me	Me	H	Me	(6a)	B	1.0:1.2	80; 36	76	(1a)	G	35
											H	24
Me	Me	Me	H	Me	(6b)	A	1.0:1.0	40; 12	62	(1b)	D	55
											E	75
Et	Me	Me	H	Me	(6c)	A	1.0:1.0	40; 18	65	(1c)	D	60
											E	25
											F	45
Ph	Me	Me	H	Me	(6d)	C	1.0:5.0	40; 340	50	(1d)	D	60
											E	85
CO_2Me	Me	Me	H	Me	(6e)	A	1.0:5.0	70; 70	83	(1e)	D, E	0[b]
											F	0
H	Me	Me	H	Ph	(6f)	B	1.2:1.0	80; 36	60	(1f)	G	30
											H	20
Me	Me	Me	H	Ph	(6g)	A	1.0:1.0	50; 20	68	(1g)	D	45
											E	65
Ph	Me	Me	H	Ph	(6h)	C	1.0:1.5	40; 340	0[c]			
H	Ph	Me	H	Ph	(6i)	A	2.0:1.0	60; 72	50	(1i)	G	0
Me	Ph	Me	H	Ph	(6j)	A	2.0:1.0	60; 84	45[d]	(1j)	E	65
H	Me	Me	$CH_2CH_2CH(Me)CH_2$		(6k)	A	1.0:1.2	50; 96	65[e]	(1k)	G	40

[a] From nitroketone (6). [b] Nitroketone (6a) formed. [c] Benzoylcyclopropane (7) (60%) formed. [d] Mixed diastereoisomers formed (ratio 4:5). [e] Only one diastereoisomer formed.

manganate–magnesium sulphate at pH 7, either directly[16b] (method G) or, with lower overall yields, after first converting the nitroketone into its ethylene ketal[16a] (method H). These conditions are known to inhibit the oxidation of the aldehyde group to a carboxylic acid; the method failed, however, with compound (6i). Yields, and conditions for converting the nitroketones (6) into the diketones (1) are also given in Table 1.

Although nine examples of compounds (1) were prepared by the method shown in Scheme 3, the approach suffers from poor availability of the enones (4), in addition to other limitations referred to above. For example, the enone (4b) was made using the methodology reported for the preparation of 4,4-diphenylbut-3-en-2-one,[20] an approach which promised to be quite general. However, it failed for the enone (4e) ($R^4 \neq H$), giving fragmentation products from both the hydroxy ketal (8b) and the aldol (9) (Scheme 4).

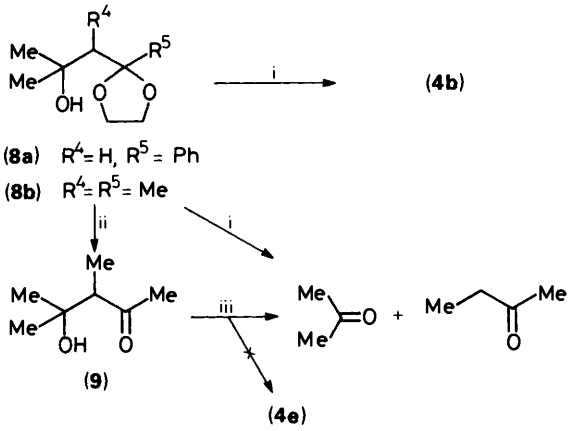
Some additional 1,4-diketones were prepared by other approaches: the cyclohexanone (1l) by Yoshikoshi's method;[6a] the cyclopentanone (1m) by the method of Hennion and



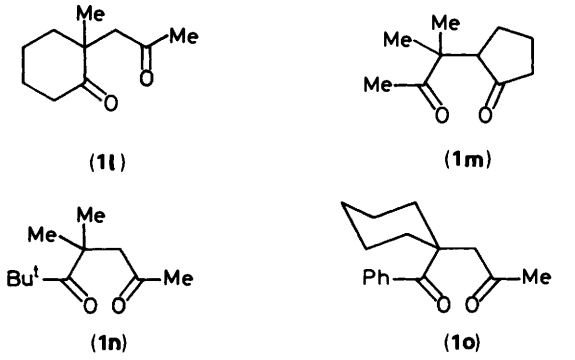
(7)

Quinn;[21] and examples (1n) and (1o) by alkylation of ketone enolates with 3-bromopropyne, followed by mercury(II)-catalysed hydration. The latter approach, in which 15–50% *O*-alkylation also occurred, used the methodology of Welch and co-workers,[22] only with sodium hydride in toluene as the base rather than lithium di-isopropylamide in tetrahydrofuran. The diketones (1a) and (1d) were also prepared in 15% and 45% overall yields respectively by this method, which failed, however, for the preparation of the diketo-ester (1e).

Reaction of 1,4-*Diketones with Ammonia.*—In studies on

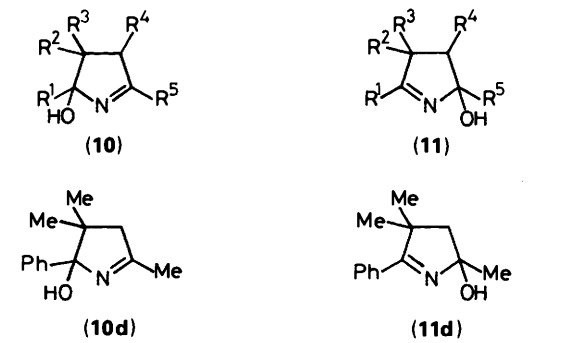


Scheme 4. *Reagents and conditions:* i, HCl–Me_2CO–H_2O, heat; ii, AcOH–H_2O, 25 °C; iii, various



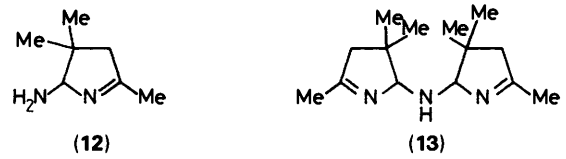
corrin synthesis, 2,2-disubstituted 1,4-diketones have been reported to give 2-hydroxy-3,4-dihydro-2*H*-pyrroles (hydroxypyrrolines) in methanolic ammonia.[23] We have isolated analogous hydroxypyrrolines from both 2-acyl-2-alkyl-[5] and simpler[24] 1,4-diketones in essentially quantitative yields by reaction with liquid ammonia. It seemed likely that the diketones (**1**) would similarly yield hydroxypyrrolines, which might subsequently be dehydrated to the 3*H*-pyrroles (**2**). From our earlier work,[24] it was anticipated that two regioisomers (**10**) and (**11**) would be formed, each comprising mixtures of diastereoisomers for $R^2 \neq R^3$ and/or $R^4 \neq H$.

Reaction of the diketone (**1d**) overnight with liquid ammonia gave a mixture (9:1 by ^1H NMR) of the hydroxypyrrolines (**10d**) and (**11d**), which could be separated by recrystallisation from benzene–hexane. The two isomers were readily distinguished from spectroscopic data: $\nu_{C=N}$ 1 645 cm^{-1} (**10d**) and 1 605 cm^{-1} (**11d**); $\delta_H(Me_2)$ 0.39 and 1.16 (**10d**) and 1.34 and 1.44 (**11d**), one methyl group in the former being strongly shielded by the phenyl substituent; and δ_H(ring CH_2) 2.13 and 2.49 (ABq, *J* 18.8 Hz) (**10d**), and 1.97 and 2.13 (ABq, *J* 13.6 Hz)



(**11d**). With time, in chloroform solution, the composition of the mixed isomers (**10d**) and (**11d**) changed, the latter becoming predominant at the expense of the former. Isomer (**10d**) is the anticipated major product from kinetic control, attack by ammonia being faster at the acetyl than at the benzoyl group in (**1d**), while (**11d**) is thermodynamically more stable, being more conjugated and less sterically crowded.

In contrast, the diketone (**1b**) gave, under the same conditions, only one hydroxypyrroline, shown to be (**11b**) both from the coupling constant (13.6 Hz) for the ring CH_2 group, and from long-range coupling shown by the imine ^{13}C carbon signal. Other 1,4-diketones gave mixed isomers in some cases, and in others either (**10**) or (**11**). Crude yields were close to quantitative, the yields in Table 2 being in most cases for pure, recrystallised isomers; exceptions are indicated in the footnotes. Reaction of the diketone (**1g**) was much slower than its isomer (**1d**), necessitating the use of a very large excess of ammonia, while the diketone (**1j**) was even less reactive, giving an inseparable mixture of diastereoisomers of (**10j**) and (**11j**) together with much unreacted diketone. The keto-aldehydes (**1**; R^1 = H) were highly reactive, and in general yielded only the hydroxypyrrolines (**10**) [mixed diastereoisomers from (**1k**)]. Occasionally, however, a small peak in the ^1H NMR spectrum *ca.* δ 7.8 revealed a trace of the isomer (**11**). For (**1a**), at least two



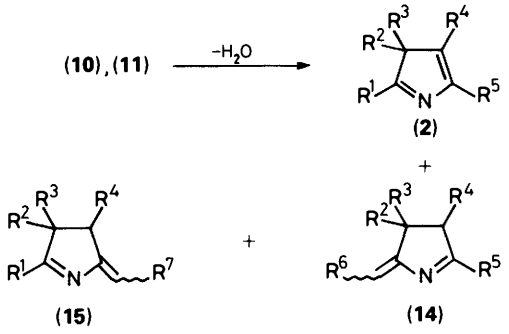
other major products were formed in addition to (**10a**), the relative amounts appearing to depend upon the quantity of ammonia and the reaction time, although results were not readily reproducible. Evidence from ^1H and ^{13}C NMR spectra suggested (**12**) and (**13**) as possible structures, the overall patterns being consistent with (**10a**) having the OH group replaced by a less electronegative substituent. Thus for R^1, R^2, and R^3, signals were observed at δ_H 4.45(q), 0.89(s), 1.15(s), and 4.64(q), 0.91(s), 1.17(s), respectively, for the two additional compounds [*cf.* 5.05(q), 1.01(s), and 1.11(s) for (**10a**)], while for C-2 and C-5, signals were found at δ_C 92.64(d) and 172.25(s), and 86.23(d) and 172.98(s) respectively [*cf.* 99.52(d) and 174.66(s) for (**10a**)]. In other respects the spectra were very similar; there was no clear evidence for two diastereoisomers of structure (**13**). Additional peaks in the ^1H NMR spectrum of a crude sample of hydroxypyrroline (**10f**) at δ 4.56(q), 0.99(s), and 1.28(s) suggested the presence of an analogous by-product. Physical, analytical, mass and IR spectroscopic data for compounds (**10**) and (**11**) are shown in Table 2, while ^1H and ^{13}C NMR data are in Table 3; numbering of substitution patterns is the same as for the diketones (**1**). Of note are the effect of phenyl conjugation on $\nu_{C=N}$ [an exception being the Bu^t derivative (**11n**)], and the facile distinction between isomers (**10**) and (**11**) from $^2J_{HH}$ for the ring methylene group (*ca.* 16.8 Hz for the former and *ca.* 13.6 Hz for the latter).

Preparation of 3H- *and* 2H-*Pyrroles.—By dehydration of hydroxypyrrolines.* Hydroxypyrrolines (**10**) and (**11**) having R^2 = H readily lose water to form 1*H*-pyrroles, possibly *via* a 3*H*-pyrrole intermediate;[24–26] however, only one example having R^2 and $R^3 \neq H$ appears to have been dehydrated to a 3*H*-pyrrole.[27] In general, where R^1 and/or R^5 bear an α-hydrogen atom, up to three isomeric products (**2**), (**14**), and (**15**) might be expected (Scheme 5); in addition, non-acidic conditions are indicated, to inhibit rearrangement of the desired product (**2**) to an isomeric 2*H*-pyrrole.[28]

Table 2. Physical, analytical, mass, and IR spectroscopic data for the hydroxypyrrolines (**10**) and (**11**).[a]

Compound (formula)	Yield[b] (%)	M.p.[c] (°C)	Found (%) (Required) C	H	N	M^+	ν_{max}/cm^{-1}	Phase
(11b) ($C_8H_{15}NO$)	85	96.5–97	68.2 (68.0)	10.4 (10.7)	10.1 (9.9)	141	3 130br s, 1 644vs, 1 436m. 1 419m, 1 370s, 1 313s, 1 254s, 1 197s, 1 152s, 954m, 901s, and 790br	Nujol
(11c) ($C_9H_{17}NO$)	40	74–74.5		*d*		155	3 160br s, 1 651vs, 1 442m, 1 409m, 1 363s, 1 283s, 1 250m, 1 202m, 1 180s, 1 155s, 1 118s, 961m, 936s, 900m, and 740br	Nujol
(10d) ($C_{13}H_{17}NO$)	40	147	76.55 (76.8)	8.15 (8.4)	6.95 (6.9)	203	3 110br s, 1 643vs, 1 492m, 1 449vs, 1 418s, 1 381s, 1 330s, 1 258m, 1 201m, 1 178m, 1 098s, 1 067vs, 1 001m, 782vs, and 712vs	KBr
(11d) ($C_{13}H_{17}NO$)	25	112	76.55 (76.8)	8.2 (8.4)	6.7 (6.9)	203	3 180br s, 1 604s, 1 575s, 1 465vs, 1 375s, 1 324s, 1 263s, 1 195vs, 1 130s, 1 073s, 958s, 895m, 788s, 765br m, and 706vs	Nujol
(10f) ($C_{12}H_{15}NO$)	35	165	76.0 (76.15)	7.85 (8.0)	7.25 (7.4)	189	3 140br s, 1 615vs, 1 577w, 1 457vs, 1 436m, 1 385m, 1 335vs, 1 275m, 1 135vs, 1 110m, 1 056s, 1 035s, 775s, and 705s	KBr
(10g) ($C_{13}H_{17}NO$)	35	123	76.95 (76.8)	8.3 (8.4)	6.95 (6.9)	203	3 220br s, 1 616vs, 1 576w, 1 457s, 1 373s, 1 346m, 1 235s, 1 203s, 1 158vs, 1 143m, 958s, 775s, and 705s	Nujol
(11g) ($C_{13}H_{17}NO$)	75[e]						3 070br s, 1 644vs, 1 489m, 1 441vs, 1 295s, 1 220m, 1 190s, 1 137vs, 1 112s, 1 000s, 947s, 770br, 738vs, and 669vs	Nujol
(10k)[f] ($C_{11}H_{19}NO$)	75	42 (dec.)		*d*		180	3 160br, s, 1 641s, 1 463s, 1 424m, 1 362s, 1 291m, 1 203m, 1 146vs, 1 117s, 995s, 842m, and 730br	Nujol
(10l), (11l)[g] ($C_{10}H_{17}NO$)	70		71.65 (71.8)	10.05 (10.25)	8.65 (8.35)	167		
(11m) ($C_{10}H_{17}NO$)	85	137[h]				167	3 110br s, 1 648s, 1 474m, 1 364m, 1 312s, 1 302s, 1 233s, 1 188vs, 1 144s, 1 074vs, 970s, 893m, 852m, and 790br	Nujol
(11n) ($C_{11}H_{21}NO$)	80	108	71.95 (72.1)	11.35 (11.55)	7.75 (7.65)	183	3 320br s, 1 618s, 1 480m, 1 409m, 1 377s, 1 321m, 1 265s, 1 205vs, 1 125s, 1 081s, 959s, 908m, and 740br	Nujol
(10o) ($C_{16}H_{21}NO$)	80	139	78.6 (78.95)	8.6 (8.7)	6.0 (5.75)	243	3 090br s, 1 653s, 1 489w, 1 455vs, 1 414s, 1 382vs, 1 321m, 1 250m, 1 230m, 1 109s, 1 051vs, 1 029s, 998s, 960m, 790br, 778vs, and 708vs	Nujol

[a] Numbering for particular substitution patterns is the same as for precursor diketones (**1**). [b] Isolated, crystallised product. [c] From benzene–light petroleum. [d] Compound too unstable for satisfactory microanalysis. [e] Crude yield; in admixture with 25% (**10g**). [f] Inseparable mixture of two diastereoisomers. [g] Inseparable mixture: one diastereoisomer of (**10l**) and two of (**11l**). [h] Lit.,[21] m.p. 134–136.5 °C.



Scheme 5.

Dehydration of hydroxypyrroline (**11b**) with basic alumina in refluxing dichloromethane, with simultaneous removal of water (4A molecular sieves: Soxhlet), yielded essentially quantitatively a mixture of the 3*H*-pyrrole (**2b**) and the exocyclic isomers (**14b**) and (**15b**) (R^6 and R^7 = H respectively) in a ratio of 62:23:15. The three isomers were readily identified from ^{1}H NMR signals in the 4–6 ppm range, integrals giving the relative amounts. Thus, signals were observed as follows: δ 5.64(q) (**2b**); 5.11 and 4.56(2 × s) (**14b**); and 5.12 and 4.66(2 × t) (**15b**). The mixture was hydrolysed when subjected to chromatography on alumina or silica, but was separated by dissolving in ice-cold 1M hydrochloric acid, followed by immediate basification with ice-cold 0.4M sodium carbonate and extraction with diethyl ether. Pure 3*H*-pyrrole (**2b**) was isolated from the ether, while under these conditions the exocyclic isomers were hydrated to (**11b**), which remained in the aqueous phase and could be recovered by extraction with dichloromethane. Attempts to further purify the 3*H*-pyrrole (**2b**) by reduced-pressure distillation, regenerated a mixture of the isomers (**2b**), (**14b**), and (**15b**) in the above ratio, demonstrating that the three compounds establish a thermodynamic equilibrium when heated above room temperature. The 2-ethyl analogue (**2c**) was similarly prepared from hydroxypyrroline (**11c**) in refluxing benzene [δ_H 5.61 (q, *J* 1.3 Hz)], but in only 15% yield. The major product (85%) which could be purified, but from which the 3*H*-pyrrole (**2c**) could not be isolated, was the ethylidene compound (**14c**) (R^6 = Me) [δ_H 4.92 (q, *J* 7 Hz)]; no trace of the isomer (**15c**) was detected.

Of interest was the difference in behaviour between the regioisomers (**10d**) and (**11d**). The former gave exclusively the 3*H*-pyrrole (**2d**) [δ_H 5.76 (q, *J* 1.3 Hz)] in refluxing benzene, although the isomer (**15d**) was detectable after prolonged heating [δ_H 5.34 and 4.84 (2 × t, *J* 1.8 Hz)]. The hydroxypyrroline (**11d**), however, was recovered unchanged under the same conditions, even after 8 h. The essential difference between the isomers (**10d**) and (**11d**) is that the former bears an acidic ring hydrogen atom, and may tautomerise to an enamine prior to dehydration; this is not the case with the latter. The isomer

Table 3. ^{1}H and ^{13}C NMR spectroscopic data for hydroxypyrrolines (**10**) and (**11**).

	$\delta_H(CDCl_3)$						$\delta_C(CDCl_3)$[a]								
Compd	R^1	R^2	R^3	R^4	R^5	OH	C-2	C-3	C-4	C-5	R^1[n]	R^2	R^3	R^4	R^5[n]
(**10a**)[b]	5.05[c]	1.01	1.11	2.28[d] 2.40[d]	2.01[c]	6.90	99.52	51.95	41.61	174.66		20.48	25.57		19.23
(**11b**)	1.92	1.14	1.23	1.76[e] 2.02[e]	1.50	6.66	98.11	52.06	50.49	180.51	14.46	26.44	27,.09		30.23
(**11c**)	1.20 2.24	1.13	1.22	1.84[e] 1.96[e]	1.53	5.78	97.88	51.89	50.04	183.86	10.88 21.06	26.31	27.02		30.00
(**10d**)	7.2–7.5	0.37	1.16	2.13[f] 2.49[f]	1.71	6.98	102.66	53.79	45.72	178.88	143.45i 126.28 127.25m 126.82p	21.56	26.76		19.88
(**11d**)	7.3–7.5 7.6–7.8	1.34	1.44	1.97[g] 2.13[g]	1.58	5.60	97.51	54.00	50.70	179.04	134.02i 128.17o, m 129.74p	27.46	28.28		29.90
(**10f**)	5.33[c]	1.10	1.24	2.73[c,f] 2.93[c,f]	7.3–7.5 7.8–7.9	5.14	100.93	49.35	42.31	173.41		21.67	26.38		134.14i 127.85o 128.50m 131.10p
(**10g**)	1.41	1.12	1.14	2.72[h] 2.94[h]	7.3–7.5 7.7–7.9	4.71	101.74	49.68	44.37	171.95	23.24[i]	23.62[i]	24.22[i]		134.41i 127.80o 128.45m 130.89p
(**11g**)[j]	1.86	1.02	1.19	1.96[e] 2.22[e]	7.2–7.5	4.68	99.57	53.63	50.38	183.92	14.41	25.90	26.49		147.73i 125.31o 127.74m 126.77p
(**10k**)[k]	5.00 5.09	0.84–1.11		1.23–2.72		5.61	99.62 99.62	55.96 56.12	43.99 41.55	179.21 182.46		22.43 25.03	26.06 25.90	32.50t, 39.55t 32.77t, 22.43d 17.17.q 33.21t, 40.09t 33.48t, 23.08d 17.17q	
(**10l**), (**11l**)[l]	1.3–1.8		1.19 1.29	2.40 2.44	1.49 1.53 1.90	4.40	98.59 99.25 99.62			177.36 183.86					27.63
(**11m**)	1.90	1.02	1.22	1.0–2.1		5.60	110.35	56.50	51.41	181.43	14.84	21.02	29.25	25.35t, 28.44t 41.01t	
(**11n**)	1.28	1.31	1.39	1.88[g] 1.91[g]	1.53		96.27	55.37	52.11	187.77	30.23 37.43	28.12	28.98		29.96
(**11o**)	7.2–7.6	0.66–2.00		2.01[m] 2.15[m]	1.58	3.10	98.38	47.51	57.04	180.51	135.11i 128.17o, m 129.20p	23.19, 23.29 25.46, 34.56 35.10			30.55

[a] Assignments confirmed by multiplicities in off-resonance decoupled spectra. [b] Mixture with other compounds; see text. [c] $^5J_{HH}$ 1.3 Hz. [d] $^2J_{HH}$ 17.6 Hz. [e] $^2J_{HH}$ 13.6 Hz. [f] $^2J_{HH}$ 16.8 Hz. [g] $^2J_{HH}$ 13.1 Hz. [h] $^2J_{HH}$ 16.2 Hz. [i] Assignments uncertain. [j] Data from mixture containing 25% (**10g**). [k] Unstable and inseparable mixture of two diastereoisomers; major isomer first. Spectra recorded at −30 °C. [l] Inseparable mixture: one diastereoisomer of (**10l**) and two of (**11l**); only limited assignments possible. [m] $^2J_{HH}$ 14.0 Hz. [n] i = *ipso*, m = *meta*, o = *ortho*, and p = *para* carbon signals.

(**11d**) was thus refluxed with *acidic* alumina in dichloromethane, and now yielded a mixture of (**2d**) and (**15d**) (9:1) cleanly. Results for the dehydration of these and other hydroxypyrrolines are given in Table 4. In some cases, mixtures were formed which could not be separated by chromatography, pH partition, or fractional distillation; rapid hydration to hydroxypyrrolines, or thermal equilibrations of the isomers (**2**), (**14**), and (**15**) were commonly observed. Dehydration of compounds (**10f**) and (**10k**) in benzene gave the 1*H*-pyrroles (**16**) and (**17**) respectively, apparently *via* thermal rearrangement of the intermediate 3*H*-pyrroles (**2f**) and (**2k**) (Scheme 6). This was confirmed by isolation of pure 3*H*-pyrrole (**2f**) [δ_H 8.01 and 6.39 (2 × d, *J* 1.34 Hz)] from dehydration of (**10f**) in the lower-boiling dichloromethane. However, under these conditions (**10k**) gave only a trace of the tetrahydro-3*H*-indole (**2k**) [δ_H 7.85(s)]; the bulk of the product, which was not isolated, lacked an alkene absorption, and showed an intense singlet at δ 1.08. It is possible that the 3*H*-pyrrole (**2k**) trimerises in a fashion similar to 3,3-dimethyl-3*H*-indole.[29] All attempts to dehydrate the t-butyl compound (**11n**) were unsuccessful, the starting material being recovered.

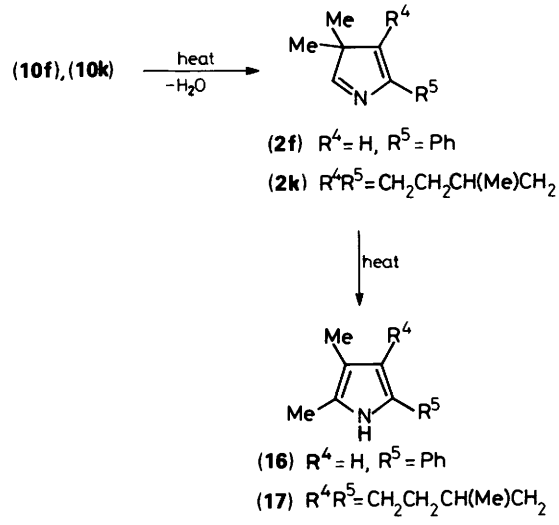
^{1}H and ^{13}C NMR data are given in Table 5, while physical, UV, IR, and mass spectroscopic data for those 3*H*-pyrroles obtained pure are given in Table 6.

By direct cyclisation of 1,4-*diketones* (**1**). Attempts were made to prepare 3*H*-pyrroles (**2**) directly from the 1,4-diketones (**1**) using ammonium acetate in acetic acid. Reaction of the diketone (**1j**) at 40 °C (14 h) successfully yielded the 3*H*-pyrrole (**2j**), while at 60 °C (24 h), only the isomeric 2*H*-pyrrole (**18j**) was isolated, apparently *via* acid-catalysed rearrangement at the higher temperature (Scheme 7). This was supported by the quantitative conversion of the 3*H*-pyrrole (**2d**) into the isomer (**18d**) after 20 h in acetic acid at 50 °C. In contrast with this, the 2*H*-pyrrole (**18j**) has been reported to be rearranged in benzene–pyridine at 270 °C to 2,3-dimethyl-4,5-diphenyl-1*H*-pyrrole, apparently *via* the (unobserved) 3*H*-pyrrole (**2j**).[30] The

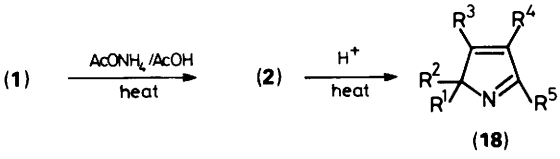
Table 4. Products from dehydration of hydroxypyrrolines (**10**) and (**11**).

Compound	R^1	R^2	R^3	R^4	R^5	Alumina	Solvent (Time/h)	Ratio of products (Yield pure isolated product/%) (2)	(14)	(15)
(**11b**)	Me	Me	Me	H	Me	Basic	CH_2Cl_2 (8)	62(46)	23	15
(**11c**)	Et	Me	Me	H	Me	Basic	Benzene (4)	15	85(75)	0
(**10d**)	Ph	Me	Me	H	Me	Basic	Benzene (4.5)	100(92)		0[a]
(**11d**)	Ph	Me	Me	H	Me	Basic	Benzene (8)		No reaction	
						Acidic	CH_2Cl_2 (24)	90		10
(**10f**)	H	Me	Me	H	Ph	Basic	Benzene (4.5)	*b*		
						Basic	CH_2Cl_2 (5)	100(88)		
(**10g**), (**11g**)	Me	Me	Me	H	Ph	Basic	Benzene (4.5)	85[c]	15[c]	
(**10k**)	H	Me	Me	$CH_2CH_2CH(Me)CH_2$		Basic	Benzene (24)	*d*		
						Basic	CH_2Cl_2 (4)	Trace[e]		
(**10l**), (**11l**)	$(CH_2)_4$		Me	H	Me	Basic	Benzene (4.5)	16[c]	82[c]	2[c]
(**11m**)	Me	Me	Me	$(CH_2)_3$		Acidic	CH_2Cl_2 (24)	60[c]	0	40[c]
(**11n**)	Bu[t]	Me	Me	H	Me	Basic	Benzene (24)		No reaction	
						Acidic	Benzene (24)		No reaction	
(**11o**)	Ph	$(CH_2)_5$		H	Me	Basic	CH_2Cl_2 (6)	100(68)		0[f]

[a] Some (**15b**) formed on prolonged heating. [b] Only 1*H*-pyrrole (**16**) formed (66%). [c] Inseparable mixture. [d] Only 1*H*-pyrrole (**17**) formed (60%). [e] See text. [f] Some (**15o**) formed on prolonged heating.



Scheme 6.



Scheme 7.

diketone (**1g**) gave a mixture of pyrroles (**2g**) and (**18g**) at 60 °C, which were successfully separated by chromatography on alumina; other diketones under the same conditions gave only 2*H*-pyrroles. Results are summarised in Table 7, while physical and spectroscopic data for the 2*H*-pyrroles and additional 3*H*-pyrroles are given in Tables 5 and 6.

Isomeric 3*H*- and 2*H*-pyrroles bearing alkyl and aryl substituents are most readily distinguished from their ^{13}C NMR spectra. Signals for the tetrahedral carbon atom, the imine, and the lowest field alkene carbon atoms are in the ranges δ 56–64, 181–189, and 149–157 for 3*H*-pyrroles, and δ 78–89, 170–174, and 168–172 for 2*H*-pyrroles, respectively. In the IR spectra, lines assigned to C=N, C=C, and C–N vibrations (bold type in Table 6) are found in the ranges 1 600–1 635, 1 515–1 580, and 1 250–1 290 cm^{-1} for the 3*H*-pyrroles, and 1 625–1 640, 1 530–1 560, and 1 320–1 360 cm^{-1} for the 2*H*-pyrroles, respectively.

Although 3*H*-pyrroles rearrange readily in acidic media, some were nevertheless characterised successfully as salts. However, care must be taken during recrystallisation; the picrate of 3*H*-pyrrole (**2b**), for example, rearranged to the picrate of the corresponding 2*H*-pyrrole (**18b**) when recrystallised from boiling ethanol, although not at a lower temperature. This may account for the observation by Wong and Ritchie that picrates of isomeric 2*H*- and 3*H*-pyrroles have the same melting points, and show almost no depression with mixed melting point.[4a]

The Paal–Knorr reaction may thus be used effectively for preparing both 3*H*-pyrroles, and, *via* rearrangement, 2*H*-pyrroles, from 2,2-disubstituted 1,4-diketones, providing novel, and potentially general, routes to both of these classes of azoles.

Experimental

UV spectra were recorded on a Shimadzu UV 240 spectrometer, and IR spectra on a Perkin-Elmer 157G instrument with polystyrene being used in calibration. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$, unless otherwise stated, on a JEOL FX90Q spectrometer with Me_4Si used as internal reference, and mass spectra on a Hitachi RMS-4 instrument. ^{13}C NMR signals refer to single carbon atoms, unless otherwise indicated.

The nitroalkanes (**5a–c**) were available commercially, as were the enones (**4a**) and (**4d**). Literature preparations were used for phenylnitromethane (**5d**),[31] methyl nitroacetate (**5e**),[32] and 1,3-diphenylbut-2-en-1-one (dypnone) (**4c**).[33] Contrary to the literature account, only the pure *trans*-isomer of the latter was isolated [δ_H 7.02 (1 H, q, *J* 1.3 Hz)].

3-*Methyl*-1-*phenylbut*-2-*en*-1-*one* (**4b**).—*Ethyl* 3,3-*ethylenedioxy*-3-*phenylpropanoate*. This was prepared in 85% yield from the reaction between ethyl benzoylacetate (21.5 g, 0.11 mol) and ethane-1,2-diol (18.0 g, 0.29 mol) in refluxing benzene (75 ml), catalysed by toluene-*p*-sulphonic acid (0.2 g). Water was removed using a Dean–Stark apparatus; ν_{max}(film) 1 745, 1 160, 1 140, 1 020, and 676 cm^{-1}; δ_H 1.12 (3 H, t), 2.96 (2 H, s), 3.96 (4 H, m), 4.09 (2 H, q), and 7.2–7.6 (5 H, m).

Table 5. ^{1}H and ^{13}C NMR spectroscopic data for 3*H*-pyrroles (**2**)[a] and 2*H*-pyrroles (**18**).[a]

	δ_H($CDCl_3$)					δ_C($CDCl_3$)[b]								
Compd	R^1	R^2	R^3	R^4	R^5	C-2	C-3	C-4	C-5	R^{1h}	R^{2h}	R^3	R^4	R^{5h}
3*H*-Pyrroles														
(**2b**)	2.09		1.11	5.64[c]	2.08[c]	188.31	56.50	128.55	149.41	14.74	21.62			16.04
(**2d**)	7.3–7.5 7.9–8.1		1.38	5.76[c]	2.19[c]	183.43	56.34	129.69	149.08	133.32i 127.74o 128.34m 132.18p	22.70			16.20
(**2f**)	8.01[d]		1.30	6.39[d]	7.3–7.5 7.8–7.9	181.04	57.58	128.27	152.06		19.93			134.02i 126.22o 128.44m 127.95p
(**2g**)[e]	2.21		1.22	6.34	7.3–7.5 7.8–7.9	188.58	57.21	127.58[f]	151.42	15.00	21.78			134.35i 126.17o 128.39m 127.80p[f]
(**2j**)	2.07	7.0–7.4	1.60	6.54	7.0–7.4 7.8–7.9	187.28	63.82	127.04[f]	151.85	14.46	137.06i 124.71o 127.42m[f] 126.01p	17.61		132.89i 125.25o 127.74m[f] 127.25p[f]
(**2l**)[e]	1.3–2.0		1.08	5.75[c]	2.14[c]									
(**2m**)[e]	2.13		1.09	1.6–2.6		181.81	57.32	146.65	157.16	15.60	20.86		24.16 25.30 26.87	
(**2o**)	7.3–7.5 7.9–8.1	1.29–2.05		6.36[c]	2.22[c]	183.92	62.62	129.52	150.39	133.97i 127.96o 128.28m 127.75p	25.03 25.89 32.29			16.47
2*H*-Pyrroles														
(**18b**)	1.19		1.95[c]	5.85[c]	2.16	78.07	170.11	120.64	172.00	23.08		12.62		18.80
(**18c**)	0.50 1.50[g] 1.93[g]	1.17	1.90[c]	5.90[c]	2.18	81.15	170.43[f]	124.38	179.92[f]	7.75 29.25	22.37	12.84		18.58
(**18d**)	7.1–7.3	1.60	1.85[c]	5.95[c]	2.26	83.32	172.16[f]	124.06	172.49[f]	139.50i 128.39o, m 126.93p	21.24	13.11		18.80
(**18g**)	1.32		2.06[c]	6.46[c]	7.3–7.5 7.8–8.0	77.90	168.48	118.80	171.78	22.21		12.03		133.54i 126.50o 127.47m 128.99p
(**18j**)	1.73	7.1–7.4	1.94[c]	6.55[c]	7.4–7.5 7.9–8.1	84.02	171.51	120.64	173.52	21.39	139.44i 128.66o[f] 128.50m[f] 127.09p	13.54		134.35i 125.73o 127.79m 130.39p
(**18l**)	1.4–2.1		1.96[c]	5.88[c]	2.16	89.06	168.59[f]	123.79	169.62[f]	26.33 34.45		12.56		18.70

[a] Numbering for particular substitution patterns are the same as for precursor diketones (**1**). [b] Assignments confirmed by multiplicities in off-resonance decoupled spectra. [c] $^4J_{HH}$ 1.3 Hz. [d] $^5J_{HH}$ 1.34 Hz. [e] Inseparable mixture of isomers. [f] Assignments with similar chemical shifts uncertain. [g] Diastereotopic CH_2; $^2J_{HH}$ 14.0 Hz, $^3J_{HH}$ 7.0 Hz. [h] i = *ipso*, m = *meta*, o = *ortho*, and p = *para* carbon signals.

4,4-*Ethylenedioxy*-2-*methyl*-4-*phenylbutan*-2-*ol* (**8a**). To an ice-cold solution of methylmagnesium iodide, prepared from magnesium turnings (26.7 g, 1.10 mol) and iodomethane (149.0 g, 1.05 mol) in anhydrous ether (600 ml), was added the above ketal-ester (113 g, 0.47 mol) in anhydrous ether (250 ml), dropwise with cooling and vigorous stirring. Stirring was continued at 25 °C for 2 h, the product was poured into ice and water (1 kg), then the mixture was filtered and separated, and the aqueous phase was extracted with ether (2 × 250 ml). The ether layers were combined, dried ($MgSO_4$), and evaporated. Distillation gave the hydroxy-ketal (**8a**) (64.7 g, 62%), b.p. 102 °C (0.5 mmHg); ν_{max}(film) 3 550, 1 220, 1 177, 1 155, 1 020, and 680 cm^{-1}; δ_H 1.25 (6 H, s), 2.17 (2 H, s), 3.51 (1 H, br s, 3.65–4.17 (4 H, m), and 7.27–7.43 (5 H, m); δ_C 30.45 (2 C, q), 50.17(t), 63.71 (2 C, t), 70.54(s), 111.33(s), 125.47 (2 C, d), 128.07(d), 128.29 (2 C, d), and 143.07(s).

2-*Methyl*-1-*phenylbut*-2-*en*-1-*one* (**4b**). A solution of the hydroxy-ketal (**8a**) (22.0 g, 0.099 mol), 12M HCl (8 ml), and water (20 ml) in acetone (200 ml) was heated under reflux for 5 h. After cooling, water (1 l) was added, the mixture was extracted with ether (3 × 250 ml), then the ether extracts were combined and dried ($MgSO_4$), and the solvent was evaporated. Distillation of the residue gave the enone (**4b**) (8.7 g, 55%), b.p. 69 °C (3 mmHg) [lit.,[9a] 104–106° (5 mmHg)]; ν_{max}(film) 1 663, 1 614, 1 235, 990, and 625 cm^{-1}; δ_H 2.01 (3 H, d, *J* 1.3 Hz), 2.21 (3 H, d, *J* 1.3 Hz), 6.75 (1 H, m, *J* 1.3 Hz), 7.41–7.53 (3 H, m), and 7.88–7.98 (2 H, m); δ_C 21.13(q), 27.90(q), 121.24(d), 128.17 (2 C, d), 128.39 (2 C, d), 132.18(d), 139.33(s), 156.40(s), and 191.45(s).

Attempted Preparation of 3,4-*Dimethylpent*-3-*en*-2-*one* (**4e**).—Ethyl 3,3-ethylenedioxy-2-methylbutanoate was prepared from

Table 6. Physical, UV, IR, and mass spectroscopic data for 3*H*-pyrroles (**2**) and 2*H*-pyrroles (**18**).

Compound	M.p. or b.p./°C (mmHg) n_D (T/°C)	UV λ_{max}/nm (log ε)	Solvent	IR[a] ν_{max} (film)/cm^{-1}	MS M^+
3*H*-Pyrroles					
(**2b**)	**1.4500**(29)	253 (3.08)	EtOH	3 070w, **1 634**s, **1 580**s, 1 464s, 1 434s, 1 377s, **1 288**s,	123
		271 (3.07)	EtOH/HCl	and 780s	
(**2d**)	38(0.05)	215 (3.97), 250sh (3.51), 303 (3.94)	EtOH	3 070m, **1 630**s, **1 523**s, 1 497s, 1 465s, 1 448s, 1 015s,	185
	1.5668(29)	214sh (3.65), 260 (3.61), 330 (3.96)	EtOH/HCl	794s, 787m, 721s, and 701vs	
(**2f**)		*b*		3 070m, **1 613**m, 1 596s, **1 563**m, 1 465s, 1 449s, 1 322m,	171
				1 271s, 764vs, 740m, 696vs, and 675m	
(**2g**)[c]				3 070m, **1 600**s, 1 578s, **1 500**m, 1 492m, 1 465s, 1 448s,	185
				1 264m, 1 032m, 764vs, 699vs, and 683m	
(**2j**)	**1.5320**(25)	217 (4.37), 268sh (3.89), 279sh (3.73)	EtOH	3 065m, **1 624**m, 1 597s, 1 573m, 1 491s, 1 447s, 1 378m,	247
		240 (4.29), 280 (3.91)	EtOH/HCl	**1 251**m, 1 059m, 1 025m, 765vs, and 699vs	
(**2o**)	**1.5025**(26)	214 (4.02), 275sh (3.71), 303 (3.85)	EtOH	3 055m, **1 625**s, **1 517**m, 1 496m, 1 442vs, **1 263**s, 780vs,	225
		215 (3.76), 263 (3.61), 328 (3.77)	EtOH/HCl	695vs, and 678m	
2*H*-Pyrroles					
(**18b**)	45(24)	233 (3.55)	EtOH	3 050w, **1 639**s, **1 552**m, 1 450m, 1 425s, 1 372s, **1 320**s,	123
	1.4497(21)	251 (3.65)	EtOH/HCl	and 803s	
(**18c**)	65(40)[d]	234 (3.50)	EtOH	3 060w, **1 637**s, **1 552**m, 1 453m, 1 439s, 1 385s, **1 332**s,	137
	1.4516(26)			and 835m	
(**18d**)		243 (3.37)	EtOH	3 060m, **1 636**s, 1 602m, **1 557**m, 1 496s, 1 447s, 1 386s,	185
		240 (3.57), 275sh (3.20)	EtOH/HCl	**1 335**s, 1 027m, 835m, 771vs, and 707vs	
(**18g**)		225 (3.52), 244 (3.76)	EtOH	3 060m, **1 629**s, 1 600m, 1 581w, **1 535**m, 1 449s,	185
		215sh (3.42), 280 (3.94)	EtOH/HCl	**1 355**vs, 1 025m, 835m, 777vs, and 696vs	
(**18j**)[e]	70[f]	215sh (4.37), 245 (4.21)	EtOH	3 060m, **1 627**s, 1 600m, 1 579w, **1 532**m, 1 490m,	247
		215sh (4.08), 285 (4.36)	EtOH/HCl	1 433vs 1 379s, **1 357**vs, 1 025s, 842s, 775vs, and 690vs	
(**18l**)	85(25)	232 (3.55)	EtOH	3 060w, **1 630**s, **1 550**m, 1 439s, 1 381s, **1 332**s, and	149
	1.4890(24)			830m	

[a] Values in bold type are assigned to pyrrole ring vibrations; see text. [b] UV spectrum was that of the hydroxypyrroline (**10f**). [c] Inseparable mixture with the exocyclic isomer (**15g**). [d] Lit., b.p. 52–56 °C (11 mmHg) (H. Booth, A. W. Johnson, M. Markham, and R. Price, *J. Chem. Soc.*, 1959, 1587). [e] IR spectrum in Nujol. [f] Lit.,[30] m.p. 70–71 °C.

Table 7. Reaction of 1,4-diketones (**1**) with ammonium acetate in acetic acid.

Diketone	R^1	R^2	R^3	R^4	R^5	Temperature (°C) (Time/h)	3*H*-Pyrrole Yield (%)[a]	2*H*-Pyrrole Yield (%)[a]
(**1b**)	Me	Me	Me	H	Me	60(14)		(**18b**) 50[b]
(**1c**)	Et	Me	Me	H	Me	60(14)		(**18c**) 40[b]
(**1d**)	Ph	Me	Me	H	Me	50(20)		(**18d**) 60
(**1g**)	Me	Me	Me	H	Ph	60(14)	(**2g**) 35[c]	(**18g**) 25[c]
(**1j**)	Me	Ph	Me	H	Ph	40(14)	(**2j**) 85	
						60(24)		(**18j**) 65
(**1l**)	$(CH_2)_4$		Me	H	Me	60(14)		(**18l**) 60

[a] Isolated, purified products. [b] Some polymerisation occurred on distillation. [c] Separated by column chromatography [Al_2O_3; eluant light petroleum–diethyl ether (1:1)].

ethyl 2-methyl-3-oxobutanoate and ethane-1,2-diol, as for ethyl 3,3-ethylenedioxy-3-phenylpropanoate above. Yield 72%; ν_{max}(film) 1 740, 1 189, 1 124, 1 060, and 1 025 cm^{-1}; δ_H 1.20 (3 H, d, *J* 7 Hz), 1.27 (3 H, t, *J* 7 Hz), 1.37 (3 H, s), 2.76 (1 H, q, *J* 7 Hz), 3.95 (4 H, s), and 4.17 (2 H, q, *J* 7 Hz). Reaction with excess methylmagnesium iodide gave 4,4-ethylenedioxy-2,3-dimethylpentan-2-ol (**8b**) (55%), b.p. 150 °C (15 mmHg); δ_H 1.01 (3 H, d, *J* 8 Hz), 1.20 (3 H, s), 1.23 (3 H, s), 1.40 (3 H, s), 1.90 (1 H, q, *J* 8 Hz), 4.03 (4 H, s), and 4.33 (1 H, br s). Hydrolysis in refluxing aqueous acid–acetone, as for the hydroxy-ketal above, gave only acetone and butanone. However, reaction in aqueous acetic acid at 25 °C for 2 days gave the aldol 4-hydroxy-3,4-dimethylpentan-2-one (**9**); ν_{max}(film) 3 500, 1 710, 1 350, 1 180, 1 130, and 930 cm^{-1}; δ_H 1.16 (2 H, d, *J* 7.5 Hz), 1.17 (3 H, s), 1.22 (3 H, s), 2.22 (3 H, s), 2.66 (1 H, q, *J* 7.5 Hz), and 3.29 (1 H, br s). All attempts to dehydrate this to the enone (**4e**) led only to acetone and butanone.

Preparation of Nitroketones (**6**).—Reactions were carried out successfully on the 0.02–0.5 mol scale. *Method A*. A solution of the appropriate nitroalkane (**5**), the enone (**4**), and Triton B (40% benzyltrimethylammonium hydroxide in methanol; 0.125 equiv. based on the nitroalkane) in dioxane (10–30 ml per 0.1 mol nitroalkane) was stirred under N_2, the course of the reaction being monitored by ^{1}H NMR. Details of the conditions and yields are given in Table 1.

Prepared by this method were: 4,4-dimethyl-5-nitrohexan-2-one (**6b**), b.p. 84 °C (13 mmHg) [lit.,[9b] 55.6–57.0 °C (0.1 mmHg)]; *m/z* 173 (M^+); ν_{max}(film) 1 720, 1 538, and 1 358 cm^{-1}; δ_H 1.05 (3 H, s), 1.14 (3 H, s), 1.46 (3 H, d, *J* 7.0 Hz), 2.14 (3 H, s), 2.44 and 2.60 (2 H, ABq, *J* 17.5 Hz), and 5.03 (1 H, q, *J* 7.0 Hz); δ_C 13.71(q), 23.29(q), 23.94(q), 31.58(q), 36.51(s), 50.81(t), 88.68(d), and 206.56(s); 4,4-dimethyl-5-nitroheptan-2-one (**6c**), b.p. 78 °C (0.2 mmHg) [lit.,[9c] 133 °C (17 mmHg)]; *m/z* 187 (M^+); ν_{max}(film) 1 721, 1 545, and 1 371 cm^{-1}; δ_H 0.93

(3 H, t, *J* 7.0 Hz), 1.08 (3 H, s), 1.17 (3 H, s), 1.6–2.2 (2 H, m), 2.12 (3 H, s), 2.39 and 2.55 (2 H, ABq, *J* 17.5 Hz), and 4.73 (1 H, dd, *J* 2.9, 11.2 Hz); δ_C 11.00(q), 21.24(t), 23.78(q), 24.32(q), 31.75(q), 36.57(s), 50.98(t), 97.02(d), and 206.40(s); *methyl* 3,3-*dimethyl*-2-*nitro*-5-*oxohexanoate* (**6e**), b.p. 90 °C (0.1 mmHg), n_D^{28} 1.4507; *m/z* 217 (M^+); ν_{max}(film) 1 756, 1 714, 1 560, 1 375, 1 215, and 1 023 cm^{-1}; δ_H 1.25 (3 H, s), 1.27 (3 H, s), 2.13 (3 H, s), 2.72 and 2.84 (2 H, ABq, *J* 18.4 Hz), 3.81 (3 H, s), and 5.87 (1 H, s); δ_C 24.60 (2 C, q), 31.26(q), 36.89(s), 51.57(t), 52.87(q), 92.91(d), 164.15(s), and 206.57(s); *semicarbazone* of (**6e**), m.p. 139 °C (ethanol) (Found: C, 43.5; H, 6.8; N, 20.15. $C_{10}H_{18}N_4O_5$ requires C, 43.8; H, 6.6; N, 20.4%); *m/z* 274 (M^+); 3,3-*dimethyl*-4-*nitro*-1-*phenylpentan*-1-*one* (**6g**), b.p. 106 °C (0.01 mmHg), n_D^{25} 1.4820 (Found: C, 66.05; H, 7.35; N, 5.55. $C_{13}H_{17}NO_3$ requires C, 66.35; H, 7.3; N, 5.95%); *m/z* 235 (M^+); ν_{max}(film) 1 684, 1 543, and 1 363 cm^{-1}; δ_H 1.15 (3 H, s), 1.20 (3 H, s), 1.50 (3 H, d, *J* 7.0 Hz), 2.90 and 3.19 (2 H, ABq, *J* 17.0 Hz), 5.17 (1 H, q, *J* 7.0 Hz), 7.28–7.56 (3 H, m), and 7.86–7.97 (2 H, m); δ_C 13.87(q), 23.78(q), 24.22(q), 36.84(s), 45.56(t), 89.01(d), 127.91 (2 C, d), 128.61 (2 C, d), 133.16(d), 137.82(s), and 198.28(s); 3-*methyl*-4-*nitro*-1,3-*diphenylbutan*-1-*one* (**6i**), b.p. 166 °C (0.001 mmHg), m.p. 55 °C (ethanol) (Found: C, 72.2; H, 6.1; N, 4.8. $C_{17}H_{17}NO_3$ requires C, 72.05; H, 6.05; N, 4.95%); *m/z* 283 (M^+); ν_{max}(film) 1 692, 1 535, and 1 367 cm^{-1}; δ_H 1.68 (3 H, s), 3.63 (2 H, s), 4.98 and 5.10 (2 H, ABq, *J* 11.5 Hz), 7.30–7.55 (8 H, m), and 7.83–7.93 (2 H, m); δ_C 24.66(q), 41.13(s), 45.84(t), 83.76(t), 125.48 (2 C, d), 127.21(d), 127.92 (2 C, d), 128.62 (2 C, d), 128.78 (2 C, d), 133.22(d), 137.45(s), 142.92(s), and 197.37(s); 3-*methyl*-4-*nitro*-1,3-*diphenylpentan*-1-*one* (**6j**); minor diastereoisomer was separated by column chromatography (SiO_2; eluant diethyl ether), m.p. 96 °C (ethanol) (Found: C, 72.8; H, 6.4; N, 4.5. $C_{18}H_{19}NO_3$ requires C, 72.7; H, 6.45; N, 4.7%); *m/z* 297 (M^+); ν_{max}(Nujol) 1 695, 1 540, and 1 352 cm^{-1}; δ_H 1.44 (3 H, d, *J* 6.5 Hz), 1.77 (3 H, s), 3.61 and 3.78 (2 H, ABq, *J* 17.9 Hz), 5.05 (1 H, q, *J* 6.5 Hz), 7.28 (5 H, s), 7.33–7.58 (3 H, m), and 7.85–7.96 (2 H, m); δ_C 14.52(q), 22.32(q), 43.23(t), 43.93(s), 91.39(d), 126.49 (2 C, d), 127.14(d), 127.79 (2 C, d), 128.39 (2 C, d), 128.61 (2 C, d), 133.10(d), 137.76(s), 141.34(s), and 196.76(s); for the major isomer of (**6j**) δ_H 1.27 (3 H, d, *J* 7.0 Hz), 1.70 (3 H, s), 3.23 and 4.02 (2 H, ABq, *J* 17.5 Hz), 5.05 (1 H, q, *J* 7.0 Hz), 7.17–7.55 (8 H, m), and 7.76–7.90 (2 H, m); δ_C 14.09(q), 18.31(q), 43.72(t), 46.38(s), 91.93(d), 126.22 (2 C, d), 126.49 (2 C, d), 126.98(d), 127.79 (2 C, d), 128.61 (4 C, d), 133.0(d), 137.65(s), 141.93(s), and 196.32(s); and 5-*methyl*-2-(1,1-*dimethyl*-2-*nitroethyl*)*cyclohexanone* (**6k**), b.p. 84 °C (0.1 mmHg), m.p. 60–60.5 °C (light petroleum) (Found: C, 62.15; H, 9.05; N, 6.55. $C_{11}H_{29}NO_3$ requires C, 61.95; H, 9.0; N, 6.55%); *m/z* 213 (M^+); ν_{max}(Nujol) 1 725, 1 546, and 1 372 cm^{-1}; δ_H 1.03 (3 H, d, *J* 5.3 Hz), 1.10 (3 H, s), 1.13 (3 H, s), 1.37–2.49 (8 H, m), and 4.29 and 5.00 (2 H, ABq, *J* 10.5 Hz); δ_C 21.72(q), 22.21(q), 24.76(q), 28.22(t), 34.56(t), 36.19(d), 36.30(s), 51.90(t), 54.82(d), 83.86(t), and 211.00(s).

Method B. To a refluxing solution of the appropriate nitroalkane (**5**) and the enone (**4**) in absolute ethanol (50 ml per 0.1 mol nitroalkane) was added in one batch sodium ethoxide (0.12 equiv. based on the nitroalkane). The mixture was refluxed for 36 h, cooled, and neutralized with acetic acid. The solvent was removed under reduced pressure, the residual oil was dissolved in ether, and the solution was washed with water, dried ($MgSO_4$), and evaporated. The crude product was distilled. Conditions and yields are in Table 1.

Prepared by this method were: 4,4-dimethyl-5-nitropentan-2-one (**6a**), b.p. 50 °C (1.3 mmHg) [lit.,[9c] 114–116 °C (15 mmHg)]; *m/z* 159 (M^+); ν_{max}(film) 1 720, 1 546, and 1 360 cm^{-1}; δ_H 1.14 (6 H, s), 2.15 (3 H, s), 2.60 (2 H, s), and 4.57 (2 H, s); δ_C 25.89 (2 C, q), 31.31(q), 34.18(s), 50.44(t), 83.43(t), and 206.78(s); and 3,3-dimethyl-4-nitro-1-phenylbutan-1-one (**6f**), b.p. 112 °C (0.1 mmHg) [lit.,[9a] 155–158 °C (4 mmHg)]; *m/z* 221 (M^+); ν_{max}(film) 1 690, 1 543, and 1 354 cm^{-1}; δ_H 1.23 (6 H, s), 3.13 (2 H, s), 4.70 (2 H, s), 7.40–7.60 (3 H, m), and 7.88–7.99 (2 H, m); δ_C 26.11 (2 C, q), 34.51(s), 45.56(t), 83.70(t), 127.85 (2 C, d), 128.66 (2 C, d), 133.22(d), 137.60(s), and 198.33(s).

Method C. A solution of phenylnitromethane (**5d**) (0.036 mol), the appropriate enone (Table 1), and DBU (0.036 mol) in dry acetonitrile (25 ml) was stirred at 40 °C for 1 week. The product was poured into ice cold water (100 ml), and the mixture was acidified to pH 2 with 1M HCl and extracted with ether (4 × 25 ml). The ether extracts were washed with water (2 × 25 ml), dried ($MgSO_4$), and evaporated, and the product was distilled.

Prepared by this method were: 4,4-*dimethyl*-5-*nitro*-5-*phenylpentan*-2-*one* (**6d**), b.p. 69 °C (0.2 mmHg); n_D^{24} 1.5270; *m/z* 235 (M^+); ν_{max}(film) 1 716, 1 553, and 1 365 cm^{-1}; δ_H 1.13 (3 H, s), 1.22 (3 H, s), 2.08 (3 H, s), 2.31 and 2.64 (2 H, ABq, *J* 17.5 Hz), 6.06 (1 H, s), and 7.31–7.57 (5 H, m); δ_C 23.84(q), 24.05(q), 31.69(q), 38.14(s), 50.81(t), 96.81(d), 128.34 (2 C, d), 129.31 (2 C, d), 129.42(d), 131.80(s), and 206.83(s); *semicarbazone* of (**6d**), m.p. 185–186 °C (95% ethanol), *m/z* 292 (M^+) (Found: C, 57.3; H, 7.05; N, 18.8. $C_{14}H_{20}N_4O_3$ requires C, 57.5; H, 6.9; N, 19.15%); and trans-1-*benzoyl*-2,2-*dimethyl*-3-*phenylcyclopropane* (**7**) from the enone (**4b**), b.p. 138 °C (0.5 mmHg), m.p. 48 °C (subl.) (Found: C, 86.1; H, 7.2. $C_{18}H_{18}O$ requires C, 86.35; H, 7.25%); *m/z* 250 (M^+); ν_{max}(Nujol) 1 656, 1 598, 1 580, 1 500, 1 450, 1 249, 1 040, and 745 cm^{-1}; δ_H 1.12 (3 H, s), 1.27 (3 H, s), 3.03 and 3.24 (2 H, ABq, *J* 6.1 Hz), 7.12–7.34 (5 H, m), 7.40–7.59 (3 H, m), and 7.94–8.06 (2 H, m); δ_C 20.37(q), 22.15(q), 32.94(s), 37.32(d), 37.59(d), 126.44(d), 128.06 (2 C, d), 128.17 (2 C, d), 128.61 (2 C, d), 128.98 (2 C, d), 132.61 (d), 132.87(s), 139.06(s), and 197.79(s).

Preparations of 1,4-*Diketones* (**1**).—*From nitroketones* (**6**). Reactions were carried out successfully on the 0.01–0.36 mol scale. Yields are in Table 1.

Method D. The nitroketone (**6**) was dissolved in ethanol (100 ml per 0.15 mol), stirred at 25 °C, and aqueous sodium hydroxide (4M; 1.3 equiv.) was added in one batch. The solution was stirred for 3.5 h, aqueous hydrochloric acid (3M; 2.5 equiv.) was added, and stirring was continued for a further 2 h. The ethanol was removed under reduced pressure, the residue was extracted with dichloromethane, and the organic phase was washed with water and dried ($MgSO_4$). The solvent was removed, and the residue purified by distillation.

Prepared by this method were: 3,3-dimethylhexane-2,5-dione (**1b**), b.p. 100 °C (26 mmHg) [lit.,[34] 77–78 °C (10 mmHg)]; *m/z* 142 (M^+); ν_{max}(film) 1 707, 1 368, and 1 132 cm^{-1}; δ_H 1.19 (6 H, s), 2.10 (3 H, s), 2.18 (3 H, s), and 2.77 (2 H, s); δ_C 25.19 (2 C, q), 25.30(q), 30.39(q), 45.61(s), 53.41(t), 206.56(s), and 212.74(s); 4,4-dimethylheptane-2,5-dione (**1c**); b.p. 110 °C (19 mmHg) [lit.,[19b] 122 °C (27 mmHg)]; *m/z* 156 (M^+); ν_{max}(film) 1 710, 1 365, and 1 104 cm^{-1}; δ_H 1.03 (3 H, t, *J* 7.0 Hz), 1.18 (6 H, s), 2.09 (3 H, s), 2.57 (2 H, q, *J* 7 Hz), and 2.78 (2 H, s); δ_C 7.80(q), 25.19 (2 C, q), 30.34 (2 C, t and q), 45.34(s), 53.69(t), 206.73(s), and 215.18(s); 2,2-dimethyl-1-phenylpentane-1,4-dione (**1d**), b.p. 90 °C (0.75 mmHg) (lit.,[7a] no b.p. quoted); *m/z* 204 (M^+); ν_{max}(film) 1 716, 1 683, 1 365, and 1 185 cm^{-1}; δ_H 1.33 (6 H, s), 2.04 (3 H, s), 2.92 (2 H, s), 7.33–7.48 (3 H, m), and 7.55–7.66 (2 H, m); δ_C 26.49 (2 C, q), 30.17(q), 45.56(s), 54.61(t), 127.20 (2 C, d), 127.90 (2 C, d), 130.23(d), 139.66(s), 206.24(s), and 209.27(s); 3,3-*dimethyl*-1-*phenylpentane*-1,4-*dione* (**1g**), b.p. 82 °C (0.2 mmHg) (Found: C, 76.35; H, 7.5. $C_{13}H_{16}O_2$ requires C, 76.45; H, 7.9%); *m/z* 204 (M^+); ν_{max}(film); 1 711, 1 690, 1 344, and 1 212 cm^{-1}; δ_H 1.28 (6 H, s), 2.27 (3 H, s), 3.34 (2 H, s), 7.40–7.56 (3 H, m), and 7.88–7.99 (2 H, m); δ_C 25.51 (2 C, q), 25.59(q), 45.50(s), 49.19(t), 128.01 (2 C, d), 128.61 (2 C, d), 133.16(d), 137.06(s), 198.06(s), and 213.06(s).

Method E. To a stirred solution of the nitroketone (**6**) in

methanol (50 ml per 0.01 mol) at 0 °C was added 30% hydrogen peroxide [8.8M; 18 mol per mol (**6**)], followed by a solution of potassium carbonate [4M; 8 mol per mol (**6**)]. Stirring was continued at 25 °C for 16 h, the mixture was acidified with 3M hydrochloric acid, extracted with dichloromethane, and the organic extracts were dried ($MgSO_4$) and evaporated.

Prepared by this method were the diketones (**1b—d, g**), whose properties were identical with those of samples prepared by Method D, and 3-*methyl*-1,3-*diphenylpentane*-1,4-*dione* (**1j**), which was purified by column chromatography [SiO_2; eluant light petroleum–diethyl ether (1:1)] (Found: C, 81.25; H, 7.05. $C_{18}H_{18}O_2$ requires C, 81.15; H, 6.80%); *m/z* 266 (M^+); ν_{max}(film) 1 715, 1 691, 1 344, 1 214, and 1 200 cm^{-1}; δ_H 1.81 (3 H, s), 2.07 (3 H, s), 3.51 and 3.81 (2 H, ABq, *J* 17.5 Hz), 7.25–7.53 (8 H, m), and 7.85–7.96 (2 H, m); δ_C 21.78(q), 25.73(q), 47.56(t), 53.96(s), 126.22 (2 C, d), 127.14(d), 127.90 (2 C, d), 128.44 (2 C, d), 128.82 (2 C, d), 132.89(d), 137.44(s), 142.10(s), 197.62(s), and 209.00(s).

Method F. The method of Nokami and co-workers[19b] was used without modification. While the nitroketone (**6c**) was converted successfully into the diketone (**1c**) (Table 1), the nitro-ester (**6e**) gave only a complex mixture.

Method G. To a stirred solution of the nitroketone (**6**) in methanol (70 ml per 0.01 mol) was added, in one batch, methanolic KOH (1.6M; 1.6 equiv.). The mixture was stirred at 25 °C for 2 h, cooled to 0–5 °C, and a freshly prepared solution containing potassium permanganate (0.05M; 1.0 equiv.) and magnesium sulphate (0.06M; 0.9 equiv.) was added dropwise. Stirring was continued for a further 1 h, the solution was filtered, and the filtrate was extracted with 2–3 portions of diethyl ether. The combined organic phases were dried ($MgSO_4$), evaporated, and the residue was purified by column chromatography [SiO_2; eluant light petroleum–diethyl ether (1:1)].

Prepared by this method were: 2,2-dimethyl-4-oxopentanal (**1a**), b.p. 92 °C (24 mmHg) [lit.,[35] 98–99 °C (38 mmHg)]; *m/z* 128 (M^+); ν_{max}(film) 1 733, 1 723, 1 354, and 1 180 cm^{-1}; δ_H 1.13 (6 H, s), 2.14 (3 H, s), 2.76 (2 H, s), and 9.57 (1 H, s); δ_C 22.16 (2 C, q), 30.50(q), 43.88(s), 51.47(t), 204.73(d), and 206.40(s); 2,2-*dimethyl*-4-*oxo*-4-*phenylbutanal* (**1f**) (Found: C, 75.95; H, 7.25. $C_{12}H_{14}O_2$ requires C, 75.75; H, 7.4%); *m/z* 190 (M^+); ν_{max}(film) 1 732, 1 683, 1 343, and 1 212 cm^{-1}; δ_H 1.21 (6 H, s), 3.30 (2 H, s), 7.44–7.58 (3 H, m), 7.88–8.00 (2 H, m), and 9.70 (1 H, s); δ_C 22.42 (2 C, q), 43.88(s), 47.02(t), 128.07 (2 C, d), 128.61 (2C, d), 133.32(d), 136.79(s), 197.79(s), and 204.78(d); and 2-*methyl*-2-(4-*methyl*-2-*oxocyclohexyl*)*propanal* (**1k**), b.p. 52 °C (0.04 mmHg), n_D^{25} 1.4720 (Found: 72.5; H, 9.9. $C_{11}H_{18}O_2$ requires C, 72.5; H, 9.95%); *m/z* 182 (M^+); ν_{max}(film) 1 726, 1 710, and 1 110 cm^{-1}; δ_H 1.00 (3 H, s), 1.02 (3 H, d, *J* 6.5 Hz), 1.14 (3 H, s), 1.39–2.78 (8 H, m), and 9.63 (1 H, s); δ_C 18.53(q), 21.89(q), 22.21(q), 26.71(t), 33.91(t), 34.83(d), 45.29(s), 50.38(t), 56.83(d), 205.92(d), and 209.93(s).

Method H. Primary nitro-ketones were converted first into nitro-ketals by reaction with ethane-1,2-diol (2.5 mmol equiv.) in refluxing benzene in the presence of toluene-*p*-sulphonic acid; water was removed by a Dean–Stark apparatus. The products were purified by distillation.

The nitroketone (**6a**) gave 4,4-ethylenedioxy-2,2-dimethyl-1-nitropentane (79%), b.p. 105 °C (20 mmHg); *m/z* 203 (M^+); ν_{max}(film) 1 545, 1 369, 1 100, and 1 035 cm^{-1}; δ_H 1.15 (6 H, s), 1.31 (3 H, s), 1.87 (2 H, s), 3.94 (4 H, s), and 4.45 (2 H, s); δ_C (25.89(q), 26.82 (2 C, q), 34.56(s), 47.02(t), 63.82 (2 C, t), 85.34(t), and 109.92(s); and the nitroketone (**6f**) gave 1,1-ethylenedioxy-3,3-dimethyl-4-nitro-1-phenylbutane (80%), b.p. 102 °C (0.4 mmHg); ν_{max}(film) 1 545, 1 365, 1 190, and 1 030 cm^{-1}; δ_H 1.11 (6 H, s), 2.07 (2 H, s), 3.60–4.10 (4 H, m), 4.50 (2 H, s), and 7.27–7.50 (5 H, m); δ_C 26.82 (2 C, q), 35.05(s), 48.05(t), 63.65 (2 C, t), 85.22(t), 110.30(s), 125.58 (2 C, d), 128.07(d), 128.29 (2 C, d), and 143.18(s).

Conversion of the nitro-ketals into ketal-aldehydes was carried out by Method G above. Prepared by this method were 4,4-ethylenedioxy-2,2-dimethylpentanal (35%), b.p. 50 °C (4 mmHg); ν_{max}(film) 1 733, 1 368, 1 250, 1 100, and 1 035 cm^{-1}; δ_H 1.09 (6 H, s), 1.28 (3 H, s), 2.07 (2 H, s), 3.86 (4 H, s), and 9.45 (1 H, s); δ_C 22.92 (2 C, q), 25.46(q), 44.37(s), 47.35(t), 63.98 (2 C, t), 109.27(s), and 204.40(d); and 4,4-ethylenedioxy-2,2-dimethyl-4-phenylbutanal (32%), b.p. 70 °C (0.04 mmHg); ν_{max}(film) 1 734, 1 220, and 1 030 cm^{-1}; δ_H 1.10 (6 H, s), 2.21 (2 H, s), 3.55–4.00 (4 H, m), 7.26–7.51 (5 H, m), and 9.70 (1 H, s); δ_C 22.97 (2 C, q), 44.86(s), 48.49(t), 63.87 (2 C, t), 109.70(s), 125.47 (2 C, d), 128.01(d), 128.23 (2 C, d), 143.07(s), and 203.86(d).

The ketals were hydrolysed to keto-aldehydes by stirring in 60% aqueous acetic acid (3 ml per g) at 25 °C for 48 h. The mixture was extracted with dichloromethane, and the organic phase was washed with aqueous $NaHCO_3$, followed by water, and dried ($MgSO_4$). The solvent was removed, and the product was purified by distillation. Prepared by this method were compounds (**1a**) and (**1f**), whose properties were identical to those of samples prepared by Method G.

2-*Methyl*-2-*oxopropylcyclohexanone* (**1l**). This was prepared using Yoshikoshi's method[6a] (52%), b.p. 56 °C (3 mmHg) [lit.,[36] 69–71 °C (0.05 mmHg)]; *m/z* 168 (M^+); ν_{max}(film) 1 705, 1 366, 1 172, and 1 125 cm^{-1}; δ_H 1.17 (3 H, s), 1.46–2.10 (6 H, m), 2.13 (3 H, s), 2.34–2.45 (2 H, m), and 2.48 and 2.91 (2 H, ABq, *J* 17.5 Hz); δ_C 21.19(t), 24.17(q), 26.27(t), 30.99(q), 37.76(t), 38.41(t), 47.13(s), 51.68(t), 206.78(s), and 214.31(s).

2-(2-*Oxo*-1,1-*dimethylpropyl*)*cyclopentanone* (**1m**). A modified version of the method of Hennion and Quinn[21] was used. A mixture of 1-pyrrolidinocyclopentene (27.4 g, 0.20 mol), triethylamine (30.6 g, 0.30 mol), and a catalytic amount of copper(I) chloride and copper powder in dry dimethylformamide (100 ml) was cooled to −25 °C under N_2, and 3-bromo-3-methylbut-1-yne (35.2 g, 0.24 mol) was added dropwise with stirring during 6 h. Stirring was continued at this temperature for 1 h, the mixture was allowed to warm to room temperature overnight, and 4M HCl (40 ml) was added. The mixture was steam distilled, the distillate was extracted with dichloromethane, the organic phase was dried ($MgSO_4$), evaporated, and distilled to give 2-(1,1-dimethylprop-2-ynyl)cyclopentanone (17.4 g, 58%), b.p. 105 °C (5 mmHg) [lit.,[21] 64 °C (2.2 mmHg)]; *m/z* 150 (M^+); ν_{max}(film) 3 290, 2 110, 1 734, 1 633, and 1 145 cm^{-1}; δ_H 1.29 (3 H, s), 1.43 (3 H, s), 1.80–2.20 (7 H, m), and 2.07 (1 H, s); δ_C 20.03(t), 26.79(q), 27.25(t), 28.74(q), 32.90(s), 39.93(t), 56.70(d), 68.54(d), 89.67(s), and 217.84(s).

A solution of the acetylenic ketone (10.0 g, 0.067 mol) in dichloromethane (10 ml) was stirred vigorously at 25 °C for 5 h with a solution of mercury(II) sulphate (0.5 g, 0.002 mol) and a catalytic amount of sulphuric acid in water (10 ml). The mixture was filtered through Celite, the filtrate was diluted with dichloromethane (25 ml), the organic phase was washed with water, dried ($MgSO_4$), and evaporated. The crude product was purified by column chromatography [SiO_2; eluant light petroleum–diethyl ether (2:3)], and distilled to give the diketone (**1m**) (9.5 g, 85%), b.p. 75 °C (0.8 mmHg) [lit.,[21] 93–94 °C (2 mmHg)]; *m/z* 168 (M^+); ν_{max}(film) 1 733, 1 712, 1 358, and 1 150 cm^{-1}; δ_H 1.17 (3 H, s), 1.21 (3 H, s), 1.66–2.62 (7 H, m), and 2.18 (3 H, s); δ_C 20.55(q), 21.39(q), 24.26(t), 25.49(t), 25.82(q), 38.82(t), 49.03(s), 56.05(d), 212.32(s), and 218.69(s).

Preparation of the diketones (**1n**) *and* (**1o**). The approach of Welch and co-workers[22] was modified. A solution of a 2-substituted monoketone (0.010 mol) in dry toluene (50 ml) was added to a suspension of sodium hydride (80% dispersion in oil; 0.4 g, 0.012 mol) in dry toluene (40 ml). The mixture was

refluxed for 12 h under N_2, cooled to 60 °C, 50% 3-bromopropyne in toluene (0.011 mol) was added, and refluxing was continued for a further 12 h. The product was cooled to <0 °C and slowly treated with water. When no further gas was evolved, ether (100 ml) was added, the mixture was washed with water, and the organic phase was evaporated. A solution of the residual 4-ketoalkyne in dichloromethane (25 ml) was combined with a solution of mercury(II) sulphate (0.5 g) and a catalytic amount of sulphuric acid in water (25 ml), and stirred vigorously at 25 °C for 5 h. The mixture was filtered through Celite, the filtrate was diluted with dichloromethane (25 ml), and the organic phase was washed with water, dried ($MgSO_4$), and evaporated. The residue was purified by column chromatography [SiO_2; eluant light petroleum–diethyl ether (1:1)].

From 2,2,4-trimethylpentan-3-one was prepared 2,2,4,4-*tetramethylheptane*-3,6-*dione* (**1n**) (35%), n_D^{26} 1.4450 (Found: C, 71.4; H, 10.95. $C_{11}H_{20}O_2$ requires C, 71.7; H, 10.95%); *m/z* 184 (M^+); ν_{max}(film) 1 719, 1 681, 1 365, and 1 046 cm^{-1}; δ_H 1.27 (9 H, s), 1.33 (6 H, s), 2.09 (3 H, s), and 2.77 (2 H, s); δ_C 26.82 (2 C, q), 28.31 (3 C, q), 30.39(q), 45.94(s), 47.55(s), 56.43(t), 206,72(s), and 217.68(s); and from benzoylcyclohexane was prepared first 1-benzoyl-1-(prop-2-ynyl)cyclohexane; ν_{max}(film) 3 270, 2 145, 1 673, 1 450, and 1 210 cm^{-1}; δ_H 1.26–1.75 (10 H, m), 2.05 (1 H, t, *J* 2.6 Hz), 2.63 (2 H, d, *J* 2.6 Hz), and 7.30–7.65 (5 H, m); δ_C 22.64 (2 C, t), 25.62(t), 27.68(t), 33.42 (2 C, t), 51.84(s), 71.51(d), 80.50(s), 126.87 (2 C, d), 128.07 (2 C, d), 130.29(d), 139.93(s), and 208.13(s); and subsequently 2,2-*pentamethylene*-1-*phenylpentane*-1,4-*dione* (**1o**) (30%), n_D^{27} 1.4875 (Found: C, 78.9; H, 8.55. $C_{16}H_{20}O_2$ requires C, 78.65; H, 8.25%); *m/z* 244 (M^+); ν_{max}(film) 1 714, 1 673, 1 362, and 1 240 cm^{-1}; δ_H 1.10–1.90 (10 H, m), 2.10 (3 H, s), 3.10 (2 H, s), and 7.27–7.65 (5 H, m); δ_C 22.10 (2 C, t), 25.57(t), 30.55(q), 33.70 (2 C, t), 48.75(s), 49.79(t), 127.14 (2 C, d), 127.85 (2 C, d), 129.80(d), 140.53(s), 206.67(s), and 210.63(s).

Reaction of 1,4-*Diketones* (**1**) *with Liquid Ammonia.*—A general procedure is described. The appropriate diketone was stirred with liquid ammonia (*ca.* 50 ml per g) under dry N_2, the ammonia being allowed to evaporate slowly during 14–18 h. For the diketone (**1g**) three times as much ammonia was used. The last traces of ammonia were removed by flushing the apparatus with dry N_2, and the residue was purified by recrystallisation, or, if too unstable, was directly dehydrated. Physical, analytical, mass and IR spectral data are given in Table 2, and ^1H and ^{13}C NMR spectroscopic data are given in Table 3.

For the reaction of (**1a**), the by-products were tentatively assigned as aminopyrrolines (**12**) (major component), δ_H 0.89(s), 1.15(s), 2.00 (d, *J* 1.7 Hz), 2.28(br s), 2.2–2.5 (ABq), and 4.45 (q, *J* 1.7 Hz); δ_C 19.50(q), 21.18(q), 25.30(q), 42.26(s), 52.06(t), 92.64(d), and 173.25(s); and (**13**) (minor component), δ_H 0.91(s), 1.17(s), *ca.* 2.0, *ca.* 2.2–2.5, and 4.64(q); δ_C 19.34(q), 20.86(q), 24.81(q), 41.39(s), 52.77(t), 86.23(d), and 172.98(s).

Dehydration of Hydroxypyrrolines (**10**) *and* (**11**).—A general procedure is described; specific details are given in Table 4. The pure hydroxypyrroline (or mixed isomers) (1 g) was dissolved in the appropriate solvent (125 ml), Al_2O_3 (5 g; grade I) was added, and the mixture was heated under reflux using a Soxhlet apparatus filled with 4A molecular sieves; the course of the reaction was monitored by ^1H NMR. The mixture was filtered, and the solvent was removed under reduced pressure to yield the essentially pure dehydration product(s). Physical and spectroscopic data for the 3*H*-pyrroles are given in Table 5 and 6; other data follow.

3H-*Pyrrole* (**2b**). The mixture of isomers (**2b**), (**14b**), and (**15b**) was dissolved in diethyl ether (30 ml) and rapidly extracted into ice-cold 1M HCl (2 × 5 ml). The combined aqueous layers were extracted with diethyl ether (5 ml), cooled in ice and salt, and basified by rapid addition of ice-cold 0.4M Na_2CO_3 (15 ml). The mixture was extracted with diethyl ether (3 × 20 ml), and the combined extracts were washed with water (15 ml), dried ($MgSO_4$), and evaporated to give essentially pure 3*H*-pyrrole (**2b**). *Picrate*, m.p. 157 °C (EtOH) (Found: C, 47.65; H, 4.55; N, 16.25. $C_{14}H_{16}N_4O_7$ requires C, 47.75; H, 4.6; N, 15.9%); *m/z* 229 and 123; δ_H 1.43 (6 H, s), 2.28 (3 H, d, *J* 1.3 Hz), 2.66 (3 H, s), 6.16 (1 H, q, *J* 1.3 Hz), and 8.88 (2 H, s); δ_C 12.68(q), 14.03(q), 20.75 (2 C, q), 57.15(s), 126.28 (2 C, d), 128.39(s), 133.10(d), 140.09(s), 141.61 (2 C, s), 161.65(s), and 197.19(s). Exocyclic isomers (**14b**) δ_H 1.17 (6 H, s), 2.07 (3 H, s), 2.50 (2 H, s), 4.56 (1 H, s), and 5.11 (1 H, s); δ_C 20.26(q), 29.25 (2 C, q), 49.62(t), 54.55(s), 99.03(t), and 178.07(s); and (**15b**) δ_H 1.15 (6 H, s), 2.12 (3 H, s), 2.43 (2 H, t, *J* 1.6 Hz), 4.66 (1 H, t, *J* 1.6 Hz), and 5.12 (1 H, t, *J* 1.6 Hz); δ_C 15.11(q), 25.24 (2 C, q), 40.52(t), 53.36(s), 100.98(t), and 173.46(s).

Exocyclic isomer (**14c**) *from hydroxypyrroline* (**11c**). B.p. 72 °C (38 mmHg); *m/z* 137 (M^+); λ_{max}(EtOH) 238 nm (log ε 3.81); ν_{max}(film) 3 035, 1 660, and 1 610 cm^{-1}; δ_H 1.10 (6 H, s), 1.91 (3 H, d, *J* 6.5 Hz), 2.13 (3 H, s), 2.45 (2 H, s), and 4.91 (1 H, q, *J* 6.5 Hz); δ_C 12.69(q), 20.00(q), 28.99 (2 C, q), 39.88(s), 54.08(t), 108.52(d), 164.75(s), and 174.83(s); *salt of* (**14c**) *with fluoroboric acid*, m.p. 109 °C (EtOH) (Found: C, 48.2; H, 7.0; N, 6.2. $C_9H_{16}BF_4N$ requires C, 48.05; H, 7.15; N, 6.2%); ν_{max}(Nujol) 3 200, 1 647, 1 406, and 1 080 cm^{-1}; δ_H 1.27 (6 H, s), 1.92 (3 H, d, *J* 7.4 Hz), 2.70 (3 H, s), 3.07 (2 H, s), and 5.36 (1 H, q, *J* 7.4 Hz); δ_C 11.91(q), 18.03(q), 28.05 (2 C, q), 38.45(s), 51.40(t), 112.46(d), 149.73(s), and 192.20(s).

Salt of 3H-*pyrrole* (**2d**) *with fluoroboric acid.* M.p. 100 °C (EtOH) (Found: C, 57.2; H, 5.8; N, 5.15. $C_{13}H_{16}BF_4N$ requires C, 57.2; H, 5.9; N, 5.15%); ν_{max}(Nujol) 3 245, 3 190, 3 115, 1 677, and 1 085 cm^{-1}; δ_H 1.67 (6 H, s), 2.38 (3 H, d, *J* 1.8 Hz), 6.30 (1 H, q, *J* 1.8 Hz), 7.6–7.8 (3 H, m), and 8.0–8.2 (2 H, m); δ_C 12.23(q), 23.07 (2 C, q), 57.04(s), 124.59(d), 130.06 (2 C, d), 130.38 (2 C, d), 135.43(d), 136.62(s), 139.00(s), and 188.30(s); exocyclic isomer (**15d**): δ_H 1.42 (6 H, s), 2.64 (2 H, dd, *J* 1.8, 2.2 Hz), 4.84 (1 H, t, *J* 1.8 Hz), and 5.34 (1 H, t, *J* 2.2 Hz) [aryl absorption masked by that of isomer (**2d**)]; δ_C 26.92 (2 C, q), 46.70(t), 49.57(s); 103.36(t), 128.39 (2 C, d), 128.82 (2 C, d), 130.23(d), 133.86(s), 160.35(s), and 183.48(s).

1H-*Pyrrole* (**16**) *from hydroxypyrroline* (**10f**). Purified by column chromatography [SiO_2; eluant light petroleum–diethyl ether (1:1)]; m.p. 102 °C (hexane) (Found: C, 83.65; H, 7.65; N, 8.2. $C_{12}H_{13}N$ requires C, 84.15; H, 7.65; N, 8.2%); *m/z* 171 (M^+); ν_{max}(Nujol) 3 440, 1 605, 1 585, 1 510, 1 250, 760, and 690 cm^{-1}; δ_H 2.04 (3 H, s), 2.19 (3 H, s), 6.27 (1 H, d, *J* 2.7 Hz), 7.1–7.4 (5 H, m), and 7.9 (1 H, br); δ_C 10.89(q), 11.11(q), 107.86(d), 116.26(s), 123.19 (2 C, d), 125.14(s), 125.41(d), 128.77 (2 C, d), 129.37(s), and 133.05(s).

Exocyclic isomer (**14g**) *from hydroxypyrrolines* (**10g**) *and* (**11g**). δ_H 1.24 (6 H, s), 2.90 (2 H, s), 4.75 (1 H, s), and 5.35 (1 H, s) [aryl absorption masked by that of isomer (**2g**)]; δ_C 29.16 (2 C, q), 39.88(s), 49.90(t), 100.94(t), 127.64 (2 C, d), 128.13 (2 C, d), 130.79(d), 173.37(s), and 173.69(s).

Tetrahydro-indole (**17**) *from hydroxypyrroline* (**10k**). Purified by column chromatography [SiO_2; eluant light petroleum–diethyl ether (1:1]; oil, *m/z* 162 (M^+); ν_{max}(film) 3 335, 1 610, 1 540, and 1 310 cm^{-1}; δ_H 1.04 (3 H, d, *J* 6.1 Hz), 1.89 (3 H, s), 2.12 (3 H, s), 1.6–2.6 (7 H, m), and 7.08 (1 H, br); δ_C 8.71(q), 10.93(q), 21.23(t), 21.88(q), 30.00(d), 31.20(t), 32.29(t), 112.02(s), 116.57(s), 121.50(s), and 124.26(s).

Exocyclic isomers from hydroxypyrrolines (**10l**) *and* (**11l**). Only limited assignments could be made for the inseparable mixture of (**2l**), (**14l**), and (**15l**). For (**14l**): δ_H 1.04 (s, CH_3), 2.09 (s, CH_3), 2.32 (s, CH_2), and 5.55 (t, *J* 3.5 Hz, CH); and for (**15l**): δ_H 4.69 (t, *J* 1.6 Hz, CH), and 5.15 (t, *J* 2.2 Hz, CH).

Exocyclic isomer (**15m**) *from hydroxypyrroline* (**11m**). Again,

only limited assignments are possible for the inseparable mixture of (**2m**) and (**15m**): δ_H 0.89 (s, CH_3), 1.21 (s, CH_3), 2.05 (s, CH_3), and 5.37 (dd, *J* 5.3, 2.2 Hz, CH).

3H-*Pyrrole* (**2o**). This was purified from traces of the exocyclic isomer (**15o**) by column chromatography [Al_2O_3; eluant light petroleum–diethyl ether (9:1)]. For isomer (**15o**), δ_H 2.70 (t, ring CH_2), 4.87 (t, *J* 1.8 Hz, CH), and 5.33 (t, *J* 2.2 Hz, CH).

Reactions of Diketones (**1**) *with Ammonium Acetate.*—A mixture of the diketone (**1**) with dry ammonium acetate (1.5 equiv.) and glacial acetic acid (10 equiv.) was heated on an oil bath; details are given in Table 7. The mixture was cooled to 0 °C, treated dropwise with ice-cold aqueous NH_3 (33%; 25 equiv.), and extracted with CH_2Cl_2 (two portions). The combined extracts were dried ($MgSO_4$) and evaporated, and the residue was purified by column chromatography [Al_2O_3; eluant light petroleum–diethyl ether (1:1)], or by distillation. Physical and spectroscopic data are given in Tables 5 and 6.

2H-*Pyrrole* (**18b**). (Found: C, 78.0; H, 10.75; N, 11.15. $C_8H_{13}N$ requires C, 78.0; H, 10.65; N, 11.35%); *picrate* m.p. 162 °C (EtOH) (Found: C, 47.5; H, 4.75; N, 15.8. $C_{14}H_{16}N_4O_7$ requires C, 47.75; H, 4.6; N, 15.9%); *m/z* 229 and 123; δ_H 1.59 (6 H, s), 2.22 (3 H, d, *J* 1.3 Hz), 2.73 (3 H, s), 6.33 (1 H, q, *J* 1.3 Hz), and 8.91 (2 H, s); δ_C (CD_2Cl_2) 13.60(q), 17.23(q), 21.72 (2 C, q), 77.20(s), 122.59(d), 126.55 (2 C, d), 128.23(s), 142.20 (3 C, s), 162.25(s), and 180.72(s).

3H-*Pyrrole* (**2j**). (Found: C, 87.25; H, 7.1; N, 5.55. $C_{18}H_{17}N$ requires C, 87.4; H, 6.95; N, 5.65%).

2H-*Pyrrole* (**18l**). *Picrate* m.p. 182 °C (EtOH) (Found: C, 51.05; H, 4.6; N, 14.8. $C_{16}H_{18}N_4O_7$ requires C, 50.8; H, 4.8; N, 14.8%); *m/z* 229 and 149; δ_H 1.9–2.2 (8 H, m), 2.23 (3 H, d, *J* 1.4 Hz), 2.62 (3 H, s), 6.33 (1 H, q, *J* 1.4 Hz), and 8.88 (2 H, s); δ_C 13.76(q), 16.96(q), 26.33 (2 C, t), 34.78 (2 C, t), 86.62(s), 122.54(d), 126.33 (2 C, d), 128.11(s), 141.99 (3 C, s), 161.92(s), and 177.42(s).

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