Synthesis of 4-Acyl- and 4-Alkoxy-carbonylpyrazoles

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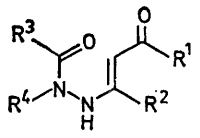
N'-Aroyl- or *N'*-acetyl, *N'*-phenyl- or *N'*-methyl-hydrazino-derivatives (1) of 1,3-dicarbonyl compounds can be converted by mild base treatment into 5-aryl- or 5-methyl-, 1-phenyl- or 1-methylpyrazoles carrying an acyl or alkoxycarbonyl group at C-4.

In the course of investigations [1] into the usefulness of *N'*-aroyl-*N'*-phenylhydrazine derivatives † (1; R^3 = Ar, R^4 = Ph) of 1,3-dicarbonyl compounds for Fischer indole synthesis, we reacted pentane-2,4-dione with *N*-benzoyl-*N*-phenylhydrazine in ethanol and obtained a mixture of two compounds, $C_{18}H_{18}N_2O_2$ and $C_{31}H_{26}N_4O$, the latter as a major product from reaction in concentrated solution; the former could be obtained cleanly by reaction in excess of the dione as solvent. That the former was the anticipated ene-hydrazine (1a) was evident from its molecular formula, the presence of an olefinic proton singlet at τ 4.90 in its n.m.r. spectrum, and i.r. carbonyl stretching at 1 615 and 1 680 cm^{-1}.

In the course of experiments designed to elucidate the structure of these two products, they were both subjected to treatment with hot ethanolic sodium hydroxide. Thereby the ene-hydrazine (1a) was found to undergo an extremely easy transformation into a product $C_{18}H_{16}N_2O$, having lost one molecule of water. The new material no longer showed a mass-spectral peak at *m/e* 105 ($PhCO^+$) which was the base peak in the spectrum of its precursor (1a) and had only one carbonyl stretching in its i.r. spectrum, at 1 650 cm^{-1}. This information, coupled with the presence of two methyl singlets at τ 7.30 and 7.90 in the n.m.r. spectrum, and the absence of absorption due to *N*-hydrogen or olefinic hydrogen, led to the adoption of the pyrazole formulation (2a) for the dehydration product.

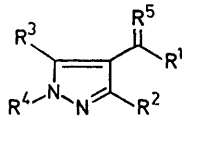
The structure of the other material, $C_{31}H_{26}N_4O$, was established by its alkaline conversion, involving hydrolytic cleavage of a benzoyl unit, into a compound of

† No stereochemistry is implied for acyclic derivatives.



(1)

	R^1	R^2	R^3	R^4
a	Me	Me	Ph	Ph
b	Ph	H	Ph	Ph
c	4-MeC_6H_4	H	Ph	Ph
d	Ph	H	4-Me	Ph
e	Ph	Me	Ph	Ph
f	$-[CH_2]_3-$		Ph	Ph
g	$-CH_2C(Me)_2CH_2-$		Ph	Ph
h	$-CH_2C(Me)_2CH_2-$		4-$MeOC_6H_4$	Ph
i	$-CH_2C(Me)_2CH_2-$		4-$O_2NC_6H_4$	Ph
j	Me	Me	4-$MeOC_6H_4$	Ph
k	Ph	Me	Me	Ph
l	$-CH_2C(Me)_2CH_2-$		Me	Ph
m	Me	Me	Ph	Me



(2)

	R^1	R^2	R^3	R^4	R^5
a	Me	Me	Ph	Ph	O
b	Me	Me	Ph	Ph	N-NHPh
c	Me	Me	Ph	Ph	N-N(COPh)Ph
d	Ph	H	Ph	Ph	O
e	4-MeC_6H_4	H	Ph	Ph	O
f	Ph	H	4-MeC_6H_4	Ph	O
g	Ph	Me	Ph	Ph	O
h	Ph	Ph	Ph	Ph	O
i	$-[CH_2]_3-$		Ph	Ph	O
j	$-CH_2C(Me)_2CH_2-$		Ph	Ph	O
k	OEt	Me	Ph	Ph	O
l	OH	Me	Ph	Ph	O
m	OH	CH_2CO_2H	Ph	Ph	O
n	OEt	Ph	Ph	Ph	O
o	$-CH_2C(Me)_2CH_2-$		4-$MeOC_6H_4$	Ph	O
p	$-CH_2C(Me)_2CH_2-$		4-$O_2NC_6H_4$	Ph	O
q	Me	Me	4-$MeOC_6H_4$	Ph	O
r	Me	Me	Me	Ph	O
s	Ph	Me	Me	Ph	O
t	Me	Me	Ph	Me	O
u	OEt	Me	Ph	Me	O

molecular formula $C_{24}H_{22}N_4$. That this product was simply the phenylhydrazone (2b) of the pyrazole ketone (2a) was easily shown by reaction of (2a) with phenylhydrazine; that the original material was the *N'*-benzoyl-*N'*-phenylhydrazone (2c) was shown by reaction of the pyrazole ketone (2a) with *N*-benzoyl-*N*-phenylhydrazine.

The conversion of (1a) into the pyrazole ketone (2a) is such an easy and efficient process that a search of the literature was made in anticipation of finding that it was an example of a well known route for the formation of pyrazoles. Surprisingly it emerged that only three previous examples were known.* In 1927 v. Auwers, a pioneer of pyrazole chemistry, reported [3] the conversion of 1,3-keto-aldehyde derivatives (1b—d) into pyrazoles (2d—f) by an exactly comparable, ethanolic alkali treatment. Accordingly we have now made a limited investigation of the re-discovered v. Auwers synthesis to assess its potential as a general approach to pyrazoles. It must be noted that the process is quite different in effect from the widely utilised [4] synthesis in which a 1,3-dicarbonyl compound reacts with hydrazine or a derivative but in which the two carbonyl carbon atoms become attached to the nitrogen atoms. In the process under consideration here, the *central* carbon of the 1,3-dicarbonyl compound becomes attached to the *carbonyl carbon* of the original *N*-acyl group. Presumably the process is initiated by base-catalysed proton abstraction from nitrogen.

RESULTS AND DISCUSSION

The 1,3-diketone *N'*-benzoyl-*N'*-phenylhydrazino-derivatives (1e—g) were prepared and shown to be transformed into the corresponding pyrazoles (2g, i, j), though somewhat less efficiently and with greater difficulty in the case of the bicyclic pyrazole ketones (2i and j). Condensation with dibenzoylmethane led, when sufficiently vigorous conditions had been found for reaction to occur, straight through to the pyrazole (2h).

Extrapolation of the v. Auwers approach to 1,3-keto-esters proved somewhat more complex, for the conditions necessary to effect initial condensation led to partial conversion into the pyrazoles and pure condensation products could not be obtained. Consequently the crude condensation product mixtures were immediately subjected to base treatment and in this way pyrazole esters and/or acids (2k—n) subsequently isolated. Heating in refluxing ethylene glycol also effected pyrazole formation.

Change of benzoyl- to *p*-methoxybenzoyl-phenylhydrazine derivatives made no difference to the reaction; thus (1h and j) were converted into the pyrazoles (2o and p), respectively; however the *p*-nitrobenzoyl analogue (1i) gave only a complex mixture on base treatment; the expected product (2p) could not be obtained.

With *N*-acetyl-*N*-phenylhydrazine, only the acyclic ketone derivatives could be made to give pyrazoles; (2r and s) were thus obtained, the latter most efficiently using dry basic conditions. With the ene-hydrazine (1l) no pyrazole formation could be achieved. With 1,3-keto-esters, initial desired condensation with *N*-acetyl-*N*-phenylhydrazine could not be effected, since loss of the acetyl group occurred first, to be followed by the subsequent orthodox [4] formation of pyrazolone.

N-Methyl-*N*-benzoylhydrazine reacted with pentane-2,4-dione to give (1m) which with base gave the pyrazole (2t). Reaction with ethyl acetoacetate, as with the phenyl analogues, proceeded directly through to a pyrazole ester, (2u), in moderate yield.

* Since this work was completed a further, though more involved, example [2] of the v. Auwers synthesis has been described.

EXPERIMENTAL

General.—See ref. 1.

4-(N'-Benzoyl-N'-phenylhydrazino)pent-3-en-2-one (1a).—*N*-Benzoyl-*N*-phenylhydrazine (5 g) was heated in refluxing pentane-2,4-dione (25 ml) for 2 h. Evaporation of solvent left an oil which crystallised, and was recrystallised from ethanol to give the *ene-hydrazine* (1a) (3.65 g), m.p. 154—156 °C; $\lambda_{max.}$ (EtOH) 229 and 280 nm (log ε 4.49 and 4.57); $\nu_{max.}$ (Nujol) 1 615s and 1 680s cm^{-1}; τ ($CDCl_3$) −2.2 (1 H, br s, NH), 4.9 (1 H, br s, C=CH), 7.9 and 8.1 (6 H, 2 × 3 H, s, 2 × CMe); *m/e* 292 (83%, M^+), 276 (20), 261 (31), 237 (62), 189 (83), 173 (91), 105 (100), and 77 (87) (Found: C, 53.7; H, 6.1; N, 9.5. $C_{18}H_{18}N_2O_2$ requires C, 73.3; H, 6.1; N, 9.9%).

4-Acetyl-3-methyl-1,5-diphenylpyrazole (2a).—The ene-hydrazine (1a) (2.10 g) was treated with aqueous sodium hydroxide (30%, 5 ml) in refluxing ethanol (15 ml) for 10 min. The solvent was evaporated and the product extracted with ether and crystallised from ether–light petroleum (60—80 °C) to give the *pyrazole* (2a) (2.0 g), m.p. 94—96 °C; $\lambda_{max.}$ (EtOH) 227 and 262 nm (log ε 4.06 and 4.21); $\nu_{max.}$ (Nujol) 1 650s cm^{-1}; τ ($CDCl_3$) 7.30 (3 H, s, Ar–Me) and 7.90 (3 H, s, COMe); *m/e* 276 (39%, M^+), 261 (100), 77 (26), and 43 (20) (Found: C, 78.2; H, 5.9; N, 10.1 $C_{18}H_{16}N_2O$ requires C, 78.6; H, 5.8; N, 10.0%).

4-Acetyl-3-methyl-1,4-diphenylpyrazole N-Benzoyl-N-phenylhydrazone (2c).—*N*-Benzoyl-*N*-phenylhydrazine hydrochloride (3 g) and pentane-2,4-dione (4 g) were heated together in refluxing ethanol (10 ml) for 1.5 h. The solvent was evaporated and the residue purified by chromatography over silica eluting with EtOAc–PhMe (1 : 1) to give the *hydrazone* (2c) (3.1 g), crystallised from ethanol, m.p. 164—165 °C; $\nu_{max.}$ (Nujol) 1 650s cm^{-1}; τ ($CDCl_3$) 7.57 (3 H, s, Ar–Me) and 8.16 (3 H, s, MeC=N); *m/e* 470 (32%, M^+), 365 (46), 276 (12), 261 (22), 105 (100), and 77 (36) (Found: C, 79.3; H, 5.7; N, 12.3. $C_{31}H_{26}N_4O$ requires C, 79.1; H, 5.5; and N, 11.9%).

4-Acetyl-3-methyl-1,5-diphenylpyrazole Phenylhydrazone (2b).—The hydrazone (2c) (2 g) was hydrolysed with aqueous sodium hydroxide (30%, 15 ml) at 95 °C for 0.5 h. After dilution with water and ether extraction the hydrazone (2b) (1.1 g) was obtained, m.p. 158—163 °C; $\nu_{max.}$ (Nujol) 3 240 cm^{-1}; τ ($CDCl_3$) 7.42 (3 H, s, Ar–Me) and 8.26 (3 H, s, MeC=N); *m/e* 366 (100, M^+), 274 (39), 261 (41), 194 (11), 165 (23), 132 (22), 91 (29), and 77 (22) (Found: C, 78.5; H, 6.3; N, 15.0. $C_{24}H_{22}N_4$ requires C, 78.6; H, 6.0; N, 15.3%).

3-(N'-Benzoyl-N'-phenylhydrazino)-1-phenylbut-2-en-1-one (1e).—*N*-Benzoyl-*N*-phenylhydrazine (4.1 g) and benzoylacetone (3.1 g) were heated together in ether (70 ml) in the

presence of glacial acetic acid (1 ml) and molecular sieves (type 4A) for 5 h. The sieves were filtered and solution evaporated to give an oil which crystallised from ether to give the *ene-hydrazine* (1e) (6.1 g), m.p. 142—144 °C; $\lambda_{max.}$ (EtOH) 277 and 235 nm (log ε 4.58 and 4.42); $\nu_{max.}$ (Nujol) 1 680s and 1 595s cm^{-1}; τ ($CDCl_3$) −2.69 (1 H, br s, NH), 4.16 (1 H, s, C=CH), and 7.90 (3 H, s, C=CMe); *m/e* 254 (44%, M^+), 170 (28), 105 (97), and 77 (100) (Found: C, 70.8; H, 5.5; N, 11.0. $C_{15}H_{14}N_2O_2$ requires C, 70.7; H, 5.8; N, 11.0%).

3-(N′-*Benzoyl*-N′-*phenylhydrazino*)*cyclohex*-2-*enone* (1f).—*N*-Benzoyl-*N*-phenylhydrazine (3 g) and cyclohexane-1,3-dione were heated in refluxing methanol (20 ml) in the presence of a few drops of acetic acid for 6 h. The product crystallised directly and could be filtered (3.3 g); more material (0.6 g) was obtained by evaporation of the filtrate and crystallisation from methanol, m.p. 169—170 °C; $\lambda_{max.}$ (EtOH) 227 and 285 nm (log ε 4.26 and 4.49); $\nu_{max.}$ (Nujol) 1 680s and 1 605s cm^{-1}; τ ($CDCl_3$) −2.70 (1 H, br s, NH) and 4.28 (1 H, s, C=CH); *m/e* 306 (8%, M^+), 105 (100), and 77 (50) (Found: C, 74.7; H, 5.7; N, 9.1. $C_{19}H_{18}N_2O_2$ requires C, 74.5; H, 5.8; N, 9.1%).

4-*Benzoyl*-3-*methyl*-1,5-*diphenylpyrazole* (2g).—This was prepared from (1e) as described for (2a), yield 93%, crystallised from ether–light petroleum (40—60 °C), m.p. 110—114 °C; $\lambda_{max.}$ (EtOH) 245 and 277 nm (log ε 4.32 and 4.15); $\nu_{max.}$ (Nujol) 1 635 cm^{-1}; τ ($CDCl_3$) 7.36 (3 H. s, Ar–Me); *m/e* 376 (4%, M^+), 251 (17), 105 (100), and 77 (84) (Found: C, 77.5; H, 5.6; N, 7.6. $C_{23}H_{20}N_2O_2$ requires C, 77.6; H, 5.6; N, 7.8%).

6,7-*Dihydro*-2,3-*diphenylindazol*-4(2H,5H)-*one* (2i).—This was prepared from (1f) as described for (2a), except reaction was for 1 h, yield 67%, crystallised from ether–light petroleum (40—60 °C), m.p. 150—152 °C; $\lambda_{max.}$ (EtOH) 231 and 277 nm (log ε 4.24 and 4.30); $\nu_{max.}$ (Nujol) 1 680s cm^{-1}; *m/e* 288 (39%, M^+), 287 (77), and 77 (97) (Found: C, 78.7; H, 5.0; N, 10.0. $C_{19}H_{16}N_2O$ requires C, 79.0; H, 5.5; N, 9.7%).

6,7-*Dihydro*-6,6-*dimethyl*-2,3-*diphenylindazol*-4(2H,5H)-*one* (2j).—This was prepared from (1g) [1] as described for (2a), except reaction was for 4 h, yield 48%, crystallised from ether–light petroleum (40—60 °C), m.p. 152—154 °C; $\lambda_{max.}$ (EtOH) 230 and 275 nm (log ε 4.2 and 4.22); $\nu_{max.}$ (Nujol) 1 670s cm^{-1}; τ ($CDCl_3$) 7.06 (2 H, s, CH_2), 7.47 (2 H, s, CH_2), and 8.73 (6 H, s, 2 × Me); *m/e* 316 (58%, M^+), 315 (100), and 77 (52) (Found: C, 79.8; H, 6.3; N, 9.1. $C_{21}H_{20}N_2O$ requires C, 79.7; H, 6.3; N, 8.8%).

4-*Benzoyl*-1,3,5-*triphenylpyrazole* (2h).—Dibenzoylmethane (0.53 g), *N*-benzoyl-*N*-phenylhydrazine (0.5 g), and toluene-*p*-sulphonic acid (100 mg) were heated together in refluxing toluene (40 ml) for 3 h in the presence of molecular sieves (4A) in a Soxhlet thimble. Evaporation of solvent and crystallisation from ether–light petroleum (40—60 °C) gave the *pyrazole* (2h) (0.92 g), m.p. 169—172 °C; $\lambda_{max.}$ (EtOH) 225 and 252 nm (log ε 4.59 and 4.66); $\nu_{max.}$ (Nujol) 1 650s cm^{-1}; *m/e* 400 (100%, M^+), 323 (86), 295 (25), 105 (88), and 77 (71) (Found: C, 83.8; H, 5.0; N, 6.3. $C_{28}H_{20}N_2O$ requires C, 84.0; H, 5.0; N, 7.0%).

Ethyl 3-*Methyl*-1.4-*diphenylpyrazole*-4-*carboxylate* (2k) *and* 3-*Methyl*-1,5-*diphenylpyrazole*-4-*carboxylic Acid* (2l).—*N*-Benzoyl-*N*-phenylhydrazine (4.0 g) and ethyl acetoacetate (2.5 g) were heated together in refluxing ethanol (20 ml) in the presence of a few drops of glacial acetic acid for 4 h. The solvent was evaporated and the residue partitioned between ether and aqueous sodium hydroxide solution. The ether layer was evaporated to give the *ester* (2k) (3.2 g), m.p. 114—116 °C; $\lambda_{max.}$ (EtOH) 230 and 262 nm (log ε 4.34 and 4.22); $\nu_{max.}$ (Nujol) 1 700s cm^{-1}; τ ($CDCl_3$) 5.75 (2 H, q, *J* 7 Hz, CH_2Me), 7.32 (3 H, s, Ar–Me), and 8.79 (3 H, t, *J* 7 Hz, CH_2Me); *m/e* 306 (99%, M^+), 288 (13), 277 (41), 261 (100), 233 (23), and 77 (93) (Found: C, 74.8; H, 6.0; N, 9.2. $C_{19}H_{18}N_2O_2$ requires C, 74.5; H, 5.8; N, 9.1%); the aqueous layer was acidified and extracted with ether to give the *acid* (2l), m.p. 202—205 °C; $\lambda_{max.}$ (EtOH) 230 and 260 nm (log ε 4.20 and 4.10); $\nu_{max.}$ (Nujol) 3 440m and 1 670s cm^{-1}; *m/e* 278 (100%, M^+), 277 (43), 261 (25), 233 (17), and 77 (36) (Found: C, 73.0; H, 5.3; N, 9.6. $C_{17}H_{14}N_2O_2$ requires C, 73.3; H, 5.2; N, 10.0%).

3-*Methoxycarbonyl*-1,4-*diphenylpyrazole*-4-*carboxylic Acid* (2m).—*N*-Benzoyl-*N*-phenylhydrazine (0.55 g), diethyl acetonedicarboxylate (0.52 g), and toluene-*p*-sulphonic acid were heated in refluxing toluene (30 ml) in the presence of molecular sieves (type 4A) in a Soxhlet thimble for 1.5 h. The solvent was evaporated and the residue heated with aqueous sodium hydroxide (30%, 10 ml) for 10 min. The mixture was diluted with water, washed with ether, acidified and extracted with ether to give an oil which was crystallised from ethanol to give the *diacid* (2m) (0.67 g), m.p. 235—240 °C; $\lambda_{max.}$ (EtOH) 225 and 255 nm (log ε 4.17 and 4.15); $\nu_{max.}$ (Nujol) 1 710s, and 1 670s cm^{-1}; τ ($CDCl_3$) 5.95 (2 H, s, CH_2); *m/e* 322 (4%, M^+), 304 (5), 277 (19), 234 (38), and 77 (100) (Found: C, 67.0; H, 4.1; N, 8.4. $C_{18}H_{14}N_2O_4$ requires C, 67.0; H, 4.3; N, 8.6%).

Ethyl 1,3,5-*Triphenylpyrazole*-4-*carboxylate* (2n).—*N*-Benzoyl-*N*-phenylhydrazine (1.0 g), ethyl benzoylacetate (0.91 g), and toluene-*p*-sulphonic acid (50 mg) were heated together in toluene (15 ml) for 3 h. The solvent was evaporated and the residue treated with aqueous sodium hydroxide (30%, 20 ml) at 95 °C for 0.5 h. The mixture was diluted with water and extracted with ether to give the *ester* (2n) (500 mg), crystallised from ethanol, m.p. 139—140 °C; $\lambda_{max.}$ (EtOH) 214 and 245 nm (log ε 4.48 and 4.39); $\nu_{max.}$ (Nujol) 1 710s cm^{-1}; τ ($CDCl_3$) 5.85 (2 H, q, *J* 7 Hz, CH_2Me) and 8.94 (3 H, t, *J* 7 Hz, CH_2Me); *m/e* 368 (100%, M^+), 339 (6), 323 (76), 295 (8), and 77 (42) (Found: C, 78.4; H, 5.5; N, 7.6. $C_{24}H_{20}N_2O_2$ requires C, 78.2; H,.5 4; N, 7.6%).

6,7-*Dihydro*-3-(4-*methoxyphenyl*)-6,6-*dimethyl*-2-*phenylindazol*-4(2H,5H)-*one* (2o).—This was prepared from (1h) [1] as described for (2a), except reaction was for 4 h, yield 48%, crystallised from ether–light petroleum (60—80 °C), m.p. 143—145 °C; $\lambda_{max.}$ (EtOH) 232 and 275 nm (log ε 4.28 and 4.24); $\nu_{max.}$ (Nujol) 1 670s cm^{-1}; τ ($CDCl_3$) 6.25 (3 H, s, MeO), 7.22 (2 H, s, CH_2), 7.60 (2 H, s, CH_2), and 8.86 (6 H, s, 2 × Me); *m/e* 346 (29%, M^+), 345 (37), 290 (10), and 77 (100) (Found: C, 76.4; H, 6.1; N, 8.4. $C_{22}H_{22}N_2O_2$ requires C, 76.3; H, 6.35; N, 8.1%).

4-(N′-4-*Methoxybenzoyl*-N′-*phenylhydrazino*)*pent*-3-*en*-2-*one* (1j).—*N*-4-Methoxybenzoyl-*N*-phenylhydrazine (1.7 g) was heated in refluxing pentane-2,4-dione (20 ml) for 2 h. The solvent was removed and the residue crystallised from ethanol to give the *ene-hydrazine* (1j) (0.17 g), m.p. 102—105 °C; $\lambda_{max.}$ 212 and 295 nm (log ε 4.56 and 4.69); $\nu_{max.}$ (Nujol) 1 680s cm^{-1}; τ ($CDCl_3$) −1.84 (1 H, br s, NH), 4.82 (1 H, s, C=CH), 6.30 (3 H, s, OMe), 7.94 (3 H, s, C=CMe), and 8.06 (3 H, s, COMe); *m/e* 324 (1% M^+), 135 (100), and 77 (14) (Found: C, 70.1; H, 6.3; N, 8.6. $C_{19}H_{20}N_2O_3$ requires C, 70.4; H, 6.2; N, 8.6%).

4-*Acetyl*-5-(4-*methoxyphenyl*)-3-*methyl*-1-*phenylpyrazole* (2q).—This was prepared from (1j) as described for (2a),

except reaction was at room temperature for 0.5 h, yield 79%, crystallised from ethanol, m.p. 126—130 °C, $\lambda_{max.}$ (EtOH) 227, and 287 nm (log ε 4.18 and 4.28); $\nu_{max.}$ (Nujol) 1 660s cm^{-1}; τ ($CDCl_3$) 6.12 (3 H, s, OMe), 7.70 (3 H, s, ArMe), and 7.74 (3 H, s, COMe); *m/e* 306 (76%, M^+), 291 (100), 275 (16), and 77 (40) (Found: C, 74.2; H, 5.9; N, 9.0. $C_{19}H_{18}N_2O_2$ requires C, 74.5; H, 5.8; N, 9.1%).

3-(N′-*Acetyl*-N′-*phenylhydrazino*)-1-*phenylbut*-2-*en*-1-*one* (1k).—*N*-Acetyl-*N*-phenylhydrazine (1.5 g), and benzoylacetone (1.6 g) were heated together in ether (15 ml) with a few drops of glacial acetic acid for 10 h in the presence of molecular sieves (type 4A). Evaporation gave an oil which slowly crystallised, and was recrystallised from ether to give the *ene-hydrazine* (1k) (1.9 g), m.p. 103—104 °C; $\lambda_{max.}$ 245 and 325 nm (log ε 4.18 and 4.33); $\nu_{max.}$ (Nujol) 1 695s, 1 680s, and 1 600s cm^{-1}; τ ($CDCl_3$) −2.85 (1 H, br s, NH), 3.99 (1 H, s, C=CH), 7.63 (3 H, s, Ar–Me), and 7.87 (3 H, s, COMe); *m/e* (21%, M^+), 251 (21), 105 (94), and 77 (100) (Found: C, 73.0; H, 6.1; N, 9.2. $C_{18}H_{18}N_2O_2$ requires C, 73.4; H, 6.1; N, 9.5%).

3-(N′-*Acetyl*-N′-*phenylhydrazino*)-5,5-*dimethylcyclohex*-2-*enone* (1l).—*N*-Acetyl-*N*-phenylhydrazine (1.0 g) and dimedone (0.93 g) were heated together in toluene (20 ml) at reflux for 7 h in the presence of molecular sieves (type 4A). The solution was cooled and the crystals of *ene-hydrazine* (1l) filtered off (1.6 g), m.p. 172—174 °C; $\lambda_{max.}$ 207 and 283 nm (log ε 4.05 and 4.41); $\nu_{max.}$ (Nujol) 1 690s cm^{-1}; τ ($CDCl_3$) 4.5 (1 H, s, C=CH), 7.8 (4 H, m, 2 × CH_2), and 8.9 (6 H, s, 2 × Me); *m/e* 272 (92%, M^+), 229 (87), and 214 (100) (Found: C, 70.7; H, 7.6; N, 9.9. $C_{16}H_{20}N_2O_2$ requires C, 70.5; H, 7.3; N, 10.2%).

4-*Acetyl*-3,5-*dimethyl*-1-*phenylpyrazole* (2r).—*N*-Acetyl-*N*-phenylhydrazine (1.4 g) was heated in refluxing pentane-2,4-dione (15 ml) for 1.5 h. The solvent was evaporated and the residue treated with aqueous potassium carbonate (30%, 15 ml) in methanol (15 ml) at 95 °C for 0.5 h. Dilution with water and extraction with ether gave the *pyrazole* (2r) (1.65 g), which was crystallised from ether–light petroleum (40—60 °C), m.p. 53—56 °C; $\lambda_{max.}$ (EtOH) 227 and 263 nm (log ε 4.18 and 4.44); $\nu_{max.}$ (Nujol) 1 670s cm^{-1}; τ ($CDCl_3$) 7.40, 7.43, and 7.45 (9 H, 3 × s, 3 × Me); *m/e* 214 (19%, M^+), 199 (100), and 77 (20) (Found: C, 72.9; H, 6.6; N, 13.0. $C_{13}H_{14}N_2O$ requires C, 72.8; H, 6.5; N, 13.0%).

4-*Benzoyl*-3,5-*dimethyl*-1-*phenylpyrazole* (2s).—The enehydrazine (1j) (1.5 g) was heated at 95 °C with sodium hydride (50% emulsion with mineral oil, 300 mg) in dry dimethylformamide (20 ml) for 5 min. The mixture was cooled, diluted with water, and extracted with ether to give an oil, which was crystallised from ether–light petroleum (40—60 °C) to give the *pyrazole* (2s) (1.1 g), m.p. 98—101 °C; $\lambda_{max.}$ 209, 250, and 275 nm (log ε 4.34, 4.17, and 4.09); $\nu_{max.}$ (Nujol) 1 650s cm^{-1}; τ ($CDCl_3$) 7.62 (6 H, s, 2 × Me); *m/e* 276 (43%, M^+), 275 (100), 261 (18), 199 (38), and 77 (40) (Found: C, 78.1; H, 5.9; N, 10.0. $C_{18}H_{16}N_2O$ requires C, 78.2; H, 5.7; N, 10.1%).

4-(N′-*Benzoyl*-N′-*methylhydrazino*)*pent*-3-*en*-2-*one* (1m).—*N*-Benzoyl-*N*-methylhydrazine (0.6 g) was heated in refluxing pentane-2,4-dione for 1 h. Evaporation of the solvent gave a crystalline residue which was recrystallised from ethanol to give the *ene-hydrazine* (1l) (0.6 g), m.p. 119—120 °C; $\lambda_{max.}$ (EtOH) 295 nm (log ε 4.20); $\nu_{max.}$ (Nujol) 1 640s and 1 610s cm^{-1}; τ ($CDCl_3$) −0.92 (1 H, br s, NH), 4.92 (1 H, s, C=CH), 6.59 (3 H, s, NMe), 7.90 (3 H, s, C=CMe), and 8.12 (3 H, s, COMe); *m/e* 232 (9%, M^+), 127 (19), 105 (100), and 77 (48) (Found: C, 66.9; H, 6.9; N, 12.0. $C_{13}H_{16}N_2O_2$ requires C, 67.2; H, 6.8; N, 12.0%).

4-*Acetyl*-1,3-*dimethyl*-5-*phenylpyrazole* (2t).—The enehydrazine (1m) (300 mg) was heated in refluxing ethanolic sodium ethoxide (5 ml, 5N) for 5 min. The solvent was evaporated and the residue partitioned between water and ether to give, on evaporation of the ether layer, crystalline material which was recrystallised from ether–light petroleum (40—60 °C) to give the *pyrazole* (2t) (230 mg), m.p. 72—73 °C; $\lambda_{max.}$ (EtOH) 229 and 257 nm (log ε 4.97 and 4.13); $\nu_{max.}$ (Nujol) 1 660s cm^{-1}; τ ($CDCl_3$) 6.31 (3 H, s, NMe), 7.36 (3 H, s, Ar–*Me*), and 7.98 (3 H, s, COMe); *m/e* 214 (43%, M^+), 200 (21), 199 (100), 128 (8), 77 (9), and 43 (7) (Found: C, 72.8; H, 6.5; N, 12.9. $C_{13}H_{14}N_2O$ requires C, 72.8; H, 6.5; N, 13.0%).

Ethyl 1,3-*Dimethyl*-5-*phenylpyrazole*-4-*carboxylate* (2u).—*N*-Benzoyl-*N*-methylhydrazine (230 mg) was reacted with ethyl acetoacetate (250 mg) in refluxing ethanol (7 ml) for 15 h. The solvent was evaporated and the residue dissolved in ether and shaken with aqueous potassium carbonate solution (30%), dried, and evaporated to give the pyrazole (2u) as an oil; $\lambda_{max.}$ (EtOH) 220 and 242 nm; $\nu_{max.}$ (Nujol) 1 700s cm^{-1}; τ ($CDCl_3$) 5.85 (2 H, q, *J* 7 Hz, CH_2Me), 6.32 (3 H, s, NMe), 7.43 (3 H, s, Ar–*Me*), and 8.88 (3 H, t, *J* 7 Hz, CH_2*Me*); *m/e* 244 (34%, M^+), 215 (13), 199 (100), 58 (16), and 43 (36) (Found: M^+ 244.121 1. $C_{14}H_{16}N_2O_2$ requires *M*, 244.121 2).

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