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THERMAL SIGMATROPIC REARRANGEMENTS OF ISOPYRAZOLES AND PYRAZOLENINES TO PYRAZOLES

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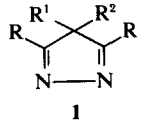
Abstract—Thermal rearrangement of 4-allyl-, 4-dimethylallyl-, and 4-propargyl-isopyrazoles proceed by [3,3]-sigmatropic processes to pyrazoles. The migration terminus is the C(3) Me group, if present, and the rearrangement is preceded by imine-enamine tautomerism. When enamine formation is not possible the rearrangment is diverted to nitrogen. Thermal rearrangements of 4-alkyl- and 4-benzyl-isopyrazoles also occur although at higher temperatures and evidence is presented suggesting [1,5]-sigmatropic processes are involved. Some pyrazolenine to pyrazole rearrangements involving migration of ester and phenyl groups are also reported.

The range of migrating groups participating in [1,j]-sigmatropic shifts is being steadily extended and now encompasses organometallic,[1] trimethylsilyl,[2] ester,[3] and cyano[4] moieties as well as the more common hydrogen, alkyl and aryl migrants. Our general interest in [1,j]- and [i,j]-shifts in heterocyclic compounds results from problems in the indole[5] and corrin[6] fields and led us to study some [1,5]- and [3,3]-shifts in isopyrazoles and pyrazolenines.

Isopyrazoles (**1**) of the type required for these studies were available by alkylation of β-diketones in an acetone-anhydrous potassium carbonate mixture either using an excess of an alkyl halide (>2 moles) giving **2**($R' = R^2$) or sequentially with one mole of two different alkyl halides (**2**; $R' \neq R^2$) Table 1. The *gem*-dialkylated β-diketones were then condensed with hydrazine[7] affording the corresponding isopyrazoles (**1**) Table 2.



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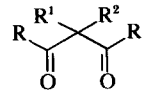

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[3,3]-Sigmatropic processes of the Claisen,[8] Claisen-Cope[9] and Cope[10] type have been reported for a number of heterocyclic systems. We extended our studies of indolenines[5] to the isopyrazoles (**3**)[11] as a further potentially tautomeric imine-enamine

Table 1. Preparation of β-diketones (**2**)

					Found (%)		Calc (%)	
R	R^1	R^2	M.p. or b.p.	Yield (%)	C	H	C	H
Me	H	Dma	71–77°/1 mm	64	—	—	—	—
Me	Me	Me	63–70°/14 mm	84	—	—	—	—
Me	Me	Et	186–195°/760 mm	71	—	—	—	—
Me	Me	Allyl	81–87°/10 mm	77	—	—	—	—
Me	Et	Allyl	95–100°/16 mm	57	71·1	9·5	71·4	9·6
Me	Me	Dma	114–117°/14 mm	51	72·4	9·9	72·5	10·0
Me	Et	Dma	75–80°/1 mm	43	73·2	10·0	73·45	10·25
Me	Me	Bz	125–132°/3 mm	56	—	—	—	—
Me	Allyl	Allyl	78–82°/0·3 mm	79	—	—	—	—
Me	Bz	Dma	50°/0·08 mm	66	79·1	8·4	79·0	8·6
Me	Bz	Bz	108–110°	64	—	—	—	—
Me	Et	Ppyl	58–62°/2·5 mm	59	72·4	8·6	72·25	8·5
Me	Ppyl	Ppyl	73–74°	70	—	—	—	—
Ph*	Me	Me	95–98°	17	—	—	—	—
Ph	Allyl	Allyl	60–63°	37	83·2	6·7	82·9	6·6

Bz = benzyl; Dma = 3,3-dimethylallyl; Ppyl = propargyl.
*not prepared by the standard synthesis.

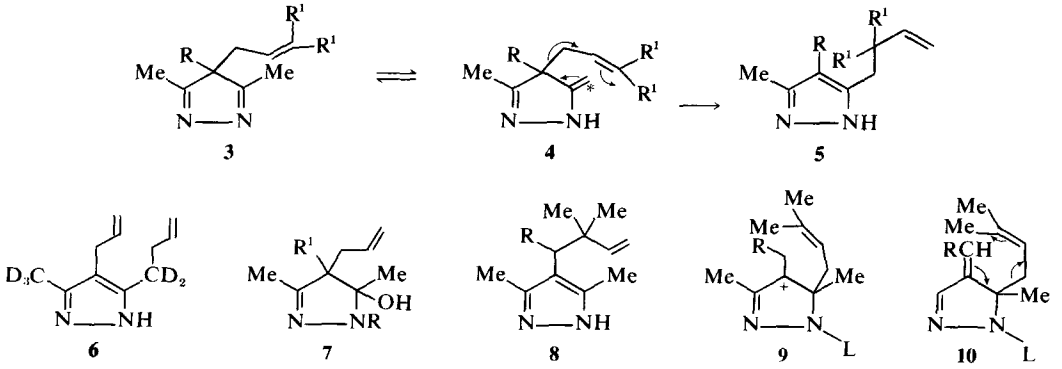
Table 2. Isopyrazoles (1)

R	R¹	R²	M.p. or b.p.	Yield (%)	Found (%) C	Found (%) H	Found (%) N	Calc (%) C	Calc (%) H	Calc (%) N
Me	Me	Et	95–96°/3 mm	85	69·1	10·0	19·9	69·5	10·2	20·25
Me	Et	Allyl	50–52°	70	72·75	9·6	16·7	73·1	9·8	17·05
Me	Me	Dma	67–69°	90	73·9	10·2	15·8	74·1	10·2	15·7
Me	Et	Dma	47–49°	54	74·7	10·3	14·7	74·95	10·5	14·55
Me	Et	Ppyl	119–120°	70	74·0	8·6	17·1	74·05	8·7	17·25
Me	Ppyl	Ppyl	145–147°	51	—	—	—	—	—	—
Ph	Me	Me	122–126°(Subl)	80	82·4	6·5	11·1	82·2	6·5	11·3
Ph	Allyl	Allyl	129–131·5°	65	83·4	6·7	9·7	83·3	7·0	9·7

Dma = 3,3-dimethylallyl; Bz = benzyl; Ppyl = propargyl.

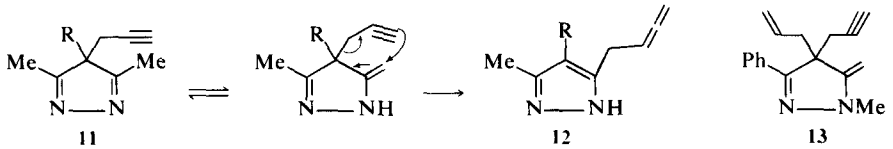
system (**3**⇄**4**) offering two possible migration termini (**3**;*) and (**4**;*) for a [3,3]-sigmatropic process. The isopyrazole (**3**; R = allyl, R′ = H) underwent quantitative (TLC) conversion to an isomeric product on heating in boiling xylene. The UV spectrum of this product exhibited a single maximum at 223 nm (ϵ_{max} 5,340), typical of a pyrazole, and an NH band in the IR at 3478 cm^{-1} indicated the absence of an N-substituent. The NMR spectrum showed only one Me group was present (τ 7·9) and a multiplet at τ 7·2–8·0 consistent with a butenyl side chain. The product was therefore formulated as **5**(R = allyl, R′ = H) and the enamine tautomer (**4**) was implicated in the rearrangement as observed for the corresponding indolenine rearrangements[5]. Although no enamine tautomer (**4**) could be detected in the NMR spectrum of **3**(R = allyl, R′ = H), deuteriation of the C(3) and C(5) Me groups occurred in D_2O-NaOD-pyridine at room temperature. Rearrangement of the deuteriated material and examination of the NMR spectrum of the product (**6**) showed the expected doublet in place of the multiplet corresponding to the saturated portion of the butenyl substituent. Analogous rearrangements in which the pyrazole enamine tautomer is generated *in situ*, via a carbinolamine (**7**), by condensation of an N-substituted hydrazine with a suitable β-diketone were reported[12] whilst our work was nearing completion. The rearrangements reported by these workers procede even at 0° showing, as in the indolenine case, that imine-enamine tautomerism is the rate determining step in the rearrangement (**3**→**5**). The isopyrazoles (**3**; R = Me and Et, R′ = H) were prepared and found to cleanly rearrange to the expected products (**5**; R = Me, R′ = H) and (**5**; R = Et, R′ = H) at 205° and 140° respectively. The corresponding dimethylallyl isopyrazoles (**3**; R = Me or Et R′ = Me) were prepared and studied to obtain evidence of the allyl inversion required by a [3,3]-sigmatropic process. Heating in boiling xylene induced a slow reaction (48hr) giving two major products in each case. One of these was the expected pyrazole (**5**; R = Me or Et, R′ = Me). The NMR spectrum of the other product showed, in each case, the presence of a terminal allyl group and enabled its site to be located on the C(4) substituent i.e. **8**(R = H or Me). Similar anomalous products were observed in some of the indolenine rearrangements[5] and they probably arise by a [1,2]-shift (**3**→**9**) catalysed by traces of Lewis acids (L) followed by deprotonation to **10**(R = H or Me) and [3,3]-sigmatropic rearrangement.

The propargyl isopyrazoles (**11**; R = propargyl or Et) were also prepared and studied. Thermal rearrangement of these derivatives in xylene gave the expected allenic pyrazoles (**12**; R = propargyl or Et) in high yield. An interesting observation on relative migratory aptitudes in these systems has been re-

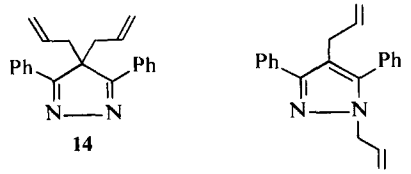


ported for the isopyrazole **13**. The relative rates of allyl to propargyl rearrangement were about 1·6 : 1.[12]

The C3 (or C5) Me group, rather than nitrogen, is thus the first choice migration terminus for 3,3-sigmatropic reactions in these allyl and propargyl isopyrazoles. An analogous preference was displayed by the related indolenines.[5] It was of interest therefore to study a case (e.g. **14**) where such a process was not possible. The isopyrazole (**14**) rearranged slowly on heating at 140° but more rapidly at higher temperatures to the N-allylpyrazole (**15**) in 93% yield thus establishing the feasibility of migration to nitrogen. However the concertedness of this latter process was not firmly established.



11 **12** **13**



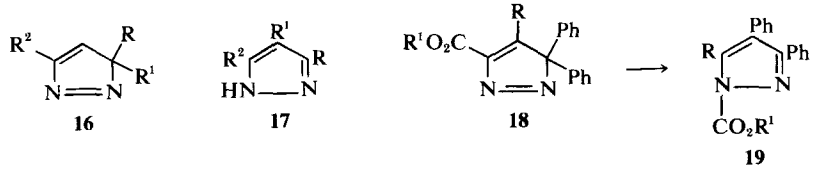
14 **15**

During an early investigation into the acid and base catalysed rearrangements of pyrazolenines, the thermal isomerisation (**16**; R = R′ = Ph, R^2 = Co_2Me) to **17**; (R = R′ = Ph; R^2 = Co_2Me) was observed on crystallisation from methanol.[13]

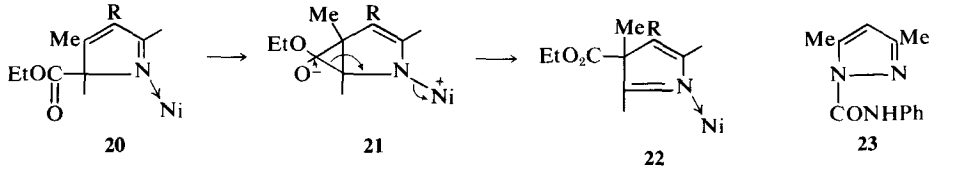
Subsequently numerous other examples of this type have come to light, usually involving migration of an aromatic substituent.[14–16] Although an earlier mechanistic rationale of these rearrangements invoked a dipolar species,[15] they are now best viewed as [1,5]-sigmatropic processes. This suggestion is born out by the cyclic progression of substitutents observed in the thermal rearrangement of **18** (R = Ph or Co_2R') to **19**(R = Ph or Co_2R')[14,15] which also indicates that an ester group has a greater migratory aptitude than a phenyl group in this system.[3b] However, as we have previously suggested,[6] unsaturated electronegative substituents, such as ester groups, have a possible alternative migration path via a cyclopropyl species open to them (e.g. **20** → **21** → **22** partial structures)[6]. Such an intermediate might intervene in the recently reported degenerate N → N rearrangement of the N-amido substituent of **23**.[7a] Although perhaps a more likely explanation in this case is that rearrangement occurs via establishment of a pyrazole-phenylisocyanate equilibrium.[18] N → N rearrangements in N-acyl pyrazoles are well documented.[17b]

Another intriguing problem present in pyrazolenines and other unsymmetrical systems is that, depending on the face of the molecule utilised, two possible directions for sigmatropic rearrangements exist (clockwise and anticlockwise). The re-si nomenclature[19] coupled with clockwise or anticlockwise designation enables such problems to be clearly identified and discussed.

However, for simplicity, in the present pyrazolenine cases in which the 3,3-substituents are identical we will consider migration towards nitrogen C(3) → N(2) as a clockwise migration and migration away from nitrogen C(3) → C(4) as an an-



16 **17** **18** **19**



20 **21** **22** **23**

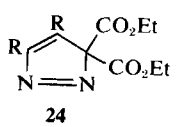
ticlockwise migration. Thus in the present context, a clockwise migration would produce a pyrazole directly whereas an anticlockwise migration would involve an isopyrazole intermediate.

Although the thermolysis of **18**(R = Co_2Me, R′ = Me) has been previously reported,[15] the isolated product was the decarboxylated pyrazole (**17**; R = R′ = Ph, R^2 = Co_2Me) and experimental data for the rearrangement was lacking. We therefore reinvestigated the thermal rearrangement of **18**(R = Co_2Me, R′ = Me) and found that heating at 100° for 18 hr in toluene gave a single major product (TLC), although monitoring the reaction by TLC indicated the formation of an intermediate. The product was isolated by chromatography on neutral alumina and proved identical with that obtained by van Alphen[13] from the acid catalysed rearrangement of **18**(R = Co_2Me, R′ = Me) and formulated as **19**(R = Co_2Me, R′ = Me). Thus an anticlockwise migration of the phenyl group occurs, followed by preferential migration of an ester group rather than a phenyl group. An unsuccessful attempt was made to synthesise the intermediate (**24**; R = Ph) by 1,3-dipolar addition of diazomalonic ester to tolan. However, diethyl diazomalonate did undergo a slow 1,3-dipolar cycloaddition to dimethyl acetylene dicarboxylate in boiling benzene. The product was not **24**(R = CO_2Me) but its rearrangement product **25**. The presence of a carbethoxy as opposed to a carbomethoxy group on nitrogen was shown by hydrolysis and decarboxylation to the pyrazole **26**. This was best achieved by stirring an ethereal solution of **25** with basic alumina (Spence H). Finally **26** was synthesised by 1,3-dipolar cycloaddition of ethyl diazoacetate to dimethyl acetylene dicarboxylate. The fact that scrambling of ester groups did not occur indicates direct migration of the C(3) ester group to nitrogen i.e. a clockwise migration. Similar direct migrations to nitrogen of ester and other unsaturated electronegative substituents (e.g. nitrile, acetyl) in pyrazolenines have recently been reported.[20] A related cyanide rearrangement (**27**→**28**) has also been observed.[21] These latter examples, and our own results, are capable of dual interpretation, either as uncomplicated [1,5]-sigmatropic shifts or as two step reactions proceeding via aziridine intermediates (e.g. **29**). The two step mechanism could well account for the different directions of migration of phenyl, on the one hand, and unsaturated electronegative groups, on the other.

A brief study has been made of the thermal rearrangements of some 4,4-dialkylisopyrazoles. Isopyrazoles are known to isomerise in the presence of concentrated acid[22] at 150–160°, and the pyrolysis of quaternary salts of isopyrazoles has also been studied[7] but the only data on neutral species is the observation that isopyrazoles with a C(4) benzyl group spontaneously rearrange, on vacuum distillation, to complex mixtures of pyrazoles by a postulated radical mechanism.[22]

Tetramethylisopyrazole (**1**; R = R^1 = R^2 = Me) was little changed on heating at 280°, but at 400° complete disappearance of starting material, with formation of one major product (**30**; R = R^1 = R^2 = Me; 75%), occurred in 0·5 hr. A small amount of cleavage product (**31**; R = R^1 = Me) was also identified spectroscopically. The high temperature required to effect rearrangement and the formation of **31** (R = R^1 = Me) suggested a radical process might be operative. Rearrangement of the deuteriomethyl derivative (**1**; R = CD_3, R^1 = R^2 = Me) gave tetramethyl pyrazole in which complete scrambling of the deuteriomethyl groups had occurred, suggesting a major contribution from concerted [1,5]-Me migrations.

Thermal rearrangement of **1** (R = R^1 = Me, R^2 = CH_2Ph) had been reported[22] to occur on distillation at 120–200° to give a complex mixture of stilbene and the pyrazoles **30** (R = Me, R^1 = Me or CH_2Ph, R^2 = CH_2Ph) and **31** (R = Me, R^1 = Me or CH_2Ph) in almost equal amounts by a radical mechanism. We find that dilute solution pyrolysis of **1** (R = R^1 = Me, R^2 = CH_2Ph) at 205° gives the 1-benzylpyrazole **30** (R = R^1 = Me, R^2 = CH_2Ph) as the major (75%) product together with cleavage product **31** (R = R^1 = Me, 18%). The dibenzyl derivative **1**(R = Me, R^1 = R^2 = CH_2Ph) rearranged at 205° to give a mixture of one major, and several minor products. Chromatographic separation gave pure samples of the major



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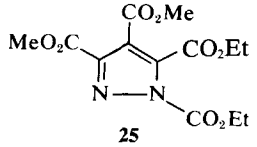

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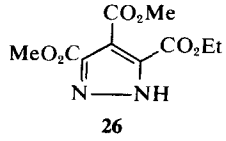

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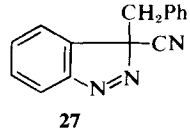

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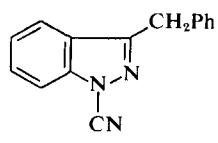

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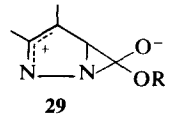

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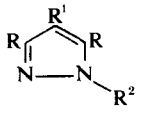
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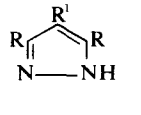
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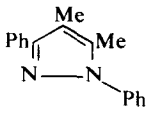
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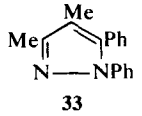
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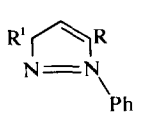
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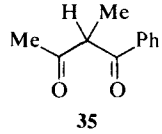
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product (**30**; R = Me, $R^1 = R^2 = CH_2Ph$; 76%) and one of the minor products (**31**; R = Me, $R^1 = CH_2Ph$; 12%).

Thermal rearrangement of **1**(R = Ph, $R^1 = R^2$ = Me) at 370–440° gave a complex mixture of products containing a small amount of cleavage product (**31**; R = Ph, R^1 = Me). Three substances isomeric with the starting material were also obtained (total yield 47%). Two of these products had similar NMR spectra with both showing aromatic and vinyl methyl signals in the ratio required for a diphenyl dimethyl pyrazole. The NMR indicated they were N-phenylpyrazoles for which three structures **30**(R = Me, $R^1 = R^2$ = Ph), **32** and **33** are possible. It was considered that the method of preparation effectively ruled out **30**(R = Me, $R^1 = R^2$ = Ph) which would require preferential migration of a Me group compared to a phenyl group. The major product (21%), compound A, was a solid m.p. 85–88° whilst the other isomer was an oil (compound B). The UV spectra of compound A (λ_{max} 266 nm) and compound B (λ_{max} 256 nm) were consistent with structure **32** for compound A and **33** for compound B. The hyposochromic effect has been well documented in pyrazole chemistry,[23] and the observed maxima closely parallel those of the model pyrazoles **34** R = Me, R^1 = Ph; λ_{max} 265 nm and **34** R = Ph, R^1 = Me; λ_{max} 254 nm).[24] The NMR spectra of the two products also supported these assignmments. Pyrazoles in which phenyl substituents (both N- and C- phenyl) are non-coplanar with the ring, by virtue of steric hindrance, exhibit essentially singlet phenyl resonances whilst those in which phenyl substituents are more nearly coplanar show multiplet phenyl resonances.[25] An examination of Dreiding models shows **33** to suffer much more steric hindrance than **32**. In particular in **32**, the C(3) phenyl group is essentially unhindered. The NMR spectrum of compound A (**32**) had an aromatic proton multiplet at τ 2·2–2·9 whilst compound B (**33**) exhibited aromatic proton resonances at τ 2·7–3·15 which consisted of a singlet at τ 3·0 superimposed on a multiplet centred at τ 2·93. Finally the mass spectra concurred with these assignments. Although many peaks were common to both spectra there were significant differences in intensities. Thus compound A (32) showed peaks at *m/e* 144 (M—PhC≡NH; 38% abundance) and *m/e* 130 (M—MeC≡NPh; 29%) and no peak at *m/e* 180 ($PhC\overset{+}{\equiv}NPh$) whereas compound B (**33**) had much less intense peaks at *m/e* 144 (20%) and *m/e* 130 (13%) and had a peak at *m/e* 180 (6%). Final confirmation of these assignments was provided by condensation of phenylhydrazine with the diketone (**35**) which it was anticipated would, by initial condensation at the more reactive methyl ketone group, lead to **33**. The product (79%) did indeed prove identical to compound B. Thus the "shunting" of substituents provides evidence for some [1,5]-sigmatropic processes in the thermal rearrangement of **1**(R = Ph, $R^1 = R^2$ = Me).

The third product from the pyrolysis mixture has not been identified. It did not prove identical with an unambiguously synthesised sample of **30**(R = Ph, $R^1 = R^2$ = Me). Moreover, although its mass spectrum indicated it was isomeric with starting material its NMR spectrum suggested a trimeric structure. Thus although the ratio of aromatic to non-aromatic protons were in the appropriate 5:3 ratio, NMR dilution studies (CCl_4) resolved two C-Me signals at τ 7·75 and 7·9 into doublets and an N-Me signal at τ 6·3 showed clear evidence of being composed of two overlapping singlets.

EXPERIMENTAL

M.ps were determined on a Kofler micro heating stage and are uncorrected. UV spectra were recorded for EtOH solns on a Unicam SP700 spectrometer, and IR spectra on a Unicam SP100 instrument. NMR spectra were measured for $CDCl_3$ solns either on a Perkin-Elmer RS10 60MHz instrument or on a Varian HA100 instrument, with TMS as internal reference. The abbreviations s, singlet d, doublet; t, triplet; q, quartet and m, multiplet are used throughout. Mass spectra data was obtained from an A.E.1. MS 902c instrument. Alumina (Spence type H) and silica gel M.F.C. (Hopkin and Williams) were used for column chromatography whereas TLC employed silica gel (May and Baker) and alumina G (Merck). Light petroleum was the fraction b.p. 60–80°.

3,3-*Disubstituted pentane*-2,4-*diones*. the anhydrous potassium carbonate-acetone method was used with excess alkyl halide for dialkylation.[26,27]

Isopyrazoles. These were prepared by condensation of the appropriate β-diketone with hydrazine hydrate in boiling EtOH in the usual way.[7,22]

[3,3]-*Sigmatropic reactions*

4,4-*Diallyl*-3,5-*dimethylisopyrazole*. A dilute soln of the isopyrazole[22] in Na-dried toluene showed no evidence (TLC; 1:1 benzene: EtOAc; alumina) of thermal reaction after being refluxed under dry N_2 for 4·5 hr. In Na-dried xylene, however, TLC monitoring indicated quantitative conversion of the isopyrazole (R_f 0·4) to a single product (R_f 0·8) *in* 5·5 hr. A *soln of* 3,5-dimethyl-4,4-diallylisopyrazole (3·00 g) in xylene (25 ml) was boiled, under N_2, for 6·5 hr, then evaporated under reduced pressure and the residue distilled on a short-path apparatus (50°/0·1 mm) giving 3-(*but*-3-*enyl*)-4-*allyl*-5-*methylpyrazole* (2·64 g, 88%) as a colourless oil, n_D^{23} 1·5081,

(Found: C, 75·0; H, 9·0; N, 16·1. $C_{11}H_{16}N_2$ requires: C, 75·0; H, 9·2; N, 15·9%); λ_{max} (EtOH) 223 nm; (ϵ_{max} 5,340), τ(CCl_4)–3·0 (s, 1H, –NH), 3·8–5·4 (m, 6H, vinyl H), 6·95 (d, 2H, CH_2–CH=CH_2), and 7·9 (s, 3H, Me), *Picrate*: yellow needles m.p. 92·5–93·5° (from benzene), (Found: C, 50·5; H, 4·4; N, 17·5. $C_{17}H_{19}N_5O_7$ requires: C, 50·4; H, 4·7; N, 17·3%).

4,4-*Diallyl*-3,5-*di* (*trideuteriomethyl*) *isopyrazole.* The isopyrazole (1·05 g) was dissolved in warm D_2O and NaOD soln (1 ml.; 30% in D_2O) added, followed by addition of sufficient dry pyridine to dissolve the ppt. Isolation and an NMR study of the product after 4 days at room temp, showed almost complete deuteriation of the C3 and C5 Me groups. Thermolysis of the deuterated sample in xylene for 6·5 hr and work-up in the usual way gave the 3-(but-3-enyl)-4-allyl-5-methylpyrazole: τ (CCl_4) –2·2 (s, 1H, –NH), 3·8–5·4 (m, 6H, vinyl H), 6·95 ((d, 2H, CH_2 –CH=CH_2), and 7·7 (d, *ca* 3H, –CD_2CH_2C(H):$C(H_2)$; overlapping a small multiplet).

4-*Allyl*-3,4,5-*trimethylisopyrazole.* The isopyrazole (2·7 g)[22] was boiled under reflux in tetralin (30 ml) for 11 hr when TLC ($CHCl_3$, Al_2O_3) showed formation of a major product (R_f 0·6). Chromatography on alumina eluting with light petroleum and then chloroform, gave, on evaporation the chloroform eluate, 5-(*but*-3-*enyl*) -3,4-*dimethylpyrazole* (2·55 g, 94%) as a colourless oil (Found: C, 71·6; H, 9·25; N, 18·3. $C_9H_{14}N_2$ requires: C, 71·95; H, 9·4; N, 18·65%), τ(CCl_4) 3·85–5·3 (m, 3H, vinyl H), 7·2–8·0 (m, 4H, methylene H), 7·9 and 8·15 (both s, 6H, 2 × Me).

4-*Allyl*-3,5-*dimethyl*-4-*ethylisopyrazole.* The isopyrazole (3 g) was boiled under reflux in dry xylene (25 ml) under dry N_2 for 19 hr. The solvent was evaporated under reduced pressure to leave a light brown oil (3·07 g). Short-path distillation (40°/0·05 mm) gave 3-(*but*-3-*enyl*)-4-*ethyl*-5-*methylpyrazole* (2·5 g, 83%) as a colourless oil, n_D^{25} 1·4997, (Found: C, 72·9; H, 9·6; N, 16·8. $C_{10}H_{16}N_2$ requires: C, 73·1; H, 9·8; N, 17·05%), τ(CCl_4) 3·95–4·55 (m, 1H, –CH=CH_2), 4·9–5·25 (m, 2H, –CH=CH_2). 7·25–7·9 (m, 6H, CH_2Me + CH_2–CH_2–CH=CH_2) 7·9 (s, 3H, Me), and 8·95 (t, 3H, CH_2Me).

4–(3,3-*Dimethylallyl*)-3,4,5-*trimethylisopyrazole* (with J. Caldwell). The isopyrazole (1·0 g) was boiled under reflux in toluene (10 ml) under N_2 for 48 hr. TLC monitoring then indicated complete disappearance of starting material with formation of two major and two minor products. Chromatography on silica gel eluting with light petroleum (to remove xylene), followed by EtOAc gave 3,5-*dimethyl*-4-(2,2-*dimethylbut*-3-*enyl*)*pyrazole* (400 mg, 40%) as a colourless oil (short path distillation 35°/0·02 mm.); n_D^{23} 1·4937. (Found: C, 74·35; H, 10·3; N, 15·05. $C_{11}H_{18}N_2$ requires: C, 74·1: H, 10·2; N, 15·7%); λ_{max} 229 nm (ϵ 6080); τ 3·7–5·2 (m, 3H, allyl protons), 7·8 (s, 6H, nuclear Me's), 8·1 (s, 2H, nuclear CH_2), and 8·3 (s, 6H, gem Me's).

The second fraction from the column was 3,4-*dimethyl*-2-(2,2-*dimethylbut*-3-*enyl*)*pyrazole* obtained as colourless prisms (petrol), (300 mg; 30%), m.p. 73–75°. (Found: C, 73·55; H, 10·23; N, 15·6%); λ_{max} 225 nm (ϵ 5660); τ 3·9–5·3 (m, 3H, allyl protons), 7·5 (s, 2H, nuclear protons), 7·85 and 8·1 (both s, 6H, 2 × Me), and 9·0 (s, 6H, gem Me's).

The final fraction from the column was shown to to 3,4,5-*trimethylpyrazole* (30 mg), colourless needles (water), m.p. 137–139°, by comparison with an authentic sample. τ 7·8 (s, 6H, 2 × Me) and 8·1 (s, 3H, Me).

4-(3, 3-*Dimethylallyl*)-3, 5-*dimethyl*-4-*ethylisopyrazole* (with J. Caldwell). The isopyrazole (2 g) in toluene was reacted, as above, for 2 days. TLC monitoring then indicated complete disappearance of starting material with formation of one major and one minor product as well as a trace of a third substance. Chromatography as above gave four products which, in order of elution, were: 3,5-*dimethyl*-4-(1,2,2-*trimethylbut*-3-*enyl*)*pyrazole* (880 mg; 44%), obtained as a colourless oil by short path distillation (34° 0·05 mm); (Found: C, 74·75; H, 10·4; N, 14·2. $C_{12}H_{20}N_2$ requires: C, 74·95; H, 10·5; N, 14·5%), λ_{max} 228 nm (ϵ 6860); τ(CCl_4) 3·8–5·3 (m, 3H, allyl protons), 7·8 (q, 1H, CH–CH_3), 7·95, 8·0 (both s, 6H, 2 × nuclear Me), 8·5 (s, 6H, gem Me's), 8·94 and 9·06 (both d, 3H, two rotamers of –CH–Me).

The second fraction contained 3,5-*dimethyl*-1-(3,3-*dimethylallyl*)-4-*ethylpyrazole* which was obtained as a colourless oil (200 mg; 10%) by short path distillation (38°/0·2 mm); (Found: C, 74·25; H, 10·9; N, 14·45%); τ 4·7 (t, 1H, CH=CMe_2), 5·45 (d, 2H, N–CH_2), 7·65 (q, 2H, CH_2Me), 7·85, 7·9 (both s, 6H, 2 × nuclear Me), 8·3 (br. s, 6H, gem Me's), and 8·95 (t, 3H, CH_2Me).

The third fraction afforded colourless prisms (from petrol) of 3-(2,2-*dimethylbut*-3-*enyl*)-4-*ethyl*-5-*methylpyrazole* (700 mg; 35%), m.p. 53–54°. (Found: C, 74·55; H, 10·7; N, 14·25%); λ_{max} 225 nm. (ϵ 5790); τ 4·85–5·25 (m, 3H, allyl protons), 7·5 (s, 2H, CH_2CMe_2), 7·65 (q, 2H, CH_2Me), 7·8 (s, 3H, Me), 8·97 (s superimposed on t, 9H, gem Me's + CH_2Me).

The final fraction contained 3,5-*dimethyl*-4-*ethylpyrazole* (100 mg), colourless prisms (aqueous EtOH) m.p. 51–52°, identified by comparison with an authentic sample. τ 7·65 (q, 2H, CH_2Me), 7·85 (s, 6H, 2 × Me), and 9·0 (t, 3H, CH_2Me).

3,5-*Dimethyl*-4-*ethyl*-4-(2-*propynyl*)*isopyrazole.* A soln of the isopyrazole (3·2 g) in dry xylene (200 ml) was boiled under reflux under N_2 for 22 hr. The solvent was removed under reduced pressure and the residue (3·9 g) purified by short-path distillation (48°/0·03 mm). 3-(*But*-1,2-*dienyl*)-4-*ethyl*-5-*methylpyrazole* (2·7 g, 84·5%) was obtained as a colourless oil, n_D^{25} 1·5289, (Found: C, 74·3; H, 8·9; N, 17·4. $C_{10}H_{14}N_2$ requires: C, 74·05; H, 8·7; N, 17·25%), τ(CCl_4) 4·7–5·15 (m, 1H, –CH=C=CH_2), 5·5 (m, 2H, CH=C=CH_2), 6·8 (m, 2H, CH_2–CH=C), 7·85 (q, 2H, CH_2Me), 7·9 (s, 3H, Me), and 9·0 (t, 3H, CH_2Me).

3,5-*Dimethyl*-4,4-*di*(2-*propynyl*)*isopyrazole.* The isopyrazole (0·7 g) was heated in dry xylene (300 ml) for 18½ hr and worked up in the usual way by short path distillation (54°/0·02 mm) to give 3-(*But*-1,2-*dienyl*)-4-*propargyl*-5-*methylpyrazole* (0·5 g, 71·5%) as a colourless oil. (Found: C, 76·4; H, 7·25; N, 16·0. $C_{11}H_{12}N_2$ requires: C, 76·71; H, 7·02; N, 16·27%), τ 4·5–5·0 (m, 1H, CH=C=CH_2), 5·3 (m, 2H, CH=C=CH_2), 6·5–6·85 (m, 4H, 2 × nuclear –CH_2–), 7·75 (s, 3H, Me) and 8·0 (t, 1H, –C≡C–H).

4,4-*Diallyl*-3,5-*diphenylisopyrazole.* In boiling xylene soln the reaction was slow, but in dilute soln in *o*-dichlorobenzene conversion of the isopyrazole (R_f 0·5) to a single product (R_f 0·9) was quantitative (TLC; 95:5 benzene:EtOAc; alumina) in 3 hr. A soln of 3,5-diphenyl-4,4-diallylisopyrazole (1·50 g) in anhyd tetralin (20 ml) was refluxed under dry N_2 for 1 hr when solvent was removed by chromatography on alumina (Spence H) with petrol. Benzene elution then gave the single product of thermolysis (R_f 0·6 by TLC: benzene; alumina), which, after molecular distillation, crystallised on standing and was characterised as 1,4-*diallyl*-3,5-*diphenyl*-*pyrazole* (1·40 g, 93%), colourless prisms m.p. 101–102°: (Found: C, 83·5; H, 6·9; N, 9·7. $C_{21}H_{20}N_2$ requires: C, 83·3; H, 7·0; N, 9·7%), λ_{max}

250 nm (ε 20,910), τ(CCl_4) 2·1–2·9 (m, 10H, aromatic H), 3·5–5·3 (m, 6H, vinyl H), 5·4 (d, 2H, N–CH_2–) and 6·75 (split d, 2H, nuclear –CH_2–).

Thermal rearrangement of 3,4,4,5-*tetramethylisopyrazole.* Freshly distilled 3,4,4,5-tetramethylisopyrazole was sealed in an ampoule under dry N_2 and heated in a Carius furnace as follows: (a) Furnace temp: 340°. Sample raised to 280° in 1 hr. Only slight change evidenced (NMR). (b) Sample kept at 280° for 13 hr. Again only slight change. (c) Furnace temp: 405°. Sample raised to 325° in 1 hr. Fractional distillation of the pyrolysate enabled partial separation into its two components. (d) Furnace temp: 540°. Sample raised to 400° in 1 hr. The product was virtually a single substance (NMR and TLC) and, on molecular distillation (25°/0·1 mm), yielded a colourless mobile oil (75%), n_D^{23} 1·4791, of high purity, identified as 1,3,4,5-tetramethylpyrazole: τ(CCl_4) 6·4 (s, 3H, N-Me), 7·95 (s, 6H, 2 × Me), and 8·15 (s, 3H, Me). τ(benzene) 7·2 (s, 3H, N-Me), 8·25, 8·7, and 8·85 (all s, 9H, 3 × Me). Methiodide: colourless needles m.p. 191–193°, (Found: C, 36·0; H, 5·5; N, 10·5. $C_8H_{15}N_2I$ requires: C, 36·1; H, 5·7; N, 10·5; I, 47·7), λ_{max} 221 nm (ε 17,940). Both NMR and TLC studies of the Crude pyrolysis mixture demonstrated the presence of 3,4,5-trimethylpyrazole.

Thermal rearrangement of deuterated 3,4,4,5-*tetramethylisopyrazole.* A soln of freshly distilled 3,4,4,5-tetramethylisopyrazole (3·0 g, 0·0242 mole) in D_2O (6 ml, 0·33 mole) containing a catalytic amount of NaOD was allowed to stand at room temp until NMR spectral monitoring indicated equilibrium to be established. (It was found necessary to add base continually to maintain the exchange of the 3- and 5-Me groups, and equilibrium was taken as established when addition of base caused no further change—2 weeks). The solvent was removed under reduced pressure, the residue dissolved in anhy ether, filtered, and evaporated to give the isopyrazole which was dried over P_2O_5 before pyrolysis. τ(D_2O) 7·85 (m, 9 units) and 8·85 (s, 28 units), *m/e* (%): 130 (3), 129 (30), 128 (59), 127 (57), 126 (33), 125 (12), 124 (2); for M^+.

After 30 min in a furnace at 520°, a sample of the above deuterated isopyrazole sealed under dry N_2 in an ampoule was raised to 370°. Work-up in the usual way gave deuterated 1,3,4,5-tetramethylpyrazole. τ(CCl_4) 6·55 (s, 9 units), 8·0 (s, 17·5 units), and 8·2 (s, 9·5 units). All signals showed subsidiary peaks and the 8·0τ singlet was itself slightly split. Addition of benzene resolved the spectrum into four singlets with their subsidiary signals. *m/e* (%): 132 (4), 131 (12), 130 (24), 129 (55), 128 (84), 127 (100), 126 (92), 125 (63), 124 (25), 123 (10); for M^+.

Thermal rearrangement of 3,4,5-*trimethyl*-4-*benzylisopyrazole.* A soln of 3,4,5-trimethyl-4-benzylisopyrazole (2·0 g, 0·01 mole)[22] in anhyd tetralin (25 ml) was refluxed under dry N_2 for 11 hr. Formation of a major product (R_f 0·7) was shown (TLC; 4:1 benzene:EtOAc; alumina) to be accompanied by a single trace product (R_f) 0·2). Reaction was complete in 5 hr and extended reflux caused no further change in the product distribution. After 11 hr the tetralin was removed by chromatography on alumina with light petroleum (1 l.), the major (R_f 0·7) product collected by subsequent chloroform elution, and the minor (R_f 0·2) material by stripping the column with MeOH. Distillation of the major product (1·5 g is isolated) on a short-path apparatus (36°/0·08 mm) yielded a colourless mobile oil, n_D^{23} 1·5450, characterised as 1-*benzyl*-3,4,5-*trimethylpyrazole* (1·2 g, 60%), (Found: C, 77·4; H, 7·9; N, 13·6. Calc. for $C_{13}H_{16}N_2$: C, 78·0; H, 8·1; N, 14·0%.), τ(CCl_4) 2·4–3·2 (m, 5H, aromatic H), 4·95 (s, 2H, PhCH_2N:), 7·9, 8·05, and 8·15 (all s, 3 × Me). The minor product (0·35 g isolated) was sublimed to give 3,4,5-trimethylpyrazole, m.p. 134–137°. A sample for analysis had m.p. 137–138° (lit.[20] m.p. 138°): (Found: C, 65·6; H, 9·2; N, 25·9. Calc. for $C_6H_{10}N_2$: C, 65·4; H, 9·2; N, 25·4%), λ_{max} 223 nm (ε 4,690), τ(CCl_4)–1·8 (s, 1H, :NH), 7·85 (s, 6H, 2 × Me), and 8·15 (s, 3H, Me).

Thermal rearrangement of 4,4-*dibenzyl*-3,5-*dimethylisopyrazole.* The isopyrazole (2·5 g, 0·91 mole)[22] in tetralin was boiled under reflux under N_2 and after 4 hr was virtually completely transformed into a major product (R_f 0·9) and two trace materials (R_f 0·5 and 0·3) as evidenced by TLC monitoring (chloroform; alumina). Reflux was continued for a further 3 hr, when the mixture was cooled, and freed from solvent by chromatography on alumina with light petroleum (500 ml) and then benzene (500 ml). Elution with chloroform completely removed the major (R_f 0·9) product, followed by the minor (R_f 0·3) product in a pure state. Molecular distillation of the major pyrolysis product gave a colourless viscous oil (1·9 g, 76%) identified as 1,4-*dibenzyl*-3,5-*dimethylpyrazole* (Found: C, 82·8; H, 7·3; N, 10·3. Calc. for $C_{19}H_{20}N_2$: C, 82·6; H, 7·3; N, 10·1%), λ_{max} 202, 228 (sh), 252 (sh), 259, 262, and 269 nm. (ε 24,880, 7,930, 648, 601, 554, and 394), τ(CCl_4) 2·6–3·2 (m, 10H, aromatic H), 4·9 (s, 2H, PhCH_2N:), 6·35 (s, 2H, PhCH_2–), 7·95 and 8·05 (both s, 6H 2 × Me). Picrate: yellow lathes m.p. 135–137° (lit.[22] m.p. 132–133°).

The minor (R_f 0·3) product (0·3 g, 12%) was identified as 4-benzyl-3,5-dimethylpyrazole by comparison with an authentic sample, whilst the R_f 0·5 material proved to be unreacted isopyrazole.

Thermal rearrangement of 4,4-dimethyl-3,5-diphenylisopyrazole. At temp between 370° and 440°, pyrolysis of the isopyrazole sealed in an ampoule under dry N_2 yielded a complex mixture. In one experiment, the sample of 3,5-diphenyl-4,4-dimethyl-isopyrazole (5·0 g, 0·02 mole) was raised to 440° in 40 min (furnace temp 540°). On cooling, the brown mobile pyrolysate deposited a crystalline material which was collected, after trituration of the mixture with light petroleum, as plates (0·15 g), m.p. 222–226°, raised to 226–228° on recrystallisation. This material was shown to be 3,5-diphenyl-4-methylpyrazole by comparison (UV and mixed m.p.) with an authentic sample (lit.[29] m.p. 222–223° or 229·5°), λ_{max} 252 nm (ε 23,400) m.m.p. 224–227°. TLC of the petrol soluble remainder indicated a complex product distribution. Column chromatography was conducted first on alumina and then rechromatography of the fractions on silica gel. In this way the second fraction from the alumina column gave two products, a yellow solid (1·05 g; compound A) and a yellow viscous oil (0·35 g; compound B) on rechromatographing on silica gel. Finally the third fraction from the alumina column gave a red viscous oil (0·95 g; compound C) on rechromatographing on silica gel.

Compound A. Crystallised as yellow star-shaped clusters, m.p. 85–88°, from light petroleum and was characterised as **29**. (Found: C, 82·4; H, 6·2; N, 11·5. $C_{17}H_{16}N_2$ requires: C, 82·2; H, 6·5; N, 11·3); λ_{max} 266 nm. (ε 18,460), τ(CCl_4) 2·2–2·9 (m, 10H, aromatic H), 7·75 (s, 3H, Me), and 7·85 (s, 3H, Me), *m/e* (%): 249 (16), 248 (M^+)? (72), 247 (38), 233 (6), 206 (7), 171 (7), 145 (6), 144 (38), 131 (5), 130 (29), 128 (6), 124 (10), 118 (19), 115 (9), 104 (13), 103 (13), 91 (8), 78 (13), 77 (100), 76 (7), 65 (6), 64 (6), 63 (6), 52 (6), 51 (39), and 50 (8).

Compound B. Distilled on a short-path apparatus (58°/0·1 mm) giving a yellow viscous oil which crystallised, on keeping, as yellow rhombs, characterised as **30**,

m.p. 47–49°, (Found: C, 81·9; H, 6·6; N, 11·0. $C_{17}H_{16}N_2$ requires: C, 82·2; H, 6·5; N, 11·3%), λ_{max} 256 nm (ε 15,220), τ(CCl_4) 2·7–3·2 (m, 10H, aromatic H), 7·8 (s, 3H, Me), and 8·1 (s, 3H, Me). *m/e* (%): 262 (16), 261 (7), 249 (26), 248 (M^+) (100), 247 (69), 233 (9), 232 (9), 206 (18), 204 (5), 180 (6), 178 (5), 171 (8), 148 (5), 144 (20), 130 (13), 128 (6), 124 (9), 123 (7), 120 (5), 118 (8), 116 (8), 115 (9), 108 (20), 107 (17), 106 (29), 105 (29), 104 (10), 103 (13), 102 (7), 91 (17), 90 (5), 89 (6), 79 (22), 78 (14), 77 (62), 76 (6), 65 (7), 64 (9), 63 (7), 52 (7), 51 (34), and 50 (11); m*: 172·0 and 246·0.

Compound (C) (19% isolated) was distilled on a short-path apparatus to give a yellow viscous oil; (Found: C, 82·4; H, 6·7; N, 11·3), λ_{max} 242 (sh) and 251 (ε 16,610 and 17,150), ν_{max} (CCl_4) 1028, 1075, 1368, 1385, 1441, 1449, 1508, 1605, 2876, 2935, 2945, 3035, and 3065 cm^{-1} (ε 44, 38, 91, 70, 93, 92, 116, 82, 20, 45, 46, 38, and 54), τ(CCl_4) 2·2–3·1 (m, 13·5 units), 6·4 (split s, 2 units), and 7·75, 7·8, 7·92 and 8·0 (all s, 4·5 units in all); *m/e* (%): 262 (6), 249 (22), 248 (M^+) (100), 247 (50), 233 (9), 232 (11), 231 (5), 206 (9), 165 (6), 149 (7), 144 (11), 130 (6), 124 (8), 118 (7), 115 (7), 104 (5), 103 (8), 89 (6), 77 (22), 58 (92), 56 (7), and 51 (9).

3,4-*Dimethyl*-1,5-*diphenylpyrazole.* A soln of phenylhydrazine (1·25 g, 0·0115 mole) in EtOH (12 ml) was added with shaking and ice-cooling to 1-phenyl-2-methylbutane-1,3-dione (2·029 g, 0·115 mole).[30] After 30 min at room temp colourless needles began to precipitate, but over the next 3 days these slowly disappeared. Concentration of the mixture left a yellow oil which, on molecular distillation (58°/0·1 mm), gave 1,5-*diphenyl*-3,4-*dimethylpyrazole* (2·25 g, 79%), identical with compound (B) isolated from pyrolysis of 4,4-dimethyl-3,5-diphenylisopyrazole. (Found: C, 81·8; H, 6·2; N, 11·2. $C_{17}H_{16}N_2$ requires: C, 82·2; H, 6·5; N, 11·3%), λ_{max} 256 nm (ε 15,490), no shift with acid; τ(CCl_4) 2·7–3·2 (m, 10H, aromatic H), 7·8 (s, 3H, Me), and 8·05 (s, 3H, Me).

1,4-*Dimethyl*-3,5-*diphenylpyrazole.* An aqueous soln of methyl hydrazine (0·32 g, 0·01 mole in 4 ml) was added to a warm ethanolic soln of 1,3-diphenyl-2-methylpropane-1,3-dione (2·38 g, 0·01 mole in 13 ml) and the mixture refluxed on a steam-bath for 17 hr. The solvent was then evaporated, the residue dissolved in ether, washed with 20% NaCl, dried $MgSO_4$, and evaporated to leave a yellow solid, m.p. 60–100°. This could not be crystallised to sharp m.p., so all residues were combined (2·5 g), refluxed in EtOH (60 ml) with methyl hydrazine (1·0 ml) for 4 days, and worked up as above to yield yellow lathes (1·95 g), m.p. 111–116° (sublimes) (from light petroleum). Recrystallisation from chloroform-light petroleum gave colourless needles (1·48 g, 59%), m.p. 112·5–116°, characterised as 1,4-dimethyl-3,5-diphenylpyrazole. (Found: C, 81·9; H, 6·2; N, 11·4. $C_{17}H_{16}N_2$ requires: C, 82·2; H, 6·5; N, 11·3%), λ_{max} 248 nm (ε 22,270), τ 2·1–2·9 (m, 10H, aromatic H), 6·2 (s, 3H, N-methyl), and 7·85 (s, 3H, Me).

Thermal rearrangements of pyrazolenines

4,5-*Dicarbomethoxy*-3,3-*diphenylpyrazolenine.* TLC monitoring of a thermolysis of the pyrazolenine (1·0 g)[13] in toluene (50 ml) at 100° indicated formation of an intermediate (R_f 0·8: benzene; alumina. R_f 0·6: benzene; neutral alumina) and its conversion to a thermally stable product (R_f 0·6: benzene; alumina. R_f 0·4: benzene; neutral alumina) in 18 hr. A pure sample of this stable product was isolated by chromatography on neutral alumina (Spence H soaked overnight in ethyl acetate and dried for 3 days at *ca* 110°) as colourless chunky crystals, m.p. 147–149°, and characterised as a diphenyl dicarbomethoxy pyrazole: (Found: C, 67·8; H, 5·0; N, 8·3. $C_{19}H_{16}N_2O_4$ requires: C, 67·9; H, 4·8; N, 8·3%), λ_{max} 228 (sh) and 314 nm (ε 5,640 and 13,360), τ(CCl_4) 2·0–3·0 (m, 10H, aromatic H), and 6·2 and 6·35 (2 × s, 6H, 2 × CO_2Me).

3,3-*Dicarbethoxy*-4,5-*dicarbomethoxypyrazolenine.* A soln of diazomalonic ester (5·71 g, 0·029 mole)[31] and dimethyl acetylene dicarboxylate (4·7 g, 0·29 mole) in anhyd ether (30 ml) showed no sign of reaction after 16 hr at room temp, nor after reflux for a further 19 hr. The solvent was evaporated and the residue refluxed in anhyd benzene. IR monitoring (on the 2150 cm^{-1} diazo peak) indicated reaction to be complete in 3 days, although a considerable amount of the diazo-compound remained, and no further change was observed after reflux for yet a further 3 days. The mixture was concentrated to a yellow oil (9·25 g) and chromatographed on an alumina with ether. Spontaneous evolution of CO_2 occurred and the column became warm, so MeOH was used to strip the support and the combined eluates evaporated to a viscous oily residue (6·3 g), which on trituration with light petroleum containing a little acetone gave yellow rhombs (0·7 g), m.p. 91–97°. Rechromatograph of the filtrate gave more *product* (2·45 g), m.p. 92–97°. The total solid (3·15 g) crystallised from chloroform-light petroleum as needles, m.p. 94–97°, and identified (below) as 5-*carbethoxy*-3,4-*dicarbomethoxypyrazole* (2·90 g, 40%). The analytical sample had m.p. 97–99°, (Found: C, 46·6; H, 4·4; N, 10·9. $C_{10}H_{12}N_2O_6$ requires: C, 46·9; H, 4·7; N, 10·9%), τ 5·6 (q, 2H, $-CO_2CH_2Me$), 6·05 and 6·1 (2 × s, 6H, $-CO_2CH_3$), and 8·65 (t, 3H, CO_2CH_2Me).

In a repeat attempt at the preparation of 3,3-dicarbethoxy-4,5-dicarbomethoxypyrazolenine conducted on the same scale as before, the yellow oily concentrate left after removal of solvent from the mixture crystallised on storage at −10°. This product was crystallised from MeOH as colourless chunky rhombs, m.p. *ca* room temp, and characterised as a dicarbethoxy dicarbomethoxy pyrazole (8·15 g, 45%): (Found C, 47·2; H, 4·7; N, 8·8. $C_{13}H_{16}N_2O_8$ requires: C, 47·6; H, 4·9; N, 8·5%), λ_{max} 238 nm. (ε 22,960), τ(CCl_4) 5·4–5·75 (m, 4H, 2 × CH_2–Me), 6·1 and 6·2 (2 × s, 6H, $-CO_2CH_3$), and 8·4–8·7 (m, 6H, 2 × CH_2Me). A sample of this pyrazole (1·0 g, 0·00305 mole) was stirred overnight over alumina (10 g) in ether (30 ml). Filtration, removal of the solvent, and crystallisation of the residue from light petroleum gave colourless needles, m.p. 97–100°, identical with 5-carbethoxy-3,4-dicarbomethoxypyrazole (0·4 g, 51%).

The tetrasubstituted pyrazole was, however, stable to chromatography on neutral alumina (prepared as previously described).

5-*Carbethoxy*-3,4-*dicarbomethoxypyrazole.* Prepared by reaction of ethyl diazoacetate (1·14 g, 0·01 mole) with dimethyl acetylene dicarboxylate (1·42 g, 0·01 mole) in dry ether (8·0 ml). After a few min the mixture became warm and refluxed. Formation of large colourless lathes was observed after 4 hr, and after 3 days the product (1·92 g, 75%), m.p. 96·5–99·5°, was collected. (Found: C, 46·8; H, 4·3; N, 10·9. $C_{10}H_{12}N_2O_6$ requires: C, 46·9; H, 4·7; N, 10·9), τ −2·3 (broad s, 1H, –NH), 5·65 (q, 2H, $-CO_2CH_2Me$), 6·1 and 6·15 (2 × s, 6H, $-CO_2CH_3$), and 8·7 (t, 3H, CH_2Me).

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