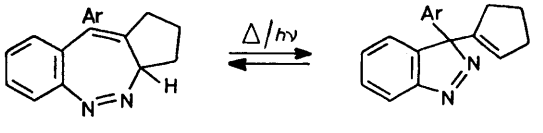
Thermal Ring Transformation of 3*H*-1,2-Diazepines to 4-Alkenyl-1*H*-pyrazoles *via* Ring Contraction and Sigmatropic Vinyl Group Migration [1]

By **Colin D. Anderson, John T. Sharp,*** and (in part) **R. Stewart Strathdee,** Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ

3*H*-1,2-Diazepines (9) undergo a thermally induced ring contraction to 4-alkenyl-1*H*-pyrazoles *via* a 1,3-azo-group migration and further rearrangements. The reaction can be rationalised as a multi-step process in which the initial azo-group migration gives an unstable 3-alkenyl-3-methyl-3*H*-pyrazole which is rapidly converted to a 4*H*-pyrazole by a [1,5] sigmatropic shift of the alkenyl group and finally to the product *via* a proton shift to nitrogen. The ring contraction step in which the azo-group migrates is thought to take place by a two-step mechanism involving either a diradical or a dipolar intermediate. Some evidence from product ratios disfavours the former.

RING transformations between five- and seven-membered heterocyclic systems have recently attracted much interest. We reported [2,3] that the 3*H*-1,2-benzodiazepines (1) undergo a thermally or photochemically induced

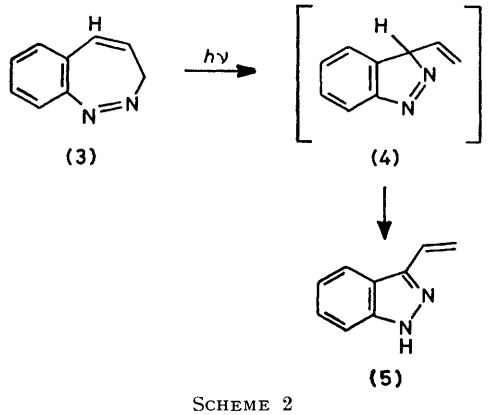


(1) (2)

SCHEME 1

reversible transformation into 3-alkenyl-3*H*-indazoles (2), Scheme 1, *via* a formal 1,3-migration of the azo-group. Tsuchiya has shown that for similar diazepines which have a hydrogen atom at the migration terminus, *e.g.* (3) (Scheme 2), the transformation is rendered irreversible by a hydrogen migration which aromatises the indazole.[4-6] Similarly, in the thermal ring expansion of the strained pyrazole (6) (Scheme 3), the reaction is driven irreversibly in the opposite direction towards the diazepine (8) by the [1,5] sigmatropic hydrogen shift which rearomatises the benzene ring.[7,8] Superficially similar ring transformations of triazepines have also been studied.[9]

With the recent availability [10,11] of the monocyclic 3*H*-1,2-diazepine system (9a/b) it was clearly of interest to examine the thermal and photochemical reactions of these compounds: the former are reported here.

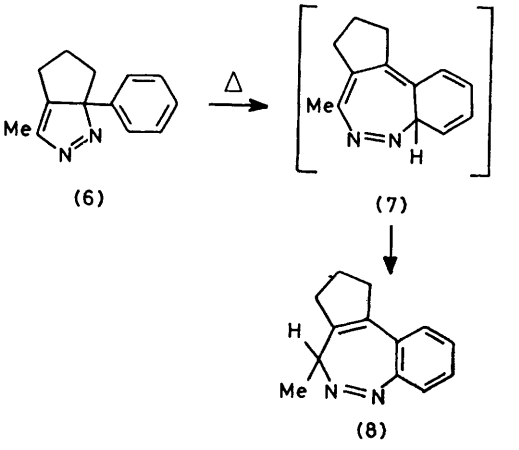


(3) (4) (5)

SCHEME 2

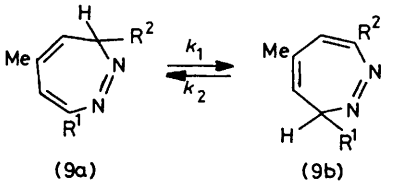
RESULTS AND DISCUSSION

The 3*H*-1,2-diazepines (9), like their benzo-annelated analogues, underwent thermal ring contraction; *e.g.* 3,5,7-trimethyl-3*H*-1,2-diazepine (10), when boiled under reflux in chlorobenzene, gave the 1*H*-pyrazole (13). The product was identified by its i.r. and n.m.r. spectra and its structure confirmed by hydrogenation to the known 3,5-dimethyl-4-propylpyrazole. It was clear from its ^{1}H n.m.r. spectrum that the pure isolated pyrazole (13) was the *E*-propenyl isomer. However the ^{1}H n.m.r. spectrum of the crude pyrazole product before recrystallisation showed that the *Z*-propenyl isomer was also present as a minor product [*E*/*Z* = 6].



(6) (7) (8)

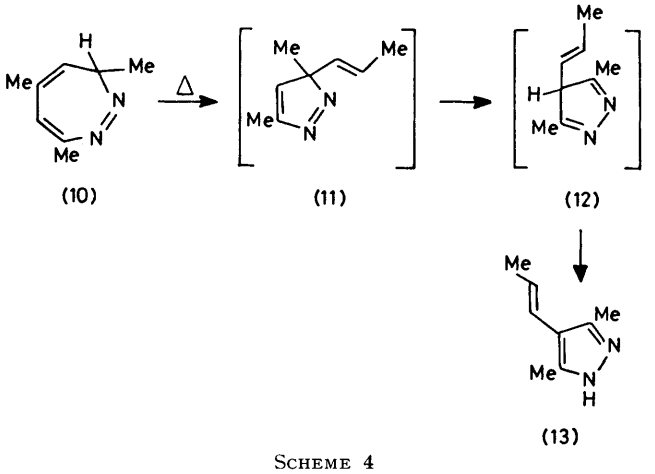
SCHEME 3



(9a) (9b)

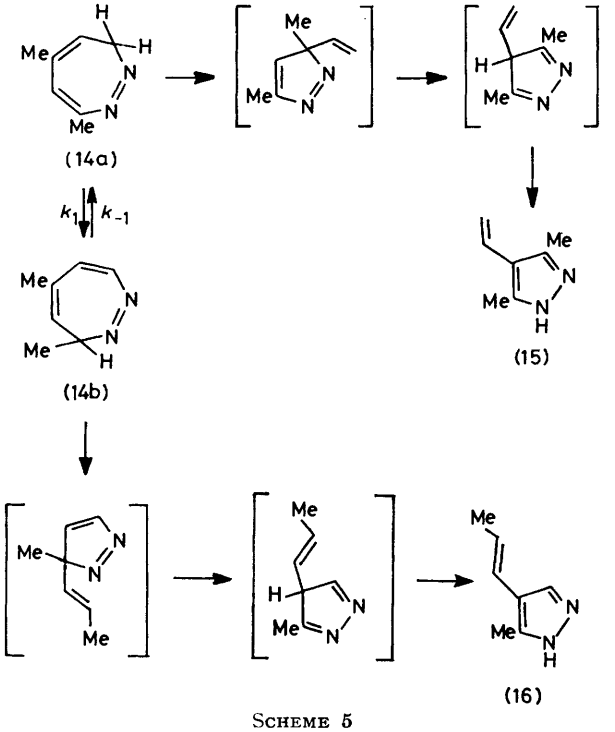
The course of the reaction can be rationalised as shown in Scheme 4. The first step is a ring-contraction which parallels those in Schemes 1 and 2 and gives the 3-methyl-3-propenyl-3*H*-pyrazole (11). This then rearranges to the 4*H*-pyrazole (12) *via* a [1,5] sigmatropic shift of the propenyl group and (12) is finally converted

to the aromatic 1*H*-pyrazole (13) by a proton shift to nitrogen. Monitoring of the reaction by h.p.l.c. produced no evidence for either of the pyrazole intermediates but there is ample precedent in pyrazole chemistry to



SCHEME 4

support the suggested scheme. The conversion of the 3*H*- to the 4*H*-pyrazole is an example of the van Alphen–Huttel rearrangement,[12,13] but this is the first case involving the migration of an alkenyl group. That it is the propenyl group in (11) which migrates rather than the methyl group is in accord with the usual high mobility of unsaturated groups in sigmatropic shifts.[14] This reaction provided one of the first demonstrations of the relative rapidity of alkenyl group migrations. Other reports have since confirmed that such shifts are fast and it has been suggested [15] that this is due to the

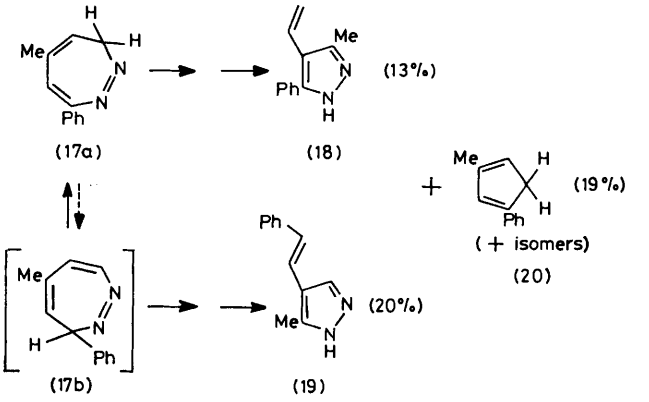


SCHEME 5

lowering of the transition state energy by a secondary π-orbital interaction similar to that proposed earlier to account for the rapid sigmatropic migrations of aryl groups. The final step in Scheme 4 would be expected to be very fast as 4-hydro-4*H*-pyrazoles are normally isolable but undergo rapid isomerisation to the aromatic 1*H*-isomers.

The pyrolysis of the diazepines (9) in which $R^1 \neq R^2$ is made more complicated than the above because of the rapid interconvertibility of the two isomers (9a) and (9b) by [1,5] sigmatropic hydrogen shifts. These hydrogen migrations are very much faster (*ca.* 10^{10}) than those in analogous cycloheptatrienes,[11] *e.g.* for (9a/b; R^1 = Me, R^2 = H) $k_1 = 0.56 \times 10^{-4}$ s^{-1} and $k_{-1} = 3.3 \times 10^{-4}$ s^{-1} at 0 °C; thus at room temperature and above, the isomers exist as an inseparable equilibrium mixture. The pyrolysis can therefore proceed *via* cleavage of the 2,3-bond in either (9a) or (9b) or both.

For the dimethyldiazepines (14a and b) (Scheme 5) which exist in a *ca.* 85 : 15 ratio at 0 °C, the major product



SCHEME 6

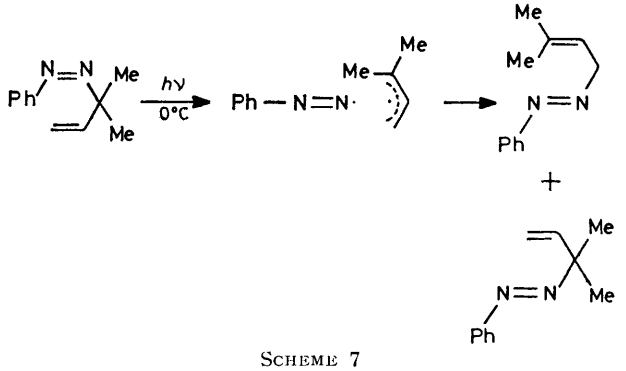
(15) was derived from (14a) and the minor product (16) from (14b). The product ratio was 92 : 8. The former was isolated pure by recrystallisation and its structure confirmed by hydrogenation to the known 4-ethyl-3,5-dimethyl-1*H*-pyrazole. The minor product (16) was an oil which could not be separated from (15) by preparative chromatography: it was detected and the product ratio was determined by both h.p.l.c. and from the ^{13}C n.m.r. spectrum of the product mixture. The crude mixture of pyrazoles obtained from the pyrolysis was then hydrogenated and the product shown by h.p.l.c. to give two peaks in the ratio 92 : 8, with retention volumes identical with those of 4-ethyl-3,5-dimethyl-1*H*-pyrazole and 3-methyl-4-propyl-1*H*-pyrazole respectively. The ^{13}C n.m.r. spectrum of this hydrogenated mixture also clearly showed minor peaks with chemical shifts identical with those of an authentic sample of 3-methyl-4-propyl-1*H*-pyrazole.

The 5-methyl-7-phenyl-3*H*-1,2-diazepine (17) exists entirely at room temperature as the (17a) isomer, due to its preferential stabilisation over (17b) by the conjugation of the phenyl group. However, pyrolysis gave the products (18) and (19) (Scheme 6) from both the

diazepine isomers, with the major reaction pathway occurring *via* the decomposition of (17b), the normally undetectable isomer. In this case the alkenylpyrazoles were separated by preparative t.l.c. and their structures confirmed by comparison of the hydrogenated pyrazoles with authentic samples prepared by conventional routes.

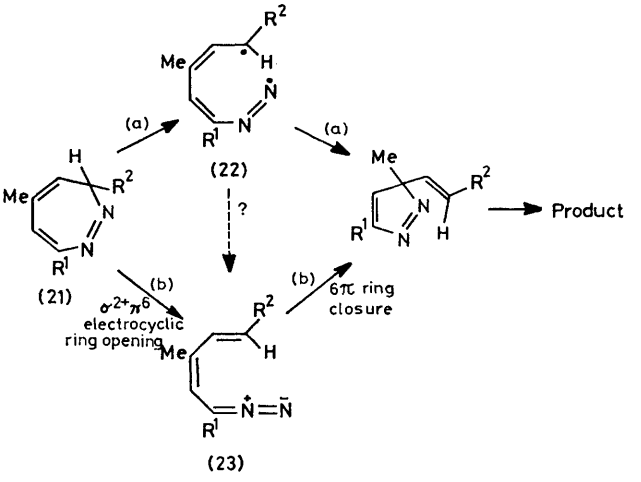
In all cases the pyrolysis reactions also produced products with high t.l.c. R_F values compared to the pyrazoles. These are presumed to be hydrocarbons formed *via* nitrogen-extrusion reactions. In the pyrolyses of (10) and (14) these compounds were not isolated because of the difficulty of separating them from the reaction solvent which was of similar volatility. A hydrocarbon product was, however, isolated from the pyrolysis of the higher molecular weight diazepine (17). This product (*m/e* 156) is considered to be a mixture of the methylphenylcyclopentadiene isomers (20) since its hydrogenation gave only 1-methyl-3-phenylcyclopentane.

Although the formation of the 1*H*-pyrazoles can be adequately rationalised by the multi-step pathways



SCHEME 7

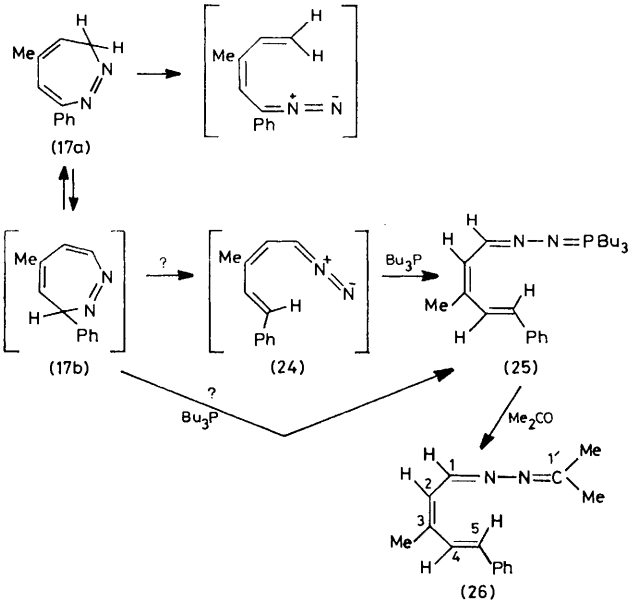
shown in Schemes 4—6, the mechanism of the first step, the ring contraction, is still obscure. This step is superficially similar to the analogous ring contractions of benzo- and thieno-diazepines [2-6] and triazepines,[9] and related also to the reaction [16] shown in Scheme 7 in that it involves the formal 1,3-migration of an azo-group. It has been suggested that the ring contractions of 1,2-benzodiazepines and 1,2-thienodiazepines may be two-step processes involving either dipolar or diradical intermediates, but there is no definitive evidence to show which mechanism is operating. However there is good (CIDNP) evidence for a stepwise radical pathway for the reaction shown in Scheme 7.[16] If the diazepine ring contraction reported here is similarly a two-step process then it can be represented as shown in Scheme 8. We attempted to determine whether the diazoalkene (23) was involved by carrying out a trapping experiment with tributylphosphine, well known for its rapid reaction with diazo-compounds to give phosphazines. The thermolysis of (17) under the usual conditions in the presence of tributylphosphine (Scheme 9) did in fact give the phosphazine (25), characterised as the acetone azine (26), but the reaction was complete in only 5 min instead of the usual 5 h. It seems very likely therefore



SCHEME 8

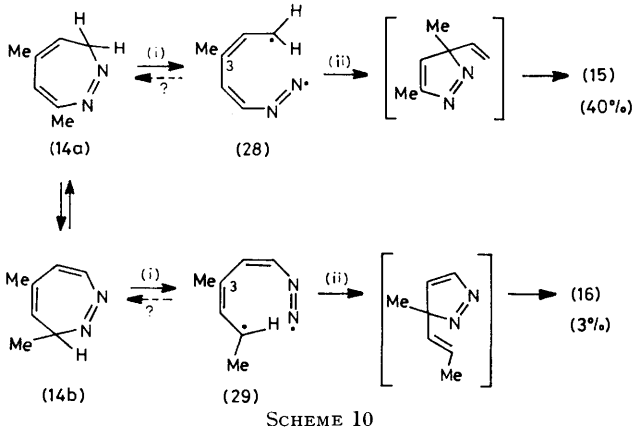
that (25) is derived not by reaction of the phosphine with a diazoalkene intermediate (24) but by its direct nucleophilic attack on the diazepine. Further work on the reactions of phosphines with 1,2-diazepines is in progress.

One feature of the thermolysis of diazepines (14) and (17) which is worthy of comment is the ratio of the two pyrazole products (15) : (16) and (18) : (19). At 12 : 1 and 1 : 1.5, respectively, these are not easily reconciled with the homolytic cleavage–recombination mechansim [pathway (a) of Scheme 8] for the ring-contraction step. It is well known that the homolysis of azo-compounds has a product-like transition state and that the rate of reaction depends strongly on the degree and nature of substitution at the incipient carbon radical.[17,18] Thus for the homolytic cleavage of (14a)/(14b) (Scheme 10), where the rate of interconversion of the two diazepines is fast compared to their decomposition rate, it would be



SCHEME 9

expected that the major decomposition pathway would be *via* (14b) to give (16), *i.e.* preferential cleavage of the 2° rather than the 1° C–N bond of (14a). However the product ratio favours (15) by *ca.* 12 : 1. Similarly, in the thermolysis of (17) (Scheme 6), it would be expected that homolytic cleavage of (17b) would be more strongly favoured than that of (17a); in fact (19) is the major product but the (19) : (18) ratio is only 1.5 : 1. For these ratios to be compatible with the homolytic mechanism, as shown for example in Scheme 10, the first step (i) at least would have to be a fast reversible process with the product-determining selectivity being exerted in the second (ii), or possibly in some later stage in the process if step (ii) were also reversible. It seems unlikely that much selectivity would be shown in step (ii) since the rates of radical combination reactions are very fast and since the positions of ring closure (C-3) are similarly



SCHEME 10

substituted in both (28) and (29). Consequently although the evidence is indirect we feel that it disfavours a radical pathway for this thermal ring contraction in contrast to the formally similar photo-induced azo-group migration shown in Scheme 7.

EXPERIMENTAL

^{1}H N.m.r. spectra were obtained on a Varian HA100 spectrometer and ^{13}C n.m.r. spectra with either Varian XL100 or CFT20 spectrometers. Chemical shifts are recorded as p.p.m. downfield from internal tetramethylsilane. Mass spectra were obtained with an A.E.I. MS902 instrument (70 eV) using a direct insertion probe.

Toluene used as pyrolysis solvent was dried over sodium wire, distilled under dry nitrogen, and stored over sodium wire. Chlorobenzene was distilled, dried by passage through alumina, and stored over molecular sieve (4A).

All the diazepine pyrolyses were carried out under nitrogen and in the dark.

Preparations of Starting Materials and Reference Samples.—The 3*H*-1,2-diazepines (10), (14), and (17) were prepared as described previously.[11]

4-*Ethyl*-3-*methyl*-5-*phenyl*-1H-*pyrazole*. Hydrazine hydrate (1.58 g, 0.032 mol) in methanol (30 ml) was added over 15 min to a stirred solution of 2-ethyl-1-phenylbutane-1,3-dione [19] (6.0 g, 0.032 mole) in methanol (30 ml) at room temperature. The mixture was then boiled under reflux for 10 min, cooled, and the solvent removed. The residue was dissolved in ether and the solution washed with water (50 ml), dried, and evaporated under reduced pressure to give a yellow oil (6.15 g). This on short-path distillation (0.1 mmHg) gave a colourless oil which solidified and was crystallised from light petroleum to give the pyrazole (5.0 g, 87%), m.p. 81—82 °C (Found: C, 77.4; H, 7.65; N, 15.0. $C_{12}H_{14}N_2$ requires C, 77.4; H, 7.6; N, 15.0%), δ(CDCl$_3$) 12.13br (s, NH), 7.1—7.6 (5 H, m, ArH), 2.51 (q, *J* 7 Hz, CH_2), 2.02 (s, 3-Me), and 1.06 (t, *J* 7 Hz, Et-C*H*$_3$).

2-(2-*Phenylethyl*)*butane*-1,3-*dione*. A mixture of 5-phenylpentan-2-one (11.0 g, 0.068 mol) and ethyl formate (6.16 g, 0.083 mol) was added to an ice-cooled suspension of powdered sodium ethoxide [from sodium (1.61 g, 0.070 mol) and ethanol (20 ml)] in dry ether (50 ml) under nitrogen. After standing overnight at room temperature the ether was removed by evaporation under reduced pressure and the residual solid was dissolved in ice-cold water (50 ml). To this was added with vigorous stirring concentrated aqueous cupric sulphate (17 g). The mixture was then extracted with ether and the ether solution dried and evaporated under reduced pressure to leave a dark green oil. Unchanged starting materials (2.2 g) were removed from this by distillation (0.1 mmHg) and from the remaining oil two copper salts were obtained by fractional crystallisation from benzene–light petroleum: (i) 6-*phenylhexane*-1,3-*dione copper salt* (3.0 g, 25%) as blue crystals, m.p. 106—108 °C (Found: C, 65.4; H, 5.9. $C_{24}H_{26}CuO_4$ requires C, 65.2; H, 5.9%), $\nu_{max.}$ (Nujol) 1 580 cm^{-1} (C=O); (ii) 2-(2-*phenylethyl*)*butane*-1,3-*dione copper salt* (0.35 g, 3%) as green crystals, m.p. 142—144 °C (Found: C, 65.0; H, 5.9. $C_{24}H_{26}CuO_4$ requires C, 65.2; H, 5.9%), $\nu_{max.}$ (Nujol) 1 595 cm^{-1} (C=O). This salt (0.316 g, 0.715 mmol) was added to dilute hydrochloric acid (2M; 20 ml) and the mixture extracted with ether (50 ml). The ether solution was washed with aqueous sodium hydrogen carbonate (2%; 2 × 20 ml) and water (20 ml) and then dried and evaporated under reduced pressure to give a white solid. This was recrystallised at −30 °C from light petroleum (b.p. 60—80 °C)–ether to give 2-(2-*phenylethyl*)*butane*-1,3-*dione* (0.23 g, 85%), m.p. 80—81 °C (Found: $M^{\cdot+}$, 190.099 254. $C_{12}H_{14}O_2$ requires *M*, 190.099 373), δ(CDCl$_3$) 14.80 (d, *J* 6 Hz, OH), 7.84 (d, *J* 6 Hz, =CH), 7.0—7.4 (5 H, m), 2.3—2.8 (m, 2 × CH_2), and 1.99 (s, Me), δ_C (CDCl$_3$) 193.7 (C-3), 178.6 (C-1), 140.7 (C-2), 128.6, 126.3, and 111.9 (tert) (aromatic), 37.5 and 29.8 (2 × CH_2), and 23.4 (CH_3).

3-*Methyl*-4-(2-*phenylethyl*)-1H-*pyrazole*. Hydrazine hydrate (0.185 g, 3.68 mmol) was added to a solution of 2-(2-phenylethyl)butane-1,3-dione (0.70 g, 3.68 mmol) in methanol (50 ml), and the mixture boiled under reflux for 10 min. After cooling and removal of the solvent under reduced pressure the residue was dissolved in ether and the ether solution washed with water (50 ml), dried, and evaporated under reduced pressure. The residual oil on short-path distillation (0.1 mmHg) gave, after standing, a white solid which was recrystallised from light petroleum (b.p. 40—60 °C) to give the pyrazole as needles (0.56 g, 82%), m.p. 55—57 °C (Found: C, 77.1; H, 7.5; N, 14.9. $C_{12}H_{14}N_2$ requires C, 77.4; H, 7.6; N, 15.0%), δ(CDCl$_3$) 10.42br (s, NH), 7.0—7.3 (6 H, m, ArH), 2.6—2.9 (m, 2 × CH_2), and 2.10 (s, Me).

3-Methyl-4-propyl-1*H*-pyrazole was prepared by a standard route [20] and gave δ(CDCl$_3$) 7.30 (s, H-5), 2.36 (t, *J* 7 Hz, CH_2), 2.22 (s, 3-Me), 1.56 (sextuplet, *J* 7 Hz, CH_2), and 0.92 (t, *J* 7 Hz, Me), δ_C(CDCl$_3$) 140.4 (C-3), 133.3 (C-5), 117.8 (C-4), and 25.45, 23.6, 13.6, and 10.1 (aliphatic).

1-*Methyl*-3-*phenylcyclopentane*. Reaction of the Grignard reagent from bromobenzene (3.82 g, 0.024 3 mol) with 3-methylcyclopentanone (2.0 g, 0.020 4 mol) and subsequent dehydration of the crude product by boiling under reflux for 4.5 h in water–ethanol (1 : 1 v/v; 60 ml) containing concentrated hydrochloric acid (1 ml) gave a mixture of 3-methyl-1-phenylcyclopent-1-ene and 4-methyl-1-phenylcyclopent-1-ene (2.58 g, 80%), b.p. 116—118 °C at 14 mmHg (Found: $M^{\cdot+}$, 158.109 690. $C_{12}H_{14}$ requires M, 158.109 545). This mixture (1.0 g, 6.34 mmol) was hydrogenated in ethanol (80 ml) using 10% palladium–charcoal (130 mg) as catalyst and worked up in the usual way to give 1-methyl-3-phenylcyclopentane (0.72 g, 71%) as an oil, b.p. 108—110 °C at 17 mmHg (lit.,[21] 93—94 °C at 12 mmHg), δ($CDCl_3$) 7.15 (5 H, s), 2.8—3.4 (1 H, m), 1.2—2.5 (7 H, m), and 1.10 (d, J 6 Hz, Me).

Pyrolysis of 3H-1,2-*Diazepines*.—3,5,7-*Trimethyl*-3H-1,2-*diazepine* (10) *in chlorobenzene*. A solution of the diazepine (0.995 g, 7.32 mmol) in chlorobenzene (80 ml) was boiled under reflux for 3 h when t.l.c. (alumina; benzene as eluant) showed that all the diazepine had been consumed. After removal of the solvent under reduced pressure, dry-column chromatography (alumina; hexane as eluant) of the residue gave (E)-3,5-*dimethyl*-4-*propenyl*-1H-*pyrazole* (13) (0.53 g, 53%), m.p. 130—132 °C [from light petroleum (b.p. 60—80 °C)] (Found: C, 70.9; H, 9.1; N, 20.85. $C_8H_{12}N_2$ requires C, 70.55; H, 8.9; N, 20.6%), $\nu_{max.}$ (Nujol) 3 120 and 3 180 cm^{-1} (NH), δ($CDCl_3$) 9.60br (s, NH), 6.19 (d of q, J 16 and 1.5 Hz, propenyl 1-H), 5.75 (d of q, J 16 and 6 Hz, propenyl 2-H), 2.27 (s, 3- and 5-Me), and 1.85 (d of d, J 6 and 1.5 Hz, propenyl Me). This pyrazole (0.049 7 g, 0.366 mmol) in ethanol (40 ml) was hydrogenated at 1 atm for 20 min using 10% palladium–charcoal (20 mg) as catalyst. Filtration, removal of the solvent under reduced pressure, and sublimation of the residue at *ca.* 0.1 mmHg, gave 3,5-dimethyl-4-propyl-1*H*-pyrazole (0.038 5 g, 80%), m.p. 77.5—78.5 °C (lit.,[22] 77.5—78.5 °C), $\nu_{max.}$ (Nujol) 3 090, 3 150, and 3 200 cm^{-1} (NH), δ($CDCl_3$) 9.88br (s, NH), 2.31 (t, J 7.5 Hz, 1′-CH_2), 2.18 (s, 3- and 5-Me), 1.47 (sextet, J 7.5 Hz, 2′-CH_2), and 0.88 (t, J 7.5 Hz, 3′-Me).

The ^{1}H n.m.r. spectrum of the crude 3,5-dimethyl-4-propenyl-1*H*-pyrazole obtained from the dry-column chromatography also showed absorptions at δ 2.16 (s, 3- and 5-Me), 1.60 (d of d, J 6 and 1.5 Hz, propenyl Me) thought to be due to the *Z*-propenyl isomer, estimated from the integrals to be *ca.* 14% of the total pyrazole product. In a control experiment, (*E*)-3,5-dimethyl-4-propenyl-1*H*-pyrazole (0.02 g) was boiled under reflux in dry chlorobenzene (15 ml) for 5 h; after evaporation of the solvent ^{1}H n.m.r. showed no isomerisation to the *Z*-propenyl isomer to have occurred.

5-*Methyl*-7-*phenyl*-3H-1,2-*diazepine* (17a). (i) *In toluene*. A solution of the diazepine (0.616 g, 0.335 mmol) in toluene (20 ml) was boiled under reflux for 5 h when t.l.c. (alumina; benzene–ether 1 : 1 as eluant) showed that all the diazepine had been consumed with the formation of a fast-running spot (R_F 0.8) and two slow-running spots (R_F *ca.* 0.1). These were separated by preparative t.l.c. (silica; ether as eluant) to give (a) a yellow oil (0.225 g), *m/e* 156 ($M^{\cdot+}$), which was shown by t.l.c. (alumina; benzene as eluant) to contain four components; this was hydrogenated at 1 atm over 10% palladium–charcoal to give 1-methyl-3-phenylcyclopentane having spectral and chromatographic properties identical with an authentic sample; (b) 3-methyl-5-phenyl-4-vinylpyrazole (18) as a pale yellow oil (0.071 g, 12%) (Found: $M^{\cdot+}$, 184.099 475. $C_{12}H_{12}N_2$ requires M, 184.100 043), $\nu_{max.}$ (Nujol) 3 150 cm^{-1} (NH), δ($CDCl_3$) 10.53br (s, NH), 7.2—7.6 (5 H, m, ArH), 6.61 (d of d, J 18 and 11.5 Hz, 1′-H), 5.27 (d of d, J 18 and 1.5 Hz, 2′-H), 5.14 (d of d, J 11.5 and 1.5 Hz, 2′-H), and 2.18 (s, Me). This pyrazole (0.035 g) in ethanol (20 ml) was hydrogenated at 1 atm for 10 min using 10% palladium–charcoal (48 mg) as catalyst. Usual work-up and vacuum sublimation gave 4-ethyl-3-methyl-5-phenyl-1*H*-pyrazole (0.034 g, 86%), m.p. 78—81 °C, mixed m.p. 78—81 °C, which had identical chromatographic and spectroscopic properties to the authentic sample; (c) 3-methyl-4-styryl-1*H*-pyrazole (19) (0.132 g, 21%), m.p. 139—140 °C (Found: C, 78.05; H, 6.5; N, 15.1. $C_{12}H_{12}N_2$ requires C, 78.2; H, 6.6; N, 15.2%), $\nu_{max.}$ (Nujol) 3 120 cm^{-1} (NH); δ($CDCl_3$) 9.78br (s, NH), 7.72br (s, 5-H), 7.1—7.6 (5 H, m, ArH), 6.96 and 6.75 (2 × d, J 16 Hz, styryl AB), and 2.40 (s, Me). This pyrazole (0.057 g, 0.31 mmol) in ethanol (20 ml) was hydrogenated at 1 atm for 10 min using 10% palladium–charcoal (45 mg) as catalyst. Usual work-up gave a quantitative yield of 3-methyl-4-(2-phenylethyl)-1*H*-pyrazole, m.p. 54—56 °C, mixed m.p. 54—57 °C, which had identical spectroscopic and chromatographic properties to an authentic sample.

In a similar experiment the yields were determined by g.l.c. A solution of the diazepine (0.086 g, 0.466 mmol) in toluene (20 ml) was boiled under reflux for 5 h when t.l.c. showed that all the diazepine had been consumed. After removal of the solvent under reduced pressure the residue was hydrogenated for 10 min at 1 atm using 10% palladium–charcoal (0.09 g) as catalyst. The yields of products, determined by g.l.c. (2½% NPGS, 120 °C for 15 min then 49 °C min^{-1} to 215 °C) using 2-cyanostilbene as internal standard, were 4-ethyl-3-methyl-5-phenyl-1*H*-pyrazole (13%), 3-methyl-4-(2-phenylethyl)-1*H*-pyrazole (20%), and 1-methyl-3-phenylcyclopentane (19%).

In a similar pyrolysis carried out in chlorobenzene for 2 h the yields were 12, 16, and 18%, respectively.

(ii) *In toluene in the presence of tributylphosphine*. A solution of the diazepine (17a) (0.078 g, 0.424 mmol) and tributylphosphine (0.20 g, 0.99 mmol) in toluene (10 ml) was kept at 100 °C for 5 min when t.l.c. (alumina; benzene as eluant) showed that all the diazepine had been consumed with the formation of a strongly polar product. Acetone (10 ml) was added and the solution kept at room temperature for 5 min when t.l.c. showed that the initial product had been converted to a new compound with R_F 0.5. Dry-column chromatography (alumina; benzene as eluant) gave 1-isopropylidenehydrazono-3-methyl-5-phenylpenta-2,4-dien-1-one (32) (0.064 g, 67%), m.p. 92—94 °C [from light petroleum (b.p. 40—60 °C) at −30 °C] (Found: C, 79.5; H, 8.0; N, 12.3. $C_{15}H_{18}N_2$ requires C, 79.6; H, 8.0; N, 12.4%), δ [assignments refer to structure (26)] ($CDCl_3$) 8.63 (d, J 10 Hz, H-1), 7.15—7.70 (5 H, m, ArH), 7.48br (d, J 16 Hz, 4-H), 6.70 (d, J 16 Hz, 5-H), 6.28br (d, J 10 Hz, 2-H), 2.10 (d, J 1 Hz, 3-Me), and 2.05 (s, 2 × isopropylidene Me), δ_C ($CDCl_3$) 167.1 (C-1′), 155.5 (C-1), 144.0 (tert), 137.1 (tert), 132.5, 128.8, 128.3, 127.0, 126.6, and 124.7 (C-2—5 and aromatic), 25.4, 20.9, and 18.5 (3 × Me).

5,7-*Dimethyl*-3H-1,2-*diazepine*/3,5-*dimethyl*-3H-1,2-*diazepine* (14a/b). A solution of the diazepine mixture (0.399 g, 3.3 mmol) in chlorobenzene (50 ml) was boiled under reflux for 5 h when t.l.c. (alumina; benzene–ether 1 : 1

as eluant) showed that the diazepines had been consumed. H.p.l.c. (15 × 0.5 cm Spherisorb S5Y using 50% water-saturated ether as eluant) showed two product peaks in the ratio 8 : 92. Removal of the solvent under reduced pressure, and dry-column chromatography (alumina; benzene as eluant) followed by vacuum sublimation and recrystallisation from light petroleum (b.p. 60—80 °C) gave a pure sample of the major product 3,5-*dimethyl*-4-*vinyl*-1H-*pyrazole* (15) (0.157 g, 40%), m.p. 120—121 °C (Found: C, 68.5; H, 8.3; N, 22.7. $C_7H_{10}N_2$ requires C, 68.8; H, 8.25; N, 22.9%), $\nu_{max.}$ (Nujol) 3 120 cm^{-1} (NH), δ($CDCl_3$) 10.10br (s, NH), 6.53 (d of d, *J* 18 and 11.5 Hz, 1′-H), 5.26 (d of d, *J* 18 and 1.5 Hz, 2′-H), 5.10 (d of d, *J* 11.5 and 1.5 Hz, 2′-H), and 2.30 (s, 3- and 5-Me). This pyrazole (0.086 g, 0.704 mmol) was hydrogenated by the usual method and the product sublimed at *ca.* 0.1 mmHg to give 4-ethyl-3,5-dimethyl-1*H*-pyrazole (0.087 g, 100%), m.p. 50—53 °C (lit.,[23] 53 °C) which had identical i.r. and n.m.r. spectra to those quoted in the literature,[23,24] δ($CDCl_3$) 11.17br (s, NH), 2.35 (q, *J* 8 Hz, CH_2), 2.20 (s, 3-and 5-Me), and 1.04 (t, *J* 8 Hz, ethyl Me).

In a similar pyrolysis the crude alkenylpyrazole product (0.24 g, 48%) obtained from the dry-column chromatography was hydrogenated at 1 atm for 20 min using 10% palladium–charcoal (0.2 g) as catalyst. Usual work-up followed by short-path distillation at 0.1 mmHg gave a quantitative yield of a semi-crystalline oil which was shown by h.p.l.c. (15 × 0.5 cm Spherisorb S5Y using 50% water-saturated ether as eluant and a detector wavelength of 230 nm) to contain two components in the ratio 8 : 92 with retention times identical with those of 3-methyl-4-propyl-1*H*-pyrazole and 4-ethyl-3,5-dimethyl-1*H*-pyrazole, respectively, δ_C($CDCl_3$) 141.2 (49), 140.4 (3), 133.0 (5), 117.7 (3), 116.8 (24), 25.4 (9), 23.6 (8), 16.1 (93), 15.7 (3), 15.0 (87), 13.6 (8), 10.5 (100), and 10.15 (8%).

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