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A STUDY OF PERISELECTIVITY IN THE THERMAL CYCLISATION REACTIONS OF DIENE-CONJUGATED DIAZO COMPOUNDS: 1,7-CYCLISATION AS A ROUTE TO 3H-1,2-DIAZEPINES AND 1,5-CYCLISATION LEADING TO NEW REARRANGEMENT REACTIONS OF 3H-PYRAZOLES[1]

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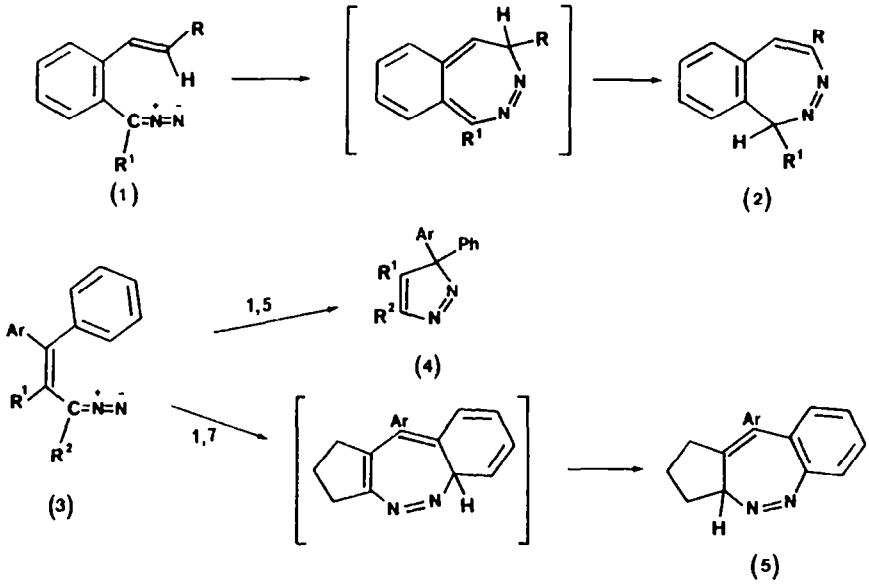
Abstract - A range of diene-conjugated diazo compounds has been generated by the thermal decomposition of the sodium salts of the tosylhydrazones of 1-acyl-1,3-dienes. Those of type (21) with a cis relationship of the diazo group and the γ,δ-double bond and having a cis hydrogen atom at the diene terminus cyclised only by 1,7 ring closure to give 3H-1,2-diazepines (23). This mode of cyclisation was inhibited by the presence of cis methyl or phenyl groups at the diene terminus eg in (45). Compounds of this type cyclised by the alternative 1,5- ring closure to give 3-alkenyl-3H-pyrazoles eg (46) as primary products. These observations are explained on the basis of a helical transition state (54) for the 8π electron 1,7-electrocyclisation reaction. Diene-conjugated diazo compounds with a trans γ,δ double bond eg (32) also cyclised predominantly by 1,5-electrocyclisation to give 3-alkenyl-3H-pyrazoles eg (33). In most cases the 3H-pyrazoles rearranged under the reaction conditions via alkenyl group and hydrogen migrations to give 1H-pyrazoles eg (34) and (37).

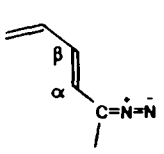
INTRODUCTION

In earlier work we have studied the reactions of conjugated diazo compounds of types (1) and (3) which have an aromatic double bond as part of the conjugated diene system. Those, eg (1)



with the aromatic bond in the α,β position cyclise at 80°C exclusively by 1,7 ring closure[2] to give 1H-2,3-benzodiazepines (2). Similar reactions are shown by analogues with α,β thiophene rings.[3] On the other hand compounds of type (3) which have the aromatic bond in the γ,δ position generally show the opposite periselectivity and favour 1,5-electrocyclisation to give 3-aryl-3H-pyrazoles (4) as the primary products. However such systems can be induced to react wholly or partly by 1,7 cyclisation to give 3H-1,2-benzodiazepines,[4,5] or their thieno analogues,[6] by the incorporation of a fused cyclopentyl ring, eg in [3, $R^1,R^2 = (CH_2)_3$] which cyclises to give only (5). It can be seen from these results that the activation energies for 1,5 and 1,7 cyclisation are not very different, and that the periselectivity is much affected by the presence and position of an aromatic double bond in the conjugated system.

This paper describes the further extension of this work to a study of the perselectivity of cyclisation in systems of type (6) and (7) containing only olefinic unsaturation. In particular



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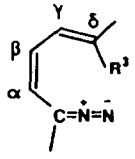

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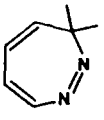


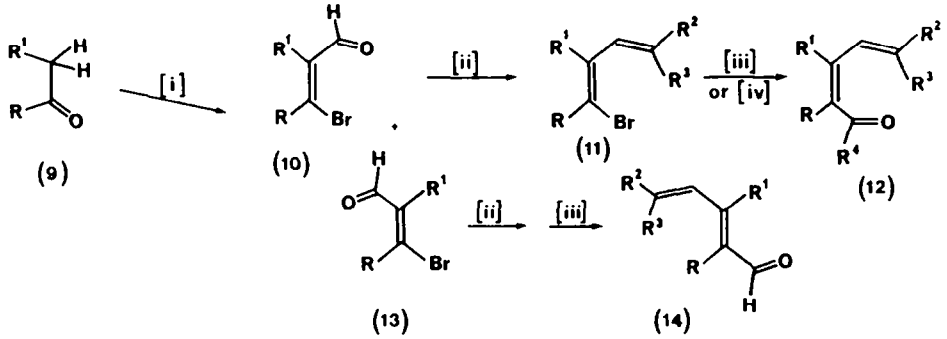
(8)

it was hoped that the cyclisation of (7) would provide a synthetic route to the interesting monocyclic 3H-1,2-diazepine system (8) hitherto only accessible by the base induced elimination of toluene-p-sulphinic acid from 3,4-dihydro-2-tosyl-1,2-diazepines. The intention was to study a range of substrates of types (6) and (7) and investigate how the partitioning between 1,5- and 1,7-cyclisation was affected by (i) the stereochemistry of the α,β double bond, and (ii) the presence or absence of cis substitutents, R^3, on the δ carbon atom in (7). This last point was of particular interest because it has been shown that the 1,7-cyclisation of compounds of type (1) is blocked when the cis hydrogen atom at the olefin terminus is replaced by a methyl or a phenyl group; the reaction then goes by an alternative pathway via loss of nitrogen to give carbene-derived products.

RESULTS AND DISCUSSION

(i) Synthesis of the Diazo Compound Precursors

As in the earlier work the diazo compounds were generated by heating the sodium salts of tosylhydrazones at 80°C in aprotic solvents. The tosylhydrazones were prepared from the 1-acyl-1,3-dienes (12) and (14). Two methods were developed for the synthesis of these aldehydes and ketones. The first, outlined in Scheme 1 was used in most cases as it is the more efficient and uses readily available starting materials. The key step is the triple functionalisation of the

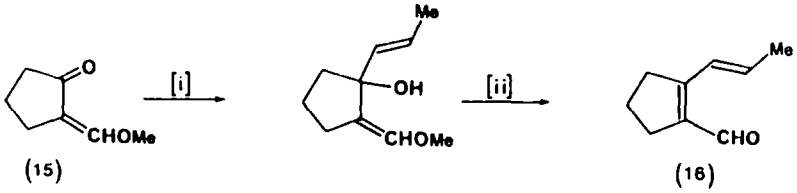


R-R^4 as indicated in Tables 1 and 2

Reagents: (i) PBr_3/D.M.F., (ii) $Ph_3\overset{+}{P}CHR^2R^3$/base, (iii) Mg or BuLi, D.M.F., (iv) Mg or BuLi, R^4CHO; ^{3}oxidation by CrO_3/pyridine or $Ba(MnO_4)_2$.

Scheme 1

α-methylene ketones (9) by Arnold's bromoformylation reaction.[7] The 2-bromo-1-formylalkenes (10) and (13) were occasionally subject to sudden exothermic polymerisation during distillation so we generally worked up the reactions by chromatography, and used the products soon after preparation. In the acyclic case (R = Me, R^1 = Ph) the isomers (10) and (13) were easily separated on a preparative scale by medium pressure liquid chromatography. The reaction conditions for the metallation of (11) were critical in some cases - particularly when R^3 = Me since the vinyl 'anion' tended to isomerise via a proton migration if the temperature was too high or if it was kept too long before reaction with the electrophile. The reactions with dimethylformamide [step (iii)] to give the aldehydes (R^4 = H) generally gave excellent yields but in the preparation of the ketones [step (iv)] the oxidation of the alcohols was achieved only in low yield despite the use of mild oxidants [CrO_3/pyridine or $Ba(MnO_4)_2$]. The reaction of the Grignard reagent of (11; R,R^1 = $(CH_2)_3$, R^2 = Ph, R^3 = H) with p-tolualdehyde gave both the expected alcohol (49%) and the ketone (12c) (36%) directly, a recorded[8] but relatively rare occurrence. The second general method utilised the reaction between alkenyl-lithium or vinyl Grignard reagents and the dimethyl acetals or methyl enol ethers of β-ketoaldehydes.[9] It was used for only one example (16) in this work.

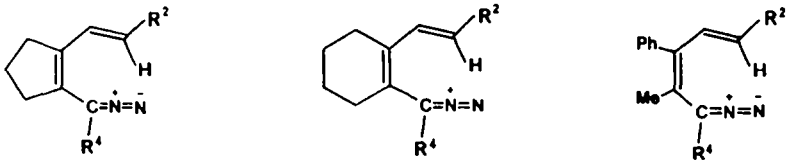


(15) (16)

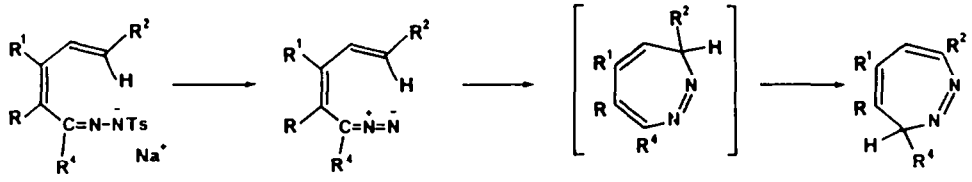
Reagents: (i) MeCH=CHLi, (ii) H^+/H_2O

(ii) Cyclisation of cis-Diazo Compounds (7) with R^3 = H

Three basic variants (17)-(19) on this type of system were studied. In (17) and (18) the required cis stereochemistry was achieved by using cycloalkenyl moieties in the α,β position, and in the acyclic case (19) by isomer separation at an early stage in the dienal synthesis. The



(17) (18) (19)



(20) (21) (22) (23)

R,R^1,R^2,R^4 as shown in Table 1

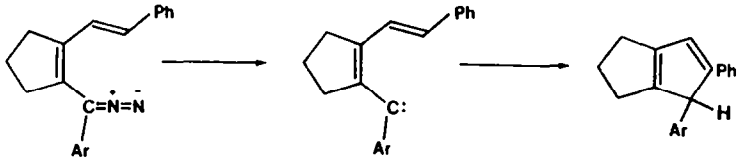
Scheme 2

initial work was carried out on the cyclopentene derivatives in a deliberate attempt to steer the reaction towards 1,7-cyclisation since it was known from earlier work on α,β-unsaturated diazo compounds that the fusion of a cyclopentyl ring on to the conjugated system disfavours 1,5-cyclisation.[4,5] However in the event it was found that this device was not required as all of the systems showed a cyclisation periselectivity which favoured 1,7 cyclisation so strongly that no pyrazoles were isolated. The diazo compounds (21), generated from the tosylhydrazone salts (20), all reacted by the path shown in Scheme 2 to give the 3H-1,2-diazepines (23) in the yields

Table 1 Cyclisations of diazo compounds (21) derived from carbonyl compounds (12, R^3 = H) giving 3H-1,2-diazepines (23)

Diazo Compound	R	R^1	R^2	R^4	Carbonyl compound precursor	Products (yield)
21a	- $(CH_2)_3$ -		Ph	H	12a	(23a) (63%)
21b	- $(CH_2)_3$ -		Ph	Me	12b	(23b) (76%)
21c	- $(CH_2)_3$ -		Ph	p-Tolyl	12c	(23c) (9%), (25) (40%)
21d	- $(CH_2)_3$		Me	H	16	(23d) (65%)
21e	- $(CH_2)_4$		Ph	H	12e	(23e) (92%)
21f	- $(CH_2)_4$		Ph	Me	12f	(23f) (56%)
21g	Me	Ph	Ph	H	12g	(23g) (71%)

pathway to give (25). This characteristic has been seen before for diazo compounds with an aryl substituent on the diazo carbon atom. Apparently the conjugation of the aromatic ring has a strong differential effect favouring the transition state for carbene formation.



(21c) (24) (25)

Ar = p-Tolyl

The formation of the 3H-1,2-diazepine (23) can be rationalised as a two-step process: firstly a 1,7 (8π electron) electrocyclisation giving the primary product (22), which was neither detected nor isolated, followed by a [1,5] sigmatropic hydrogen shift to give (23). Such hydrogen migrations in 3H-1,2-diazepines are known to be fast[10,11] so the formation of (23) must reflect its higher thermodynamic stability than that of (22). Two factors contribute to this: (i) the R^2 group (Ph or Me) is brought into conjugation or hyperconjugation with the conjugated diene system, and (ii) the double bonds exocyclic to the carbocyclic rings in cases where R,R^1 = $-(CH_2)_n-$ are moved to more stable locations.

The structures of the diazepines were assigned by comparison of their ^1H and ^{13}C n.m.r. spectra (see Experimental section and Table 2), and mass spectrometry fragmentation patterns with data from other 3H-1,2-diazepines[10,11], prepared by the elimination of toluene-p-sulphinic acid from 3,4-dihydro-2-tosyl-1,2-diazepines, 1H-2,3-benzodiazepines[2,3] and 3H-1,2-benzodiazepines.[4,5] In particular they showed the following characteristic features: (i) all gave mass spectra having small parent ions and major fragmentation by loss of N_2, (ii) the ^{13}C chemical shifts of the saturated carbon adjacent to the azo group (C-3) were in the range 66-82 ppm, whereas 3H-pyrazoles eg (4) have chemical shifts of ca 94-106 ppm for the analogous carbon atom,[4,5] and (iii) in cases where there were two hydrogen atoms on C-3 they had widely separated chemical shifts (ca 3.6 ppm) and gave temperature dependent spectra owing to ring inversion.[2,3] The ^1H n.m.r. spectrum of (23b) showed chemical shift equivalence of the methyl group on C-3 and its adjacent proton, but this was broken by addition of a shift reagent and then showed the expected coupling.

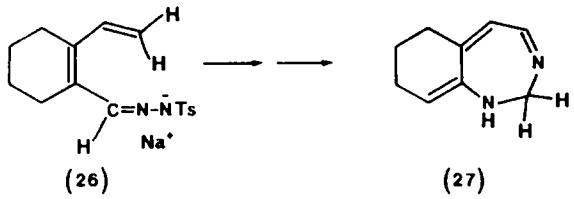
There was only one exception to the isolation of 3H-1,2-diazepines from tosylhydrazone salts of this general type. The sodium salt of 1-formyl-2-vinylcyclohexene tosylhydrazone (26) under the same reaction conditions gave as the sole isolable product an unstable colourless oil (71%) which we have provisionally formulated as a cyclohexa[d][1,3]diazepine (27). Work to confirm

Table 2 ^{13}C N.m.r. data of 3H-1,2-diazepines and pyrazoles

Compound	MHz	Chemical shift (δ)
23a	20	24.03, 33.30, 35.51 (C-6,C-7,C-8), 67.37 (C-1), 110.40 (C-5), 125.58, 127.79 (tert.), 127.98, 128.47, 137.30 (tert.), 140.14 (tert.), 154.76 (tert.)
23b	20	15.98 (Me), 23.50 (C-7), 32.13, 33.48 (C-6,C-8), 72.82 (C-1), 109.96 (C-5), 125.52, 127.93, 128.44, 132.77 (tert.), 137.22 (tert.), 138.92 (tert.), 154.44 (tert.)
23c	90	21.19 (Me), 23,60, 33.52, 33.88 (C-6,C-7,C-8), 81.94 (C-1), 110.19 (C-5), 125.69, 128.18, 128.31, 129.05, 129.14, 132.89 (tert.), 135.63 (tert.), 137.16 (tert), 137.25 (tert.), 138.96 (tert.), 154.29 (tert.)
23d	20	21.14 (Me), 24.20, 33.17, 35.38 (C-6,C-7,C-8), 66.52 (C-1), 112.45 (C-5), 126.83 (tert.), 139.42 (tert.), 152.79 (tert.)
23e	90	22.42 (C-7,C-8), 29.13, 31.31 (C-6,C-9), 71.58 (C-1), 116.68 (C-5), 123.57 (tert.), 125.61, 127.99, 128.50, 134.34 (tert.), 137.30 (tert.), 154.10 (tert.)
23f	90	15.03 (Me), 22.34, 22.44, 26.39, 29.72 (C-6,C-7,C-8,C-9), 74.69 (C-1), 116.38 (C-5), 125.63, 127.34 (tert.), 127.99, 128.53, 134.12 (tert.), 137.24 (tert.), 153.83 (tert.)
23g†	90	20.50 (Me), 71.92 (C-3), 114.70 (olefinic), 120.74 (tert.), 124.81, 126.61, 127.47, 127.84, 128.75, 136.32 (tert.), 138.29 (tert.), 138.96 (tert.), 153.76 (tert.)
31a‡	50	10.6 (Me), 17.5 (Me), 20.8 (2 x Me), 24.9 (Me_2C), 111.7 (tert.), 121.3 (olefinic), 122.2 (olefinic), 139.9 (tert.), 149.7 (tert.)
31b†	50	10.5 (2 x Me), 113.0 (tert.), 119.4, 124.9, 125.1, 125.7, 127.7, 138.1 (tert.), 141.2 (tert.)
34	90	8.8 (Me), 115.0 (tert.), 124.7, 125.4, 127.4, 127.7 (2 x CH), 127.9, 128.7, 129.2, 129.6 (tert.), 134.0 (tert.), 140.4 (tert.), 140.8 (C-3).
37*	20	9.3 (Me), 111.1 (tert.), 126.3, 127.2, 127.4, 127.6, 128.2, 128.5, 128.8, 137.0 (tert.).
47	20	9.0 (Me), 16.5 (Me), 114.4 (tert.), 123.3, 126.0, 127.3, 128.0, 128.2, 128.3, 129.5, 130.0 (tert.), 132.8 (tert.), 140.5 (C-3), 141.0 (tert.)
Z-47	90	8.9 (Me), 21.4 (Me), 114.4 (tert.), 122.2, 126.9, 127.1, 127.2, 127.65, 127.72, 129.1, 130.0 (tert.), 135.6 (tert.), 138.4 (tert.), 140.4 (C-3), 140.6 (tert.)
50	20	9.2 (Me), 18.0 (Me), 112.4 (tert.), 115.3 (olefinic), 125.9, 127.4, 127.5, 128.2, 128.4, 132.3 (tert.), 139.7 (tert.), 143.1 (tert.), 143.7 (tert.), 146.0 (tert.)
52a	90	16.3 (Me), 21.6, 24.8, 28.6, 41.6 (C-4 to C-7), 95.6 (C-7a), 120.2 (olefinic), 125.9, 127.3, 128.1, 137.1 (C-3), 143.3 (tert.), 143.5 (tert.), 161.5 (tert.)
53a	50	16.6 (Me), 20.5, 21.6, 22.6, 22.9 (C-4 to C-7), 116.2 (tert.), 121.7 126.2, 127.5, 128.4, 132.0 (tert.), 138.1 (C-3), 139.2 (tert.), 141.5 (tert.)
52b	50	17.9 (Me), 26.7 (Me), 21.4, 24.8, 28.7, 41.4 (C-4 to C-7), 95.6 (C-7a), 117.1 (olefinic), 136.8 (C-3), 140.7 (tert.), 161.5 (tert.)
44	20	8.5 (Me), 26.3 (1'-CH_2), 34.7 (2'-CH_2), 114.7 (tert.), 125.4, 126.0, 127.6, 128.2 (2 x CH), 128.8, 139.0 (tert.), 140.1 (tert.), 140.3 (C-3).
39		9.8 (Me), 36.9 (2'-CH_2), 53.3 (1'-CH_2), 113.1 (tert.), 126.4, 126.9, 127.2, 128.2 (2 x CH), 128.3, 128.6, 129.8, 134.2 (tert.), 138.1 (tert.), 149.6 (tert.)
40	90	8.7 (Me), 36.7 (2'-CH_2), 50.8 (1'-CH_2), 114.3 (tert.), 126.4, 128.1, 128.3, 128.4, 129.7, 130.4 (tert.), 138.3 (tert.), 139.1 (C-3), 141.1 (tert.).
42	90	8.5 (Me), 27.6 (1'-CH_2), 35.2 (2'-CH_2), 110.5 (tert.), 126.0, 127.3, 127.5, 128.3 (2 x CH), 128.5, 132.4 (tert.), 141.3 (tert.), 145.2 (tert.), 146.9 (tert.)
Hydrogenation product of (47)	90	8.7 (Me), 18.0 (Me), 40.4 (2'-CH), 56.4 (1'-CH_2), 114.1 (tert.), 126.4, 127.0, 128.0, 128.2, 128.3, 129.8, 130.5 (tert.), 139.0 (C-3), 141.3 (tert.), 143.4 (tert.)
Hydrogenation product of (50)	90	8.7 (Me), 21.2 (Me), 34.3 (1'-CH_2), 39.9 (2'-CH), 111.7 (tert.), 126.3, 126.9, 127.3, 127.5, 128.4, 128.5, 132.8 (tert.), 145.4 (tert.), 146.3 (tert.)

‡ In perdeuterioacetone * In perdeuteriodimethyl sulphoxide

the structure of this compound, and on the factors which lead to the operation of this apparently new rearrangement is still in progress and will be reported in full later.

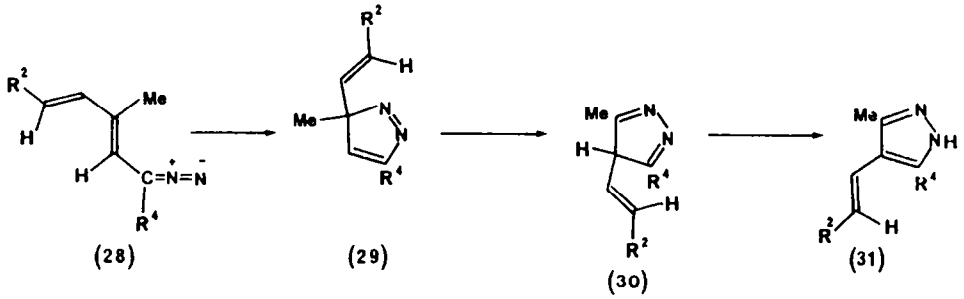


(26) (27)

(iii) Cyclisations of trans-Diazo Compounds (6)

Systems with a trans arrangement of the diazo group and the γ,δ-double bond eg (28) and (32) were studied for two reasons (i) to find out whether any trans → cis isomerisation of the α,β-double bond would occur under the reaction conditions and so allow diazepine formation, and (ii) in the expectation that 1,5 cyclisation would occur, with the intention of preparing a sample of the 3-vinyl-3H-pyrazole (33) which would result from the 1,5 cyclisation of (21g). This compound was required to allow a positive check to be made for its presence as a minor product in the cyclisation of (21g).

Two types of trans diazo compounds were studied: those with a substituent on the α-carbon atom eg (32), and those without eg (28). Each gave a different reaction path but in neither case was the primary product - the 3-vinyl-3H-pyrazole (29) or (33) - isolated.



(28) (29) (30) (31)

(28a)-(31a); R^2 = Me, R^4 = Pr^i (28b)-(31b); R^2 = Ph, R^4 = Me

Scheme 3

The tosylhydrazone precursors for the diazo compounds (28a) and (28b) had been prepared in earlier work for the study of their acid catalysed cyclisation reactions.[11,12] The decomposition of their sodium salts at 80°C, Scheme 3, gave the 1H-pyrazoles (31) as the only isolable products. The yields are given in Table 3. Their formation requires 1,5-electrocyclisation to give the

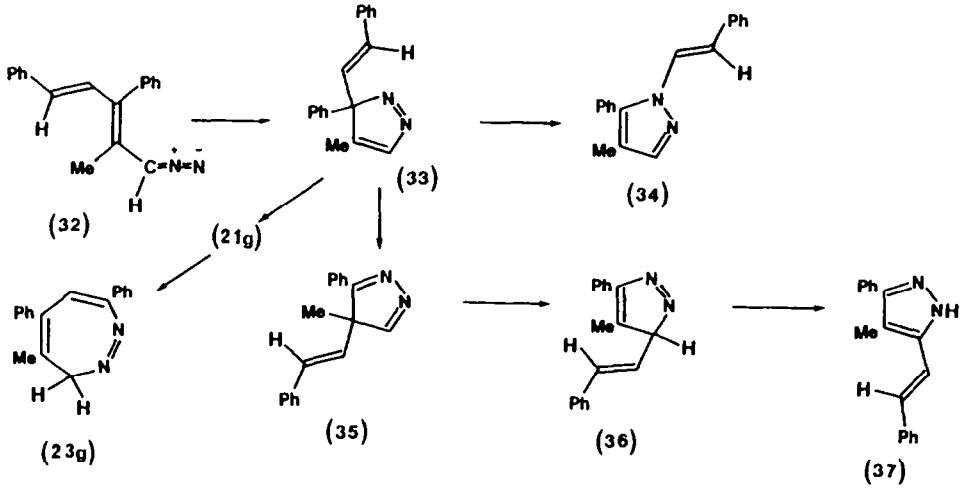
Table 3 Cyclisation of diazo compounds to give pyrazoles

Diazo compound	Carbonyl compound precursor	Products (yield)
28a	ref 11	(31a) (62%)
28b	ref 12	(31b) (55%)
32 (80°C)	14g	(23g) (13%), (34) (33%), (37) (20%)
32 (110°C)		(23g) (6%), (34) (7%), (37) (61%)
45	12i	(47) (32%) + Z isomer (5%), (50) (30%)
51a	12j	(52a) (42%), (53a) (9%)
51b	12k	(52b) (11%)

3H-pyrazole (29) followed by successive [1,5]-vinyl, and hydrogen migrations. This 3H- to 4H- to 1H-pyrazole rearrangement sequence has been observed before, in the thermal decomposition of 3H-1,2-diazepines,[13] and was discussed in that paper. The absence of any 3H-1,2-diazepines in the products suggests that the α,β trans diazo compound does not isomerise either by bond

rotation in the delocalised system or by retro-cyclisation of (29).

The structures of the pyrazoles (31) were assigned by comparison of their spectra with data from compounds of the same type.[4,5] In particular the ^{1}H n.m.r. spectra clearly showed the presence of the intact alkenyl group, and the ^{1}H and ^{13}C n.m.r. spectra of (31b) showed the expected chemical shift equivalence of the two methyl groups.



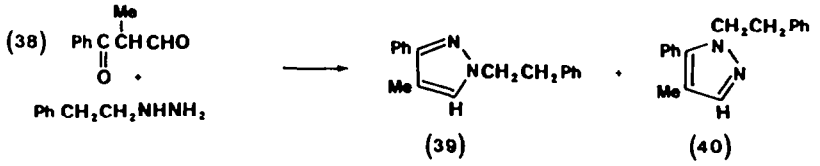
Scheme 4

The cyclisation reactions of the diazo compound (32), which has a methyl substituent on the α-carbon, were more complex and gave three products, Scheme 4 and Table 3, the 3H-1,2-diazepine (23g) and the two 1H-pyrazoles (34) and (37). It is suggested that the pyrazoles are formed in competing rearrangement processes from the primary product (33). The 1-styryl-1H-pyrazole (34) is formed by a [1,5] C → N migration of the alkenyl group. It is notable that a shift of this type was not observed in the rearrangement of (29).[13] The other pyrazole (37) is produced via a sequence of three migrations. The first a [1,5] C → C shift of the styryl group parallels the (29) to (30) rearrangement in Scheme 3 and gives the 4H-pyrazole (35). This compound differs from (30) in that it lacks a hydrogen atom on the saturated carbon and cannot aromatise directly. Instead it undergoes a further [1,5] migration which takes the styryl group on to a hydrogen bearing carbon atom and gives the 3H-pyrazole (36). This compound as is well known for such species then aromatises by a hydrogen shift to give the isolated product (37).* In this sequence it seems likely that the formation of (36) from (35) will be slow since it is known that 3H- are less thermodynamically stable than 4H-pyrazoles and the equilibrium must therefore favour (35). However the reaction sequence is driven towards (37) by the final irreversible aromatisation step. The slowness of the (35) → (36) conversion probably accounts for the occurrence of the C → N styryl shift giving (34). Both C → C and C → N [1,5] sigmatropic migrations are well known in 3H-pyrazole chemistry but groups of low or moderate migrating ability normally show only the shift to carbon eg (29) → (30). It seems likely that the shift to nitrogen has become kinetically competitive in this case because the rate of formation of (37) is much reduced [cf that of (31)] by the relative slowness of the conversion of (35) into (36). In this context it is interesting that (37) becomes the major product (61%) and the yield of (34) drops to (7%) when the cyclisation is carried out at 110°C rather than 80°C. A control experiment showed that (34) does not isomerise to give (37) at this temperature. The greater tendency toward the C → N shift in (33) than in (29) may also be due to some activating effect of the 3-phenyl group, as 3,3-diphenyl-3H-pyrazoles are known to undergo both types of migration.[15]

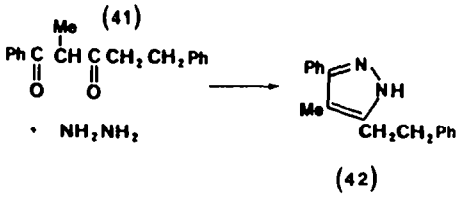
* The pyrazole (37) could be formed via a similar migration sequence involving shifts of the phenyl rather than the styryl group. Unsaturated groups are known to migrate rapidly in [1,5] shifts in five-membered rings[14] but data on the relative mobility of phenyl and vinyl groups are scarce.

The formation of a low yield of the 3H-1,2-diazepine (23g) from the isomerically pure tosylhydrazone precursor to (32) must indicate either the isomerisation of (32) by bond rotation or the formation of the cis diazo compound by the electrocyclic ring opening of the 3H-pyrazole (33).

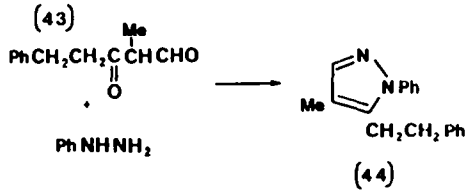
The formulations of the pyrazole products as (34) and (37) is supported by their i.r., and ^{1}H and ^{13}C n.m.r. spectra (see Experimental section and Table 2). Their structures were confirmed by hydrogenation to give products which were identical with the 'authentic' samples (40) and (42) prepared by standard routes as shown in Schemes 5 and 6. The 5-phenethyl derivative



Scheme 5



Scheme 6



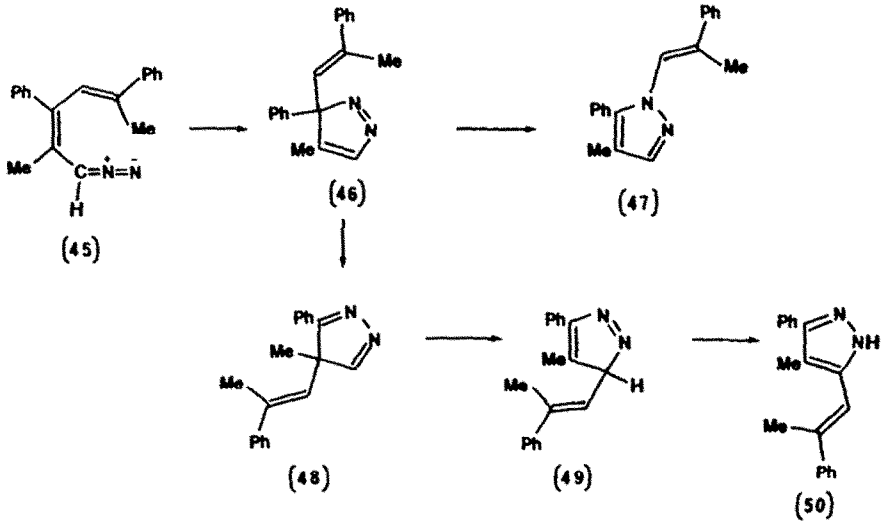
Scheme 7

(42) was prepared unambiguously, Scheme 6, by the reaction of hydrazine hydrate with the 1,3-diketone (41). The route to (40), Scheme 5, by the reaction of the β-ketoaldehyde (38) with phenethylhydrazine however gave the expected two products. The difficulty in differentiating between pairs of isomers of this type is well documented[16] but in this case we were able to do so by using the nuclear Overhauser effect. The effect on peak enhancement of the pyrazole ring proton of irradiation at the resonance frequencies of the phenethyl 1' and 2' protons was measured. One isomer gave enhancements of 7% and 1% respectively while the other gave 1% and 0.5%. Thus the former was assigned structure (39) with the closer proximity of the interacting nuclei. Isomer (40) was identical with the hydrogenation product of (34). The isomer (44) was also synthesised for comparison, by the route shown in Scheme 7, but corresponded to neither of the hydrogenated cyclisation products.

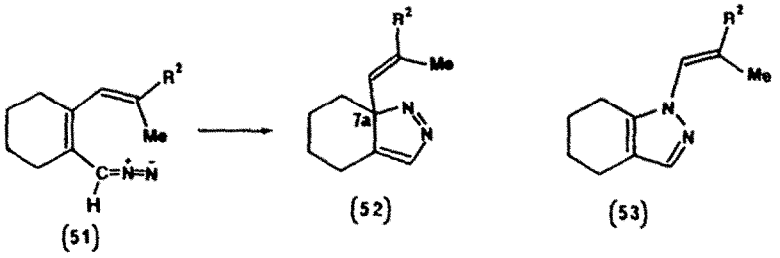
(iv) Cyclisations of cis-Diazo Compounds (7) with R^3 = Me or Ph

Three diazo compounds of this type were studied: (45), (51a), and (51b). All are structural analogues of the diazo compounds (21) in Scheme 2, but modified by the replacement of the cis hydrogen atom at the diene terminus by a methyl or phenyl group. This had the remarkable effect of completely inhibiting the 1,7 mode of cyclisation - the exclusive ring closure path in (21) - so that none of this group gave any isolable diazepines and all cyclised instead via 1,5 ring closure. Thus (45), which contained a ca 3 : 1 mixture of the E and Z isomers of the γ,δ double bond, gave only the 1H-pyrazoles (47) and (50), Scheme 8 (only the E,E isomer shown) The yields are shown in Table 3. These are formed via the same reaction paths as previously observed in the cyclisation of the trans diazo compound (32), Scheme 4. They were identified by comparison of their n.m.r. and mass spectra and those of their hydrogenated derivatives with the spectra of (34), (37), (40) and (42).

The reactions of the cyclohexene derivatives (51), Scheme 9, similarly gave no diazepines, but moderate to low yields of the pentahydroindazoles (52) and/or (53). The accountance in these reactions was low. Several other products which could not be obtained pure were formed in low yields together with much polymeric material. Compound (52a) is formulated as a 3H-pyrazole derivative on spectroscopic evidence. Its ^{1}H n.m.r. spectrum showed the presence of



Scheme 8



(51a)-(53a); R^2 = Ph (51b)-(52b); R^2 = Me

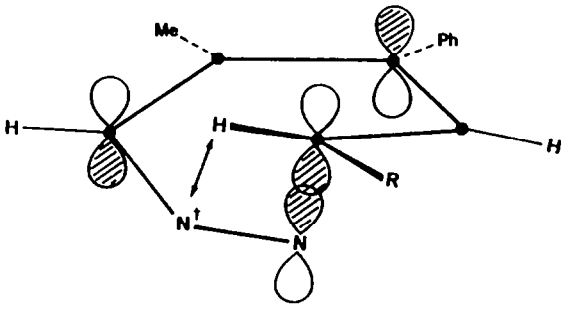
Scheme 9

the intact 2-phenylpropenyl group and the ^{13}C n.m.r. spectrum showed the C-7a absorption at 95.6 ppm, a position similar to that in the 7a-phenyl analogue (99.8 ppm) prepared previously,[5] and typical for 3H-pyrazoles.[4,5] A control experiment showed that (53a) was formed by the thermal rearrangement of (52a). Its spectra were similar to those of the other N-alkenylpyrazoles obtained above.

(v) Mechanisms of the Cyclisation Reactions

The results of the cyclisations of diazo compounds of type (21), Scheme 2, show that 1,7- is very strongly favoured over 1,5-cyclisation. This situation is however reversed in compounds of type (45), Scheme 8 and (51), Scheme 9, which have a cis methyl group at the diene terminus. The presence of a substituent at this position apparently raises the activation energy for 1,7 ring closure so much that 1,5 cyclisation becomes the preferred reaction path. This result therefore parallels the earlier observation that 1,7 ring closure in (1) is blocked by cis methyl or phenyl substituents, but in that case the reaction is diverted to give only carbene-derived products.[17]

It has been shown that the 1,5 ring closure of α,β-unsaturated diazo compounds - like that of many other conjugated 1,3-dipolar intermediates - is a concerted electrocyclisation process.[18] The formation of the 3H-1,2-diazepines in Scheme 2, can be most simply rationalised as a similar 8π electron pericyclic process. The experimental observations summarised above can then be accommodated by a transition state geometry for 1,7-electrocyclisation as shown in (54). Assuming that the HOMO of the system has the nodal properties of ψ_4 of a heptatrienyl anion (the isoelectronic hydrocarbon analogue) then it formally requires a conrotatory ring closure in the planar delocalised system. However the whole conjugated system cannot lie coplanar without



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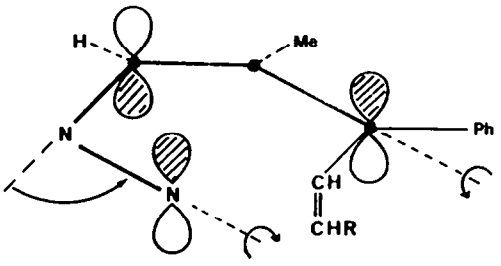
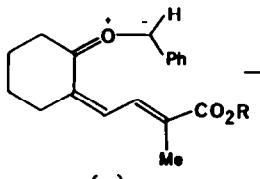


(55)

considerable distortion of the 120° bond angles at the trigonal carbon atoms and it seems much more likely that it will adopt the helical transition state shown. This has an easily accessible geometry which brings the terminal atoms into a bonding overlap and requires only the minimum angular distortion of the diazo group from its preferred linear geometry (see below). As the terminal atoms approach each other by bond rotation of the C–C single bonds this will reduce the pitch of the helix and so increase the conjugation around the system. This stabilising effect will assist the development of the transition state. In this transition state the steric interaction [⟷ in (54)] between the cis hydrogen atom and $N^{\dagger}$ of the diazo group is small and will not impede the approach of the terminal atoms. However models show that a methyl group at that position [as in (45) and (51)] comes into a significant steric interaction with $N^{\dagger}$. This would raise the activation energy for 1,7-electrocyclisation either by inhibiting orbital overlap between the terminal atoms or by twisting the γ,δ double bond out of conjugation. The N terminus in (54) rules out any differentiation between dis- and con-rotation but it is of interest to note that Eberbach has shown that the analogous diene-conjugated carbonyl ylide system (56) does undergo conrotatory closure.[19] It also appears from his results that cis substituents at the diene terminus disfavour but do not prevent 1,7 cyclisation in systems of this type[20] eg (60).



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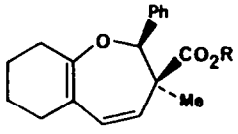

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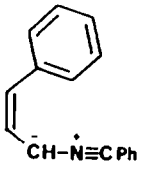

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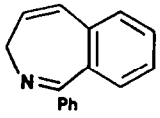

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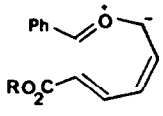

(60)

The other question of interest is why 1,7- is preferred over 1,5-electrocyclisation in the unhindered diazo compounds of type (21). Huisgen has analysed the range of possible stereo-electronic pathways for 1,5 cyclisation[18] and one of these is depicted in (55). Irrespective of the detail it would appear that 1,5 cyclisation will require considerable in-plane bending of the diazo group at an early stage in the development of the transition state, before C/N orbital overlap can provide much stabilising effect. Calculations have shown that there is a substantial energy barrier to the in-plane bending of the C–N–N angle for diazomethane[21,22] and it

thus seems likely that this is a major contribution to the higher activation energy for the 1,5 cyclisation. In this context it is interesting to note the report by Padwa[23] that the nitrile ylide (58) - which has an orthogonal double bond like the diazo group[24] - also cyclises exclusively by the 1,7 mode. In contrast carbonyl ylides such as (60), which belong to the bent allyl type of 1,3-dipole, undergo both 1,5 and 1,7 ring closure.[20]

Acknowledgment

We thank the S.E.R.C. and the University of Edinburgh for support (I.R.R.).

EXPERIMENTAL

N.m.r. spectra were obtained on the following instruments: Varian HA100 (^{1}H, 100 MHz), Bruker WP200 (^{1}H, 200 MHz; ^{13}C, 50 MHz), Bruker WH360 (^{1}H, 360 MHz; ^{13}C, 90 MHz), Varian CFT20 (^{13}C, 20 MHz). All samples were run as solution in deuteriochloroform unless otherwise stated. Chemical shifts are recorded as δ values. In the ^{13}C spectra carbon multiplicity was established by single frequency off resonance decoupling or by distortionless enhancement by polarisation transfer (DEPT). Mass spectra were obtained using an AEI MS902 spectrometer with electron ionisation at 70 eV unless otherwise stated. Preparative chromatography on silica was carried out by the medium pressure technique[25] (<100 p.s.i.) using either 1000 x 15 or 1000 x 25 mm columns packed with Merck Kieselgel 60. Eluting solvents were based on petroleum ether b.p. 40-60°C, referred to as 'petroleum'. Chromatography on alumina used material from Laporte Industries (Grade H, 100/200 mesh) deactivated to Grade III, and gravity elution. 'Evaporation' of solvents indicates evaporation under reduced pressure using a rotary evaporator.

Phosphonium salts. Benzyltriphenylphosphonium bromide,[26] isopropyltriphenylphosphonium bromide[27] and methyltriphenylphosphonium iodide[28] were prepared by literature routes. 1-Phenylethyltriphenylphosphonium bromide. A mixture of 1-phenylethyl bromide[29] (20.2 g, 0.11 mol) and triphenylphosphine (28.7 g, 0.11 mol) in benzene (100 ml) was boiled under reflux for 24 h. The precipitated salt was recrystallised from ethanol (39.2 g, 80%), m.p. 230-232°C (Found: C, 69.55; H, 5.5. $C_{26}H_{24}BrP$ requires C, 69.8 ; H, 5.4%); δ_H (100 MHz) 1.78 (3 H, dd J 19 and 7 Hz, CH_3), 6.53 (1 H, m, CH), 7.0-7.28 (5 H, m, aromatic), 7.41-7.92 (15 H, m, aromatic); δ_P (24.2 MHz) 26.76.

Preparation of α,β:γ,δ-Unsaturated Aldehydes and Ketones and their Tosylhydrazones.

1-Bromo-2-formylalkenes (10). 1-Bromo-2-formylcyclopentene (54%) and 1-bromo-2-formylcyclohexene (27%) were prepared as described by Arnold.[7]

E- and Z-3-Bromo-2-phenylbut-2-enal. Phosphorus tribromide (50.7 g, 0.186 mol) was added over 30 min with stirring and ice cooling to a solution of dimethylformamide (16.4 g, 0.220 mol) in dry chloroform (60 ml). After 30 min a white precipitate formed. Benzyl methyl ketone (10.0 g, 0.075 mol) in dry chloroform (30 ml) was added dropwise and the mixture was stirred for 24 h at room temperature. After evaporation of the solvent the residue was cooled in ice and ice (2000 g) was added. Solid sodium bicarbonate was then added until the mixture was neutral. Extraction with ether (3 x 500 ml), washing with sodium bicarbonate solution and then water, drying, and evaporation gave a viscous black oil. Short column chromatography on silica to remove the tar followed by m.p.l.c. (silica, 25 vol % ether in petroleum) gave (a) Z-3-bromo-2-phenylbut-2-enal as a yellow oil (4.72 g, 28%)(Found: m/z 223.983310. $C_{10}H_9{}^{79}BrO$ requires m/z 223.983726); ν_{max} (film) 1675 (C=O) and 1605 cm^{-1} (C=C); δ_H 2.43 (3 H, s, Me), 6.98-7.47 (5 H, m, phenyl), 10.25 (1 H, s, CHO); m/z 226 (21%), 224 (21), 145 (12), 117 (100), 115 (96). The 2,4-dinitrophenylhydrazone derivative had m.p. 153-155°C (Found: C, 47.2; H, 3.2; N, 13.6 $C_{16}H_{13}BrN_4O_4$ requires C, 47.4; H, 3.2; N, 13.8%), (b)E-3-bromo-2-phenylbut-2-enal as a yellow oil (3.36 g, 20%) (Found: m/z 223.982653. $C_{10}H_9{}^{79}BrO$ requires m/z 223.983726; ν_{max} (liquid) 1670 (C=O) and 1615 cm^{-1} (C=C); δ_H 2.93 (3 H, s, Me), 7.07-7.48 (5 H, m, phenyl), 10.06 (1 H, s, CHO); m/z 226 (32%), 224 (32), 145 (23), 144 (20), 117 (100), 115 (73). The 2,4-dinitrophenylhydrazone derivative had m.p. 147-149°C (Found: C, 47.2; H, 3.3; N, 13.9. $C_{16}H_{13}BrN_4O_4$ requires C, 47.4; H, 3.2; N, 13.8%).

These bromoaldehydes were unstable and were stored at low temperature and used as soon as possible after preparation.

1-Bromo-1,3-dienes (11)

(a) 1-Bromo-2-(2-phenylethenyl)cyclopentene. A solution of sodium ethoxide, prepared from sodium (0.950 g, 41.4 mmol) in dry ethanol (50 ml) was added dropwise to a stirred suspension of benzyltriphenylphosphonium bromide (17.9 g, 41.4 mmol) in dry ethanol (200 ml). This mixture was stirred for 1 h at room temperature and then 1-bromo-2-formylcyclopentene (7.24 g, 41.4 mmol) was added dropwise to the mixture at 0°C. The reaction mixture was stirred at room temperature for 12 h and then heated under reflux for 5 min. The precipitate of sodium bromide was removed by filtration and the solvent was evaporated to leave a brown oil. Triphenylphosphine oxide was removed by gravity chromatography (alumina, petroleum) to give 1-bromo-2-(2-phenylethenyl)cyclopentene (8.48 g) as a mixture of E/Z isomers (2:1). The two isomers were separated by m.p.l.c. (silica, petroleum) to give: (1) E-1-bromo-2-(2-phenylethenyl)cyclopentene (5.5 g, 53%), as white crystals, m.p. 61-62°C (from petroleum) (Found: C, 62.5; H, 5.42. $C_{13}H_{13}Br$ requires C, 62.7; H, 5.3%); δ_H 1.6-2.75 (6 H, m, cyclopentyl), 6.41 and 7.09 (2 H, AB, J 16 Hz, olefinic), 7.15-7.65 (5 H, m, phenyl); m/z 250 (79%), 248 (79), 169 (76), 141 (100), 91 (37). (2) Z-1-bromo-2-(2-phenylethenyl)cyclopentene (2.6 g, 25%) as white crystals, m.p. 35-40°C (from petroleum) (Found: C, 62.85; H, 5.3. $C_{13}H_{13}Br$ requires C, 62.7; H, 5.3%); δ_H 1.6-2.3 and 2.5-2.75 (6 H, m, cyclopentyl), 6.34 and 6.64 (2 H, AB, J 12 Hz, olefinic), 7.05-7.4 (5 H, m, phenyl); m/z 250 (63%), 248 (63), 169 (67), 141 (100), 91 (52).

(b) 1-Bromo-2-(2-phenylethenyl)cyclohexene. A reaction similar to (a) above but using 1-bromo-2-formylcyclohexene gave the bromodiene (30.6 g, 84%) as a ca 2:1 mixture of E and Z isomers (Found: m/z 262.036093. $C_{14}H_{15}{}^{79}Br$ requires m/z 262.035760); δ_H 1.4-1.85 and 2.1-2.75 [8 H, m, cyclohexyl (E and Z isomers)], 7.05-7.5 [6 H, m, phenyl (E and Z isomers)], 6.51 (d, J 16 Hz, E CH=), 6.16 and 6.43 (d, J 12 Hz, Z CH=CH); m/z 264 (31%), 262 (33), 183 (23), 141 (100), 91 (28).

(c) E-1-Bromo-2-(2-phenylpropenyl)cyclohexene. To a stirred suspension of 1-phenylethyltriphenylphosphonium bromide (22 g, 49.2 mmol) in dry ether (500 ml) at 0°C was added n-butyl lithium (1.50 M in hexane, 32.8 ml , 49.2 mmol). The mixture was stirred for 1 h at room temperature to generate the ylid, cooled to 0°C and 1-bromo-2-formylcyclohexene (9.3 g, 49.2 mmol) in dry ether was added dropwise. The resulting mixture was stirred for 1 h at 0°C, 2 h at room temperature and heated under reflux for 1 h. The reaction was allowed to cool before the addition of water (200 ml). The aqueous layer was separated, extracted with ether (2 x 200 ml) and the combined organic layer dried. Evaporation of the solvent gave a yellow oil. Triphenylphosphine oxide was removed by chromatography (alumina, petroleum) to give 1-bromo-2-(2-phenylpropenyl)cyclohexene as an E/Z mixture (9.9 g, 73%). M.p.l.c. (silica, petroleum) of the mixture gave E-1-bromo-2-(2-phenylpropenyl)cyclohexene (9.7 g, 71%) as an oil, b.p. 170°C at 0.1 mmHg (Found: C, 66.1; H, 6.3. $C_{15}H_{17}Br$ requires C, 65.0, H, 6.2%); δ_H 1.62-1.82, 2.11-2.40 and 2.48-2.78 (8 H, m, cyclohexyl), 2.03 (3 H, d, 1 Hz, Me), 6.21 (1 H, m, olefinic), 7.12-7.63 (5 H, m, phenyl); m/z 278 (25%), 276 (25), 197 (97), 155 (100).

(d) 1-Bromo-2-(2-methylpropenyl)cyclohexene. A reaction similar to (c) was carried out using isopropyltriphenylphosphonium bromide (20.4 g, 53 mmol), ether (500 ml), n-butyl-lithium (1.5 M in hexane, 35.3 ml, 53 mmol), stirred for 2 h at room temperature, followed by the addition of 1-bromo-2-formylcyclohexene (10.0 g, 53 mmol) in ether (50 ml). The mixture was stirred for 2 h at room temperature and heated under reflux for 2 h. The usual work-up [(c) above] gave 1-bromo-2-(2-methylpropenyl)cyclohexene (9.0 g, 79%) as an oil b.p. 80°C at 1.0 mmHg (Found: m/z, 214.033547. $C_{10}H_{15}{}^{79}Br$ requires m/z 214.035670); δ_H 1.5-1.91, 2.0-2.31, and 2.42-2.63 (8 H, m, cyclohexyl), 1.63 (3 H, d, J 1 Hz, Me), 1.78 (3 H, d, J 1 Hz, Me), 5.60 (1 H, m, olefinic); m/z 216 (45%), 214 (45), 135 (100).

(e) 1-Bromo-2-vinylcyclohexene. Lithium di-isopropylamide was generated at 0°C from di-isopropylamine (11.8 g, 0.116 mol), N,N,N',N'-tetramethylethylenediamine (13.5 g, 0.116 mol) and n-butyl-lithium (1.4 M in hexane, 82.8 ml, 0.116 mol), and added, under nitrogen, to methyltriphenylphosphonium iodide (51.2 g, 0.126 mol) in dry ether (600 ml) via a direct transfer needle. The resulting mixture was stirred 1 h at room temperature and then 1-bromo-2-formylcyclohexene (20.0 g, 0.106 mol) in dry ether (100 ml) was added dropwise and stirred for 4 h. The usual work-up [(c) above] gave 1-bromo-2-vinylcyclohexene as an oil (11.4 g, 58%), b.p. 90°C at 1 mmHg (Found: m/z, 186.004563. $C_8H_{11}{}^{79}Br$ requires m/z 186.004461); ν_{max} (liquid) 1630 cm^{-1} (C=C); δ_H 1.42-1.86 and 2.08-2.71 (8 H, m, cyclohexyl), 5.0-5.42 (2 H, m, $=CH_2$), 6.91 (1 H, d of d, J 17 and 10 Hz =CH); m/z 188 (50%) 186 (50), 107 (65), 91 (45), 79 (100).

(f) E,-E-4-Bromo-1,3-diphenylpenta-1,3-diene. To a stirred suspension of benzyltriphenylphosphonium bromide (8.42 g, 19.5 mmol) in dry ether (200 ml) at 0°C was added n-butyl-lithium (1.2 M in hexane, 16.2 ml, 19.5 mmol) and stirred for 1 h at room temperature to generate the ylid. The mixture was cooled to 0°C and Z-3-bromo-2-phenylbut-2-enal (4.38 g, 19.5 mmol) in dry ether (25 ml) added dropwise. The mixture was stirred for 1 h at room temperature, heated under reflux for 1 h, cooled to 0°C, and hydrolysed by the dropwise addition of a solution of ammonium chloride (10%, w/v, 100 ml). The usual work-up [(c) above] gave E,E-4-bromo-1,3-diphenylpenta-1,3-diene (4.89 g, 84%), m.p. 51-54°C (from pentane) (Found: C, 68.1; H, 5.3 $C_{17}H_{15}Br$ requires C, 68.2; H, 5.05%); δ_H 2.20 (3 H, s, Me), 5.97 and 7.55 (2 H, AB, J 16 Hz, olefinic), 7.0-7.45 (10 H, m, phenyl); m/z 300 (79%), 298 (79), 219 (100), 204 (94), 141 (26), 115 (40).

(g) E,E-2-Bromo-3,5-diphenylhexa-2,4-diene. A reaction similar to (c) using 1-phenylethyltriphenylphosphonium bromide (17.5 g, 39.1 mmol) and Z-3-bromo-2-phenyl-2-butenal (8.00 g, 35.5 mmol) gave, after the usual work-up and chromatography, E,E-2-bromo-3,5-diphenylhexa-2,4-diene (9.95 g, 89%), m.p. 58.5-59.5°C (Found: C, 69.2; H, 5.3 $C_{18}H_{17}Br$ requires C, 69.0; H, 5.5%); δ_H 1.69 (3 H, d, J 2 Hz, =CPhMe), 2.37 (3 H, d, J 1 Hz, =CMeBr), 6.67 (1 H, m, olefinic), 7.11-7.57 (10 H, m, phenyl); m/z 314 (32%), 312 (32), 233 (100), 218 (98), 115 (45), 91 (68).

(h) 4-Bromo-1,3-diphenylpenta-1,3-diene as an E,Z and Z,Z mixture. A reaction similar to (d) using benzytriphenylphosphonium bromide (18.0 g, 41.5 mmol) and E-3-bromo-2-phenyl-2-butenal (8.48 g, 37.7 mmol) gave, after the usual work up and chromatography, a 3:1 mixture of E,Z- and Z,Z -4-bromo-1,3-diphenylpenta-1,3-diene as an oil (10.3 g, 91%) (Found: m/z, 298.034470. $C_{17}H_{15}{}^{79}Br$ requires m/z, 298.035760); δ_H 2.12 (3 H, s, Z,Z Me), 2.63 (3 H, s, E,Z Me), 6.05 and 6.46 (2 H, AB, J 12 Hz, Z,Z olefinic), 6.01 (1 H, one half of AB, J 16 Hz, E,Z olefinic), 7.07-7.60 (21 H, m, phenyl and E,Z olefinic); m/z 300 (59%), 298 (59), 219 (100), 204 (68), 141 (18), 115 (27), 91 (25).

α, β: γ, δ-Unsaturated carbonyl compounds and their tosylhydrazones

Unless stated otherwise the tosylhydrazones were prepared by mixing equimolar warm (35-40°C), ethanolic solutions of the carbonyl compound and p-toluenesulphonylhydrazide and adding a few drops of concentrated hydrochloric acid. The tosylhydrazone was usually deposited on standing but in some cases evaporation of the solvent and chromatography were required. The tosylhydrazones all gave ^1H n.m.r. spectra consistent with their structures.

1-Acyl-2-alkenylcyclopentenes. (i) E-1-Formyl-2-(2-phenylethenyl)cyclopentene (12a). A Grignard reagent was prepared by the addition of a solution of E-1-bromo-2-(2-phenylethenyl)-cyclopentene (1.4 g, 5.62 mmol) in dry T.H.F. (60 ml) to a stirred suspension of magnesium (0.13 g, 5.62 mmol) in refluxing T.H.F. over 2 h, and then stirred for a further 4 h. This was cooled to 0°C in an ice bath and dry dimethylformamide (0.62 g, 8.4 mmol) in dry T.H.F. (20 ml)

was added dropwise. The reaction mixture was stirred overnight at room temperature, heated under reflux for 1 h, and cooled before the addition of a solution of ammonium chloride (25% w/v, 50 ml). Most of the solvent was removed at reduced pressure, ether (100 ml) was added and the organic phase was separated. The aqueous layer was extracted with ether (3 x 100 ml). The combined organic layers were washed with water (2 x 100 ml) and dried. Evaporation of the solvent gave a dark orange solid (0.76 g). Recrystallisation from ethanol yielded yellow crystals of E-1-formyl-2-(2-phenylethenyl)cyclopentene (0.69 g, 62%) m.p. 103-104°C (Found: C, 84.6; H, 7.25. $C_{14}H_{14}O$ requires C, 84.8; H, 7.1%); ν_{max} (Nujol) 1640 cm^{-1} (C=O); δ_H 1.75-2.1 and 2.55-2.95 (6 H, m, cyclopentyl), 6.80 and 7.62 (2 H, AB, J 16 Hz, olefinics), 7.2-7.6 (5 H, m, phenyl), 10.30 (1 H, s, CHO). Tosylhydrazone (58%) m.p. 147°C (from ethanol) (Found: C, 68.6; H, 6.2; N, 7.5. $C_{21}H_{22}N_2O_2S$ requires C, 68.8; H, 6.05; N, 7.6%); ν_{max} (Nujol) 3210 cm^{-1} (NH).

(ii) E-1-Acetyl-2-(2-phenylethenyl)cyclopentene (12b). Acetaldehyde (5.0 g, 113 mmol) in ether (50 ml) was added dropwise to a Grignard reagent at 0°C prepared from E-1-bromo-2-(2-phenylethenyl)cyclopentene (14.0 g, 56.2 mmol) and magnesium (1.37 g, 56.4 mmol) in ether (175 ml). The mixture was stirred for 5 h at 0°C and 1 h at room temperature. The usual work-up gave a brown oil which was chromatographed (alumina, 30 vol % ether in petroleum) to give E-1-(1-hydroxyethyl)-2-(2-phenylethenyl)cyclopentene (9.86 g, 82%) as yellow crystals m.p. 50-52°C (from light petroleum/ethanol) (Found: C, 83.9; H, 8.4. $C_{15}H_{18}O$ requires C, 84.1; H, 8.5%); ν_{max} (melt) 3380 cm^{-1} (OH); δ_H 1.33 (3 H, d, J 6 Hz, Me), 1.70-2.80 (7 H, m, cyclopentyl and OH), 5.00 (1 H, q, J 6 Hz, CH-Me), 6.48 (1 H, d, J 16 Hz, olefinic), 7.06-7.6 (6 H, m, phenyl and one olefinic). Chromium trioxide (24.6 g, 0.246 mol) was added over 15 min with stirring and ice cooling to dry pyridine (200 ml). The alcohol prepared above (7.54 g, 0.035 mol) in pyridine (30 ml) was added with cooling, the mixture was stirred for 3 h at 0°C and then 18 h at room temperature, ether (1000 ml) added and the dark precipitate was filtered off and washed with ether (3 x 200ml). Water (500 ml) was added to the combined ether layers, the aqueous layer was separated and extracted with ether (2 x 200 ml). The combined ether layers were washed with a solution of 1 M hydrochloric acid (3 x 300 ml), a solution of sodium bicarbonate (20% w/v, 3 x 250 ml), water (2 x 500 ml) and dried. The ether was evaporated under reduced pressure to give a brown oil. T.l.c. indicated one major product and extensive polymerisation. The product was isolated by chromatography (m.p.l.c., silica, ether:petrol 40/60, 1:3) to give a dark yellow oil which was distilled by Kugelrohr apparatus to give E-1-acetyl-2-(2-phenylethenyl)cyclopentene (1.13 g, 15%), b.p. 190° at 0.6 mmHg (Found: m/z 212.118566. $C_{15}H_{16}O$ requires m/z 212.120109; ν_{max} (liquid) 1670 cm^{-1} (C=O); δ_H 1.90 (2 H, quintet, J 7 Hz, cyclopentyl), 2.25 (3 H, s, Me), 2.78 (4 H, t, J 7 Hz, cyclopentyl), 6.77 (1 H, d, J 17 Hz, olefinic), 7.1-7.65 (5 H, m, phenyl), 7.95 (1 H, d, J 17 Hz, olefinic). Other methods of oxidation gave similar low yields of the ketone. The tosylhydrazone was prepared by the usual method and purified by chromatography (silica, 25 vol % ether in petroleum) to give white crystals (52%), m.p. 142-145°C (from ethanol) (Found: C, 69.2; H, 6.6; N, 7.2. $C_{22}H_{24}N_2O_2S$ requires C, 69.4; H, 6.4; N, 7.4%); ν_{max} (Nujol) 3240 cm^{-1} (NH).

(iii) E-1-(p-Toluoyl)-2-(2-phenylethenyl)cyclopentene (12c). A similar reaction to (ii) using the halide (6.5 g, 26.1 mmol), magnesium (0.63 g, 26.1 mmol) and p-tolualdehyde (4.6 g, 38.0 mmol) gave a brown oil which was chromatographed (alumina, 25 vol % ether in petroleum) to give (a) E-1-(p-toluoyl)-2-(2-phenylethenyl)cyclopentene (2.7 g, 36%) as yellow crystals m.p. 56-57°C (from ethanol/light petroleum) (Found: C, 87.4; H. 7.1. $C_{21}H_{20}O$ requires C, 87.5; H, 7.0%); ν_{max} (melt) 1640 cm^{-1} (C=O); δ_H 1.94-2.22 (2 H, m, cyclopentyl), 2.43 (3 H, s, Me), 2.77-3.12 (4 H, m, cyclopentyl), 6.65 and 7.07 (2 H, AB, J 16 Hz), 7.15-7.40 (7 H, m, aromatic), 7.77 (2 H, one half of AB, J 8 Hz, tosyl ArH). The 2,4-dinitrophenylhydrazone derivative had m.p. 195-198°C (Found: C, 69.0; H, 5.15; N, 11.8. $C_{27}H_{24}N_4O_4$ requires C, 69.2; H, 5.2; N, 12.0%), and (b) E(1-hydroxy-1-phenylethyl)-2-(2-phenylethenyl)cyclopentene (3.3 g, 49%) as white crystals m.p. 102-103°C (from ethanol/pentane) (Found: C, 86.7; H, 7.7 $C_{21}H_{22}O$ requires C, 86.85; H, 7.6%); ν_{max} (melt) 3380 cm^{-1} (O-H); δ_H 1.42-2.0 (2 H, m, cyclopentyl), 2.05-2.80 (5 H, m, cyclopentyl and OH), 2.28 (3 H, s, Me), 5.87 (1 H, s, CH-OH), 6.51 (1 H, one half of AB, J 16 Hz, olefinic), 6.93-7.50 (10 H, m, aromatic).

The tosylhydrazone was prepared by warming the usual reaction mixture at 50°C for 1 h. Evaporation of the solvent, addition of dichloromethane, washing with water, drying and evaporation gave a brown solid. Chromatography (silica, 25 vol% ether in petroleum) gave the tosylhydrazone (71%), m.p. 178-180°C (from ethanol/petroleum)(Found: C, 73.6; H, 6.3; N, 5.8. $C_{28}H_{28}N_2O_2S$ requires C, 73.65; H, 6.2; N, 6.1%); ν_{max} (Nujol) 3175 cm^{-1} (NH).

(iv) E-1-Formyl-2-(2-propenyl)cyclopentene (16). A lithium reagent was prepared from 1-bromopropene (5.33 g, 44 mmol) and lithium (0.616 g, 88 mmol) in dry ether (50 ml). The lithium reagent was decanted and then added dropwise to a rapidly stirred solution of 2-methoxy enecyclopentanone[9] (3.70 g, 30 mmol) in dry ether (50 ml) at -50°C. After the addition was complete the mixture was allowed to warm to room temperature and stirred for a further 12 h. Hydrolysis was carried out by the careful addition of hydrochloric acid (10%, 100 ml) at 0°C after which the reaction micture was stirred for a further 8 h. The aqueous layer was washed with ether (3 x 30 ml), the ether extracts were combined with the organic layer, dried and the solvent was evaporated to give a brown oil. Chromatography (silica, ether:petrol 40/60, 1:4) gave E-1-formyl-2-(2-propenyl)-cyclopentene as a colourless liquid (1.27 g, 31.8%), b.p. 83-84°C at 1.5 mmHg (Found: m/z 136.087861. $C_9H_{12}O$ requires m/z 136.088810); ν_{max} (film) 1710 cm^{-1} (C=O); δ_H 1.7-2.1 and 2.5-2.9 (9 H, m, cyclopentyl including Me at 1.91, d, J 6 Hz), 6.1 (1 H, dq, J 16 Hz, J' 6 Hz, CH=CHMe), 7.0 (1 H, d, J 16 Hz, CH=CHMe), 10.17 (1 H, s, CHO). The 2,4-dinitrophenylhydrazone derivative had m.p. 187-188°C (Found: C, 57.2; H, 5.0; N, 17.8. $C_{15}H_{16}N_4O_4$ requires C, 57.0; H, 5.10; N, 17.7%).

Tosylhydrazone. The aldehyde (0.22 g, 1.62 mmol) and p-toluenesulphonyl hydrazide (0.30 g, 1.62 mmol) were stirred in ethanol (20 ml) containing concentrated hydrochloric acid (1 drop) for 2 h. The reaction mixture was neutralised by the addition of solid sodium bicarbonate and most of the

solvent removed at reduced pressure. Dichloromethane (50 ml) was added, and the organic phase separated, washed with water (25 ml) and dried. The solvent was evaporated and the resulting brown oil chromatographed (silica, ether:petrol 40/60, 1:4) to give E-1-formyl-2-(2-propenyl)-cyclopentene tosylhydrazone as a white solid (0.27 g, 54%), m.p. 111-113°C (from ethanol) (Found: C, 63.1; H, 6.8; N, 9.3. $C_{16}H_{20}N_2O_2S$ requires C, 63.1; H, 6.6; N, 9.2%); ν_{max} (Nujol) 3180 cm^{-1} (N-H).

1-Acyl-2-alkenylcyclohexenes. (v) 1-Formyl-2-(2-phenylethenyl)cyclohexene (12e). A reaction similar to (i) was carried out using 1-bromo-2-(2-phenylethenyl)cyclohexene (as a mixture of E and Z isomers) (28.5 g, 0.108 mol), magnesium (2.62 g, 0.108 mol), and dimethylformamide (11.8 g, 0.162 mol). The reaction mixture was stirred at room temperature for 12 h and then worked up in the usual way. Chromatography (silica, 25 vol % ether in petroleum) gave 1-formyl-2-(2-phenylethenyl)cyclohexene (14.0 g, 61%) as yellow crystals m.p. 82-83°C (from ethanol) (Found: m/z 212.120366. $C_{15}H_{16}O$ requires m/z 212.120109; ν_{max} (Nujol) 1645 cm^{-1} (C=O); ^1H n.m.r. showed the presence of E and Z isomers in the ratio ca 9:1, E isomer: 1.5-1.85 and 2.25-2.65 (8 H, m, cyclohexyl), 6.81 and 7.72 (2 H, AB, J 16 Hz, olefinic), 7.2-7.55 (5H, m, aromatic), 10.38 (1 H, s, CHO). The 2,4-dinitrophenylhydrazone derivative had m.p. 215-218°C (Found: C, 64.1; H, 5.05; N, 14.0. $C_{21}H_{20}N_4O_4$ requires C, 64.3; H, 5.1; N, 14.3%). The tosylhydrazone was prepared by the usual method. Chromatography (silica; petroleum 40 vol %, dichloromethane 40 vol %, ether 20 vol %) gave the E-tosylhydrazone (92%), m.p. 125-126°C (from ethanol)(Found: C, 69.2; H, 6.2; N, 7.1. $C_{22}H_{24}N_2O_2S$ requires C, 69.4; H, 6.4; N, 7.4%); ν_{max} (Nujol) 3210 cm^{-1} (NH).

(vi) E-1-Formyl-2-(2-phenylpropenyl)cyclohexene (12j). n-Butyl-lithium (1.5 M in hexane, 26 ml, 39.0 mmol) was added to a solution of E-1-bromo-2-(2-phenylpropenyl)cyclohexene (10.7 g, 38.6 mmol) in anhydrous T.H.F. (150 ml) under N_2, at -78°C. After stirring for 30 min, anhydrous dimethylformamide (8.5 g, 116 mmol) in dry T.H.F. (30 ml) was added dropwise with stirring. The reaction was stirred at -78°C for 4 h, hydrolysed with ammonium chloride solution (25%, w/v, 50 ml) and the mixture allowed to warm to room temperature. Most of the solvent was removed at reduced pressure, ether (200 ml) was added and the aqueous layer separated, extracted with ether (2 x 100 ml) and the combined ether layer washed with water (50 ml) and dried. Evaporation of the solvent gave a brown oil which was chromatographed (silica, ether:petrol 40/60, 1:4) to give E-1-formyl-2-(2-phenylpropenyl)cyclohexene (5.0 g, 58%) as a pale yellow oil (Found: m/z 226.134625. $C_{16}H_{18}O$ requires m/z 226.135758); ν_{max} (film) 1660 cm^{-1} (C=O); δ_H 1.6-1.8 and 2.1-2.5 (8 H, m, cyclohexyl), 2.00 (3 H, d, J 1 Hz, Me), 6.42 (1 H, br q, olefinic), 7.22-7.58 (5 H, m, phenyl), 9.80 (1 H, s, CHO). The 2,4-dinitrophenylhydrazone derivative had m.p. 195-196°C (from ethanol) (Found: C, 64.9; H, 5.4; N, 13.8. $C_{22}H_{22}N_4O_4$ requires C, 65.0; H, 5.45; N, 13.8%). Tosylhydrazone (84%) m.p. 135-136°C (Found: C, 69.9; H, 6.4; N, 7.0. $C_{23}H_{26}N_2O_2S$ requires C, 70.0; H, 6.6; N, 7.1%); ν_{max} (Nujol) 3175 cm^{-1} (N-H).

(vii) 1-Formyl-2-(2-methylpropenyl)cyclohexene (12k). A reaction similar to (vi) but at -60°C was carried out using 1-bromo-2-(2-methylpropenyl)cyclohexene (6.1 g, 28 mmol) and dimethylformamide (3.2 g, 44 mmol). The reaction mixture was stirred for 3 h at -60°C and worked up as described above. Chromatography (silica, 16 vol % ether in petroleum) gave (a) recovered bromodiene (3.2 g, 52%) and (b) 1-formyl-2-(2-methylpropenyl)cyclohexene as an oil (1.6 g, 35%) (Found: m/z 164.120407. $C_{11}H_{16}O$ requires m/z 164.120109; ν_{max} (film) 1670 cm^{-1} (C=O); δ_H 1.45-1.8 and 2.05-2.5 (8 H, m, cyclohexyl), 1.59 (3 H, d, J 1 Hz, Me), 1.83 (3 H, d, J 1 Hz, Me), 5.74 (1 H, br m, olefinic, 9.65 (1 H, s, CHO). The 2,4-dinitrophenylhydrazone derivative had m.p. 167-169°C (Found: m/z 344.147723. $C_{17}H_{20}N_4O_4$ requires m/z 344.148445).

p-Toluenesulphonylhydrazide (0.77 g, 4.15 mmol) in ethanol (20 ml) was added to 1-formyl-2-(2-methylpropenyl)cyclohexene (0.68 g, 4.15 mmol) in ethanol (20 ml) and concentrated hydrochloric acid (1 drop) added. After 2 h t.l.c. indicated the reaction had gone to completion, but no crystals were deposited after 20 h. The solvent was removed at reduced pressure and dichloromethane (100 ml) was added. The organic layer was separated, washed with water (2 x 50 ml), dried, and evaporated to give a brown oil. Chromatography (silica, 25 vol % ether in petroleum) gave 1-formyl-2-(2-methylpropenyl)cyclohexene tosylhydrazone as unstable white crystals (obtained on concentration of chromatography fractions to a reduced volume), m.p. 103-104°C (Found: C, 64.8; H, 7.2; N, 8.3 $C_{18}H_{24}N_2O_2S$ requires C, 65.0; H, 7.3; N, 8.4%); ν_{max} (Nujol) 3180 cm^{-1} (N-H).

(viii) 1-Formyl-2-vinylcyclohexene. n-Butyl-lithium (1.5 M, 33 ml, 49.5 mmol) was added under dry nitrogen to a solution of 1-bromo-2-vinylcyclohexene (6.25 g, 33.4 mmol) in dry T.H.F. (100 ml) at -110°C and stirred for 3 min. Dry dimethylformamide (7.30 g, 100 mmol) in dry T.H.F. (30 ml) was added and the reaction allowed to warm to -78°C before stirring for 3 h. The usual work up gave an oil shown by t.l.c. and h.p.l.c. to consist mainly of the desired product. Extensive decomposition however occurred during preparative chromatography (silica, 20 vol % ether in petroleum) which gave 1-formyl-2-vinylcyclohexene as an oil (1.38 g, 30%) (Found: m/z 136.088254. $C_9H_{12}O$ requires m/z 136.088810); ν_{max} (liquid) 1665 cm^{-1} (C=O); δ_H 1.5-1.9 and 2.15-2.7 (8 H, cyclohexyl), 5.55 (2 H, m, $=CH_2$), 7.39 (1 H, d of d, J 17 and 11 Hz, =C-H), 10.4 (1 H, s, CHO). In subsequent preparations this aldehyde was converted to the tosylhydrazone without prior purification.

p-Toluenesulphonylhydrazide (1.5 g, 8.1 mmol) in ethanol (40 ml) was added to the aldehyde (1.1 g, 8.1 mmol) in ethanol (40 ml) and reaction stirred for 2 h when t.l.c. indicated that the reaction was complete. The solvent was removed under reduced pressure and the resulting solid was recrystallised from ethanol to give 1-formyl-2-vinylcyclohexene tosylhydrazone as unstable, light sensitive white crystals (1.61 g, 65%), m.p. 111-113°C (Found: C, 63.3; H, 6.4; N, 9.2. $C_{16}H_{20}N_2O_2S$ requires C, 63.1; H, 6.6; N, 9.2%); ν_{max} (Nujol) 3170 cm^{-1} (N-H).

(ix) E-1-Acetyl-2-(2-phenylethenyl)cyclohexene (12f). A reaction similar to (ii) was carried out in T.H.F. using E-1-bromo-2-(2-phenylethenyl)cyclohexene (5.8 g, 22.2 mmol), magnesium (0.54 g, 22.2 mmol) and acetaldehyde (2.9 g, 66.6 mmol). The usual work up and chromatography (alumina, 25 vol % ether in petroleum) gave E-1-(1-hydroxyethyl)-2-(2-phenylethenyl)cyclohexene

as an oil (3.07 g, 61%)(Found: m/z 228.151044. $C_{16}H_{20}O$ requires m/z 228.151407; ν_{max} (liquid) 3380 cm^{-1} (O-H); δ_H 1.23 (3 H, d, J 7 Hz, Me), 1.46-1.80 and 2.08-2.80 (9 H, m, OH and cyclohexyl), 5.11 (1 H, q, J 7 Hz, CH-Me), 6.45 (1 H, one half of AB, J 16 Hz, olefinic), 7.1-7.48 (6 H, m, aromatic and olefinic); m/z 228 (42%), 213 (67), 91 (100). A mixture of this alcohol (3.9 g, 17.1 mmol) and barium manganate (76 g, 0.297 mol) in dichloromethane (250 ml) was heated under reflux for 14 days when t.l.c. indicated complete reaction. The solid was filtered off through magnesium sulphate and washed with dichloromethane. The filtrate and washings were combined and evaporated to give a brown oil which was chromatographed (silica, 25 vol % ether in petroleum) to give E-1-acetyl-2-(2-phenylethenyl)cyclohexene (1.21 g, 31%) as yellow crystals m.p. 32-34°C (from ethanol/pentane) (Found: C, 85.2; H, 7.8. $C_{16}H_{18}O$ requires C, 84.9; H, 8.0%); ν_{max} (melt) 1675 cm^{-1} (C=O); δ_H 1.59-1.89 (4 H, m, cyclohexyl), 2.28 (3 H, s, Me), 2.17-2.58 (4 H, m, cyclohexyl), 6.64 (1 H, one half of AB, J 16 Hz, olefinic), 7.0-7.47 (6 H, m, phenyl and olefinic). Oxidation using chromium trioxide in pyridine [c.f. (ii)] gave the same product in 11% yield. Preparation of the tosylhydrazone by the usual method gave a low yield but evaporation of the mother liquor and chromatography (silica, 25 vol % ether in petroleum) gave a total yield of 75%, m.p. 140-142°C (from ethanol) (Found: C, 70.2; H, 6.6; N, 7.3. $C_{23}H_{26}N_2O_2S$ requires C, 70.0; H, 6.6; N, 7.1%); ν_{max} (Nujol) 3180 cm^{-1} (NH).

Acyclic α,β:γ,δ unsaturated aldehydes. (x) E,E-3,5-Diphenyl-2-methylpenta-2,4-dienal (12g). n-Butyl-lithium (1.5 M in hexane, 8.3 ml, 12.5 mmol) was added under dry nitrogen, to a solution of E,E-4-bromo-1,3-diphenylpenta-1,3-diene (3.4 g, 11.4 mmol) in dry T.H.F. (100 ml) at -110°C. The mixture was allowed to warm to -80°C over 10 min and stirred 40 min. Dry dimethylformamide (3.7 g, 50.0 mmol) in dry T.H.F. (10 ml) was added and the mixture stirred for 5 h at -80°C. The usual work up and chromatography (silica, 20 vol % ether in petroleum) gave E,E-3,5-diphenyl-2-methylpenta-2,4-dienal (3.9 g, 81%), m.p. 116-119°C (from ethanol/pentane) (Found: C, 86.8; H, 6.5. $C_{18}H_{16}O$ requires C, 87.1; H, 6.5%); ν_{max} (Nujol) 1645 cm^{-1} (C=O); δ_H 1.70 (3 H, s, Me), 6.32 and 7.92 (2 H, AB, J 16 Hz, olefinic), 7.1-7.6 (10 H, m, phenyl), 10.57 (1 H, s CHO). Tosylhydrazone (79%), m.p. 130-131°C (Found: C, 72.3; H, 5.9; N, 6.6. $C_{25}H_{24}N_2O_2S$ requires C, 72.1; H, 5.8; N, 6.7%); ν_{max} (Nujol) 3190 cm^{-1} (N-H).

(xi) E,E-3,5-Diphenyl-2-methylhexa-2,4-dienal (12i). n-Butyl-lithium (1.5 M in hexane, 10.2 ml, 15.4 mmol) was added under dry nitrogen to a solution of E,E-2-bromo-3,5-dphenylhexa-2,4-diene (4.37 g, 14.0 mmol) in dry T.H.F. (100 ml) at -110°C, stirred for 30 seconds and dry dimethylformamide (6.11 g, 84.0 mmol) in dry T.H.F. (20 ml) added. The mixture was stirred for 4 h at -110°C and the reaction hydrolysed by the addition of a solution of ammonium chloride (10% w/v, 100 ml), warmed to room temperature and ether (250 ml) added. Extraction, drying, evaporation and chromatography (silica, 25 vol % ether in petroleum) gave E,E-3,5-diphenyl-2-methylhexa-2,4-dienal as a yellow oil (2,75 g, 75%) (Found: m/z 262.135403. $C_{19}H_{18}O$ requires m/z 262.135758); ν_{max} (liquid) 1670 cm^{-1} (C=O); δ_H 1.92 (3 H, d, J 2 Hz, Me), 2.03 (3 H, d, J 1 Hz, Me), 6.58 (1 H, m, olefinic), 7.09-7.59 (10 H, m, phenyl), 9.95 (1 H, s, CHO). The 2,4-dinitrophenylhydrazone derivative had m.p. 172-173°C (Found: C, 67.9; H, 5.10; N, 12.7. $C_{25}H_{22}N_4O_4$ requires C, 67.9; H, 5.0; N, 12.7%). Tosylhydrazone (77%), m.p. 160-162°C (from ethanol) (Found: C, 72.3; H, 6.0; N, 6.8. $C_{26}H_{26}N_2O_2S$ requires C, 72.5; H, 6.1; N, 6.5%); ν_{max} (Nujol) 3180 cm^{-1} (N-H).

(xii) Z,E-3,5-Diphenyl-2-methylpenta-2,4-dienal (14g). n-Butyl-lithium (1.5 M in hexane, 13.6 ml, 20.4 mmol) was added under dry nitrogen to a solution of E,Z- and Z,Z-4-bromo-1,3-diphenylpenta-1,3-diene (E,Z:Z,Z, 3:1) (6.11 g, 20.4 mmol) in dry T.H.F. (150 ml) at -110°C. The mixture was allowed to warm to -78°C over 10 min and dry dimethylformamide (4.47 g, 61.3 mmol) in dry T.H.F. (20 ml) added and stirred for 5 h. Work up as in (xi) and chromatography (silica, 20 vol % ether in petroleum) gave Z,E-3,5-diphenyl-2-methylpenta-2,4-dienal (2.71 g, 53%), m.p. 62-63°C (from ethanol/pentane) (Found: C, 86.85; H, 6.30. $C_{18}H_{16}O$ requires C, 87.1; H, 6.5%); ν_{max} (melt) 1660 cm^{-1} (C=O); δ_H 2.11 (3 H, s, Me), 6.42 and 7.58 (2 H, AB, J 16 Hz, olefinic), 7.0-7.48 (10 H, m, phenyl), 9.38 (1 H, s, CHO). Tosylhydrazone (69%), m.p. 162-163°C (from ethanol) (Found: C, 72.3; H, 5.80; N, 6.9. $C_{25}H_{24}N_2O_2S$ requires C, 72.1; H, 5.8; N, 6.7%); ν_{max} (Nujol) 3140 cm^{-1} (N-H).

Thermal Decomposition of the Sodium Salts of the Tosylhydrazones. - The sodium salts were prepared by the addition of the solid tosylhydrazone (ca 5% molar excess) to a solution of sodium ethoxide in dry ethanol. The solution was then stirred in the dark for 0.5 h. In some cases, the sodium salt precipitated out at this stage. The ethanol was evaporated under reduced pressure, under anhydrous conditions, and with a temperature below 45°C. The sodium salt was then dried under high vacuum over phosphorus pentoxide for at least 12 h in the dark.

Freshly distilled dry solvent was added and the reaction mixture boiled under reflux. with stirring, under dry nitrogen in the dark. During the decomposition, small samples of the reaction mixture were withdrawn and shaken with water to hydrolyse any residual sodium salt, and extracted with ether. The ether layer was analysed for unreacted tosylhydrazone by t.l.c., and the reaction continued until no tosylhydrazone remained. After cooling the sodium p-toluenesulphinate was removed by filtration through Celite and the filtrate was evaporated to give the crude product. Chromatography columns were wrapped in foil to exclude light.

Acylcyclopentene tosylhydrazones. E-1-Formyl-2-(2-propenyl)cyclopentene tosylhydrazone (21d)* The tosylhydrazone (0.31 g, 1.02 mmol) salt was boiled under reflux for 1 h in cyclohexane (50 ml). Chromatography (alumina, 20 vol % ether in petroleum) gave 6,7,8-trihydro-4-methyl-1H-cyclopenta[d][1,2]diazepine (23d) as a yellow oil (98 mg, 65%), b.p. 80°C at 0.3 mmHg (Found: C, 72.9; H, 8.3; N, 18.8. $C_9H_{12}N_2$ requires C, 72.9; H, 8.2, N, 18.9%); δ_H 1.80-1.97 (3 H, m, cyclopentyl CH_2 and ax 1-H), 2.32 (3 H, s, Me), 2.34-2.69 (4 H, m, cyclopentyl CH_2), 5.84 (1 H, d, J 8 Hz, eq 1-H), 5.86 (1 H, s, 5-H).

* The number in parenthesis after each tosylhydrazone refers to the structure of the diazo compound being generated.

E-1-Formyl-2-(2-phenylethenyl)cyclopentene tosylhydrazone (21a). The tosylhydrazone (0.34 g, 0.93 mmol) salt was boiled under reflux for 1 h in cyclohexane (100 ml); chromatography (alumina, 20 vol % ether in petroleum) gave 6,7,8-trihydro-4-phenyl-1H-cyclopenta[d][1,2]diazepine (23a) (123 mg, 63%), as an oil (Found: m/z 210.116074. $C_{14}H_{14}N_2$ requires m/z 210.115693); δ_H 1.75-2.39 (3 H, m, cyclopentyl CH_2 and ax 1-H), 2.40-3.10 (4 H, m, cyclopentyl CH_2), 6.08 (1 H, d, J 9 Hz, 1-H), 6.38 (1 H, s, 5-H), 7.13-7.53 (3 H, m, aromatic), 7.65-7.85 (2 H, m, aromatic).
E-1-Acetyl-2-(2-phenylethenyl)cyclopentene tosylhydrazone (21b). The tosylhydrazone (0.53 g, 1.40 mmol) in cyclohexane (100 ml) was boiled under reflux for 1.5 h; chromatography (alumina, 10% ether in petroleum) gave 6,7,8-trihydro-1-methyl-4-phenyl-1H-cyclopenta[d][1,2]diazepine (23b) (0.23 g, 76%), as a yellow oil (Found: m/z 224.130249. $C_{15}H_{16}N_2$ requires m/z 224.131342); δ_H (360 MHz) 1.93-2.12 (2 H, m, cyclopentyl CH_2), 2.52-2.83 (4 H, m, cyclopentyl CH_2) with a 2.11 (4 H, s, Me and ax 1-H) superimposed (the addition of Eu(fod)$_3$ shifted the peaks at δ2.11 to higher frequencies as the expected d and q, J = 7 Hz), 6.39 (1 H, s, 5-H), 7.30-7.44 (3 H, m, aromatic), 7.77-7.81 (2 H, m, aromatic).
E-1-(p-Toluoyl)-2-(2-phenylethenyl)cyclopentene tosylhydrazone (21c). The tosylhydrazone (0.50 g, 1.08 mmol) in cyclohexane (100 ml) was boiled under reflux for 1 h; chromatography (silica, 10 vol % ether in petroleum) gave (a) 3H-4,5,6-trihydro-2-phenyl-3-p-tolylpentalene (25) (118 mg, 40%) as an oil (Found: m/z 272.155653. $C_{21}H_{20}$ requires m/z 272.156493; δ_H 2.12-2.82 (6 H, m, cyclopentyl), 2.28 (3 H, s, Me), 3.26 (1 H, br, s, CH), 6.68-7.50 (10 H, m, aromatic and olefinic); δ_C (90 MHz) 20.9 (Me), 28.2 (C-5), 29.6 (C-4), 40.2 (C-6), 64.8 (C-3), 125.8 (C-1), 127.6 (aromatic CH), 128.0 (aromatic CH), 128.4 (aromatic CH), 128.9 (aromatic CH), 134.0 (tert.), 136.2 (tert.), 137.9 (tert.), 142.0 (tert.), 147.9 (tert.), 152.1 (tert.); m/z 272 (100%), 105 (20), 91 (15). (b) 6,7,8-trihydro-4-phenyl-1-p-tolyl-1H-cyclopenta[d][1,2]-diazepine (23c) (24 mg, 9%) as a yellow oil (Found: m/z 300.164265. $C_{21}H_{20}N_2$ requires m/z 300.162641); δ_H (100 MHz) 1.81-3.08 (7 H, m, cyclopentyl CH_2 and ax 1-H) with 2.39 (3 H, s, tolyl Me) superimposed, 6.50 (1 H, br, s, 5-H), 6.85-7.90 (9 H, m, aromatic).

Acylcyclohexene tosylhydrazones. E-1-Formyl-2-(2-phenylethenyl)cyclohexene toshylhydrazone (21e). The tosylhydrazone (1.05 g, 2.76 mmol) salt in cyclohexane (100 ml) was boiled under reflux for 1 h, filtered through Celite and the filtrate evaporated to give 6,7,8,9-tetrahydro-4-phenyl-1H-cyclohexa[d][1,2]diazepine (23e) (0.57 g, 92%), m.p. 111-113°C (from ethanol/pentane) (Found: C, 80.1; H, 7.3 ; N, 12.4. $C_{15}H_{16}N_2$ requires C, 80.3; H, 7.2; N, 12.5%); δ_H 1.60-1.95 (4H, m, cyclohexyl), 2.15-2.90 (5 H, m, cyclohexyl and ax 1-H), 5.82 (1 H, d, J 8 Hz, eq 1-H), 6.28 (1 H, s, 5-H), 7.10-7.52 (3 H, m, aromatic), 7.62-7.90 (2 H, m, aromatic).
E-1-Acetyl-2-(2-phenylethenyl)cyclohexene tosylhydrazone (21f). The tosylhydrazone (0.50 g, 1.28 mmol) salt in cyclohexane (100 ml) was boiled under reflux for 2.5 h; chromatography (alumina, 25% ether in petroleum) gave 6,7,8,9-tetrahydro-1-methyl-4-phenyl-1H-cyclohexa[d][1,2]-diazepine (23f) as a yellow oil (168 mg, 56%) (Found: m/z 238.145250. $C_{16}H_{18}N_2$ requires m/z 238.145250; δ_H (360 MHz) 1.37-1.87 (4 H, m, cyclohexyl), 2.32-2.54 (4 H, m, cyclohexyl), 2.02 (3 H, d, J 6.4 Hz, Me), 2.12 (1 H, br, q, J 6.4 Hz, 1-H), 6.30 (1 H, s, 5-H), 7.30-7.43 (3 H, m, aromatic), 7.78-7.81 (2 H, m, aromatic).
E-1-Formyl-2-(2-phenylpropenyl)cyclohexene tosylhydrazone (51a). The tosylhydrazone (3.37 g, 8.56 mmol) salt in cyclohexane (120 ml) was heated under reflux. A red colour was generated due to the diazo compound and the reaction was monitored by I.R. (2060 cm^{-1}) until the diazo compound had been consumed (2 h). Filtration and evaporation of the filtrate gave a black oil shown by t.l.c. to contain two major components, many minor products and polymeric material. Chromatography (alumina, 20 vol% ether in petroleum) gave (a) E-4,5,6,7-tetrahydro-1-(2-phenylpropenyl)indazole (53a) as a pale yellow oil (191 mg, 9.4%) (Found: m/z 238.145712. $C_{16}H_{18}N_2$ requires m/z 238.146991); δ_H 1.25-1.90 (4 H, m, cyclohexyl), 2.34 (3 H, d, J 1.5 Hz), 2.45-2.65 (4 H, m, cyclohexyl), 6.84 (1 H, q, J 1.5 Hz, olefinic), 7.20-7.54 (6 H, m, aromatic); m/z 238 (65%), 237 (30), 136 (25), 135 (100). This product was identical by t.l.c., ^{1}H n.m.r. and ^{13}C n.m.r. to the product obtained from thermolysis of E-4,5,6,7-tetrahydro-7a-(2-phenylpropenyl)-indazole in 1,2-dimethoxyethane, (b) E-4,5,6,7-tetrahydro-7a-(2-phenylpropenyl)indazole (52a) (0.865 g, 42%), m.p. 71-72°C (from dichloromethane/pentane) (Found: C, 80.9; H, 7.4; N, 11.7. $C_{16}H_{18}N_2$ requires C, 80.6; H, 7.6; N, 11.75%); δ_H (360 MHz) [0.52-0.60 (1 H, d of t, J 12.9 and 4.2 Hz), 1.09-1.24 (1 H, m), 1.61-1.76 (2 H, m), 2.03-2.29 (2 H, m), 2.90 (1 H, d of d, J 13.1 and 3 Hz), 2.99-3.04 (1 H, m), cyclohexyl], 1.64 (3 H, d, J 1.2 Hz, Me), 5.82 (1 H, br, q, J 1.2 Hz, olefinic), 7.21-7.36 (5 H, m, aromatic), 7.46 (1 H, d, J 1.1 Hz, 3-H).
1-Formyl-2-(2-methylpropenyl)cyclohexane tosylhydrazone (51b). The tosylhydrazone (0.92 g, 2.77 mmol) salt in cyclohexane (100 ml) was boiled under reflux for 2 h; flash chromatography (silica, 20 vol % ether in petroleum) gave E-4,5,6,7-tetrahydro-7a-(2-methylpropenyl)indazole (52b) as a yellow oil (54 mg, 11%) (Found: m/z 176.131342. $C_{11}H_{16}N_2$ requires m/z 176.130457), as the only isolable product, δ_H (80 MHz) [0.40-0.60 (1 H, m), 0.80-2.03 (5 H, m), 2.73-2.92 (2 H, m), cyclohexyl], 1.69 (3 H, d, 1.3 Hz, Me), 1.75 (3 H, d, 1.1 Hz, Me), 5.29 (1 H, br, m, olefinic), 7.34 (1 H, d, 1.5 Hz, 3-H).

Acyclic dienal tosylhydrazones. E,E-3,5-Diphenyl-2-methylpenta-2,4-dienal tosylhydrazone (21g). The tosylhydrazone (0.67 g, 1.62 mmol) salt in cyclohexane was boiled under reflux for 1 h. Work up and chromatography (alumina, 20% ether in petroleum) gave 4-methyl-5,7-diphenyl-3H-1,2-diazepine (23g). (0.30 g, 71%) as a yellow oil (Found: m/z 260.129349. $C_{18}H_{16}N_2$ requires m/z 260.131342); δ_H (100 MHz) 2.11 (3 H, s, Me), 2.35 (1 H, d of d, J 8 and 1 Hz, ax 3-H), 6.09 (1 H, d, J 8 Hz, eq 3-H), 6.49 (1 H, s, 6-H), 7.05-7.50 (8 H, m, aromatic), 7.62-7.88 (2 H, m, aromatic).
Z,E-3,5-Diphenyl-2-methylpenta-2,4-dienal tosylhydrazone (32). The tosylhydrazone (0.60 g, 1.44 mmol) salt in cyclohexane (100 ml) was boiled under reflux for 1 h. Work up and chromatography (silica, 25% ether in petroleum) gave: (a) 4-Methyl-5,7-diphenyl-3H-1,2-diazepine (23g) (50 mg, 13%), identical with that obtained above, (b) E-4-Methyl-5-phenyl-1-(2-phenylethenyl)-1H-pyrazole (34) as a yellow oil (122 mg, 33%) (Found: m/z 260.129863. $C_{18}H_{16}N_2$ requires m/z 260.131342); δ_H 2.06 (3 H, s, 4-Me), 6.26 (1 H, d, J 11 Hz, 2'-H), 6.66 (1 H, d, J 11 Hz, 1'-H), 6.81-7.75 (10 H, m, aromatic), 7.50 (1 H, s, 3-H); m/z 260 (100), 259 (100),

183 (57), 158 (98), 130 (55%). Hydrogenation of this pyrazole (35 mg) in methanol (25 ml) at atmospheric pressure using 10% palladium on charcoal (34 mg) as catalyst gave 4-methyl-5-phenyl-1-phenethyl-1H-pyrazole (24 mg, 69%) as an oil (Found: m/z 262.145682. $C_{18}H_{18}N_2$ requires m/z 262.146991) with identical spectra and physical characteristics to an authentic sample (see later), (c) E-4-Methyl-3-phenyl-5-(2-phenylethenyl)-1H-pyrazole (37) (74 mg, 20%), m.p. 193-194°C (from ethanol) (Found: C, 82.8; H, 5.9; N, 10.6. $C_{18}H_{16}N_2$ requires C, 83.0; H, 6.2; N, 10.8%); δ_H (100 MHz) (C_2D_6SO) 2.28 (3 H, s, 4-Me), 7.10-7.80 (12 H, m, aromatic and olefinic), 12.96 (1 H, br, NH); m/z 260 (100), 259 (87), 156 (14), 130 (18), 77 (19%). Hydrogenation of this pyrazole (52 mg) in methanol (30 ml) at atmospheric pressure for 20 min using 10% palladium on charcoal (40 mg) as catalyst gave a brown oil which was purified by preparative t.l.c. (silica, 33% ether in petroleum) to give 4-methyl-3-phenyl-5-phenethylpyrazole (30 mg, 57%), m.p. 102-103°C (from ethanol) (Found: C, 82.3; H, 6.90; N, 10.6. $C_{18}H_{18}N_2$ requires C, 82.4; H, 6.90; N, 10.7%) with identical spectral and physical characteristics to an authentic sample (see later).

In a similar experiment carried out in refluxing toluene the yields were: 4-methyl-5,7-diphenyl-3H-[1,2]-diazepine (6%), E-4-methyl-5-phenyl-1-(2-phenylethenyl)-1H-pyrazole (7%), E-4-methyl-3-phenyl-5-(2-phenylethenyl)-1H-pyrazole (61%).

E,E-3,5-Diphenyl-2-methylhexa-2,4-dienal tosylhydrazone (45). The tosylhydrazone (3.39 g, 7.88 mmol) salt in cyclohexane (200 ml) was boiled under reflux for 1 h. Work up and chromatography (alumina, 25% ether in petroleum) gave: (a) E-4-Methyl-5-phenyl-1-(2-phenylpropenyl)-1H-pyrazole (47) (0.67 g, 32%), as a yellow oil (Found: m/z 274.145588. $C_{19}H_{18}N_2$ requires m/z 274.146991); δ_H (360 MHz) 2.09 (3 H, s, 4-Me), 2.21 (3 H, d, J 2 Hz, =CMePh), 6.81 (1 H, br, q, J 2 Hz, 1'-H), 7.15-7.45 (10 H, m, aromatic), 7.55 (1 H, s, 3-H); m/z 274 (27), 273 (15), 171 (100), 125 (24%). This pyrazole (84 mg, 0.32 mmol) in methanol (25 ml) was hydrogenated for 20 min at atmospheric pressure using 10% palladium on charcoal (48 mg) as catalyst. Filtration, evaporation and preparative t.l.c. (silica, 20% ether in petroleum) gave 4-methyl-5-phenyl-1-(2-phenylpropyl)-1H-pyrazole (64 mg, 76%) as an oil (Found: m/z 276.162641. $C_{19}H_{20}N_2$ requires m/z 276.160337); δ_H 1.12 (3 H, d, J 7 Hz, 2'-Me), 1.88 (3 H, s, 4-Me), 3.34 (1 H, sextet, J 7 Hz, 2'-H), 4.08 (2 H, d, J 7 Hz, 1'-H_2), 6.80-7.50 (11 H, m, aromatic and 3-H).

(b) Z-4-Methyl-5-phenyl-1-(2-phenylpropenyl)-1H-pyrazole (0.11 g, 5%) as an oil (Found: m/z 274.145852. $C_{19}H_{18}N_2$ requires m/z 274.146991); δ_H (360 MHz) 1.94 (3 H, s, 4-Me), 2.01 (3 H, d, J 1.5 Hz, 2'-Me), 6.78 (1 H, br, q, J 1.5 Hz, 1'-H), 6.58-6.62 and 6.87-7.24 (10 H, m, aromatic), 7.43 (1 H, s, 3-H). Hydrogenation gave a saturated pyrazole identical with that prepared in (a) above.

(c) E-4-Methyl-3-phenyl-5-(2-phenylpropenyl)-1H-pyrazole (50) (0.62 g, 30%), m.p. 145-146°C (from ethanol/pentane) (Found: C, 83.25; H, 6.6; N, 10.3. $C_{19}H_{18}N_2$ requires C, 83.2; H, 6.6; N, 10.2%); ν_{max} (Nujol) 3260 cm^{-1} (NH); δ_H (100 MHz) 2.19 (3 H, s, 4-Me), 2.34 (3 H, d, J 2 Hz, 2'-Me), 6.54 (1 H, br, q, J 2 Hz, 1'-H), 7.15-7.63 (10 H, m, aromatic), 9.60 (1 H, br, NH); m/z 274 (100), 273 (98), 259 (12), 115 (36), 105 (35), 91 (30%). Hydrogenation of this pyrazole (37 mg, 0.14 mmol) as described above and purification by preparative t.l.c. (silica, 50 vol % ether in petroleum) gave 4-methyl-3-phenyl-5-(2-phenylpropyl)-1H-pyrazole (23 mg, 62%) as an oil (Found: m/z 276.161921. $C_{19}H_{20}N_2$ requires m/z 276.162641); ν_{max} (Nujol) 3180 cm^{-1} (NH); δ_H (360 MHz) 1.30 (3 H, d, J 7 Hz, 2'-Me), 2.00 (3 H, s, 4-Me), 2.86 (2 H, m, 1'-H_2), 3.09 (1 H, sextet, J 7 Hz, 2'-H), 6.26 (1 H, br, NH), 7.18-7.56 (10 H, m, aromatic).

E,E-2,5-Dimethylocta-4,6-dien-3-one tosylhydrazone (28a). The tosylhydrazone (0.44 g, 1.38 mmol) salt in cyclohexane (60 ml) was boiled under reflux for 1½ h; chromatography (alumina, 50% ether in petroleum) gave E-3-isopropyl-5-methyl-4-propenyl-1H-pyrazole (31a) (0.14 g, 62%), m.p. 56-59°C (Found: m/z 164.129099. $C_{10}H_{16}N_2$ requires m/z 164.131342); ν_{max} (Nujol) 3160 cm^{-1} br (NH); δ_H (80 MHz) 1.25 (6 H, d, J 7 Hz, $CHMe_2$), 1.80 (3 H, d of d, J 6.2 and 1.4 Hz, 2'-Me), 2.21 (3 H, s, 5-Me), 3.07 (1 H, septet, J 7 Hz, $CHMe_2$), 5.70 (1 H, d of q, J 16 and 6.2 Hz, 2'-H), 6.27 (1 H, d of q, J 16 and 1.4 Hz, 1'-H), 8.56 (1 H, br, NH).

4-Methyl-6-phenylhexa-3,5-dien-2-one tosylhydrazone (28b). The tosylhydrazone (0.56 g, 1.58 mmol) salt in cyclohexane (60 ml) was boiled under reflux for 30 min. Flash chromatography (silica, 33% ether in petroleum) gave E-3,5-dimethyl-4-(2-phenylethenyl)-1H-pyrazole (31b) (0.17 g, 55%), m.p. 179-180°C (Found: C, 78.6; H, 6.9; N, 14.30. $C_{13}H_{14}N_2$ requires C, 78.75; H, 7.1; N, 14.1%); ν_{max} (Nujol) 3160 cm^{-1}, br (NH); δ_H (80 MHz) 2.39 (6 H, s, 3- and 5-Me), 6.69 (1 H, d, J 17 Hz, 2'-H), 6.93 (1 H, d, J 17 Hz, 1'-H), 7.21-7.48 (6 H, m, aromatic and NH).

Preparation of Pyrazoles for Comparison

4-Methyl-5-phenethyl-1-phenyl-1H-pyrazole (44). (i) 2-Methyl-3-oxo-5-phenylpentanal. A solution of 1-phenylpentan-3-one[30] (5.0 g, 31 mmol) and ethyl formate (2.29 g, 31 mmol) in ether (50 ml) was added dropwise to dry sodium ethoxide powder (2.1 g, 31 mmol) in ether (25 ml) at 0°C. After stirring for 7 h at room temperature, the mixture was cooled to 0°C, and hydrolysed by the addition of hydrochloric acid (2 M, 25 ml). The aqueous layer was separated, extracted with ether (2 x 200ml) and the organic layer washed withsodium bicarbonate solution (10% w/v, 2 x 50 ml), water (2 x 50 ml), and dried over anhydrous sodium sulphate. The solvent was evaporated and the resulting brown oil distilled to give 2-methyl-3-oxo-5-phenylpentanal (3.1 g, 54%), b.p. 98-100°C at 0.4 mmHg as a clear oil which solidified and was crystallised from pentane/ethanol, m.p. 60-62°C (Found: C, 76.0 ; H, 7.1. $C_{12}H_{14}O$ requires C, 75.8; H, 7.4%); ν_{max} (Nujol) 3150 cm^{-1} (OH), 1670 and 1605 cm^{-1} (C=O); δ_H 1.70 (3 H, s, Me), 2.59-3.10 (4 H, m), 7.00-7.47 (5 H, m, phenyl), 7.65 (1 H, d, J 9 Hz, =CH-OH), 14.60 (1 H, d, J 9 Hz, O-H); m/z 190 (86%), 162 (21), 105 (87), 91 (100), 85 (98). (ii) 4-Methyl-5-phenethyl-1-phenyl-1H-pyrazole. A solution of 2-methyl-3-oxo-5-phenylpentanal (0.71 g, 3.72 mmol) and phenylhydrazine hydrochloride (0.54 g, 3.72 mmol) in methanol (30 ml) was boiled under reflux for 40 min. The solvent was evaporated, dichloromethane (100 ml) added and the solution was washed with water (2 x 30 ml). The organic layer was separated, dried and evaporated to give an oil which on chromatography (silica, 50 vol % ether in petroleum) gave 4-methyl-5-phenethyl-1-phenyl-1H-pyrazole (0.45 g, 46%) as an oil (Found: m/z 262.146967. $C_{18}H_{18}N_2$ requires m/z 262.146991); δ_H 1.97 (3 H, s, 4-Me), 2.5-2.73 (2 H, m, 1'-H_2), 2.8-3.1 (2 H, m, 2'-H_2), 6.80-7.05 (2 H, m, aromatic), 7.10-7.50 (9 H, m, aromatic and NH).

4-Methyl-3-phenyl-1-phenethyl-1H-pyrazole (39) and 4-methyl-5-phenyl-1-phenethyl-1H-pyrazole (40). 2-Benzoylpropanal[31] (1.0 g, 6.2 mmol) and 2-phenylethylhydrazine[32] (0.84 g, 6.2 mmol) in ethanol (50 ml) containing conc. hydrochloric acid (1 drop) were heated under reflux for 8 h. The mixture was worked up as described in the previous experiment. Chromatography (silica, 25% ether in petroleum) gave (a) 4-methyl-3-phenyl-1-phenethyl-1H-pyrazole (39) (0.27 g, 17%) as an oil (Found: m/z 262.145168. $C_{18}H_{18}N_2$ requires m/z 262.146991); δ_H (200 MHz) 2.22 (3 H, d, 0.8 Hz, 4-Me), 3.22 (2 H, t, J 7.3 Hz, 2'-H_2), 4.33 (2 H, t, J 7.3 Jz, 1'-H_2), 7.06 (1 H, br, q, J 0.1 Hz, 5-H), 7.14-7.50 (8 H, m, aromatic), 7.73-7.78 (2 H, m, aromatic), (b) 4-Methyl-5-phenyl-1-phenethyl-1H-pyrazole (40) (0.58 g, 36%) as an oil (Found: m/z 262.146967. $C_{18}H_{18}N_2$ requires m/z 262.146991); δ_H (200 MHz) 1.97 (3 H, s, 4-Me), 3.08 (2 H, t, J 7.5 Hz, 2'-H_2), 4.20 (2 H, t, J 7.5 Hz, 1'-H_2), 7.47 (1 H, s, 3-H), 6.92-7.39 (10 H, m, aromatic).

4-Methyl-3-phenyl-5-phenethyl-1H-pyrazole (42). (i) 1,5-Diphenyl-2-methylpenta-1,3-dione. A mixture of 1,5-diphenylpenta-1,3-dione[33] (1.4 g, 5.6 mmol), methyl iodide (0.97 g, 6.84 mmol) and anhydrous potassium carbonate (0.76 g, 5.6 mmol) in dry acetone (60 ml) was boiled under reflux for 24 h. Most of the solvent was evaporated and dichloromethane (60 ml) and water (60 ml) were added. The aqueous layer was separated, extracted with dichloromethane (2 x 30 ml) and the combined organic layers were dried and evaporated to give a yellow oil. Chromatography (silica, 25% ether in petroleum) gave 1,5-diphenyl-2-methylpenta-1,3-dione (1.20 g, 81%) as an oil (Found: m/z 266.129778. $C_{18}H_{18}O_2$ requires m/z 266.130672); ν_{max} (film) 1720 (C=O) and 1675 cm^{-1} (C=O); δ_H 1.38 (3 H, d, J 7 Hz, Me), 2.55-2.30 (4 H, m, 2 x CH_2), 4.43 (1 H, q, H 7 Hz, CH), 6.95-7.95 (10 H, m, aromatic). (ii) 4-Methyl-3-phenyl-5-phenethyl-1H-pyrazole. A mixture of 1,5-diphenyl-2-methylpenta-1,3-dione (0.89 g, 3.35 mmol) and hydrazine hydrate (0.17 g, 3.35 mmol) in methanol (15 ml) was boiled under reflux for 1 h. The usual work up and chromatography (silica, 33% ether in petroleum) gave 4-methyl-3-phenyl-5-phenethylpyrazole (0.58 g, 66%), m.p. 103-104°C (Found: C, 82.3; H, 6.8; N, 10.6. $C_{18}H_{18}N_2$ requires C, 82.4; H, 6.9; N, 10.7%); ν_{max} (Nujol) 3240 cm^{-1} (NH); δ_H (100 MHz) 2.02 (3 H, s, 4-Me), 2.87 (4 H, s, CH_2CH_2), 7.05-7.60 (10 H, m, aromatic), 7.65 (1 H, br, NH).

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