Electrocyclic Aromatic Substitution by the Diazo Group. Part 2.[1] Ring Size Effects on the Cyclisation of 1-Aryl-3-diazoalkenes: a New Rearrangement of 3*H*-Pyrazoles to 3*H*-1,2-Benzodiazepines [2]

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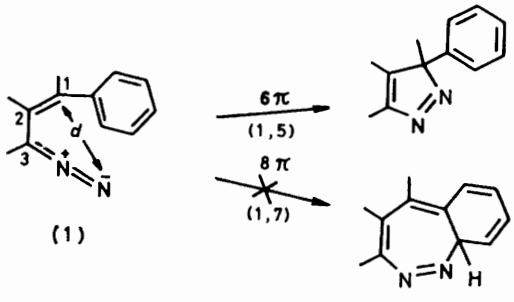
The reactions of the unsaturated diazo compounds derived from the tosylhydrazone salts of 1-acyl-2-arylcycloalkenes have been studied and the results compared with the analogous reactions of 1-diazo-2-diarylmethylenecycloalkanones. In 1-aryl-2-(1-diazoethyl)cyclopentenes (18) the cyclopentyl ring has a less inhibiting effect on the 6π-electron cyclisation than in (2), and compounds (18) are the first 1-aryl-3-diazo-alkenes to undergo both 6π- and 8π-electron cyclisation to give the 3*H*-pyrazoles (20) and 3*H*-1,2-benzodiazepines (21). The strained pyrazoles (20) undergo a novel thermal ring transformation to give the diazepines (21) rather than the usual van Alphen–Huttel rearrangement of 3*H*-pyrazoles. An increase in the size of the annelated ring results in the usual preference for 6π-electron cyclisation, *e.g.* 1-phenyl-2-(1-diazoethyl)cyclohexene (24) gives a 3*H*-pyrazole (25) which on heating does not ring expand to a diazepine but undergoes an unusual van Alphen–Huttel rearrangement involving shift of an alkyl- rather than an aryl-group. 1-Phenyl-2-(1-diazophenylmethyl)cyclopentene (32), 3-phenyl-2-(1-diazoethyl)indene (35), and 1-methyl-2-(1-diazoethyl)cyclopentene (37) do not cyclise but react only *via* loss of nitrogen to give carbene-derived products.

In a recent investigation [1] into the cyclisation reactions of 1-aryl-3-diazoalkenes (1) we showed that although the normally preferred mode of cyclisation was *via* a 6π-electron 1,5-ring closure to give pyrazoles (Scheme 1) this process could be inhibited by the fusion of a cyclopentyl ring at C-2,C-3. Such compounds, *e.g.* (2), cyclised only *via* the alternative 8π-electron 1,7-ring closure to give 3*H*-1,2-benzodiazepines (4) (Scheme 2). Similarly, analogues of (2) with two alkyl groups on the β-carbon, *e.g.* (6), also failed to give 3*H*-pyrazoles but reacted instead *via* carbene formation (Scheme 3). This inhibition of the 6π-electron 1,5-cyclisation was attributed (*a*) to the effect of the cyclopentyl ring in increasing the separation [*d* in (1)] between the terminal

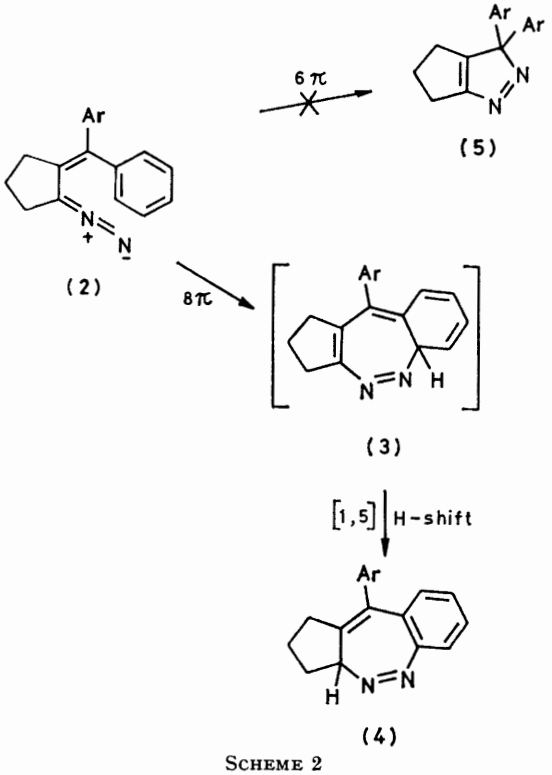


Scheme 1

nitrogen and the β-carbon atoms, so raising the activation energy for 1,5-closure relative to that for the competing 1,7-closure (*e.g.* Scheme 2) or carbenic (*e.g.* Scheme 3) processes; and/or (*b*) to the related ring strain effect of the fused cyclopentyl ring in destabilising the potential pyrazole products (5) and (9).

The 1,7-cyclisation (Scheme 2) provided the first route to 3*H*-1,2-diazepines and also the first example of electrocyclic aromatic substitution by the diazo group, *i.e.* electrocyclic ring closure followed by a sigmatropic shift. It is interesting that in the more recent [3] analogous photo-induced cyclisation of the nitrile ylide (10) to give the benzazepine (11), the 1,7-electrocyclisation is the preferred reaction.

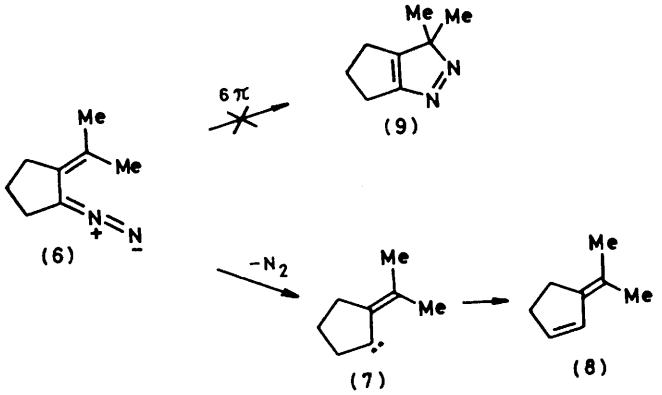
In this paper we describe a further study of the ways in which structural modifications in 1-aryl-3-diazo-



Scheme 2

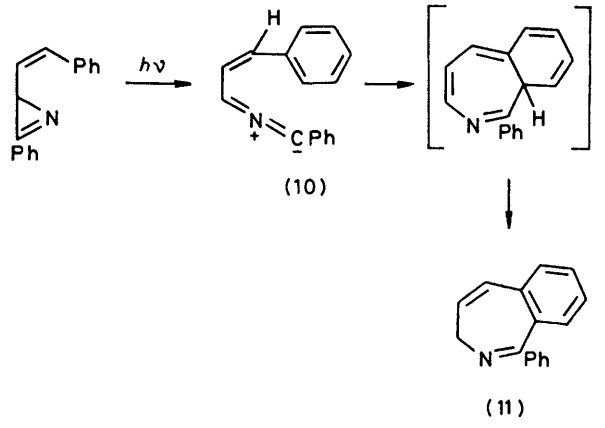
alkenes (1) affect both the periselectivity of the 6π- and 8π-electrocyclisation processes and the competing carbene formation. Since the annelation of a cyclopentyl ring at C-2,C-3 in (1) had produced such a profound effect on its mode of reaction it was of interest to investigate the effects of a similar fusion at C-1,C-2. The differences resulting from the two types of annelation are illustrated

in structures (12)—(14). Assuming that the 6π-electrocyclisation requires a planar transition state,[1] and that the bond angles are as shown, then although the cyclopentyl ring increases the separation between the reacting sites in both (13) and (14) compared to the acyclic case (12), the effect is less for (14). Thus if this *is* a critical factor, then formation of 3*H*-pyrazole would be expected to be less disfavoured for (14) than for (13). However in (13) the diazo-group is kept in conjugation with the α,β-double bond by the virtual planarity of the five-membered ring, in contrast with (14) which has free rotation about the 1,2-bond. This should result in a higher activation entropy for both the 6π- and 8π-electrocyclisation reactions of (14) making them less



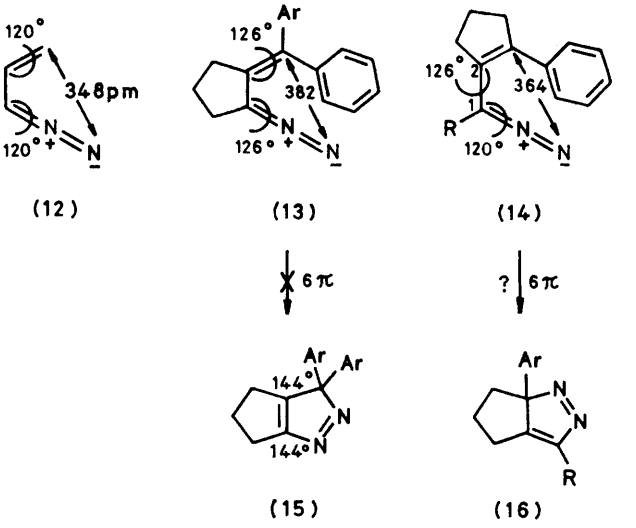
SCHEME 3

competitive with formation of carbene. This hindrance to the ring closure reactions of (14) would be expected to be exacerbated by a large R group whose steric interaction with the adjacent cyclopentyl CH_2 group would inhibit the conjugation of the diazo-function with

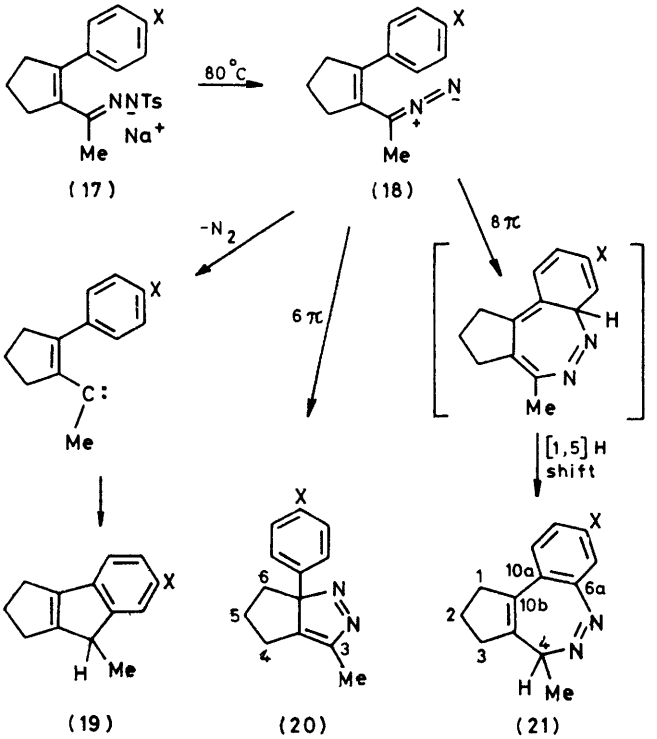


the remainder of the π-system. For the potential 3*H*-pyrazoles (15) and (16), the relative degree of destabilisation by the fused cyclopentyl ring is difficult to estimate; (15) with its alkene bond endocyclic to both rings probably has the greater angle strain but (16) with a saturated carbon at the ring junction will have greater torsional destabilisation.

The results for compounds of type (14) show that, in contrast to (13), both 6π- and 8π-cyclisations are possible and that carbene reactions do, as predicted, compete more effectively and, in some cases, completely dominate the reactions.



In the case where R = Me the diazo-compounds (18) (Scheme 4) reacted *via* all three modes; these are the only 3-aryl-1-diazoalkenes so far studied which react by both 6π- and 8π-cyclisation. The products were



	Yield (%)	
a; X = H	46	32
b; X = Me	43	37
c; X = F	36	38

SCHEME 4

identified by their analytical and spectroscopic data and by hydrogenation of (19a) to 1,2,3,3a,4,8b-hexahydro-4-methylcyclopent[*a*]indene. The 3*H*-pyrazoles and 3*H*-1,2-benzodiazepines had characteristic mass and ^{1}H and ^{13}C n.m.r. spectra (Tables 1 and 2).[1,4] The yields shown

TABLE 1

^{13}C N.m.r. data of 3*H*-pyrazoles, 4*H*-pyrazoles, and 3*H*-1,2-benzodiazepines *

Compound	Chemical shift
(20a)	Me 11.6; C-4—6 19.5, 31.9, 33.9; C-6a 110.2; aromatic 127.1, 128.0, 128.6, 135.1 (tert.); olefinic 148.5 (tert.), 168.8 (tert.)
(20b)	Me 11.7; Me (tolyl) 21.0; C-4—6 19.5, 31.9, 33.7; C-6a 109.8; aromatic 126.8, 129.2, 131.8 (tert.), 137.5 (tert.); olefinic 148.1 (tert.), 160.7 (tert.)
(20c)	Me 11.7; C-4—6 19.4, 31.8, 33.9; C-6a 109.3; aromatic C-1′ 130.6 (J_{CF} 3 Hz), C-2′ 128.7 (J_{CF} 8 Hz), C-3′ 115.4 (J_{CF} 22 Hz), C-4′ 162.2 (J_{CF} 245 Hz); olefinic 148.5 (tert.), 160.3 (tert.)
(25)	Me 11.1; C-4—7 21.6, 24.8, 28.1, 37.2; C-7a 99.8; aromatic 127.4, 127.9, 128.8, 134.1 (tert.); olefinic 147.5, 150.7
(28)	Me 19.1; C-4—7 21.7, 21.9, 22.3, 22.6; C-3 96.7; aromatic 125.7, 127.8, 128.8, 135.4 (tert.); olefinic 152.4, 152.9
(26)	Me 13.1; C-2′—5′ 27.8, 33.5; C-3, C-5, 177.9, 181.1; C-4 67.9; aromatic 127.6, 128.7, 130.4
(27)	Me 12.5; C-4—7 21.3, 26.9, 29.3, 33.8, C-3, C-7a 180.2, 181.9; C-3a 63.3; aromatic 126.3, 128.0, 129.6, 133.2 (tert.)
(21a)	Me 16.7; C-1—3 22.7, 32.6, 33.2; C-4 67.1; aromatic and olefinic 125.3 (tert.), 125.5, 126.2, 127.6, 128.6, 136.1 (tert.), 138.7 (tert.), 150.6 (tert.)
(21b)	Me 16.7; Me (tolyl) 21.2; C-1—3 22.7, 32.6, 33.0; C-4 67.0; aromatic and olefinic 122.6 (tert.), 125.8, 128.2, 128.9, 135.3 (tert.), 135.9 (tert.), 137.3 (tert.), 150.3 (tert.)
(21c)	Me 16.6; C-1—3 22.6, 32.7, 33.1; C-4 67.6; C-3a, C-10b 135.5, 137.7; C-10a 121.5; C-10 128.1 (J_{CF} 8 Hz); C-6a 151.2 (J_{CF} 8 Hz); C 7 116.1 (J_{CF} 23 Hz); C-9 113.6 (J_{CF} 22 Hz); C-8 159.1 (J_{CF} 248 Hz)

* Deuteriochloroform as solvent; chemical shifts are quoted in p.p.m. downfield from tetramethylsilane.

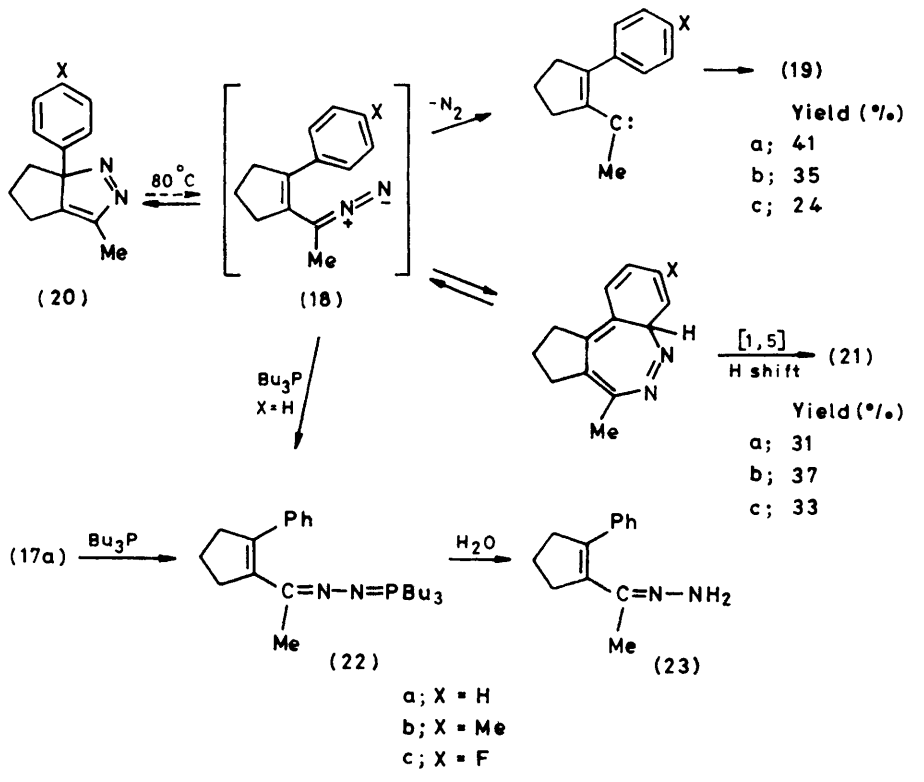
TABLE 2

Mass spectral data of 3*H*-1,2-benzodiazepines and 3*H*-pyrazoles

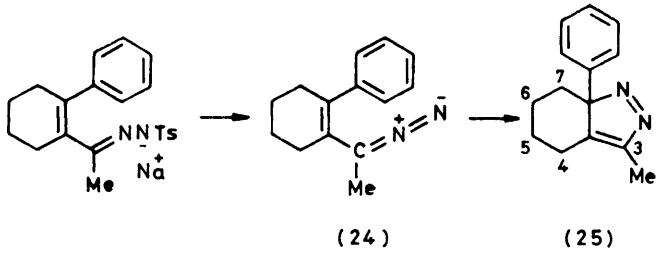
Compound		*m/e* (%)
(21a)	X = H	198(11), 170(63), 155(32), 142(100), 141(40)
(21b)	X = Me	212(14), 184(81), 169(32), 156(100)
(21c)	X = F	216(10), 188(64), 173(27), 160(100), 159 (44)
(20a)	X = H	198(2), 170(70), 155(28), 142(100)
(20b)	X = Me	212(1), 184(60), 169(32), 156(100)
(20c)	X = F	216(1), 188(66), 173(21), 160(100)

in Scheme 4 were those obtained after reaction times just long enough for complete consumption of the tosylhydrazone salts (17). Monitoring of the reaction of (17a) by h.p.l.c., however, showed that the pyrazole to diazepine ratio was high in the early stages of the reaction (*e.g.* 12 : 1 after 1.5 h) and fell steadily as the reaction progressed. This suggested that the 6π ring closure was the kinetically favoured process but that the pyrazole (20) was subsequently being transformed into the more stable diazepine (21). This was shown to be so by heating samples of the pyrazoles (20) at 80 °C (Scheme 5) when they decomposed to give both the diazepines (21) and the cyclopentindenes (19). This pyrazole to diazepine rearrangement provided the second example of a five to seven membered ring transformation involving the formal 1,3-migration of an azo group; this reaction however is irreversible, unlike the previous example [5] in which the equilibrium between a benzodiazepine and a 3*H*-indazole favoured the latter by *ca.* 2 : 1. This conversion of (20) into (21) is a new type of thermal reaction for 3*H*-pyrazoles which usually undergo the van Alphen–Huttel rearrangement [6] in which one of the groups on the saturated carbon migrates to an adjacent atom to give either a 1*H*- or 4*H*-pyrazole (*e.g.* Scheme 6). It seems most likely that the decomposition of pyrazole (20) involves a reverse of the cyclisation process (Scheme 5) and that although the equilibrium between the pyrazole and the diazo-compound lies heavily on the side of the pyrazole, the reaction is driven to the right by the irreversible (at this temperature) sigmatropic hydrogen shift giving (21) and the irreversible loss of nitrogen *en route* to (19). The intermediacy of the diazo compound (18a) in this reaction is supported by the observation that when (20a) was thermolysed in the presence of tributylphosphine neither (19a) nor (21a) were formed, the diazo compound instead being trapped to give the phosphazene (22) which on hydrolytic work-up gave the hydrazone (23) (61%). Control reactions showed that the diazepine (21a) did not react with tributylphosphine under these conditions and that the diazo compound (18a) generated directly from the tosylhydrazone salt (17a) did react to give (23). That the decomposition of the pyrazole (20a) is faster (*ca.* 5×) in the presence of the tributylphosphine is due to the relative rapidity of the trapping reaction compared to the product-forming steps leading to (19) and (21) in Scheme 5. It could be argued that (22) is formed not by the route shown in Scheme 5 but *via* direct bimolecular reaction between the pyrazole and the tributylphosphine; this however seems unlikely since the closely related pyrazole (25) fails to give a similar reaction (see below).

The effect of the cyclopentyl ring in (18) in restraining pyrazole formation and promoting diazepine formation (Scheme 4) is confirmed by comparison with the reactions of the cyclohexyl analogue (24) whose cyclisation gave (25) as the major product. The low isolated yield (33%) was due to decomposition during column chromatography. This pyrazole (25) is much more thermally stable than (20) but, on prolonged heating in dimethoxyethane, decomposed by the 'normal' van Alphen–Huttel rearrangement (Scheme 6) to give the 4*H*-pyrazole (26) (95%) rather than *via* the novel ring opening reaction of (20) which is induced by the higher ring strain in that system. That it is the alkyl group in (25) which undergoes the 1,5-shift giving (26) rather than the alternative migration of phenyl to give (27) is at first sight surprising since in sigmatropic shifts aryl groups usually migrate much more readily than alkyl groups.[7]

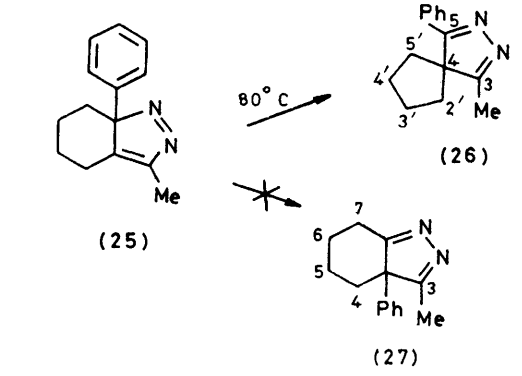


SCHEME 5

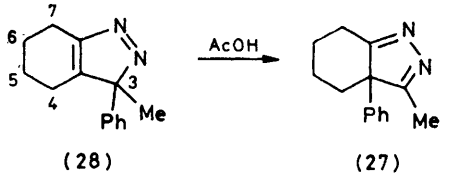


The formulation of the product as (26) is strongly supported by its ^{13}C n.m.r. spectrum (Table 1) which showed a peak for C-4 at 68 p.p.m. and two different C=N peaks at 178 and 181 p.p.m., values agreeing well with those for other 4*H*-pyrazoles,[8] but only two peaks for the CH_2 groups which fits for the symmetrical (26) but not for (27). For comparison, a sample of (27) was prepared in moderate yield by the acid-catalysed rearrangement of (28); its ^{13}C n.m.r. spectrum (Table 1) was again characteristic for a 4*H*-pyrazole and showed the expected four different CH_2 absorptions.

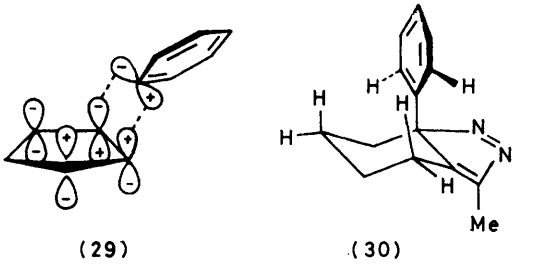
The high mobility of aryl and other unsaturated groups in sigmatropic shifts has been attributed to the lowering of the transition state energy by a secondary orbital interaction (29) involving the *p*-orbital on the migrating carbon.[7,9,10] However for (25) a Dreiding



SCHEME 6

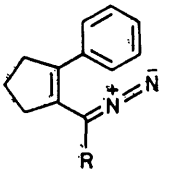


model shows that a transition state involving this kind of interaction is sterically inaccessible in both the chair



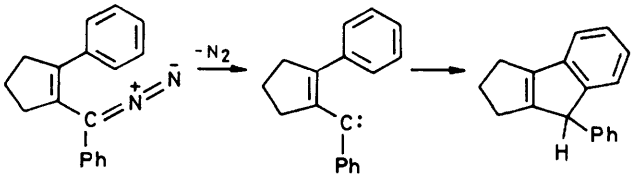
(30) and skew-boat conformations due to severe van der Waals interactions between the CH_2 groups of the cyclohexyl ring and the *ortho* hydrogen atoms of the benzene ring. This interaction prevents the rotation of the latter into a position where *p*-orbital overlap is possible. Thus the failure of the phenyl group to migrate is explicable on kinetic grounds, and in addition the product (27) of such a migration would, like its precursor (25), be destabilised by having an 'axial' phenyl group. Either or both of these factors result in alkyl migration being the preferred reaction pathway in this case.

Returning to the effects of structure on the reactions of compounds of type (31) we have found that the



(31)

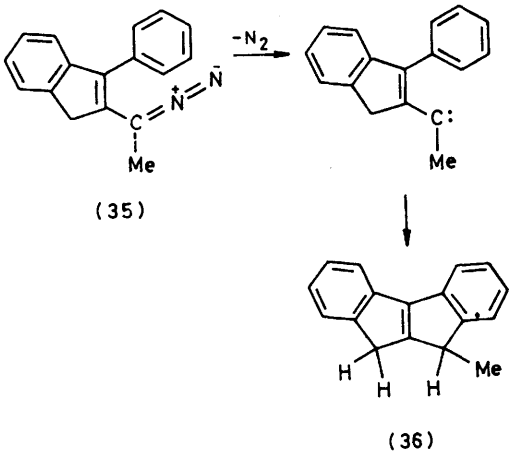
partitioning of reaction between the electrocyclisation and carbenic modes is much affected by relatively minor modifications. For example, although (18) reacted predominantly *via* electrocyclisation (Scheme 4), the replacement of methyl by phenyl, *i.e.* to give (32), resulted in the complete dominance of the carbenic reaction to give (34) (95%); no heterocyclic products were detected. The conjugation of the α phenyl group with the diazo-function in (32) will doubtless lower its ground state energy compared to that of (18) but the phenyl conjugation also apparently lowers the activation energy for carbene formation while having relatively little effect in stabilising the transition states for the electrocyclisation reactions. That this result is not due solely to the bulk of the phenyl group inhibiting conjugation between the diazo-group and the alkene bond is shown by the similar effect of conjugating the alkene



(32) (33) (34)

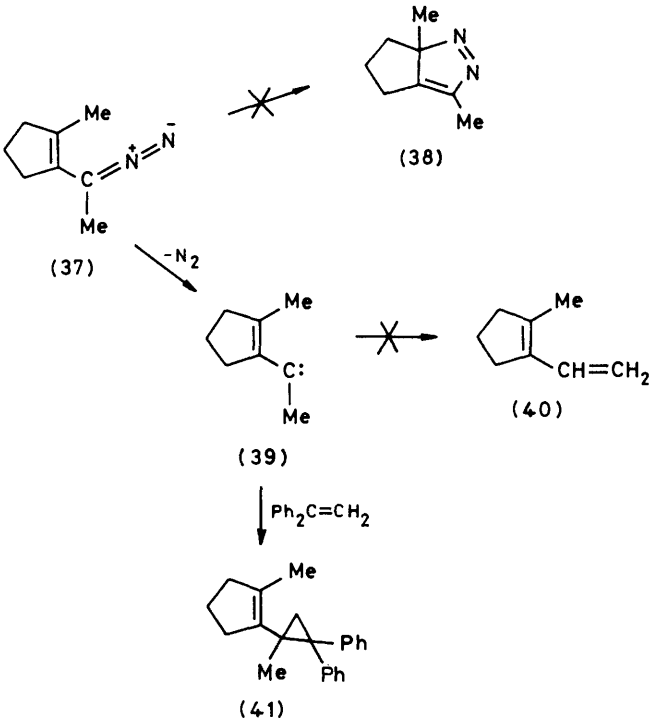
bond with a fused benzene ring as in (35); again the electrocyclisation reactions became uncompetitive and the only isolable product was the hydrocarbon (36) (95%). The competitiveness of the electrocyclisation reactions of (31) was not increased by reducing the size of R: the diazo compound (31; R = H) derived from 2-phenylcyclopentene-1-carbaldehyde tosylhydrazone salt gave 2-phenylcyclopentene-1-carbaldehyde azine (5%) as the only identified product.

We have also briefly examined the reactions of (37) and as with (6) (Scheme 3) the cyclopentyl ring prevented pyrazole (38) formation so that nitrogen was eliminated in the major reaction pathway to give the carbene (39). However whereas the carbene (7) reacted by a characteristic singlet carbene rearrangement to give



(35) (36)

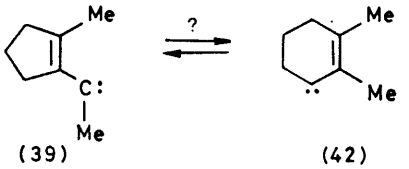
(8), the apparently similar carbene (39) did not likewise give (40) as a major product. Multiple inseparable products were obtained from (37) in a variety of solvents. A trapping reaction with cyclohexene failed to give any isolable adduct but with 1,1-diphenylethene the adduct



(37) (38) (39) (40) (41)

(41) was obtained in 44% yield. This reactivity pattern is typical of a triplet carbene and it appears that (39) crosses rapidly to that state whereas (7) does not. We have considered the possible interconversion of (39) and (42) *via* a carbene–carbene rearrangement and although this does not occur rapidly in the liquid phase, since (39)

and (42) give different adducts with 1,1-diphenylethene, it may be possible at higher temperatures as both are converted into similar mixtures of toluene and xylenes on flash vacuum pyrolysis at 700 °C.[11]



(39) (42)

To summarise, it has been shown that the fusion of a cyclopentyl ring at C-1,C-2 of (1) does, as predicted, discourage the formation of 3*H*-pyrazoles and thus for the β-aryl compounds (18) provides a route to the benzo[*c*]cyclopenta[*e*][1,2]diazepines (21). This effect however is less marked than for compounds of type (13) and in general carbene formation competes more effectively with the electrocyclisation reactions for (14) than for (13).

EXPERIMENTAL

^{1}H N.m.r. spectra were obtained on Varian EM-360 (60 MHz) and HA100 (100 MHz) spectrometers and ^{13}C n.m.r. spectra on a Varian XL 100 instrument. Mass spectra were obtained on an A.E.I. MS902 spectrometer and on a V.G. Micromass 12B coupled gas chromatograph–mass spectrometer. The cyclohexane and 1,2-dimethoxyethane used in the diazo-compound cyclisation reactions were distilled under nitrogen from calcium hydride immediately before use.

Preparation of the Unsaturated Aldehyde and Ketones.—The following compounds were prepared by the literature routes indicated and had correct characteristics: 1-acetyl-2-methylcyclopentene,[12,13] 1-benzoyl-2-phenylcyclopentene,[14] and (*E*)-2-(methylphenylmethylene)cyclohexanone.[15]

1-*Acetyl*-2-*phenylcyclopentene*. This was prepared by an adaptation of the method of Groves and Jones.[16] Acetic anhydride (87.8 g, 0.86 mol) and 1-phenylcyclopentene [17] (100 g, 0.69 mol) were dissolved in carbon disulphide (350 ml). The solution was cooled to 0 °C and anhydrous zinc chloride (101 g, 0.74 mol) was added with stirring. The mixture was stirred at room temperature for 24 h and then poured onto crushed ice. The product was extracted with ether; the ether solution was washed with water, potassium bicarbonate solution, water again, and then dried and evaporated to leave a red–brown oil (127 g). Distillation gave 3-acetyl-2-phenylcyclopentene (60.6 g, 47%), b.p. 120—122 °C at 1 mmHg; $\nu_{max.}$ (film) 1 710 cm^{-1} (C=O); τ($CDCl_3$) 2.6—2.9 (5 H, m), 3.7 (1 H, m), 6.2 (1 H, m), 7.3—8.0 (4 H, m), and 8.1 (s, Me). This product was dissolved in methanol (350 ml) and added to potassium hydroxide (30 g) in methanol (500 ml) and the solution kept at room temperature. G.l.c. (2% NPGS, 170 °C) showed the equilibration of the 3- and 1-acetyl-2-phenylcyclopentenes to be complete after 24 h and showed approximately equal amounts of each. The solution was poured into water (600 ml) and the product extracted with ether. The ether solution was washed with water, dried, and evaporated to leave a yellow oil which was distilled, b.p. 98—103 °C at 0.3 mmHg, to yield a *ca.* 1 : 1 mixture of 1- and 3-acetyl-2-phenylcyclopentenes (45.1 g), from which the more volatile 1-*acetyl*-2-*phenylcyclopentene*, b.p. 73—74 °C at 0.1 mmHg, was obtained pure by fractionation on a Fischer Spaltrohr System MMS 200 distillation apparatus (Found: C, 83.9; H, 7.5. $C_{13}H_{14}O$ requires C, 83.8; H, 7.6%). $\nu_{max.}$ (film) 1 620—1 680 cm^{-1} (C=C, C=O); τ($CDCl_3$) 2.6—2.9 (5 H, m), 7.0—7.3 (4 H, m), 7.9—8.3 (2 H, m), and 8.1 (s, Me).

The following ketones were prepared by analogous routes. Separation from the 3-acetyl isomers was achieved either by fractional distillation as above or by medium-pressure column chromatography on silica (1 000 × 15 mm, Merck Silica Gel 60) using dichloromethane as eluant: 1-*acetyl*-2-p-*tolylcyclopentene*, b.p. 90 °C at 0.2 mmHg (Found: C, 84.05; H, 8.1. $C_{14}H_{16}O$ requires C, 84.0; H, 8.1%), $\nu_{max.}$ (film) 1 660 cm^{-1} (C=O), τ($CDCl_3$) 2.85 (4 H, s), 7.0—7.4 (4 H, m), 7.63 (s, Me), 7.8—8.2 (2 H, m), and 8.06 (s, Me); 1-*acetyl*-2-p-*fluorophenylcyclopentene*, b.p. 73—75 °C at 0.02 mmHg (Found: C, 76.4; H, 6.4. $C_{13}H_{13}OF$ requires C, 76.5; H, 6.4%), $\nu_{max.}$ (film) 1 660 cm^{-1} (C=O), τ($CDCl_3$) 2.7—3.2 (4 H, m), 7.0—7.3 (4 H, m), 7.6—8.5 (2 H, m), and 8.04 (s, CH_3); 1-*acetyl*-2-*phenylcyclohexene*, b.p. 74—76 °C at 0.02 mmHg (Found: C, 84.0; H, 8.3. $C_{14}H_{16}O$ requires C, 84.0; H, 8.1%), $\nu_{max.}$ (film) 1 665 cm^{-1} (C=O), τ($CDCl_3$) 2.6—2.9 (5 H, m), 7.4—7.9 (4 H, m), 8.0—8.4 (2 H, m), and 8.33 (s, Me) (in this preparation excess of acetic anhydride was used as the reaction solvent); 2-*acetyl*-3-*phenylindene*, m.p. 74—74.5 °C (Found: C, 87.4; H, 6.3. $C_{17}H_{14}O$ requires C, 87.2; H, 6.0%), $\nu_{max.}$ (Nujol) 1 645 cm^{-1} (C=O), τ($CDCl_3$) 2.4—3.1 (9 H, m), 6.17 (s, CH_2), and 8.01 (s, Me) (the base-catalysed isomerisation step was not required in this preparation).

2-*Phenylcyclopentene*-1-*carbaldehyde*. This was prepared by an adaptation of the method of Schmidle and Barnett.[18] 1-Phenylcyclopentene [17] (72 g, 0.5 mol) was added slowly with stirring to a solution of dimethylformamide (40 g, 0.55 mol) and phosphorus oxychloride (84.5 g, 0.55 mol) in 1,2-dichloroethane (150 ml) kept at 5 °C. The solution was then boiled under reflux for 15 min, cooled, and a solution of sodium acetate (278 g, 2.75 mol) in water (600 ml) was added. The mixture was boiled under reflux for 15 min, cooled, and the product extracted with ether. The ether extract was washed with water, dried, and evaporated to leave a brown oil (100 g) which was chromatographed on alumina to give 2-*phenylcyclopentene*-1-*carbaldehyde* (16.2 g, 19%) (Found: C, 83.6; H, 7.3. $C_{12}H_{12}O$ requires C, 83.7; H, 7.0%), $\nu_{max.}$ (film) 1 630—1 680 cm^{-1} (C=O, C=C), τ($CDCl_3$) 0.2 (1 H, s), 2.65 (5 H, s), and 6.8—8.2 (6 H, m).

Preparation of the p-*Tolylsulphonylhydrazones*.—Except where details are given below, the tosylhydrazones (Table 3) were prepared by the addition of the ketone, or for solid ketones, a solution of the ketone in the minimum volume of ethanol, to a solution at 50 °C of *p*-toluenesulphonylhydrazine (1 mol. equiv.) in ethanol containing a few drops of hydrochloric acid. The solution was allowed to stand in the dark at room temperature until the condensation was complete. The precipitated tosylhydrazones were filtered off, washed with ether, and dried over phosphorus pentaoxide at *ca.* 0.1 mmHg before use.

2-*Phenylcyclopentene*-1-*carbaldehyde tosylhydrazone*. *p*-Toluenesulphonylhydrazine (13.0 g, 0.07 mol) was added to a solution of 2-phenylcyclopentene-1-carbaldehyde (12.0 g, 0.07 mol) in ether (400 ml). The mixture was shaken and kept at room temperature for 3 days when t.l.c. (alumina, methylene chloride) showed that the aldehyde had all reacted. The solution was concentrated to *ca.* 100 ml using a

TABLE 3

Tosylhydrazones of the unsaturated aldehydes and ketones

Carbonyl compound	Yield (%)	M.p.* (°C)	Formula of hydrazone	C (%) Found	C (%) Calc.	H (%) Found	H (%) Calc.	N (%) Found	N (%) Calc.	$\bar{\nu}$ NH (cm^{-1})
1-Acetyl-2-methylcyclopentene	60	122—123 †	$C_{15}H_{20}N_2SO_2$	61.8	61.6	6.6	6.9	9.7	9.6	3 210
1-Benzoyl-2-phenylcyclopentene	56	145—148 †,[a]	$C_{25}H_{24}N_2SO_2$	72.0	72.1	5.9	5.8	6.7	6.7	3 220
1-Acetyl-2-phenylcyclopentene	56	135—136 †	$C_{20}H_{22}N_2SO_2$	67.6	67.8	6.0	6.3	8.1	7.9	3 165
1-Acetyl-2-*p*-tolylcyclopentene	65	143—144 †	$C_{21}H_{24}N_2SO_2$	68.3	68.5	6.4	6.6	7.7	7.6	3 175
1-Acetyl-2-*p*-fluorophenylcyclopentene	82	143—145 †	$C_{20}H_{21}FN_2SO_2$	64.8	64.5	6.0	5.7	7.8	7.5	3 175
2-Phenylcyclopentencarbaldehyde-1-al	61	110—111 †,[b]	$C_{19}H_{20}N_2SO_2$	67.2	67.1	6.1	5.9	8.2	8.2	3 165
1-Acetyl-2-phenylcyclohexene	80	145—146 †	$C_{21}H_{24}N_2SO_2$	68.5	68.5	6.6	6.6	7.7	7.6	3 195
2-Acetyl-3-phenylindene	85	204—207 †	$C_{24}H_{22}N_2SO_2$	72.0	71.6	5.7	5.5	7.2	7.0	3 180
(*E*)-2-(Methylphenylmethylene)cyclohexanone	62	136—140	$C_{21}H_{24}N_2SO_2$	68.2	68.5	6.5	6.6	7.5	7.6	3 180

* After recrystallisation from ethanol, except for [a] ethanol–benzene and [b] light petroleum–ether. † Decomp.

rotary evaporator and the yellow precipitate (18.8 g) was filtered off. Recrystallisation from light petroleum–ether gave the tosylhydrazone (14.7 g, 61%).

Thermal Decomposition of the p-*Tolylsulphonylhydrazone Sodium Salts.*—The sodium salts were prepared by the addition of the tosylhydrazone to a solution made by dissolving an equimolar quantity of sodium in dry ethanol. Generally a slight excess of the tosylhydrazone (1—2%) was used to ensure that no unchanged base was left to cause isomerisation of the products.[1,4] The mixture was stirred until all the tosylhydrazone had dissolved. The solvent was then removed by evaporation at *ca.* 10 mmHg under anhydrous conditions, keeping the temperature below 35 °C. The residual salts were dried at *ca.* 0.1 mmHg for at least 12 h. The reaction solvent was then added and the mixture boiled under reflux under nitrogen in the dark until all the starting material had been consumed (t.l.c.). Unless otherwise stated reactions were worked up by cooling, filtration of the precipitated sodium *p*-toluenesulphinate, and evaporation of the filtrate under reduced pressure.

1-*Acetyl*-2-*phenylcyclopentene tosylhydrazone salt* (17a). (a) *In* 1,2-*dimethoxyethane*. The tosylhydrazone (2.89 g, 8.15 mmol) was refluxed in 1,2-dimethoxyethane (50 ml) for 9 h to give after the usual work-up a brown oil. Dry-column chromatography (alumina, light petroleum) gave 1,2,3,4-*tetrahydro*-4-*methylcyclopent*[a]*indene* (19a) (0.271 g, 20%), 1,2,3,4-*tetrahydro*-4-*methylbenzo*[c]*cyclopenta*[e][1,2]-*diazepine* (21a) (0.520 g, 32%), and 4,5,6,6a-*tetrahydro*-3-*methyl*-6a-*phenylcyclopenta*[c]*pyrazole* (20a) (0.740 g, 46%). The cyclopentindene (19a), pure by g.l.c. (1% SE30, 110 °C), was an oil (Found: $M^{+\cdot}$, 170.109 216. $C_{13}H_{14}$ requires M, 170.109 545), $\nu_{max.}$ (film) 1 630 cm^{-1} (C=C), τ($CDCl_3$) 2.6—3.0 (4 H, m), 6.74br (1 H, q, J 7 Hz), 7.3—7.8 (6 H, m), and 8.74 (d, J 7 Hz, Me). The cyclopentindene (19a) (0.141 g, 0.83 mmol) in ethanol (30 ml) was hydrogenated for 50 min at 4 atm. in a Parr hydrogenator using 10% palladium–charcoal (0.093 g) as catalyst. Filtration, evaporation of the solvent, and distillation of the residue at 0.05 mmHg gave 1,2,3,3a,4,8b-*hexahydro*-4-*methylcyclopent*[a]*indene* (57 mg, 41%) as an oil (Found: *m/e*, 172.125 083. $C_{13}H_{16}$ requires M, 172.125 194), τ($CDCl_3$) 2.7—3.0 (4 H, m), 6.47 (1 H, t of d, J 8 and 4 Hz), 6.69 (1 H, quint, J 7 Hz), 7.24 (1 H, quint, J 8 Hz), and 8.74 (d, J 7 Hz, Me) superimposed on 7.7—8.9 (m) (total 9 H). The diazepine (21a) had m.p. 50—52 °C (from light petroleum–ether 10 : 1) (Found: C, 78.5; H, 7.1; N, 14.0. $C_{13}H_{14}N_2$ requires C, 78.8; H, 7 1; N, 14.1%), τ($CDCl_3$) 2.26 (1 H, m), 2.5—2.8 (3 H, m), 6.7—7.15 (1 H, m), 7.15—7.75 (4 H, m), and 7.93 (d, J 7 Hz, Me) superimposed on 7.75—8.3 (m) (total 5 H). The pyrazole (20a) was an oil (Found: C, 78.8; H, 7.7; N, 13.9. $C_{13}H_{14}N_2$ requires C, 78.9; H, 7.1; N, 14.1%), τ($CDCl_3$) 2.5—2.9 (5 H, m) and 7.69 (s, Me) superimposed on 7.3—8.8 (m) (total 9 H) (Found: $M^{+\cdot}$, 198.115 902, $M^{+\cdot}$ − 28, 170.109 384. $C_{13}H_{14}N_2$ requires M, 198.115 693, $C_{13}H_{14}$ requires *m/e* 170.109 545).

In a similar reaction of (17a) (1.39 g, 3.93 mmol) in 1,2-dimethoxyethane (20 ml) the ratio (20a) : (21a) was monitored by h.p.l.c. (alumina, methylene chloride) using a u.v. detector at 258 nm [ε (21a) 9 290, ε (20a) 2 360]. The (20a) : (21a) ratio was 12 after 1.5 h, 7 after 2.8 h, and 4 after 5.0 h.

(b) *In* 1,2-*dimethoxyethane in the presence of the tributylphosphine.* The sodium salt (17a) (1.60 g, 4.5 mmol) and tri-n-butylphosphine (1.82 g, 9.0 mmol) were boiled under reflux in 1,2-dimethoxyethane (20 ml) for 9 h. Usual work-up gave a brown oil which (h.p.l.c.) did not contain the pyrazole (20a) or the diazepine (21a). Dry column chromatography (alumina, ether) gave 1-*acetyl*-2-*phenylcyclopentene hydrazone* (23) (0.637 g, 71%), m.p. 102—103 °C (from light petroleum–ethanol 6 : 1) (Found: C, 77.8; H, 8.2; N, 13.9. $C_{13}H_{16}N_2$ requires C, 78.0; H, 8.1; N, 14.0%), $\nu_{max.}$ (Nujol) 3 365, 3 280, and 3 215 cm^{-1} (NH), τ($CDCl_3$) 2.8 (5 H, s), 4.85br (s, NH_2), 7.0—7.4 (4 H, m), 7.8—8.3 (2 H, m), and 8.48 (s, Me). This product (0.062 g) was further characterised as the azine formed by condensation with acetone (2 ml). The acetone was evaporated on a steam-bath leaving the azine as a yellow oil (Found: $M^{+\cdot}$, 240.160 831. $C_{16}H_{20}N_2$ requires M, 240.162 641), τ($CDCl_3$) 2.8 (5 H, s), 6.9—7.3 (4 H, m), 7.7—8.2 (2 H, m), 8.00 (s, Me), 8.20 (s, Me), and 8.36 (s, Me).

1-*Acetyl*-2-p-*tolylcyclopentene tosylhydrazone salt* (17b). The tosylhydrazone (2.25 g, 6.12 mmol) salt was refluxed in 1,2-dimethoxyethane (40 ml) for 4 h. After the usual work-up, chromatography (alumina, light petroleum–ether) gave 1,2,3,4-*tetrahydro*-4,6-*dimethylcyclopent*[a]*indene* (19b) (0.219 g, 20%) as an oil, 1,2,3,4-*tetrahydro*-4,8-*dimethylbenzo*[c]*cyclopenta*[e][1,2]*diazepine* (21b) (0.472 g, 37%), and 4,5,6,6a-*tetrahydro*-3-*methyl*-6a-p-*tolylcyclopenta*[c]*pyrazole* (20b) (0.553 g, 43%). The cyclopentindene (19b), pure by t.l.c. (alumina, light petroleum), was an oil (Found: $M^{+\cdot}$, 184.124 632. $C_{14}H_{16}$ requires *m/e* 184.125 194), τ($CDCl_3$) 2.8—3.1 (3 H, m), 6.82br (1 H, q, J 8 Hz), 7.68 (s, Me) superimposed on 7.3—7.8 (m) (total 9 H), and 8.78 (d, J 8 Hz, Me). The diazepine (21b) had m.p. 89—90 °C (from light petroleum) (Found: C, 79.3; H, 7.9; N, 13.6. $C_{14}H_{16}N_2$ requires C, 79.2; H, 7.6; N, 13.2%), τ($CDCl_3$) 2.46 (1 H, d, J 1.5 Hz), 2.71 (1 H, d, J 8 Hz), 2.91 (1 H, d of d, J 8 and 1.5 Hz), and 7.62 (s, CH_3) and 7.96 (d, J 6 Hz, CH_3) superimposed on 6.7—8.4 (m) (total 12 H). The pyrazole (20b) was a pale brown oil, pure by t.l.c., but which could not be obtained colourless by chromatography

(Found: $M^{+\cdot}$, 212.131 085, $M^{+\cdot} - 28$, 184.124 994. $C_{14}H_{16}N_2$ requires M, 212.131 342, $C_{14}H_{16}$ requires m/e 184.125 194), τ($CDCl_3$) 2.6—3.0 (4 H, m) and 7.64 (s, Me) and 7.67 (s, Me) superimposed on 7.2—8.8 (m) (total 12 H).

1-*Acetyl*-2-p-*fluorophenylcyclopentene tosylhydrazone salt* (17c). The tosylhydrazone (3.25 g, 8.72 mmol) salt in 1,2-dimethoxyethane (40 ml) for 6 h, after the usual work-up and chromatography (alumina, light petroleum–ether) gave 6-*fluoro*-1,2,3,4-*tetrahydro*-4-*methylcyclopent*[a]*indene* (19c) (0.443 g, 27%), 8-*fluoro*-1,2,3,4-*tetrahydro*-4-*methylbenzo*[c]*cyclopenta*[e][1,2]*diazepine* (21c) (0.709 g, 38%), and 6a-p-*fluorophenyl*-4,5,6,6a-*tetrahydro*-3-*methylcyclopenta*[c]*pyrazole* (20c) (0.678 g, 36%). The cyclopentindene (19c), pure t.l.c. (alumina, petroleum), was an oil (Found: $M^{+\cdot}$, 188.099 147. $C_{13}H_{13}F$ requires M, 188.100 122), τ($CDCl_3$) 2.8—3.3 (3 H, m), 6.80 (1 H, q, J 7 Hz), 7.3—7.8 (6 H, m), and 8.77 (d, J 7 Hz, Me). The diazepine (21c) had m.p. 80—81 °C (from light petroleum–ether 10 : 1) (Found: C, 72.0; H, 6.3; N, 13.1. $C_{13}H_{13}N_2F$ requires C, 72.2; H, 6.1; N, 13.0%), τ($CDCl_3$) 2.4—3.1 (3 H, m) and 7.93 (d, J 6 Hz, Me) superimposed on 6.6—8.8 (m) (total 10 H). The pyrazole (20c), pure by t.l.c. (alumina, benzene), was an oil (Found: $M^{+\cdot}$, 216.106 012, $M^{+\cdot} - 28$, 188.100 414. $C_{13}H_{13}N_2F$ requires M, 216.106 269, $C_{13}H_{13}F$ requires m/e 188.100 122), τ($CDCl_3$) 2.65 (2 H, d of d, J_o 9 Hz, J_{HF} 5 Hz), 3.00 (2 H, t, J_o 9 Hz), and 7.67 (s, Me) superimposed on 7.2—8.8 (m) (total 9 H).

1-*Acetyl*-2-*phenylcyclohexene tosylhydrazone salt*. The tosylhydrazone salt (3.90 g, 10.6 mmol) was refluxed in 1,2-dimethoxyethane (70 ml) for 4 h and after the usual work-up gave a brown oil which showed a single spot on t.l.c. (alumina, methylene chloride) and one major peak (>95% of total peak area) by h.p.l.c. (alumina, methylene chloride–hexane). Chromatography (alumina, methylene chloride) followed by recrystallisation from light petroleum–ethanol gave 5,6,7,7a-*tetrahydro*-3-*methyl*-7a-*phenyl*-4H-*indazole* (25) (0.75 g, 33%), m.p. 66—67 °C (Found: C, 78.9; H, 7.7; N, 13.2%; $M^{+\cdot}$ 212.131 085, $M^{+\cdot} - 28$, 184.124 813. $C_{14}H_{16}N_2$ requires C, 79.2; H, 7.6; N, 13.2%; M, 212.131 342; $C_{14}H_{16}$ requires m/e 184.125 194), τ($CDCl_3$) 2.4—3.2 (5 H, m) and 7.56 (s, Me) superimposed on 6.5—9.4 (m) (total 11 H). A control experiment showed that (25) partly decomposes on chromatography on alumina.

2-*Acetyl*-3-*phenylindene tosylhydrazone salt* (with D. Munro). The tosylhydrazone (5.07 g, 12.6 mmol) salt in 1,2-dimethoxyethane (60 ml) for 40 min gave after the usual work-up a yellow solid. Chromatography on silica gave 9,10-*dihydro*-9-*methylindeno*[1,2-a]*indene* (36) (2.58 g, 95%) as white crystals. Recrystallisation from ethanol gave the pure product (1.91 g, 70%), m.p. 114—115 °C (Found: C, 93.7; H, 6.4. $C_{17}H_{14}$ requires C, 93.6; H, 6.5%), τ($CDCl$)$_3$ 2.2—3.0 (8 H, m), 6.33 (1 H, q, J 8 Hz), 6.45 (2 H, s), and 8.58 (d, J 8 Hz, Me). Other material (0.49 g) eluted from the column appeared to be polymeric (n.m.r.).

(E)-2-(*Methylphenylmethylene*)*cyclohexanone tosylhydrazone salt* (with K. A. Wall). The tosylhydrazone (2.42 g, 6.57 mmol) was refluxed in 1,2-dimethoxyethane (50 ml) for 30 h, worked up in the usual way, and chromatographed (alumina, methylene chloride) to give 4,5,6,7-*tetrahydro*-3-*methyl*-3-*phenyl*-3H-*indazole* (28) (0.807 g, 58%), m.p. 64—65 °C (from light petroleum–ethanol) (Found: C, 79.3; H, 7.2; N, 13.2. $C_{14}H_{16}N_2$ requires C, 79.2; H, 7.6; N, 13.2%), τ($CDCl_3$) 2.6—3.1 (5 H, m), 7.15br (2 H, m), 7.82br (2 H, m), and 8.35 (s, Me) superimposed on 8.1—8.7 (m) (total 7 H).

2-*Phenylcyclopentene*-1-*carbaldehyde tosylhydrazone salt*. The tosylhydrazone (2.45 g, 7.20 mmol) salt, refluxed in 1,2-dimethoxyethane (40 ml) for 4 h, gave, after the usual work-up, a brown oil (1.47 g) containing (t.l.c.) six components. The mixture was separated into two fractions $R_F > 0.7$ (0.388 g) and $R_F < 0.3$ (0.955 g) by dry-column chromatography. Trituration of the latter with ether gave 2-*phenylcyclopentene*-1-*carbaldehyde azine* (0.059 g, 5%) as yellow needles (from benzene), m.p. 205—206 °C (decomp.) (Found: 84.8; H, 7.2; N, 8.5. $C_{24}H_{24}N_2$ requires C, 84.7; H, 7.1; N, 8.2%), τ($CDCl_3$) 1.54 (2 H, s), 2.6—2.8 (10 H, m), 7.1 (8 H, m), and 8.0 (4 H, m).

1-*Benzoyl*-2-*phenylcyclopentene tosylhydrazone salt*. The tosylhydrazone (0.659 g, 1.58 mmol) was boiled under reflux in cyclohexane (25 ml) for 20 h when t.l.c. (alumina, light petroleum) showed a single product. Usual work-up gave a yellow solid (^{1}H n.m.r. spectrum virtually identical with that of the pure product) which was sublimed (135 °C at 0.1 mmHg) to give 1,2,3,4-*tetrahydro*-4-*phenylcyclopent*[a]*indene* (34) (0.348 g, 95%), m.p. 57—58 °C (Found: C, 93.3; H, 6.7. $C_{18}H_{16}$ requires C, 93.1; H, 6.9%), τ(CCl_4) 2.6—3.1 (9 H, m), 5.75 (1 H, m), and 7.2—7.8 (6 H, m). This compound (0.20 g, 0.862 mmol) in ethanol (50 ml) containing a few drops of perchloric acid was hydrogenated at 2.5 atm. in a Parr hydrogenator using 10% palladium–charcoal (0.05 g) as catalyst. After filtration and evaporation the residue was distilled at 0.05 mmHg to give 1,2,3,3a,4,8b-*hexahydro*-4-*phenylcyclopent*[a]*indene* (0.138 g, 68%) (Found: C, 92.4; H, 7.8. $C_{18}H_{18}$ requires C, 92.3; H, 7.7%), τ($CDCl_3$) 2.5—3.1 (9 H, m), 5.41 (1 H, d, J 9 Hz), 6.36 (1 H, t of d, J 8 and 4 Hz), 7.00 (1 H, quint, J 8 Hz), and 7.7—9.1 (6 H, m).

1-*Acetyl*-2-*methylcyclopentene tosylhydrazone salt*. (a) Decomposition of the salt in a variety of aprotic solvents gave almost quantitative evolution of nitrogen with the formation of complex mixtures of products, *e.g.* in toluene g.l.c. showed ten major peaks. Analysis by g.c.–m.s. of the products formed in cyclohexene showed that none had a molecular ion m/e 190 as expected for the carbene–cyclohexene adduct. Separation of these mixtures was not attempted.

(b) *In cyclohexane in the presence of* 1,1-*diphenylethene*. The tosylhydrazone (3.17 g, 10.85 mmol) salt and 1,1-diphenylethene (11.2 g, 62.3 mmol) in cyclohexane (25 ml) were boiled under reflux for 20 h. Usual work-up gave a yellow liquid (12.38 g) shown by g.l.c. (1% SE30, 130—170 °C) to contain 1,1-diphenylethene and one other component. After distillation to remove the 1,1-diphenylethene the residue was separated by dry-column chromatography (alumina–light petroleum) to give 1-methyl-2-(1-methyl-2,2-diphenylcyclopropyl)cyclopentene (41) (1.33 g, 44%) (Found: C, 91.9; H, 8.1. $C_{22}H_{24}$ requires C, 91.6; H, 8.4%), τ($CDCl_3$) 2.5—3.1 (10 H, m), 8.32br (s, Me), 8.96 (s, Me), 7.8—9.0 (6 H, m), 8.15 (1 H, d, J 5 Hz), and 8.72 (1 H, d, J 5 Hz).

Thermal Decomposition of the 6a-*Aryl*-4,5,6,6a-*tetrahydro*-3-*methylcyclopenta*[c]*pyrazoles* (20).—4,5,6,6a-*Tetrahydro*-3-*methyl*-6a-*phenylcyclopenta*[c]*pyrazole* (20a). (i) The pyrazole (161 mg, 0.81 mmol) was boiled under reflux in 1,2-dimethoxyethane (20 ml) in the dark under nitrogen. T.l.c. (alumina, toluene) showed full reaction after 23 h. The solvent was evaporated under reduced pressure to leave a yellow oil which contained (^{1}H n.m.r.) the diazepine (21a) and the cyclopentindene (19a) in the ratio 1 : 2, confirmed by h.p.l.c. (alumina, methylene chloride). The

products were separated by dry-column chromatography (alumina, toluene) to give the cyclopentindene (19a) (56 mg, 41%) and the diazepine (21a) (50 mg, 31%), identical with authentic samples. A brown oil (32 mg; R_F 0) was recovered from the dry-column. This had not been present before chromatography (t.l.c.).

(ii) *In the presence of tributylphosphine.* The pyrazole (20a) (225 mg, 1.14 mmol) and tributylphosphine (445 mg, 2.25 mmol) in 1,2-dimethoxyethane were boiled under reflux in the dark under nitrogen. H.p.l.c. (alumina, methylene chloride–hexane 1 : 1) showed complete reaction after 4.3 h. After evaporation, dry-column chromatography (alumina, ether) of the residue gave 1-acetyl-2-phenylcyclopentene hydrazone (23) (139 mg, 61%), identical with an authentic sample. As a control the diazepine (21a) (45 mg, 0.23 mmol) and tributylphosphine (91 mg, 0.45 mmol) in 1,2-dimethoxyethane (1 ml) were boiled under reflux in the dark under nitrogen for 9 h. The mixture was cooled and water (1 drop) was added to hydrolyse any phosphazine present. T.l.c. (alumina, benzene) showed that no 1-acetyl-2-phenylcyclopentene hydrazone had been formed. Chromatography (alumina, light petroleum–methylene chloride) gave recovered diazepine (21a) (43 mg).

4,5,6,6a-*Tetrahydro*-3-*methyl*-6a-p-*tolylcyclopenta*[c]*pyrazole* (20b). Similarly the pyrazole (20b) (182 mg, 0.86 mmol) was boiled under reflux in 1,2-dimethoxyethane (15 ml) for 18 h to give the cyclopentindene (19b) (55 mg, 35%), the diazepine (21b) (67 mg, 37%), and an unidentified brown oil (18 mg).

6a-p-*Fluorophenyl*-4,5,6,6a-*tetrahydro*-3-*methylcyclopenta*[c]*pyrazole* (20c). In a similar reaction the pyrazole (403 mg, 1.86 mmol) was boiled under reflux in 1,2-dimethoxyethane (15 ml) for 12 h to give the cyclopentindene (19c) (85 mg, 24%), the diazepine (21c) (126 mg, 33%), and a brown oil (95 mg) shown by ^{1}H n.m.r. to contain *ca.* 10% unchanged pyrazole (20c).

Thermal and Acid-catalysed Rearrangements of 5,6,7,7a-*Tetrahydro*-4H-*indazoles.*—*Thermolysis of* 5,6,7,7a-*tetrahydro*-3-*methyl*-7a-*phenyl*-4H-*indazole* (25). (i) The indazole (563 mg, 2.65 mmol) in 1,2-dimethoxyethane (50 ml) was boiled under reflux in the dark under nitrogen for 5 days. After removal of the solvent under reduced pressure, dry-column chromatography (alumina, methylene chloride) of the residue gave 3-*methyl*-5-*phenyl*-4H-*pyrazole*-4-*spirocyclopentane* (26) (539 mg, 95%) as white crystals, m.p 62—64 °C after sublimation at 0.1 mmHg [Found: C, 79.1; H, 7.9; N, 13.3%; $M^{+\cdot}$ 212.130 464, $M^{+\cdot}$ − 28, 184.125 356 and 184.099 656 (12 : 1). $C_{14}H_{16}N_2$ requires C, 79.2; H, 7.6; N, 13.2%; *M*, 212.131 342, $C_{14}H_{16}$ requires *m/e* 184.125 194, $C_{12}H_{12}N_2$ requires *m/e*, 184.100 043], τ($CDCl_3$) 2.0—2.3 (2 H, m), 2.5—2.8 (3 H, m), and 7.73 (s, Me) superimposed on 7.4—8.3 (8 H, m).

(ii) *In the presence of tributylphosphine.* The indazole (25) (208 mg, 0.98 mmol) and tributylphosphine (396 mg, 1.96 mmol) in 1,2-dimethoxyethane (4.5 ml) were boiled under reflux in the dark under nitrogen for 5 days. Work-up as above gave the pyrazole (26) (194 mg, 50%), identical with an authentic sample, and a brown oil (22 mg) which did not contain 1-acetyl-2-phenylcyclohexene hydrazone.

Acid catalysed rearrangement of 5,6,7,7a-*tetrahydro*-3-*methyl*-3-*phenyl*-4H-*indazole* (28). A solution of the indazole (0.438 g, 1.40 mmol) in glacial acetic acid (30 ml) was kept at 95 °C under nitrogen for 30 min. After neutralisation with aqueous sodium bicarbonate the product was extracted into ether. The ether solution was dried and evaporated and the residue separated by dry-column chromatography (alumina, methylene chloride) to give 4,5,6,7-*tetrahydro*-3-*methyl*-3a-*phenyl*-3H-*indazole* (27) (150 mg, 34%) as an oil, pure by t.l.c. (Found: $M^{+\cdot}$, 212.131 706, $M^{+\cdot}$ − 28, 184.125 175. $C_{14}H_{16}N_2$ requires *M*, 212.131 342, $C_{14}H_{16}$ requires *m/e*, 184.125 194), τ($CDCl_3$) 2.6—3.2 (5 H, m) and 8.05 (s, Me) superimposed on 6.8—9.0 (8 H, m).

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