Steric Effects in the Reactions of αβ-Unsaturated Ketone *p*-Tolylsulphonylhydrazones: a Route to 1,2-Benzodiazepines *via* 1,7-Ring Closure of 1,1-Diaryl-3-diazoalkenes [1]

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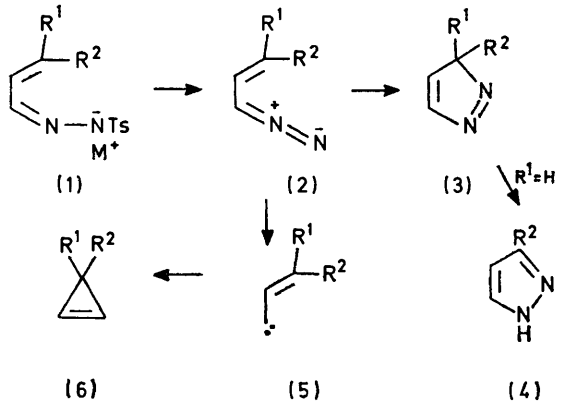
The influence of steric effects and substituents on the reactions of the sodium salts of αβ-unsaturated ketone tosylhydrazones has been studied. The tosylhydrazone salts of acyclic αβ-unsaturated ketones and those of 2-methylenecyclohexanones underwent ready thermal 1,5-ring closure to give pyrazoles but the reactions of some 2-methylenecyclopentanone tosylhydrazones were atypical. Although 2-methylenecyclopentanone tosylhydrazone salts having a β-hydrogen atom cyclised to give 1*H*-pyrazoles in high yield, the ββ-dialkyl and the ββ-diaryl analogues both failed to give 3*H*-pyrazoles: the former decomposed by a carbenic route to give dienes and the latter underwent 1,7-ring closure to give 3*H*-1,2-benzodiazepines. The effect of solvent proticity on some of these reactions has been investigated, and the mechanisms of pyrazole and benzodiazepine formation are discussed. The ^{13}C n.m.r. spectra of 3*H*-pyrazoles, 3*H*-1,2-benzodiazepines, and 1*H*-2,3-benzodiazepines show that ring size strongly affects the chemical shift of the saturated carbon atom attached to the azo-group.

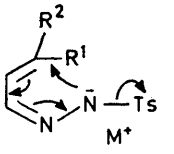
In 1935 Adamson and Kenner reported that 3-diazopropene (2; $R^1 = R^2 = H$) slowly cyclised at room temperature to give pyrazole [2] (4; $R^2 = H$); more recently, a kinetic study has shown that such reactions take place by a concerted process.[3] Diazoalkenes for this reaction can be generated most conveniently by thermal decomposition of the tosylhydrazone salts of αβ-unsaturated carbonyl compounds (1). Closs [4,5] has shown that such decompositions can take two paths: (i) ring closure to give pyrazoles, and (ii) loss of nitrogen to give carbene-derived products, *e.g.* (6) (Scheme 1). Since it is well established that the thermal decomposition of tosylhydrazone salts proceeds *via* diazo-compounds, it seems likely that the reactions follow Scheme 1; indeed in some cases the transient red colour of a



Scheme 1

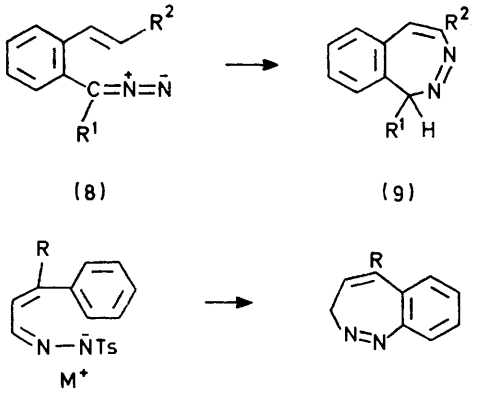
diazoalkene can be observed. It is not certain, however, that the pyrazoles are always formed in this way; their genesis could involve ring closure of the tosylhydrazone salt with concerted loss of the toluene-*p*-sulphinate anion (7).

We have recently shown that diazo-compounds with αβ-aromatic and γδ-olefinic unsaturation, *e.g.* (8), undergo 1,7-ring closure to give 2,3-benzodiazepines (9).[6] Part of this paper describes some studies on the formation of the previously unknown 3*H*-1,2-benzodiazepines (11)



(7)

from systems (10) similar to (8) but having αβ-olefinic and γδ-aromatic unsaturation. The first part, however, is concerned with tosylhydrazones with only αβ-olefinic unsaturation and shows how some steric factors and substituents affect the partition between the carbenic and



the cyclisation reaction (Scheme 1); the same factors are seen to influence the partition between 1,5- and 1,7-ring closure in (10).

[1] Preliminary report, R. H. Findlay, J. T. Sharp, and P. B. Thorogood, *Chem. Comm.*, 1970, 909.
[2] D. W. Adamson and J. Kenner, *J. Chem. Soc.*, 1935, 286.
[3] J. L. Brewbaker and H. Hart, *J. Amer. Chem. Soc.*, 1969, **91**, 711.
[4] G. L. Closs, L. E. Closs, and W. A. Böll, *J. Amer. Chem. Soc.*, 1963, **85**, 3796.
[5] G. L. Closs and W. A. Böll, *Angew. Chem. Internat. Edn.*, 1963, **2**, 399.
[6] A. A. Reid, J. T. Sharp, H. R. Sood, and P. B. Thorogood, *J.C.S. Perkin I*, 1973, 2543.

EXPERIMENTAL

^{1}H N.m.r. spectra were obtained on Perkin-Elmer R10 and Varian HA100 spectrometers and ^{13}C n.m.r. spectra on a Varian XL100 spectrometer.

Preparation of Unsaturated Ketones.—These (Table 1) were prepared by standard routes or as described below.

trans-2-*Ethylidenecyclopentanone.* 2-(2-Hydroxyethyl)-cyclopentanone [7] (b.p. 58—60° at 0·1 mmHg; lit.,[7] 91—97° at 0·8 mmHg) (25·6 g) and toluene-*p*-sulphonic acid (0·6 g) were boiled under reflux in benzene (150 ml) for 2 min. After extraction with water (2 × 50 ml) and drying, evaporation of the benzene solution gave a brown oil which was distilled to give 2-ethylidenecyclopentanone (15·0 g, 68%), b.p. 74—78° at 13 mmHg (lit.,[8] 85—89° at 18 mmHg); $\nu_{max.}$ (film) 1725 (C=O) and 1660 cm^{-1} (C=C).

cis-2-*Benzylidenecyclohexanone.* This was prepared by an adaption of Hassner and Meads' method.[9] *trans*-2-Benzylidenecyclohexanone [10] (8·4 g, 0·045 mol) in dry methanol (1100 ml) was irradiated at the b.p. with a Hanovia 100 W medium-pressure lamp through quartz. The reaction was followed by u.v. spectroscopy. After 8 h $\lambda_{max.}$ had shifted from 289 to 276 nm and was unchanged by further irradiation, but g.l.c. (2% NPGS, 140°) showed that 30% of the *trans*-isomer was still present. A portion of the mixture (100 ml) was further diluted with methanol (1000 ml) and irradiated for a further 3·5 h; g.l.c. then showed that only 5% of the *trans*-isomer remained. The methanol was removed under reduced pressure and the residue flash-distilled to give *cis*-2-benzylidenecyclohexanone as a yellow solid, b.p. *ca.* 112° at 0·01 mmHg, giving yellow crystals, m.p. 32—34° (from petroleum), shown to be a single compound by g.l.c. (2% NPGS; 140°).

TABLE 1

p-Tolylsulphonylhydrazones of the unsaturated ketones

Ketone	Tosyl-hydrazone salt	Formula of hydrazone	C(%) Found	C(%) Calc.	H (%) Found	H (%) Calc.	N (%) Found	N (%) Calc.	Yield (%)	M.p. (°C)	Cryst. solvent *	ν_{NH}/cm^{-1}
2-Cyclohexylidenecyclo-hexanone [b]	(12b)	$C_{19}H_{26}N_2O_2S$	65·6	65·9	7·4	7·6	7·9	8·1	67	152—153 †	B–E	3195
2-Isopropylidenecyclo-pentanone [c]	(12c)	$C_{15}H_{20}N_2O_2S$	61·4	61·6	7·1	6·9	9·7	9·6	72	196—197 †	C–E	3205
2-Cyclopentylidene-cyclopentanone [d]	(12d)	$C_{17}H_{22}N_2O_2S$	63·8	64·1	6·9	7·0	8·9	8·8	90	176 †	C–E	3180
trans-2-Ethylidene-cyclopentanone [e]	(17a) [f]	$C_{14}H_{18}N_2O_2S$	60·3	60·4	6·7	6·5	10·0	10·1	46	152—153 †	B–M	3190
trans-2-Benzylidene-cyclopentanone [g]	(17b)	$C_{19}H_{20}N_2O_2S$	66·95	67·05	5·85	5·9	8·5	8·25	81	187—188 †	B–EA	3200
trans-2-Benzylidene-cyclohexanone [h]	(17c)	$C_{20}H_{22}N_2O_2S$	67·95	67·8	6·45	6·3	7·95	7·9	96	152—153 †	T	3240
cis-2-Benzylidenecyclo-hexanone [e]	(36; X = H) [f]								95	136 †		3200
4,4-Diphenylbut-3-en-2-one [i]	(30)	$C_{23}H_{22}N_2O_2S$	70·7	70·75	5·8	5·7	6·95	7·2	90	162—164	B–M	3200
3,4-Diphenylbut-3-en-2-one [k]	(31)	$C_{23}H_{22}N_2O_2S$	71·0	70·75	5·8	5·7	7·35	7·2	81	153—154	B–E	3160
2-(Di-*p*-tolylmethylene)-cyclohexanone [e]	(32)	$C_{28}H_{30}N_2O_2S$	73·3	73·3	6·85	6·6	6·4	6·1	89	159 †	B–EA	3250
trans-2-(4-Nitrobenzylidene) cyclohexanone [l]		$C_{20}H_{21}N_3O_4S$	60·2	60·1	5·2	5·3	10·45	10·5	75	164 †	C	3230
trans-2-(3-Methoxybenzylidene)-cyclohexanone [m]		$C_{21}H_{24}N_2O_3S$	65·45	65·6	6·6	6·3	7·6	7·3	64	129—130 †	E–EA	3205
2-Diphenylmethylene-cyclopentanone [e]	(37a)	$C_{25}H_{24}N_2O_2S$	72·0	72·1	5·7	5·8	6·85	6·7	90	166 †	E–B	3180
2-(Di-*p*-tolylmethylene)-cyclopentanone [e]	(37b)	$C_{27}H_{28}N_2O_2S$	72·65	72·95	6·2	6·35	6·4	6·3	72	178 †	E–EA	3250
2-[Bis-(*m*-methoxyphenyl)-methylene]cyclopentanone [e]	(37c)	$C_{27}H_{28}N_2O_4S$	67·7	68·15	6·3	5·9	5·7	5·9	78	148—149 †	E–P	3230
2-[Bis-(*p*-trifluoromethyl-phenyl)methylene]-cyclopentanone [e]	(37d)	$C_{27}H_{22}F_6N_2O_2S$	58·8	58·7	4·0	4·0	5·4	5·1	62	186—187 †	P–EA	3230
2-[Bis-(*p*-fluorophenyl)-methylene]cyclopentanone	(37e)	$C_{25}H_{22}F_2N_2O_2S$	66·7	66·4	4·8	4·9	6·5	6·2	82	204—206 †		3200

* B = benzene, E = ethanol, C = chloroform, M = methanol, EA = ethyl acetate, T = toluene, P = petroleum. † Decomp.

[a] Spectra run as mull in Nujol. [b] J. Reese, *Ber.*, 1942, **75**, 384. [c] G. Vavon and A. Apchié, *Bull. Soc. chim. France*, 1928, **43**, 667. [d] D. Varech, C. Ouannes, and J. Jacques, *Bull. Soc. chim. France*, 1965, 1662. [e] Ketone preparation described in text. [f] Tosylhydrazone preparation described in text. [g] W. S. Emerson, G. H. Birum, and R. I. Longley, *J. Amer. Chem. Soc.*, 1953, **75**, 1312. [h] Ref. 10. [i] G. Wittig and H. Reiff, *Angew. Chem. Internat. Edn.*, 1968, **7**, 7. [j] ^{1}H N.m.r. spectrum showed the presence of *syn* and *anti* isomers. [k] H. E. Zimmermann, L. Singer, and B. S. Thyagarajan, *J. Amer. Chem. Soc.*, 1959, **81**, 108. [l] V. F. Sedova and V. P. Mamaev, *Khim. geterotsikl. Soedinenii, Sb.* 1: *Azotsoderzhashchie Geterotsikl.*, 1967, 349 (*Chem. Abs.*, 1969, **70**, 87,722d.) [m] Ref. 12.

2-(*Di*-p-*tolylmethylene*)*cyclohexanone.* This was prepared by the reaction of the Grignard reagent from *p*-bromotoluene (40·0 g, 0·23 mol) with ethyl 2,2-ethylenedioxycyclohexanecarboxylate [11] (25·0 g, 0·12 mol). After decomposition of the complex with aqueous ammonium chloride and extraction with ether a yellow oil was obtained which solidified on cooling. Recrystallisation of a small sample gave (2,2-*ethylenedioxycyclohexyl*)*di*-p-*tolylmethanol* as needles, m.p. 162—163° (Found: C, 78·2; H, 7·95. $C_{23}H_{28}O_3$ requires C, 78·4; H, 8·0%); $\nu_{max.}$ (Nujol) 3385 cm^{-1} (OH). The bulk of the product was mixed with methanol (135 ml), water (90 ml), and concentrated hydrochloric acid

[7] J. Skoda, *Bull. Soc. chim. France*, 1946, 327.
[8] R. Jacquier and G. Maury, *Bull. Soc. chim. France*, 1967, 306.
[9] A. Hassner and T. C. Mead, *Tetrahedron*, 1964, **20**, 2201.
[10] H. M. Walton, *J. Org. Chem.*, 1957, **22**, 1161.
[11] H. R. Snyder, L. A. Brooks, and S. H. Shapiro, *Org. Synth.*, Coll. Vol. 2, 1943, p. 531.

(4 ml) and boiled under reflux with vigorous stirring for 4 h. Work-up in the usual way gave 2-(*di*-p-*tolylmethylene*)*cyclohexanone* as yellow plates (11·4 g, 33%), m.p. 149° (Found: C, 86·55; H, 7·75. $C_{21}H_{22}O$ requires C, 86·85; H, 7·6%); $\nu_{max.}$ (Nujol) 1680 cm^{-1} (C=O).

cis-2-(3-*Methoxybenzylidene*)*cyclohexanone*. A solution of *trans*-2-(3-methoxybenzylidene)cyclohexanone [12] (2·1 g) in methanol (750 ml) was heated under reflux under nitrogen and irradiated with a 100 W Hanovia medium-pressure u.v. lamp through silica. The reaction was monitored by u.v. and after 8 h there was no further shift in the band at 282 nm. Evaporation of the methanol under reduced pressure left an oil which was flash-distilled under high vacuum to give the *cis*-ketone (1·71 g, 82%); $\nu_{max.}$ (film) 1670 cm^{-1} (C=O).

2-*Diphenylmethylenecyclopentanone*. Phenylmagnesium bromide was prepared by addition of bromobenzene (52·0 g, 0·33 mol) in dry ether (125 ml) to magnesium (8·5 g, 0·35 mol) in ether (35 ml) under dry nitrogen. The mixture was boiled under reflux for 20 min and then a solution of ethyl 2,2-ethylenedioxycyclopentanecarboxylate [13,14] (32·5 g, 0·163 mol) in ether (75 ml) was added slowly with vigorous stirring. The mixture was boiled and stirred for 30 min, cooled, and aqueous ammonium chloride (200 ml; 37% w/v) was added slowly to decompose the complex. The ether layer was separated and the aqueous layer extracted with ether (2 × 100 ml); the ethereal solutions were combined and concentrated to give a yellow oil. The oil was added to a mixture of methanol (80 ml), water (55 ml), and concentrated hydrochloric acid (4 ml) and the mixture was heated under reflux with vigorous stirring for 5 h. On cooling a yellow solid separated which was filtered off. Evaporation of the aqueous methanol under reduced pressure left a residue which was shaken with petroleum (50 ml) and set aside at *ca.* −5° for 48 h to give more yellow solid. The yellow product was recrystallised from ethanol to give 2-diphenylmethylenecyclopentanone (12·3 g, 30%) as yellow needles, m.p. 115—116° (lit.,[15] 114—115°) (Found: C, 86·95; H, 6·7. Calc. for $C_{18}H_{16}O$: C, 87·1; H, 6·5%); τ ($CDCl_3$) 2·6—3·0 (10H, m), 7·23 (t, *J* 7 Hz, CH_2), 7·68 (t, *J* 7 Hz, CH_2), 8·14 (quint, *J* 7 Hz, CH_2); $\nu_{max.}$ (Nujol) 1700 cm^{-1} (C=O).

The following ketones were prepared in a similar way, but the duration of the final acid-catalysed hydrolysis/dehydration step varied for each example. In all cases the formation of the unsaturated ketone was monitored by g.l.c. (3% QF1, 200—230°) and the reaction was continued until the peak due to the diaryl-(2-oxocyclopentyl)methanol had disappeared. The intermediate tertiary alcohol was isolated only in the unsubstituted case, by stopping the hydrolysis reaction after 2 h and recrystallising the product from acetic acid to give (2-*oxocyclopentyl*)*diphenylmethanol*, m.p. 152—153°, as needles (Found: C, 81·4; H, 6·8. $C_{18}H_{18}O_2$ requires C, 81·2; H, 6·8%); $\nu_{max.}$ (Nujol) 3420 (OH), and 1730 cm^{-1} (C=O), g.l.c. retention time relative to 2-diphenylmethylenecyclopentanone, 0·31 on a 3% QF1 column at 220°.

2-(*Di*-p-*tolylmethylene*)*cyclopentanone* (36%) had m.p. 142—143° (Found: C, 86·85; H, 7·55. $C_{20}H_{20}O$ requires C, 86·9; H, 7·3%); $\nu_{max.}$ (Nujol) 1700 and 1715 cm^{-1} (C=O). 2-[*Bis*-(m-*methoxyphenyl*)*methylene*]*cyclopentanone* (30%) had m.p. 106° (Found: C, 77·7; H, 6·65. $C_{20}H_{20}O_3$ requires C, 77·9; H, 6·5%); $\nu_{max.}$ (Nujol) 1700 cm^{-1} (C=O). 2-[*Bis*-(p-*trifluoromethylphenyl*)*methylene*]*cyclopentanone* (34%) had m.p. 74° (Found: C, 62·65; H, 3·6. $C_{20}H_{14}F_6O$ requires C, 62·5; H, 3·7%); $\nu_{max.}$ (Nujol) 1715 cm^{-1} (C=O). 2-[*Bis*-(p-*fluorophenyl*)*methylene*]*cyclopentanone* (24%) had m.p. 147—148° (Found: C, 76·1; H, 4·9. $C_{18}H_{14}F_2O$ requires C, 76·0; H, 5·0%); $\nu_{max.}$ (Nujol) 1710 cm^{-1} (C=O).

Preparation of the p-*Tolylsulphonylhydrazones*.—Except where details are given below, the tosylhydrazones (Table 1) were prepared by admixture of warm (50°) ethanolic solutions of the unsaturated ketone and *p*-tolylsulphonylhydrazine (1 mol. equiv.) with addition of a few drops of concentrated hydrochloric acid. The product usually crystallised in good yield overnight. The tosylhydrazones of the 2-diarylmethylenecyclopentanones when prepared in or recrystallised from ethanol generally contained some solvated ethanol which could not be removed by vacuum drying; this was removed by dissolving the tosylhydrazones in chloroform followed by evaporation under reduced pressure.

2-*Ethylidenecyclopentanone tosylhydrazone* (17a). All attempts to prepare this by the usual method gave yellow solutions containing two products (t.l.c.) which did not crystallise. The unsaturated ketone (5·0 g) was added to a suspension of *p*-tolylsulphonylhydrazine (8·45 g) in methanol (50 ml) at room temperature. After *ca.* 10 min the *p*-tolylsulphonylhydrazine had dissolved and the product began to crystallise. After 6·5 h 2-ethylidenecyclopentanone tosylhydrazone (5·8 g, 46%) was filtered off and recrystallised from methanol–benzene.

cis-2-*Benzylidenecyclohexanone tosylhydrazone*. This was prepared by mixing a solution of the *cis*-ketone (1·0 g, 0·0054 mol) in ethanol (5 ml) with *p*-tolylsulphonylhydrazine (1·0 g, 0·0054 mol) dissolved in ethanol (7 ml) containing concentrated hydrochloric acid (0·05 ml). The mixture was rapidly warmed to 40°, and then cooled in ice. *cis*-2-Benzylidenecyclohexanone tosylhydrazone (1·8 g, 95%) was filtered off after 0·1 h; after washing with petroleum and ethanol (*ca.* 5 ml of each) it had m.p. 136° (decomp); $\nu_{max.}$ (Nujol) 3200 cm^{-1} (NH); τ [$(CD_3)_2SO$] −0·4 (s, NH), 2·48 and 2·88 (AA′BB′q, J_{AB} 8 Hz), 2·9—3·2 (5H, m), 3·8br (s, =CH−), 7·3—7·8 and 8·0—8·6 (8H, m), and 7·68 (s, CH_3). Recrystallisation from benzene gave the *trans*-isomer, τ [$(CD_3)_2SO$] −0·28 (s, NH), 2·17 and 2·57 (AA′BB′q, J_{AB} 8 Hz), 2·72br (5H, s), 3·34br (s, =CH−), 7·61 (s, CH_3), and 7·2—7·8 and 8·2—8·7 (8H, m).

cis-2-(3-*Methoxybenzylidene*)*cyclohexanone tosylhydrazone*. All attempts to prepare this gave the *trans*-tosylhydrazone.

Thermal Decomposition of Tosylhydrazone Sodium Salts.—The general procedure for the preparation and drying of the sodium salts and the work-up of the decomposition products are described for 2-ethylidenecyclopentanone tosylhydrazone. For subsequent experiments the solvent used and reaction time are given and any deviations from the standard procedure are noted. Unless otherwise stated the reactions were carried out in dry freshly distilled solvent at its b.p., under nitrogen, and in the dark.

trans-2-*Ethylidenecyclopentanone tosylhydrazone salt* (17a). (a) *In toluene*. The tosylhydrazone (2·86 g, 0·0103 mol) was added to a solution made by dissolving sodium (0·2371 g, 0·0103 mol) in dry ethanol (40 ml). The solution was stirred at room temperature in the dark for *ca.* 15 min

[12] R. Baltzly, E. Lorz, P. B. Russell, and F. M. Smith, *J. Amer. Chem. Soc.*, 1955, **77**, 624.

[13] R. P. Linstead and E. M. Meade, *J. Chem. Soc.*, 1934, 935.

[14] C. Black, G. L. Buchanan, and A. W. Jarvie, *J. Chem. Soc.*, 1956, 2971.

[15] R. T. Conley and B. E. Nowak, *J. Org. Chem.*, 1962, **27**, 1965.

and the solvent was evaporated off under reduced pressure below 40°. The residual salt was dried in the flask under high vacuum (P_2O_5) overnight. Dry toluene (40 ml) was added and the mixture was heated under reflux for 25 h; t.l.c. then showed that all the starting material had been consumed. The precipitated sodium toluene-*p*-sulphinate was filtered off and the filtrate was evaporated under reduced pressure to leave a white solid. This was recrystallised from benzene–petroleum to give 1,4,5,6-tetrahydro-3-methylcyclopentapyrazole (20a) (0·80 g, 64%), m.p. 139—140° (lit.,[16] 138—139°). (Found: C, 68·7; H, 8·1; N, 22·7. Calc. for $C_7H_{10}N_2$: C, 68·8; H, 8·25; N, 22·9%); ^{1}H n.m.r. data identical with those reported.[16]

(b) *In 2-methoxyethanol.* The tosylhydrazone (5·8 g, 0·021 mol) was added to a solution of sodium (0·46 g, 0·020 mol) in 2-methoxyethanol (40 ml) and the solution was boiled under reflux for 24 h. The mixture was poured into saturated sodium chloride solution (250 ml) and extracted with ether (3 × 20 ml). The extract was dried and evaporated to give the pyrazole (20a) (2·02 g, 79%), m.p. and mixed m.p. 139—141° (from benzene–petroleum).

2-*Cyclohexylidenecyclohexanone tosylhydrazone salt* (12b). (a) *Vacuum pyrolysis.* The tosylhydrazone (2·65 g) salt admixed with dry sand (8 g) was pyrolysed in a distillation flask connected to an ice-cooled receiver and a trap cooled in liquid nitrogen. The apparatus was evacuated to 0·05 mmHg and the flask was heated in an oil-bath at 140—150°; a pale yellow oil (1·34 g) distilled into the receiver. This was redistilled to give 3,4,5,6-*tetrahydrocyclopentapyrazole*-3-*spirocyclohexane* (14b) (1·19 g, 82%), b.p. 77—78° at 0·03 mmHg as an oil which solidified, m.p. 48—50° (Found: C, 75·7; H, 9·3; N, 14·5. $C_{12}H_{18}N_2$ requires C, 75·7; H, 9·5; N, 14·7%); τ ($CDCl_3$) 7·26 (2H, m) and 7·6—9·0 (16H, m).

(b) *In toluene* (3 h). The tosylhydrazone (4·32 g) salt gave an oil (1·78 g), b.p. 80—120° at 2 mmHg, shown by g.l.c. (1% SE30, 140°) to consist mainly of the 3*H*-pyrazole (14b) (63% yield), along with bi(cyclohex-1-enyl) (4%) and 3-cyclohexylidenecyclohexene (1%), identified by comparison (g.l.c. and g.l.c.–mass spectrometry) with authentic samples. Also present were three other components (<5%) which were not identified. A control experiment showed that (14b) was not converted into the dienes when boiled under reflux in toluene (12 h).

(c) *In 2-methoxyethanol* (11 h). The tosylhydrazone (11·15 g) salt in 2-methoxyethanol (120 ml) gave an oil (4·77 g) b.p. 70—120° at 0·5 mmHg, shown by g.l.c. (1% SE30, 140°) to contain the 3*H*-pyrazole (14b) (62%) yield, bi(cyclohex-1-enyl) (5%), 3-cyclohexylidenecyclohexene (1%), and two other components (*ca.* 2 and 5%) of molecular weight 238 (g.l.c.–mass spectrometry).

2-*Isopropylidenecyclopentanone tosylhydrazone salt* (12c). (a) *Vacuum pyrolysis.* The sodium salt (4·54 g) mixed with dry sand (15·25 g) was pyrolysed at 120—150° as described for (12b). A purple liquid (1·15 g) was collected; $\nu_{max.}$ (film) 2050 cm^{-1} (C=$\overset{+}{N}$=$\overset{-}{N}$). The liquid was distilled, with evolution of nitrogen, to give colourless 3-*isopropylidenecyclopentene* (0·95 g, 61%), b.p. 56° at 10 mmHg; g.l.c. (10% SIL, 65°; 5% PEGA, 50°) showed only a single peak (Found: C, 88·5; H, 11·5. C_8H_{12} requires C, 88·8; H, 11·2%); τ (CCl_4) 3·70 and 4·13 (broad distorted doublets, –CH=CH–, *J ca.* 6 Hz), 7·59 (m, 2 × CH_2), and 8·28 and 8·34 (overlapping singlets, 2 × CH_3). Hydrogenation of the product (0·5 g) at atmospheric pressure over 10% palladium–carbon gave a quantitative yield of isopropylcyclopentane, b.p. 126° (lit.,[17] 128—129°) (Found: C, 85·8; H, 14·1. Calc. for C_8H_{16}: C, 85·6; H, 14·4%); τ ($CDCl_3$) 8·0—9·0 (10H, m) and 9·15br (d, 2 × CH_3).

(b) *In cyclohexane.* Little decomposition of the tosylhydrazone salt occurred in 24 h.

(c) *In toluene.* The tosylhydrazone (2·77 g) salt was boiled under reflux in toluene (30 ml) for 14 h. G.l.c. (10% SIL, 65°; 5% PEGA, 50°; *p*-xylene as internal standard) showed that 3-isopropylidenecyclopentene was present in 74% yield.

2-*Cyclopentylidenecyclopentanone tosylhydrazone salt* (12d). (a) *In toluene* (24 h). The tosylhydrazone (9·33 g) salt was boiled under reflux in toluene (90 ml) for 24 h. G.l.c. (10% APL, 120°; APL capillary 130°) and t.l.c. (alumina; benzene) showed only one product. Distillation gave 3-*cyclopentylidenecyclopentene* (2·75 g, 70%), b.p. 85° at 11 mmHg (Found: C, 89·2; H, 10·9. $C_{10}H_{14}$ requires C, 89·5; H, 10·5%); τ (CCl_4) 3·85 (1H, m), 4·15 (1H, m), 7·4—8·05 (8H, m), and 8·2—8·4 (4H, m). The product was hydrogenated at atmospheric pressure over 10% palladium–carbon to give a single product, b.p. 70° at 11 mmHg, identical (g.l.c. on 50 m APL capillary, 130°) with bi(cyclopentyl) produced by the Wolff–Kishner reduction of 2-cyclopentylcyclopentanone; τ (CCl_4) 9·1—10·1 (m).

(b) *In 2-methoxyethanol* (24 h). The tosylhydrazone (12·93 g) salt gave an oil (5·29 g), b.p. 65—135° at 9 mmHg, which was shown by g.l.c. (2·5% OVI, 165°) to contain three components (40 : 7 : 53%). Distillation gave bi(cyclopent-1-enyl), b.p. 80—85° at 9—10 mmHg, and 2-cyclopentylidenecyclopentyl-(2-methoxyethyl) ether, b.p. 131° at 9—10 mmHg, corresponding to the first and last g.l.c. peaks respectively. Yields, estimated from the ^{1}H n.m.r. spectrum of the crude product, were 29% for the diene and 44% for the ether. The bi(cyclopent-1-enyl), τ ($CDCl_3$) 4·45br (2H, s), 7·4—7·8 (8H, m), and 8·11 (4H, dist. q), was converted into Diels–Alder adducts with maleic anhydride (76%; m.p. 101—102°; lit.,[18] 104°) and *p*-benzoquinone (32%; m.p. 120—122°; lit.,[18] 124°). 2-*Cyclopentylidenecyclopentyl* (2-*methoxyethyl*) *ether* (Found: C, 74·0; H, 10·5. $C_{13}H_{22}O_2$ requires C, 74·2; H, 10·5%) showed τ ($CDCl_3$) 5·78br (1H, s), 6·48 (4H, s), 6·66 (3H, s), 7·5—8·0 (6H, m), and 8·0—8·6 (8H, m) [similar to the spectrum of 2-cyclopentylidenecyclopentanol prepared by reduction of 2-cyclopentylidenecyclopentanone with sodium borohydride: τ ($CDCl_3$) 5·53br (1H, s), 6·89br (s, OH, removed on shaking with D_2O), and 7·4—8·2 (m, 14H)].

trans-2-*Benzylidenecyclopentanone tosylhydrazone salt* (17b). (a) *In cyclohexane* (25 h). The tosylhydrazone was recovered unchanged in 98% yield.

(b) *In toluene* (16·5 h). The tosylhydrazone (1·36 g) salt gave a solid product (0·69 g) which was recrystallised from ethanol to give 1,3,4,5-tetrahydro-3-phenylcyclopentapyrazole (20b) (0·52 g, 71%), m.p. 142—143° (lit.,[19] 144°) (Found: C, 78·05; H, 6·5; N, 15·05. Calc. for $C_{12}H_{12}N_2$: C, 78·2; H, 6·6; N, 15·2%); $\nu_{max.}$ (Nujol) 3140 cm^{-1} (NH), τ ($CDCl_3$) 0·3br (s, NH), 2·2—2·8 (6H, m), and 7·0—7·6 (6H, m).

(c) *In 2-methoxyethanol* (24 h). The tosylhydrazone (13·6 g) salt gave the same product as in (b) (6·1 g, 83%).

[16] R. Jacquier and G. Maury, *Bull. Soc. chim. France*, 1967, 316.
[17] F. Eisenlohr, *Fortschr. Chem. Phys.*, 1926, **18**, 75.
[18] E. de Barry Barnett and C. A. Lawrence, *J. Chem. Soc.*, 1935, 1104.
[19] T. Sato and S. Watanabe, *Bull. Chem. Soc. Japan*, 1968, **41**, 3017.

trans-2-*Benzylidenecyclohexanone tosylhydrazone salt* (17c) *in toluene*. The tosylhydrazone (5·15 g) salt was heated at 80° in toluene for 15 h and gave *tetrahydro-3-phenyl-1H-indazole* (20c), m.p. 127—128° (2·23 g, 77%). The product recrystallised from ethanol–petroleum contained ethanol which could not be removed by vacuum drying, and the compound was purified by sublimation at 130° and 0·05 mmHg (Found: C, 78·85; H, 7·05; N, 14·15. $C_{13}H_{14}N_2$ requires C, 78·75; H, 7·1; N, 14·15%); $\nu_{max.}$ (CCl_4) 3200—3140br cm^{-1} (NH); τ (CCl_4) −0·85br (s, NH), 2·2—2·85 (5H, m), 7·1—7·6 (4H, m), and 8·0—8·4 (4H, m).

cis-2-*Benzylidenecyclohexanone tosylhydrazone salt* (36) *in cyclohexane* (16 h). The tosylhydrazone (0·98 g) salt gave the indazole (20c) (0·40 g, 78%), m.p. and mixed m.p. 127—128°.

4,4-*Diphenylbut-3-en-2-one tosylhydrazone salt* (30). (a) *In dimethoxyethane*. The sodium salt was prepared by adding a solution of the tosylhydrazone (1·06 g, 0·00272 mol) in dimethoxyethane (15 ml) to a solution of sodium (0·069 g, 0·00304 mol) in ethanol (20 ml). The solvents were evaporated off under vacuum and any residual ethanol was removed by dissolving the salt in dimethoxyethane (20 ml) and again evaporating under vacuum. The residual salt was dried under vacuum overnight. Dimethoxyethane (30 ml), freshly distilled from calcium hydride, was added and the mixture was boiled under reflux for 1 h. The usual work-up gave a pale yellow solid (0·62 g, 98%), which was shown by n.m.r. spectroscopy to contain 3,3-diphenyl-5-methylpyrazole (84%) and 3(5)-methyl-4,5(3)-diphenylpyrazole (16%). Recrystallisation from dry benzene–petroleum gave 3,3-*diphenyl-5-methylpyrazole*, m.p. 99—101° (Found: C, 81·7; H, 6·1; N, 12·1. $C_{16}H_{14}N_2$ requires C, 82·0; H, 6·0; N, 12·0%); τ 2·72 (10H, s), 3·01 (1H, q, J 1·5 Hz), and 7·54 (d, J 1·5 Hz, CH_3). After determining the m.p. (99—101°) the sample was kept at 120—130° for a few minutes; it solidified and melted again at 178—179°.

(b) *In cyclohexane*. A similar experiment using cyclohexane which was freshly distilled from calcium hydride gave a result similar to that in (a). However, an experiment in which the sodium salt was prepared in the usual way and sodium-dried cyclohexane was used gave only 3(5)-methyl-4,5(3)-diphenylpyrazole (68%), m.p. and mixed m.p. 178—179°.

Reaction of diphenyldiazomethane with propyne. Diphenyldiazomethane was prepared by oxidising benzophenone hydrazone (5·0 g) with silver oxide (8·9 g) in dry ether (60 ml) at room temperature for 30 min. The solution was filtered, placed in a steel-tube reactor, and cooled to −70° while propyne (30 g) was added. The reactor was sealed and kept at room temperature for 14 weeks. The ethereal solution was kept overnight at −20°, then pale yellow crystals (0·65 g) of benzophenone azine, m.p. and mixed m.p. 159—160°, were filtered off. The mother liquor was concentrated to give white crystals (1·20 g), shown by t.l.c. to contain one major component contaminated with benzophenone azine. Dry-column chromatography gave 3,3-diphenyl-5-methylpyrazole (0·41 g), m.p. 99—101°, i.r. and n.m.r. spectra identical with those reported above. This 3*H*-pyrazole (50 mg) was boiled under reflux in ethanol (10 ml) for 2 h and was quantitatively converted into 3(5)-methyl-4,5(3)-diphenylpyrazole, m.p. and mixed m.p. 179—180°. 3,3-Diphenyl-5-methylpyrazole (50 mg) in cyclohexane (10 ml), freshly distilled from calcium hydride, was boiled under reflux for 20 h and the solvent was then evaporated off under vacuum. The n.m.r. spectrum of the whole product showed *ca.* 50% conversion into 3(5)-methyl-4,5(3)-diphenylpyrazole. The conversion was completed by boiling the mixture in ethanol for 1·5 h to give the 1*H*-pyrazole (31), m.p. and mixed m.p. 178—179°.

trans-3,4-*Diphenylbut-3-en-2-one tosylhydrazone salt* (33) *in cyclohexane* (24 h). The tosylhydrazone (0·60 g) salt gave 3(5)-methyl-4,5(3)-diphenylpyrazole (0·23 g, 64%), m.p. 178—179° (lit.,[19] 179—180°) (from ethanol–petroleum) (Found: C, 81·95; H, 6·1; N, 12·05. Calc. for $C_{16}H_{14}N_2$: C, 82·0; H, 6·0; N, 12·0%); $\nu_{max.}$ (Nujol) 3200—3040br cm^{-1} (NH); τ ($CDCl_3$) −1·25br (s, NH), 2·5—2·9 (10H, m), and 7·90 (s, CH_3).

2-(*Di*-p-*tolylmethylene*)*cyclohexanone tosylhydrazone salt* (34) *in cyclohexane* (14 h). The tosylhydrazone (4·12 g) salt gave a colourless solid (2·57 g) which was recrystallised from ethanol–petroleum to give 4,5,6,7-*tetrahydro*-3,3-*di*-p-*tolyl*-3H-*indazole* (35) (1·97 g, 73%) as needles, m.p. 101—102° (Found: C, 83·2; H, 7·4; N, 9·25. $C_{21}H_{22}N_2$ requires C, 83·4; H, 7·3; N, 9·3%); τ ($CDCl_3$) 3·0 (8H, s), 7·0—7·3 (4H, m), 8·0—8·4 (4H, m), and 7·7 (s, 2 × CH_3); $\nu_{max.}$ (Nujol) 1650 cm^{-1} (N=N). No red colouration was observed during the reaction.

trans-2-(4-*Nitrobenzylidene*)*cyclohexanone tosylhydrazone salt*. (a) *In cyclohexane and* (b) *in toluene*. T.l.c. showed that little decomposition of the tosylhydrazone salt took place in 20 h.

(c) *In t-butylbenzene* (7 h). The tosylhydrazone (1·45 g) salt gave a yellow oil which could not be crystallised. The oil was chromatographed on silica gel to give 4,5,6,7-*tetrahydro*-(4-*nitrophenyl*)*indazole* (0·73 g, 83%), m.p. 183—185° as pale yellow crystals (Found: C, 64·5; H, 5·5; N, 17·2. $C_{13}H_{13}N_3O_2$ requires C, 64·2; H, 5·4; N, 17·3%); $\nu_{max.}$ (Nujol) 3240br cm^{-1} (NH); τ ($CDCl_3$) 1·78 (2H, d),2·18 (2H, d), 7·1—7·5 (4H, m), and 8·0—8·4 (4H, m).

trans-2-(3-*Methoxybenzylidene*)*cyclohexanone tosylhydrazone salt*. (a) *In t-butylbenzene*. The tosylhydrazone (1·08 g) salt was heated at 100° in t-butylbenzene for 5 h; t.l.c. then showed that the reaction was complete. The product was a yellow oil which was purified by distillation (170° at 0·05 mmHg) to give 4,5,6,7-*tetrahydro*-3-(3-*methoxyphenyl*)-*indazole* (0·51 g, 79%) as a pale yellow viscous oil (Found: C, 73·2; H, 7·05; N, 11·7. $C_{14}H_{16}N_2O$ requires C, 73·7; H, 7·1; N, 12·3%); $\nu_{max.}$ (CCl_4) 3000—3200br and 3460 cm^{-1} (NH); τ (CCl_4) 1·1 (s, NH), 2·6—2·9 (3H, m), 3·15 (1H, q), 6·25 (s, CH_3), 7·1—7·6 (4H, m), and 8·0—8·4 (4H, m).

2-*Diphenylmethylenecyclopentanone tosylhydrazone salt* (37a). (a) *In cyclohexane*. The sodium salt of the tosylhydrazone (4·99 g) was boiled under reflux in cyclohexane (150 ml) for 25 h. Initially the solution turned brown and then assumed a deep red colour which eventually faded to give a yellow solution and a white precipitate. The precipitate (2·06 g) was filtered off and dissolved in water and the solution was acidified with hydrochloric acid giving a white precipitate. This was filtered off under nitrogen and recrystallised from water to give toluene-*p*-sulphinic acid (1·54 g, 82%), m.p. 83—84° (lit.,[20] 85°). The yellow filtrate was evaporated under reduced pressure to give a yellow solid (2·77 g) which afforded 1,2,3,3a-*tetrahydro*-10-*phenylbenzo*[c]*cyclopenta*[f][1,2]*diazepine* (39a) (2·38 g) as yellow needles, m.p. 159—160° (from ethanol). The mother liquor was evaporated and the residual oil was chromatographed on silica to give a colourless oil (0·14 g), which could not be crystallised, and more benzodiazepine (0·13 g, total 80%)

[20] Heilbron's ' Dictionary of Organic Compounds,' Eyre and Spottiswoode, London, 1965.

(Found: C, 82·9; H, 6·2; N, 10·75. $C_{18}H_{16}N_2$ requires C, 83·05; H, 6·2; N, 10·8%); $\nu_{max.}$ (Nujol) 1570w and 1600w cm^{-1} (C=C, N=N); τ ($CDCl_3$) 2·22br (1H, d, *J* 8 Hz), 2·4—3·0 (8H, m), 6·85br (1H, d, *J ca.* 9 Hz), and 7·1—8·0 (6H, m).

(b) *In cyclohexane in the presence of tributylphosphine.* The tosylhydrazone salt (1·4 g, 0·0032 mol) and tributylphosphine (1·2 g, 0·006 mol) in cyclohexane (30 ml) were heated at 70° for 4 h and then boiled under reflux for a further 4 h. No red colour was observed at any time. The mixture was cooled and the white precipitate of sodium toluene-*p*-sulphinate (0·55 g) was filtered off. Evaporation of the filtrate gave a yellow solid which was recrystallised from ethanol–petroleum to give 2-*diphenylmethylenecyclopentanone hydrazone* (0·71 g, 85%), m.p. 125—126°, as yellow needles (Found: C, 82·25; H, 6·9; N, 10·35. $C_{18}H_{18}N_2$ requires C, 82·4; H, 6·9; N, 10·7%); $\nu_{max.}$ (Nujol) 3350 and 3200br cm^{-1} (NH); τ ($CDCl_3$) 2·8 (10H, s), 5·1br (s, NH_2), 7·43 (t, *J* 7 Hz, CH_2), 7·69 (t, *J* 7 Hz, CH_2), and 8·21 (q, *J* 7 Hz, CH_2). This product was further characterised as the azine formed by condensation with acetone. Acetone (1 drop) was added to a solution of the hydrazone (0·09 g) in ethanol. The mixture was warmed to 60° and set aside to crystallise. The product was recrystallised from ethanol–petroleum to give 1-*isopropylidenehydrazono*-2-*diphenylmethylenecyclopentanone* (0·08 g), m.p. 109—110° (Found: C, 83·1; H, 7·65; N, 9·25. $C_{21}H_{22}N_2$ requires C, 83·4; H, 7·3; N, 9·3%); τ ($CDCl_3$) 2·75 (10H, s), 7·37br (t, *J* 7 Hz, 2 × CH_2), 7·09 (s, CH_2 superimposed on m, CH_2), and 8·67 (s, CH_2).

2-(*Di*-p-*tolylmethylene*)*cyclopentanone tosylhydrazone salt* (37b) *in cyclohexane* (25 h). The tosylhydrazone (5·36 g) salt gave 1,2,3,3a-*tetrahydro*-7-*methyl*-10-p-*tolylbenzo*[c]*cyclopenta*[f][1,2]*diazepine* (39b) as yellow plates (2·36 g, 68%), m.p. 177—178° (from ethanol) (Found: C, 82·95; H, 6·85; N, 9·6. $C_{20}H_{20}N_2$ requires C, 83·3; H, 7·0; N, 9·7%); $\nu_{max.}$ (Nujol) 1610w and 1570w cm^{-1} (N=N, C=C); τ ($CDCl_3$) 2·39br (1H, s,), 2·75—3·0 (6H, m), 6·83br (1H, d, *J ca.* 9 Hz), 7·57 (s, CH_2), 7·63 (s, CH_2), and 7·1—8·0 (6H, m).

2-[*Bis*-(m-*methoxyphenyl*)*methylene*]*cyclopentanone tosylhydrazone salt* (37c) *in cyclohexane* (14 h). The tosylhydrazone (1·95 g) salt gave 1,2,3,3a-*tetrahydro*-6-*methoxy*-10-(m-*methoxyphenyl*)*benzo*[c]*cyclopenta*[f][1,2]*diazepine* (39c) (0·89 g, 68%), m.p. 149—150° (from ethanol) (Found: C, 75·15; H, 6·45; N, 8·75. $C_{20}H_{20}N_2O_2$ requires C, 75·0; H, 6·3; N, 8·7%); $\nu_{max.}$ (Nujol) 1605w and 1580w cm^{-1} (N=N, C=C); τ ($CDCl_3$) 2·80—3·45 (7H, m), 6·88br (1H, d, *J ca.* 9 Hz), 7·1—8·2 (6H, m), 6·1 (s, CH_3), and 6·35 (s, CH_3).

2-[*Bis*-(p-*trifluoromethylphenyl*)*methylene*]*cyclopentanone tosylhydrazone salt* (37d) *in cyclohexane* (20 h). The tosylhydrazone (3·58 g) salt gave an orange solid (2·01 g) which was recrystallised from benzene–ethanol to give 2-[*bis*-(p-*trifluoromethylphenyl*)*methylene*]*cyclopentanone azine* as an orange solid (0·175 g). The mother liquor was evaporated and the residue was chromatographed on silica gel (2 × 45 cm). Elution with petroleum containing an increasing proportion of benzene gave more of the azine (total 0·54 g), m.p. 241—242° (decomp.), mixed m.p. with an authentic sample 235—237° (decomp.) (Found: C, 62·85; H, 3·45; N, 3·35. $C_{40}H_{28}F_{12}N_2$ requires C, 62·8; H, 3·7; N, 3·7%); $\nu_{max.}$ (Nujol) 1615 cm^{-1} (C=N); τ ($CDCl_3$) 2·35—2·9 (16H, m), 7·25—7·6 (4H, m), and 8·1—8·55 (8H, m). Elution with benzene containing an increasing proportion of ether gave a yellow solid which was recrystallised to give 1,2,3,3a-*tetrahydro*-7-(*trifluoromethyl*)-10-(p-*trifluoromethylphenyl*)-*benzo*[c]*cyclopenta*[f][1,2]*diazepine* (39d) (1·44 g, 56%), m.p. 106° (Found: C, 60·55; H, 3·55; N, 6·9. $C_{20}H_{14}F_6N_2$ requires C, 60·6; H, 3·6; N, 7·1%); $\nu_{max.}$ (Nujol) 1620w cm^{-1} (C=C and/or N=N); τ ($CDCl_3$) 2·0 (1H, s), 2·2—3·0 (6H, m), 6·75br (1H, d, *J ca.* 9 Hz), and 7·1—8·0 (6H, m).

2-[*Bis*-(p-*fluorophenyl*)*methylene*]*cyclopentanone tosylhydrazone salt* (37e) *in cyclohexane* (22 h) (with G. M. Baird). The tosylhydrazone (2·097 g) salt gave a dark yellow oil which crystallised from ethanol to give 1,2,3,3a-*tetrahydro*-7-*fluoro*10-(p-*fluorophenyl*)*benzo*[c]*cyclopenta*[f][1,2]*diazepine* (39e) (0·52 g, 38%), m.p. 129—132° (Found: C, 72·9; H, 5·1; N, 9·4. $C_{18}H_{14}F_2N_2$ requires C, 73·0; N, 4·8; H, 9·5%); $\nu_{max.}$ (Nujol) 1560w and 1600w cm^{-1} (C=C, N=N), τ ($CDCl_3$) 2·53 (1H, dd, $J_{H.F}$ 9, J_m 2·5 Hz), 2·7—3·2 (6H, m), 6·82br (1H, d, *J ca.* 9 Hz), and 7·1—7·9 (6H, m).

Base-catalysed Rearrangement of the Benzo[c]*cyclopenta*[f]-[1,2]*diazepine* (39a) (with Mrs. K. L. M. Stanley).—The benzodiazepine (0·035 g) was added to a degassed 0·02M-solution of sodium in ethanol (20 ml) and the solution was boiled under reflux under nitrogen for 18 h. The solvent was removed under reduced pressure, water (10 ml) was added, and the mixture was extracted with ether (2 × 10 ml). The extract was dried and evaporated to give an orange solid (30 mg), shown by t.l.c. to contain only one component, which was recrystallised from degassed ethanol to give 1,2,3,5-*tetrahydro*-10-*phenylbenzo*[c]*cyclopenta*[f]-[1,2]*diazepine* (40), m.p. 176—177° (Found: C, 83·1; H, 6·2; N, 10·8. $C_{18}H_{16}N_2$ requires C, 83·05; H, 6·2; N, 10·8%); $\nu_{max.}$ (Nujol) 3245 cm^{-1} (NH), τ ($CDCl_3$) 2·5—3·55 (9H, m), 7·52 (t, *J* 7 Hz, CH_2), 7·63 (t, *J* 7 Hz, CH_2), 8·33 (distorted quint, *J* 7 Hz, CH_2); τ (C_6D_6) 2·6—3·6 (8H, m), 3·82br (1H, d, *J* 8 Hz), 7·66 (t, 7 Hz, CH_2), 7·92 (t, *J* 7 Hz, CH_2), and 8·68 (distorted quint, *J* 7 Hz, CH_2). The 3*H*-benzodiazepine (73 mg) was also isomerised to the 1*H*-isomer when boiled under reflux in ethanol (10 ml) containing hydrochloric acid (0·023 g) for 0·5 h.

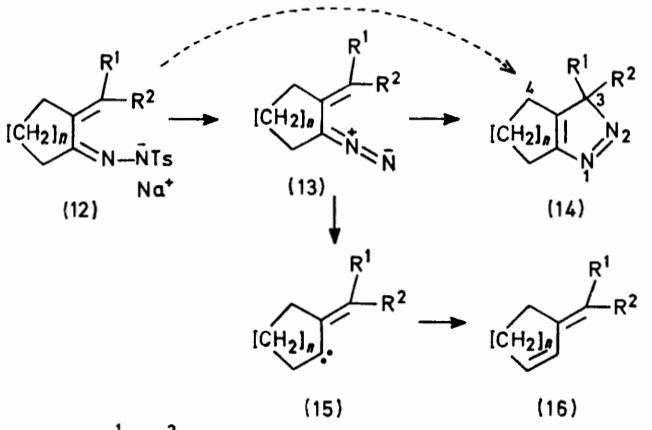
2-*Diphenylmethylenecyclopentanone Phenylhydrazone* (with Mrs. K. L. M. Stanley).—A solution of 2-diphenylmethylenecyclopentanone (0·50 g) and phenylhydrazine (1·0 g) in butanol (10 ml) was boiled under reflux under nitrogen, overnight. A solid separated on cooling which was recrystallised from degassed ethanol to give the *phenylhydrazone* (0·26 g), m.p. 113—116° (decomp.) (Found: C, 85·1; H, 6·7; N, 8·3. $C_{24}H_{22}N_2$ requires C, 85·2; H, 6·6; N, 8·3%); $\nu_{max.}$ (Nujol) 3350 cm^{-1} (NH); τ ($CDCl_3$) 2·6—3·5 (13H, m), 3·72br (2H, d, *J* 8 Hz), 7·35 (t, *J* 7 Hz, CH_2), 7·65 (t, *J* 7 Hz, CH_2), and 8·17 (distorted quint, *J* 7 Hz, CH_2).

Hydrogenation of the Benzo[c]*cyclopenta*[f][1,2]*diazepine* (39b).—A mixture of the diazepine (0·5 g) and 10% palladium–charcoal (0·2 g) in ethanol (200 ml) was hydrogenated at atmospheric pressure for 56 h; more catalyst (0·2 g) was added after 24 and 48 h. The mixture was filtered and the filtrate evaporated under vacuum to give a pale yellow solid. This was recrystallised from ethanol–petroleum to give 2-[2-*amino*-4-*methyl*-α-(p-*tolyl*)*benzyl*]-*cyclopentylamine* (44) (0·16 g, 31%), m.p. 162—163° (decomp.), as needles (Found: C, 81·4; H, 8·9; N, 9·65. $C_{20}H_{26}N_2$ requires C, 81·6; H, 8·9; N, 9·5%); $\nu_{max.}$ (Nujol) 3260br cm^{-1} (NH); τ ($CDCl_3$) 2·85br (5H, s), 3·45br (2H, s), 5·2br (1H, s), 6·2—6·6br (m, NH_2), 7·65 (s, CH_3), 7·79 (s, CH_3), and 7·4—8·6 (10H, m). The diamine (0·05 g) was acetylated with acetic anhydride in pyridine to give the NN′-*diacetyl derivative* (0·037 g, 58%), m.p. 228—229° (decomp.) (from 80% ethanol) (Found: C, 76·1; H, 7·75; N, 7·65. $C_{24}H_{30}N_2O_2$ requires C, 76·2; H, 8·0; N, 7·4%); $\nu_{max.}$ (Nujol) 3340 (NH) and 1630 cm^{-1} (C=O); τ (CCl_4) 2·92

(4H, s), 3·35 (s, NH), 3·58 (3H, s), 5·65br (1H, s), and 7·4—9·0 (20H, m).

RESULTS AND DISCUSSION

Most of this report is concerned with the distinct differences in reactivity between the sodium salts of the tosylhydrazones of α-methylenecyclopentanones (12;



a; n = 2, R^1 = R^2 = Me
b; n = 2, R^1 = R^2 = $[CH_2]_5$
c; n = 1, R^1 = R^2 = Me
d; n = 1, R^1 = R^2 = $[CH_2]_4$
e; n = 2, R^1 = Ph, R^2 = Me

SCHEME 2

$n = 1$) and those of analogous α-methylenecyclohexanones (12; $n = 2$) and acyclic unsaturated ketones. The courses of many of these reactions, particularly those of the methylenecyclopentanone derivatives, depend also on the nature of the substituents on the double bond and on the proticity [21] of the reaction solvent.

(i) *Tosylhydrazones of Mono- and Di-alkyl-substituted α-Methylenecycloalkanones.*—The products of the thermal decomposition of the tosylhydrazone salts (12), in which the double bond carries two alkyl substituents, depend strongly on ring size: the cyclohexanone derivatives (12a, b, and e) give 3*H*-pyrazoles (14) in high yield, whereas the cyclopentanone derivatives (12c and d) give the dienes (16) and no 3*H*-pyrazoles.

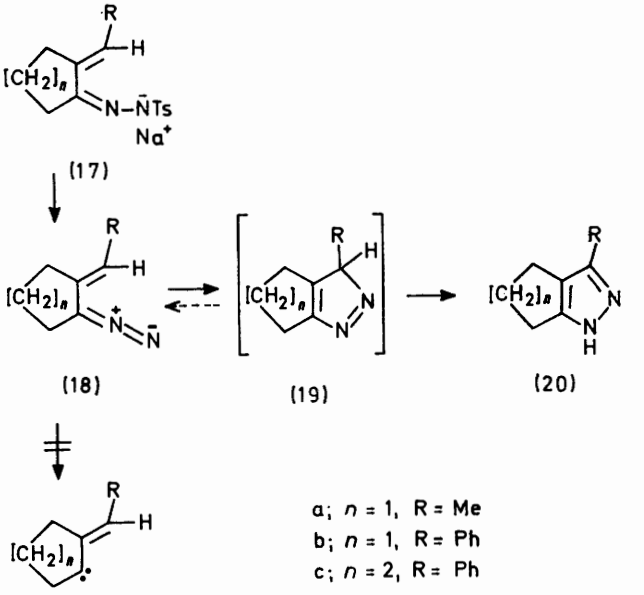
In the α-(dialkylmethylene)cyclohexanone tosylhydrazone series, it has previously been shown [22] that (12a) is converted to the 3*H*-pyrazole (14a) (76%) by heating under vacuum at 90—140°. We have shown that (12b) similarly gives (14b) (82%), and that when the reaction is carried out under aprotic conditions in refluxing toluene it again gives (14b) in substantial (63%) yield with only *ca.* 1% of the diene (16b) and 4% of the isomeric bi(cyclohex-1-enyl). A control experiment showed that the dienes are formed from the tosylhydrazone salt and not in a secondary reaction by thermal decomposition of the 3*H*-pyrazole (14b).*

* Compound (14b) does however decompose at higher temperatures, *e.g.* flash vacuum pyrolysis at 450° gives bi(cyclohex-1-enyl) (16%), 3-cyclohexylidenecyclohexene (37%), and two isomers of the pyrazole (47%) resulting from van Alphen rearrangement.[23]

In contrast the α-(dialkylmethylene)cyclopentanone tosylhydrazone salts (12c and d) gave no 3*H*-pyrazole when they decomposed under the same reaction conditions. In a vacuum pyrolysis experiment (12c) gave the diene (16c) (61%), and on decomposition in toluene (12c) gave (16c) (74%) and (12d) gave (16d) (70%). These dienes (16) are clearly formed from the singlet carbenes (15) generated by loss of nitrogen from the diazo-intermediates (13). The formation of dienes rather than cyclopropenes,[4] is no doubt due to the additional strain which would be contributed to the latter by the presence of the fused cyclopentane ring.[22]

In view of this distinct discontinuity of behaviour on reducing the ring size in (12) we also examined the reactions of a series of analogous tosylhydrazones bearing only one (*trans*) substituent at the terminus of the double bond (17a—c). In direct contrast to those above, these reactions showed no dependence on ring size: all the compounds examined gave pyrazoles in good yield [(20a) 64%; (20b) 71%; (20c) 77%]. The 3*H*-pyrazoles (19a—c) which were the initial cyclisation products were not isolated but rearranged by hydrogen migration [24] to give the more stable, aromatic 1*H*-pyrazoles (20a—c).

It seems likely that the dominance of the carbenic mode of decomposition for (12c and d) is due to their having some structural feature which inhibits the cyclisation process rather than some characteristic which accelerates



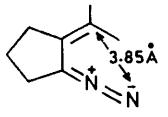
a; n = 1, R = Me
b; n = 1, R = Ph
c; n = 2, R = Ph

SCHEME 3

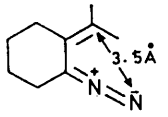
the competing elimination of nitrogen. If 3*H*-pyrazole formation occurs *via* diazo-alkene intermediates [(13); Scheme 2], then this 6 π-electron disrotatory ring closure would require a conformation of the diazoalkene in which

[21] J. H. Bayless, L. Friedman, F. B. Cook, and H. Shechter, *J. Amer. Chem. Soc.*, 1968, **90**, 531.
[22] G. L. Closs, W. A. Böll, H. Heyn, and V. Dev, *J. Amer. Chem. Soc.*, 1968, **90**, 173.
[23] A. M. Anderson, J. Dingwall, and J. T. Sharp, unpublished observations.
[24] A. Ledwith and D. Parry, *J. Chem. Soc.* (*B*), 1967, 41.

all five atoms of the conjugated system are approximately coplanar, and in which the diazo-group is sufficiently distorted from its preferred linear configuration [25] to allow bond formation. The ability of a molecule to attain this conformation and hence the rate of the cyclisation process might be expected to be very sensitive to steric factors. Models constructed from Drieding units and from a similarly fashioned diazo-group (C–N, 1·30 Å; N–N, 1·14 Å) [25] show that the separation between the termini of the π-system is *ca.* 0·35 Å greater for (21) than for (22). The former would therefore require a greater distortion of the diazo-group to achieve cyclisation; and ring closure would give a more strained 3*H*-pyrazole than that formed from (22). These additional constraints



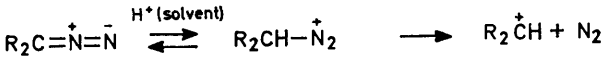
(21)



(22)

imposed by the presence of the five-membered ring are evidently sufficient to inhibit cyclisation in (12c and d) in favour of carbene formation. The contrasting success of the cyclisation for (17a and b), in which the *cis*-alkyl groups are replaced by hydrogen atoms, may reflect lower steric hindrance in the transition state due to the reduction in size of the *cis*-substituent or it may be related to the higher stability of the final products in these reactions [the aromatic 1*H*-pyrazoles (20)]. The ring closure of the diazoalkenes is *a priori* a reversible process and even though the equilibrium between (18a and b) and (19a and b) may lie heavily in favour of the diazoalkenes owing to the factors discussed above, the fast and irreversible isomerisation to the 1*H*-pyrazoles (20a and b) could serve to drive the reaction to the right. We hoped to differentiate between these two explanations by synthesising and attempting to cyclise *cis*-2-benzylidenecyclopentanone tosylhydrazone [*cis*-(17b)], but this compound could not be prepared.

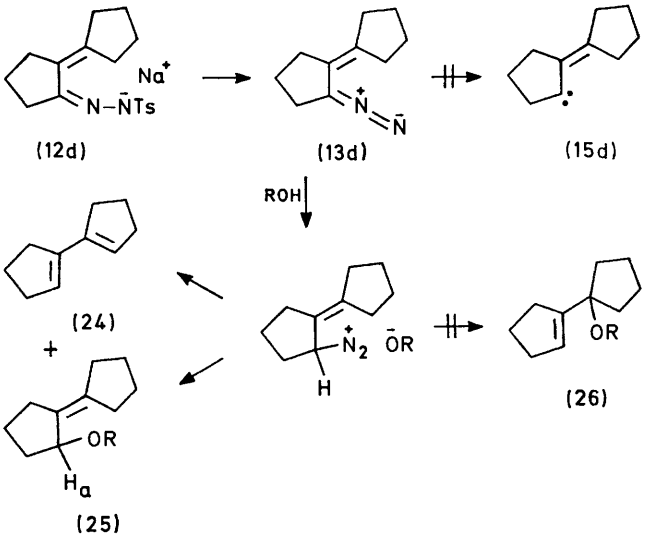
Since no colour due to diazo-intermediates was observed during any of the solution reactions of (12) and (17), we sought further evidence for their participation. When diazo-compounds are generated in protic [21] solvents they can be protonated to give diazonium ions, *e.g.* (23), and hence carbonium-ion-derived products.



(23)

The tosylhydrazone salts (12b) and (17a and b) were therefore decomposed in 2-methoxyethanol in the hope that protonation of the diazoalkene intermediates (if present) would be competitive with cyclisation, leading to the formation of some carbonium-ion-derived products at the expense of the pyrazoles. This, however, was not observed and (12b) and (17a and b) again gave the pyrazoles (14b) (62%), (20a) (79%) and (20b) (83%) in yields as high as or higher than found under aprotic conditions at a similar temperature. Compound (12b) did also give small yields (*ca.* 2 and 5%) of two compounds of molecular weight 238 which are probably ethers derived by a route analogous to that shown in Scheme 4, but since the yields were small and there was no significant diversion of the reaction from pyrazole formation, this cannot be taken as evidence for a common precursor.

The only reaction found to be sensitive to solvent proticity was the decomposition of (12d) which, in 2-methoxyethanol, gave compounds (24) (29%) and (25) (44%) (Scheme 4), whereas it had given exclusively (16d) under aprotic conditions. The structure of the ether (25) was deduced mainly from its ^{1}H n.m.r. spectrum which had no peak due to an olefinic proton, so excluding the alternative formulation (26), but contained a broad singlet (τ 5·78) due to H_a [see (25)] at a similar chemical shift to that of the analogous proton in 2-cyclopentylidenecyclopentanol (τ 5·53). A small peak (<5%) close to that of (25) in the g.l.c. trace of the crude reaction mixture may be due to (26). Protonation of (13d) by solvent is evidently very fast compared with nitrogen loss to give (15).



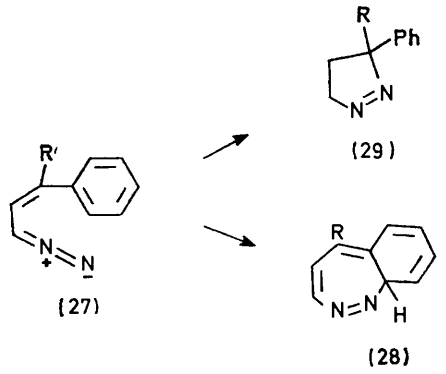
SCHEME 4

These experiments in protic solvents have not, therefore, resolved the uncertainty about diazoalkene participation in pyrazole formation; such intermediates are clearly involved in the decomposition of (12c and d) but if they are also involved in the formation of (14a and b) and (20a—c) then ring closure must be fast compared with protonation by solvent.

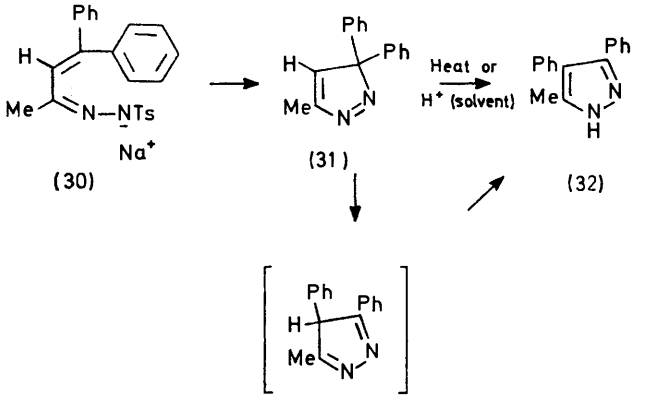
(ii) *Tosylhydrazones of* β-*Mono- and* ββ-*Di-aryl* αβ-*Unsaturated Ketones.*—β-Aryl αβ-unsaturated diazoalkenes, *e.g.* (27), in which the aryl group is *cis* to the diazo-function, are potentially capable of undergoing 1,7-ring closure to give 1,2-benzodiazepines (28) as well as 1,5-closure to give pyrazoles (29).[6] We have investigated

[25] G. W. Cowell and A. Ledwith, *Quart. Rev.*, 1970, **19**, 120.

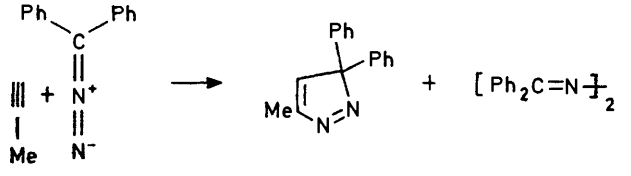
a range of such compounds in an effort to define the structural characteristics in (27) which are necessary to make 1,7-ring closure the preferred mode of reaction.



Acyclic systems give exclusively pyrazoles; *e.g.* (30), when cyclised under rigidly aprotic conditions, gave predominantly (31) (84%) and the rearranged pyrazole (32) (16%). The 3*H*-pyrazole (31) is extremely susceptible



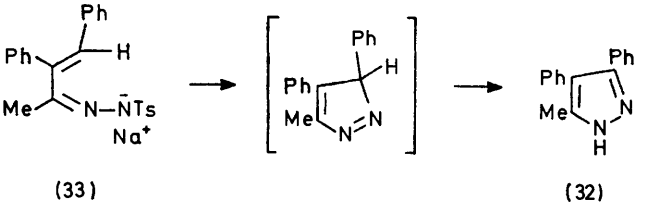
to acid-catalysed and thermal rearrangement to (32) and any trace of residual ethanol in the tosylhydrazone salt (prepared by using sodium ethoxide) led to the isolation of only (32) from the cyclisation reaction. The identity of (31) followed from its characteristic mass (Table 2) and ^{13}C n.m.r. (Table 3) spectra, and from comparison with a sample prepared by an alternative route (Scheme 5).



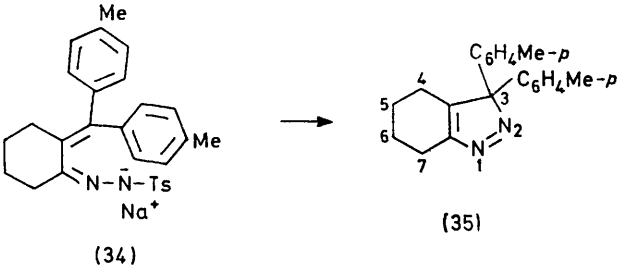
SCHEME 5

The rearranged pyrazole (32) had an N–H stretching absorption in its i.r. spectrum and its identity was confirmed by comparison with a sample prepared by cyclisation of the sodium salt of the tosylhydrazone (33) of *trans*-3,4-diphenylbut-3-en-2-one, which gave (32) in 64% yield.

The tosylhydrazone salts of α-diarylmethylenecyclohexanones also cyclised to give exclusively pyrazoles,



e.g. (34) gave (35) in 73% yield. The structure of (35) again followed from its mass (Table 2) and n.m.r. spectra.



The ^1H n.m.r. spectrum was consistent with the structure and had a single absorption at τ 7·7 for the two methyl groups [*cf.* (39b) in which the two methyl groups have different chemical shifts, τ 7·57 nd 7·63]. In the ^{13}C n.m.r. spectrum (Table 3) the tertiary C-3 gave an absorption 104·1 p.p.m. from Me_4Si (a position typical of 3*H*-pyrazoles).

TABLE 2

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

Compound	*m/e* (%)
(14b)	41(26), 53(11), 55(13), 65(13), 67(29), 77(27), 78(18), 79(87), 80(41), 81(39), 91(100), 92(36), 93(42), 94(59), 95(12), 105(53), 106(27), 107(27), 119(57), 120(22), 121(11), 133(52), 134(26), 147(34), 162(77), 163(11), 190(8)
(31)	128(12), 165(25), 189(24), 190(14), 191(100), 192(16), 202(12), 203(14), 204(10), 205(23), 206(63), 207(11), 234(9)
(35)	167(17), 182(22), 202(12), 203(10), 215(32), 216(23), 217(19), 218(13), 229(19), 230(17), 231(54), 232(20), 233(13), 245(64), 246(32), 259(41), 273(13), 274(100), 275(22), 302(5)
(39a)	165(16), 191(37), 202(54), 203(61), 204(100), 205(18), 215(18), 216(10), 217(10), 232(49), 233(10), 260(1)
(39b)	202(33), 203(15), 205(12), 215(31), 216(23), 217(56), 218(13), 219(22), 229(20), 230(16), 231(20), 232(100), 233(24), 245(35), 260(68), 261(30), 288(<1%)
(39c)	178(12), 189(16), 190(12), 191(11), 202(12), 203(13), 205(11), 215(10), 218(11), 221(14), 233(23), 234(26), 249(15), 251(15), 261(34), 264(42), 277(23), 292(100), 293(22), 320(13)
(39e)	201(11), 227(29), 238(37), 239(54), 240(100), 241(17), 251(10), 268(36), 296(<1%)

* Spectra obtained on a Micromass 12 spectrometer (source temperature *ca.* 150°; 40 eV); samples introduced by direct-insertion probe.

Attempts were also made to synthesise a range of *cis*-α-(arylmethylene)cyclohexanone tosylhydrazones (36) to test whether variation of X might induce 1,7- rather than 1,5-cyclisation. The *trans*-compounds (X = H, *p*-NO_2,

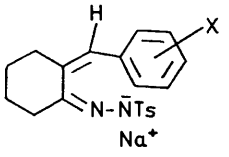
TABLE 3

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

Compound	Chemical shift from Me_4Si (p.p.m.)
(14b)	C-3 93·9; C-3a, -7a 151·6, 153·2; C-4—7 and $[CH_2]_5$ 31·3, 25·5, 23·8, 22·6, 22·5, 22·3, 21·8
(14e) †	C-3 96·7; C-3a, -7a 152·4, 152·9; C-1′ 135·4; C-2′—4′ 128·8, 127·8, 125·8; C-4—7 22·6, 22·3, 21·9, 21·7; CH_3 19·1
(35)	C-3 104·1; C-3a, -7a 150·9, 153·5; C-1′ 137·6; C-4′ 134·4; C-2′, -3′ 129·3, 127·7; C-4—7 23·3, 22·8, 22·4, 22·2; CH_3 21·0
(31)	C-3, 105·5; C-4 137·5; C-5 153·3; CH_3 13·0; C-1′ 137·0; C-2′—4′ 128·6, 128·0, 127·6
(39a)	C-1—3 26·8, 32·4, 32·6; C-3a 74·7; aromatic and olefinic 152·1 (tert.), 143·5 (tert.), 139·4 (tert.), 132·8 (tert.), 130·4, 130·0, 129·2, 128·2, 127·5, 127·4, 127·0, 125·6
(39b)	C-1—3 26·8, 32·2, 32·6; C-3a 74·5; 2 × CH_3 21·0, 21·1; aromatic and olefinic 151·8 (tert.), 141·8 (tert.), 136·8 (tert.), 136·4 (tert.), 135·3 (tert.), 132·4 (tert.), 129·7, 128·9, 128·7, 128·1, 127·9, 127·1

* Recorded on an XL-100 spectrometer (deuteriochloroform as solvent). † Prepared by K. A. Wall as part of an undergraduate project.

or *m*-MeO) were readily prepared and cyclised to give 1*H*-pyrazoles in good yield as expected, but it proved difficult to synthesise the *cis*-tosylhydrazones since the



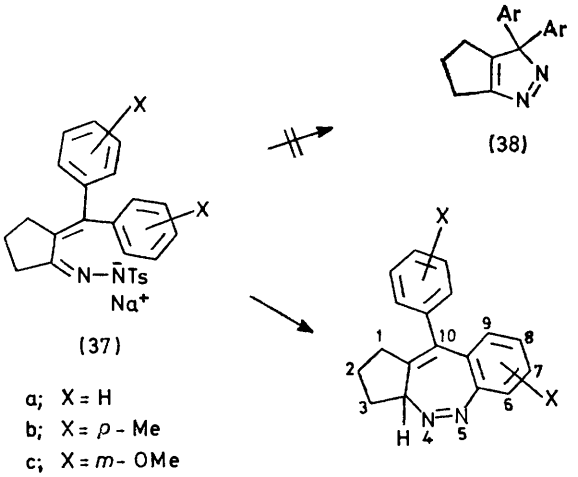
(36)

cis-ketones tended to isomerise back to the more stable *trans*-forms under the conditions used for making the tosylhydrazones. Only one pure *cis*-tosylhydrazone (36; X = H) was prepared, and it cyclised to give the pyrazole (19c).

As in the α-(dialkylmethylene) series (12), a reduction in the ring size produced a clear-cut change in the mode of reaction and like (12c and d) the α-(diarylmethylene)-cyclopentanone tosylhydrazone salts (37) failed to cyclise to 3*H*-pyrazoles (38). However unlike (12c and d) they did not take the alternative carbene path to any major extent, but instead underwent 1,7-ring closure to give the novel 1,2-benzodiazepines (39) in substantial yields (Scheme 6). The reactions were generally clean and the diazepines could be obtained by filtering off the precipitated sodium toluene-*p*-sulphinate, removal of the solvent (cyclohexane or 1,2-dimethoxyethane) by evaporation, and recrystallising the residue from ethanol. Small quantities of hydrocarbon products (unidentified) were also obtained and for (37d) 2-[bis-(*p*-trifluoromethyl phenyl)methylene]cyclopentanone azine was also isolated (22%).

Structures and Spectra of the Benzodiazepines.—The diazepines are all yellow crystalline compounds, stable at room temperature as solids, but readily isomerised [26] and decomposed [27] by light when in solution. Their mass spectra (Table 2) are consistent with the proposed structures and are typical of cyclic azo-compounds in showing small molecular ion peaks and large ($M^+ - N_2$) peaks. For example, the unsubstituted benzodiazepine (39a) had a parent peak at *m/e* 260 (1%), the ($M^+ - 28$) peak at *m/e* 232 (49%), with the base peak at *m/e* 204 corresponding to further loss of $CH_2{\cdot}CH_2$ from the cyclopentyl ring.

The ^1H n.m.r. spectrum of (39a) showed nine aromatic and seven aliphatic protons. The aromatic 6-proton in (39a) absorbed at lower field (τ 2·22) than the remainder giving a doublet (J_o 8 Hz) slightly broadened by longer-range coupling. The analogous *ortho*-protons in azobenzene are similarly more deshielded by the azo-group (τ 1·95—2·15) than the *meta*- and *para*-protons (τ 2·3—2·6). In the products in which C-7 carried a non-coupling substituent (39b and d) the 6-proton gave a broad singlet, while in (39e) it was clearly coupled to both the *ortho*-fluorine atom and the *meta*-proton. The absence



a; X = H
b; X = *p*-Me
c; X = *m*-OMe
d; X = *p*-CF_3
e; X = *p*-F

	Yield %
a; X = H,	80
b; X = 7-Me, *p*-Me	68
c; X = 6-OMe, *m*-OMe	68
d; X = 7-CF_3, *p*-CF_3	56
e; X = 7-F, *p*-F	38

SCHEME 6

of this low-field aromatic absorption in the product of cyclisation of (39c) allowed a differentiation between the two possible reaction products [(39; X = 8-OMe, *p*-OMe) and (39; X = 6-OMe, *p*-OMe)]. The 6-proton in the former would be expected to absorb near τ 2·2 since the (*meta*) methoxy-group at C-8 would not cause a significant upfield shift.[28] Since no absorption occurs below τ 2·8 the product is formulated as (39c). The

[26] J. N. Done, J. H. Knox, R. McEwan, and J. T. Sharp, *J.C.S. Chem. Comm.*, 1974, 532.

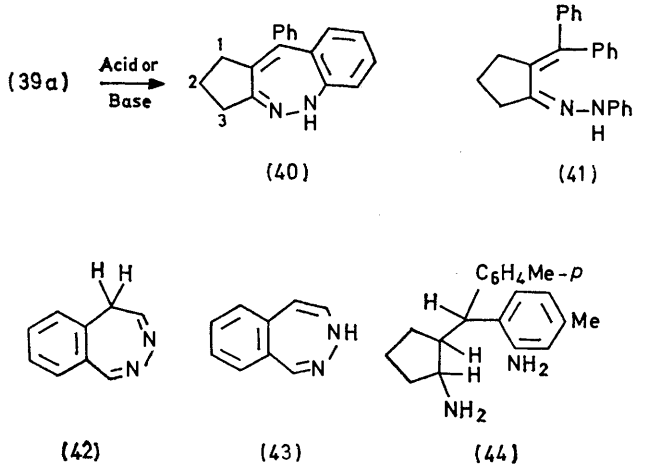
[27] R. McEwan and J. T. Sharp, *J.C.S. Chem. Comm.*, 1973, 85.

[28] W. W. Paudler, 'Nuclear Magnetic Resonance,' Allyn and Bacon, Boston, 1971, p. 105.

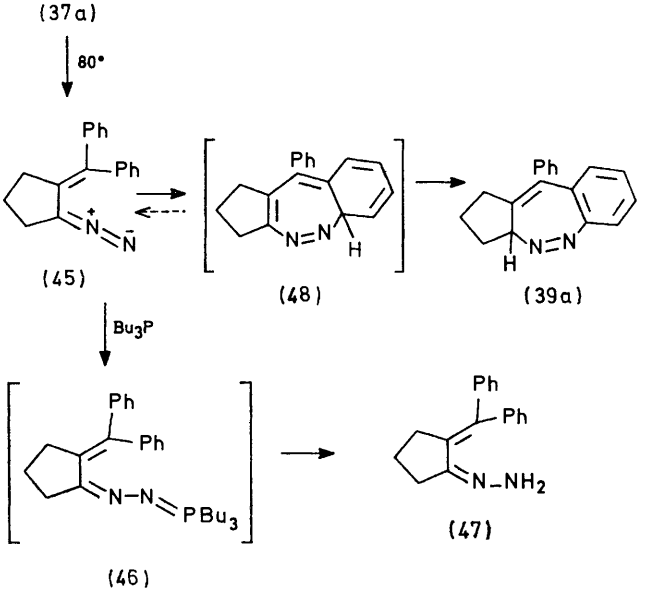
spectra of all the diazepines also showed a broad distorted doublet at τ 6·8—6·9, attributed to the 3-proton *cis* to the azo-group and subject to its deshielding influences,[6] and not to the 3a-proton as suggested in our preliminary report.[1] In connection with studies on the mechanism of thermolysis of benzodiazepines we have recently prepared the [3-^{2}H]analogue of (39a), which showed no peak at τ 6·85 but had a broad singlet at τ 7·23 (3a-H).[29]

The ^{13}C n.m.r. spectra of two of the benzodiazepines were also obtained; these make an interesting comparison with those of the 3*H*-pyrazoles (Table 3). The peaks were identified, where possible, by their chemical shifts and by off-resonance decoupling. In the 3*H*-pyrazoles the saturated carbon atom (C-3) is strongly deshielded by the attached azo-group, absorbing at 93·9—105·5 p.p.m. from Me_4Si. With two alkyl groups attached (14b) the chemical shift was 93·9 p.p.m. and replacement of these by aryl groups caused further deshielding at 96·7 p.p.m. in (14e), and 104·1 and 105·5 p.p.m. in (35) and (31). In 3*H*-indazoles C-3 has a similar chemical shift, *e.g.* 103·3 p.p.m. for 4,7-dimethoxy-3,3-diphenyl-3*H*-indazole.[26] Analogous carbon atoms in seven-membered rings, however, are much less deshielded; for example C-3a in the 1,2-benzodiazepines absorbed at 74·7 (39a) and 74·5 p.p.m. (39b), and in the 2,3-benzodiazepines (9; $R^1 = R^2 = H$, and $R^1 = Me$, $R^2 = Ph$) C-1 absorbed at 69·0 and 71·7 p.p.m. from Me_4Si, respectively.[29] Ring size has a similar but less marked effect in the hydrocarbon analogues, *e.g.* the sp^3 carbon atoms in cyclopentadiene,[30] cycloheptatriene [31] and 7*H*-benzocycloheptene [31] absorb at 41·6, 28·8, and 27·2 p.p.m. from Me_4Si, respectively.

The diazepine (39a) rearranges to the more stable isomer (40) under basic conditions so it is important that



an excess of base is not used in the formation of the tosylhydrazone salts for cyclisation. The i.r. spectrum of (40) showed an N–H stretching absorption at 3240 cm^{-1} and its mass spectrum clearly showed the absence of an azo-group. Its ^{1}H n.m.r. spectrum lacked the broad peak at τ 6·85 due to the 3-proton in (39a) but was very similar to that of 2-(diphenylmethylene)cyclopentanone phenylhydrazone (41) in having two triplets and a distorted quintet due to the protons attached to the cyclopentyl ring. Like related phenylhydrazones, (40) was rapidly oxidised in air. This rearrangement makes an interesting contrast with that of the 2,3-benzodiazepine



SCHEME 7

(9).[6] In both cases the rearrangement destroys the unstable azo-group, but in the latter case to give the 5*H*-isomer (42) and not the 3*H*-isomer (43) analogous to (40). It is probable that the potentially antiaromatic character of (43) sufficiently destabilises it relative to (42) to prevent its formation; but for (39a) no rearrangement is possible other than to (40) which would transform the azo-group and still maintain the aromatic character of the fused benzene ring.

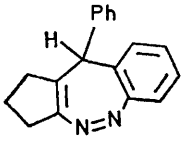
Hydrogenation of (39b) gave a diamine formulated as (44) which was acetylated to give the diamide.

Mechanism of Diazepine Formation.—In contrast to the cyclisations leading to 3*H*-pyrazoles, in which the reaction mixtures stayed colourless throughout, the formation of the diazepines was accompanied by a deep red colouration in the early stages which faded to yellow on completion. This clearly indicated the presence of a diazo-intermediate (45), which was shown to be a diazepine precursor by a trapping experiment with tributylphosphine. Although the presence of triphenylphosphine had no effect on the course of the reaction, tributylphosphine completely suppressed the red colour and led to the isolation of the hydrazone (47) (85%) instead of the diazepine. The identity of the 2-(diphenylmethylene)-cyclopentanone hydrazone was confirmed by comparison with authentic material and by conversion into an azine with acetone. The diazo-intermediate (45) apparently

[29] E. Stefaniuk, H. R. Sood, and J. T. Sharp, in preparation.
[30] J. B. Stothers, ' Carbon-13 N.M.R. Spectroscopy,' Academic Press, New York and London, 1972, p. 82.
[31] H. Günther and T. Keller, *Chem. Ber.*, 1970, **103**, 3231.

reacts more rapidly with tributylphosphine than it cyclises, and gives the phosphazine (46) which is hydrolysed during work-up to give the hydrazone.

It is suggested that the diazepines are formed by the mechanism shown in Scheme 7, in which the diazoalkene undergoes a 1,7-conrotatory ring closure to give (48) followed by a hydrogen shift which restores aromatic stabilisation. This final hydrogen migration is best rationalised as a concerted sigmatropic shift rather than as a base-catalysed process since only a [1,5] (allowed



(49)

suprafacial) migration is observed and not the sterically impossible [1,3] or [1,7] (antarafacial) migrations which would have given (49) or the more stable (40); and a base-catalysed process would be expected to yield (40), the most thermodynamically stable isomer.

The effects of substituents in the aromatic ring of (37) on the ring-closure reaction have not yet been fully investigated; the reactions of (37d and e), however, do show that *para*-electron-withdrawing groups reduce the yield of benzodiazepine. Such groups are known to stabilise diazo-alkanes and to have a small retarding effect on the 1,5-ring closure of diazoalkenes,[3] and it appears that here their effect is to reduce the rate of 1,7-ring closure relative to that of the competing nitrogen elimination. The effect of the asymmetrically placed methoxy-group in (37c) is also notable in that it directs cyclisation to the more hindered position *ortho* to itself rather than to the more accessible *para*-position. We hope to rationalise these results when we have completed a more extensive study of substituent effects.

This work shows that it is possible to devise molecular systems based on (27) which will undergo 1,7-ring closure to provide a synthesis of 1,2-benzodiazepines, but that it is not so versatile a synthesis as that of 2,3-benzodiazepines (9),[6] since its success depends on the incorporation of some structural features to inhibit the alternative highly-competitive 1,5-closure to pyrazoles.

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