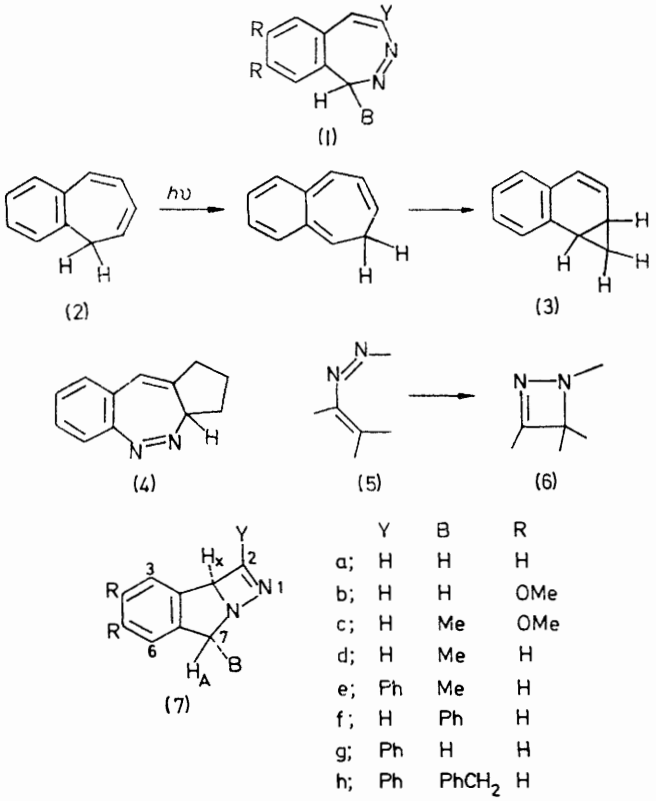
Photochemical Reactions of 1*H*-2,3-Benzodiazepines: Valence Isomerisation of a 1,2-Diazabutadiene to a Diazetine

By **Andrew A. Reid, H. Raj Sood,** and **John T. Sharp,*** Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ

1*H*-2,3-Benzodiazepines (1) rapidly undergo photoisomerisation to 2a,7-dihydro[1,2]diazeto[4,1-*a*]isoindoles (7), in contrast to their carbocyclic analogues (benzocycloheptenes), which react predominantly by [1,7] hydrogen migration and ring contraction. The photoproducts (7) decompose thermally either by extrusion of YCN (where Y is the 2-substituent) or *via* reversion to their benzodiazepine precursors, which subsequently eliminate nitrogen or rearrange.

In continuation of our studies on the synthesis and reactivity of 1,2-diazepines we have investigated the the photochemical reactivity of 1*H*-2,3-benzodiazepines (1).[1] There are several possible reaction paths and we were particularly interested to determine whether these compounds (*a*) would emulate their carbocyclic analogues and undergo a [1,7] hydrogen shift followed by ring contraction,[2] *e.g.* (2) ⟶ (3), or (*b*) would extrude nitrogen as do the 1,2-benzodiazepines[3] (4) and many other types of cyclic azo-compound, or (*c*) would react *via* electrocyclic ring closure of the 1,2-diazabutadiene unit to give 1,2-diazetines, *e.g.* (6) from (5).

In fact the photoreaction of the 1*H*-2,3-benzodiazepines (1) took path (*c*), resulting in rapid and virtually quantitative isomerisation to the 2a,7-dihydro[1,2]diazeto-[4,1-*a*]isoindoles (7) (Table 1). The products were isolated, usually in an analytically pure state, by evaporation of the reaction solution under reduced pressure. Those of low molecular weight, *e.g.* (7a), were volatile enough to allow vacuum sublimation without decomposition but more highly substituted compounds, *e.g.* (7e), partly decomposed (at *ca.* 110 °C) to give red or blue sublimates. At high temperatures the photoproducts decompose by two routes: (i) extrusion of YCN, and (ii) thermal reversion to the 1*H*-benzodiazepine (1) and its subsequent thermal decomposition or rearrangement. For example, heating compound (7h) at 168 °C in boiling t-butylbenzene gave (Scheme 1) benzonitrile (30%) *via* route (i) and probably the isoindole (8), but the latter could not be isolated or trapped by Diels–Alder reactions. The pyrolysis also gave *cis,trans*- and *trans,*-



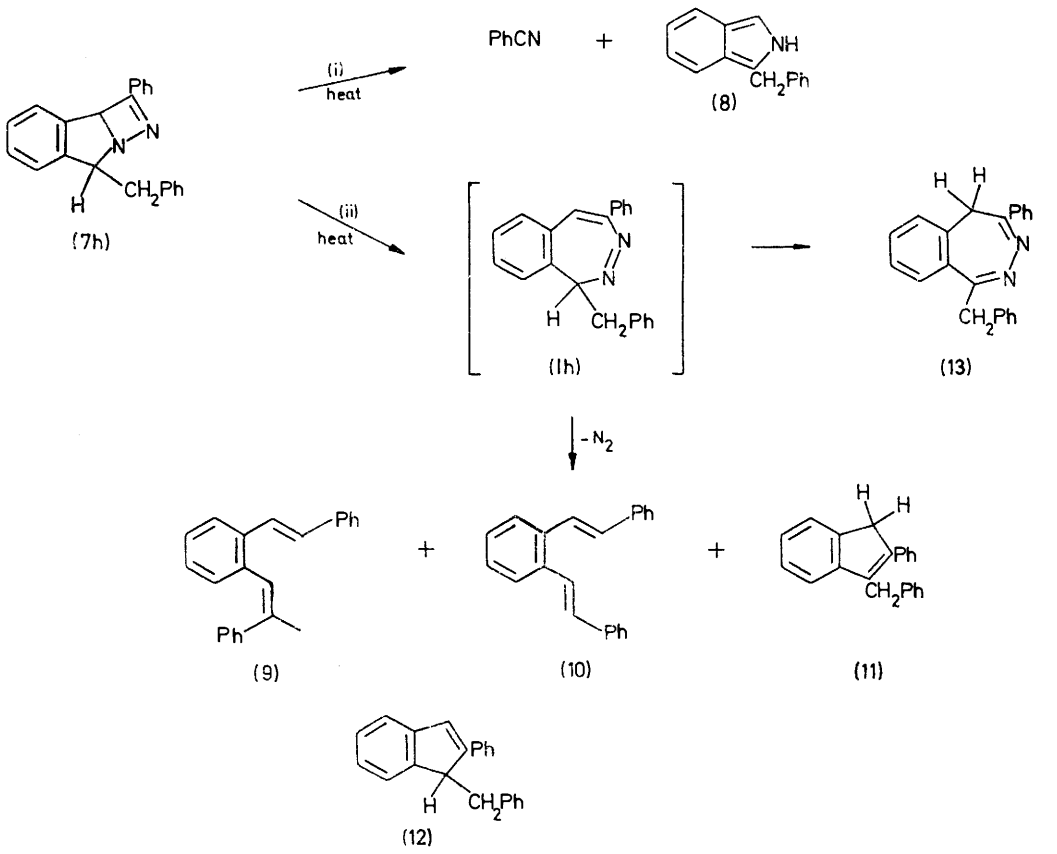
	Y	B	R
a;	H	H	H
b;	H	H	OMe
c;	H	Me	OMe
d;	H	Me	H
e;	Ph	Me	H
f;	H	Ph	H
g;	Ph	H	H
h;	Ph	$PhCH_2$	H

[1] Preliminary report, A. A. Reid, J. T. Sharp, and S. J. Murray, *J.C.S. Chem. Comm.*, 1972, 827.

[2] M. Pomerantz and G. W. Gruber, *J. Amer. Chem. Soc.*, 1971, **93**, 6615.

[3] (*a*) R. McEwan and J. T. Sharp, *J.C.S. Chem. Comm.*, 1973, 85; (*b*) J. N. Done, J. H. Knox, R. McEwan, and J. T. Sharp, *ibid.*, 1974, 532.

trans-o-distyrylbenzenes [(9), 23%; (10), 35%] together with two isomeric compounds which are probably indenes (*ca.* 6%) and the 5*H*-2,3-benzodiazepine (13)



SCHEME 1

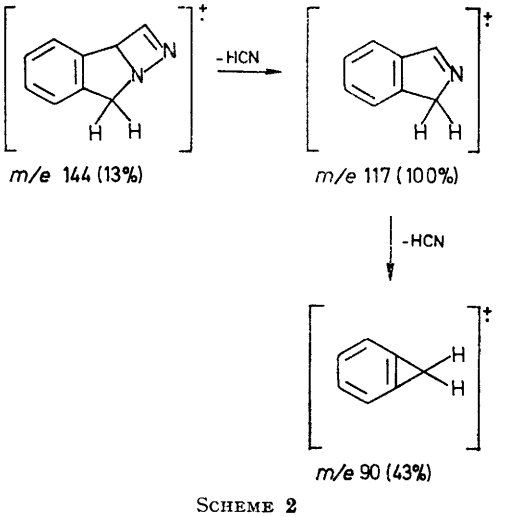
(2%) resulting from a [1,5] hydrogen shift in (1h). That these products are derived by route (ii) is supported by the formation of the same compounds directly from (1h) under similar conditions.[4,*] The flash vacuum pyrolysis (500 °C) of (7f) also proceeded predominantly by route (ii) giving a colourless product whose ^{1}H n.m.r. spectrum showed *ca.* 65% of 3-phenylindene [also formed in 87% yield by the pyrolysis of (1f)[4]] and another compound only absorbing in the aromatic region. That the latter was 1-phenylisoindole or an isomer is supported by the mass spectrum of the mixture, which had a substantial peak at *m/e* 193 with the correct high resolution mass value. The failure to isolate isoindoles from these pyrolyses is perhaps not surprising in view of their known instability to air and heat; for example 1-phenylisoindole[5] is resinified in air, and decomposes slowly at room temperature and at its m.p. (98 °C).

The mass spectra of the photoproducts (Table 2) showed the major fragmentation path of the molecular ion to be analogous to route (i) of the thermal decomposition. All the compounds (7) showed small parent peaks with base or major peaks due to $M^+ - YCN$.

* A mechanistic study of the thermal and acid-catalysed decomposition of 1*H*-2,3-benzodiazepines will be reported later.

The unsubstituted compound (7a) also showed a substantial peak at *m/e* 90 (43%), due to loss of a further molecule of HCN (Scheme 2).

The ^{1}H n.m.r. spectra of the products (Table 3) are consistent with the formulation (7) and, like those of

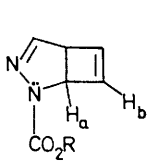


SCHEME 2

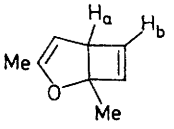
[4] A. A. Reid, J. T. Sharp, and E. Stefaniuk, unpublished observations.

[5] D. F. Veber and W. Lwowski, *J. Amer. Chem. Soc.*, 1964, **86**, 4152.

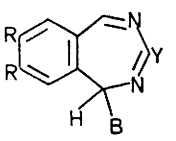
similar compounds,[6] *e.g.* (14) and (15) (J_{ab} 0), show no coupling between the 2- and 2a-(H_X) protons. The C-7 methylene groups in (7a, b, and g) gave characteristic AB patterns (J_{AB} 16 Hz) with both doublets further split



(14)

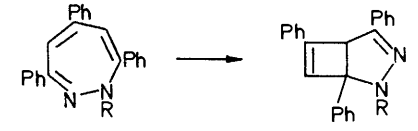


(15)

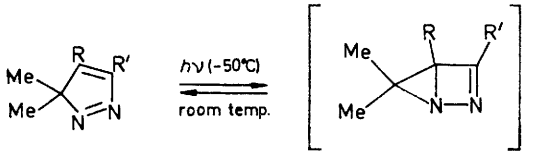


(16)

(17)



(18)

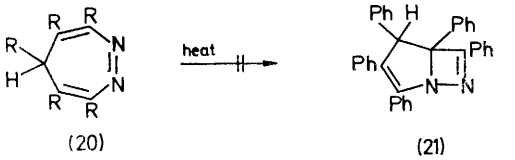


(19)

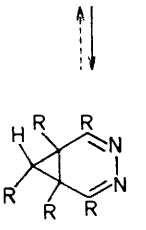
by long-range coupling to the 2- and 2a-protons. Homobenzylic coupling was observed between the 2a-proton (H_x) and the *endo*-proton on C-7 (*ca.* 2 Hz) but there was negligible coupling (<1 Hz) with the *exo*-proton and this assignment of the larger coupling to the *trans* interaction with the *endo*-proton, as previously reported for other dihydroisoindoles,[7] is consistent with the formulation of (7c—f and h) as the least hindered isomers with the substituents on C-7 in the *exo*-position. The spectra of the two compounds (7a and b) lacking both C-7 (*exo*) and C-2 substituents, also showed a further five-bond coupling (J 1.9 Hz) between the 2- and 7-(*exo*) protons.

The ^{1}H n.m.r. and mass spectral data are not inconsistent with product structures such as (16), but these can be excluded on two counts: (i) the ^{13}C n.m.r. spectra (Table 4) show only one peak (174—179 p.p.m.) in the region expected for >C=N–, whereas (16) should give two peaks, and (ii) the AB pattern from the C-7 methylene group in the ^{1}H n.m.r. spectrum of (7g) does not broaden and coalesce with temperature increase as would be expected for (16) or alternative diazepine structures.

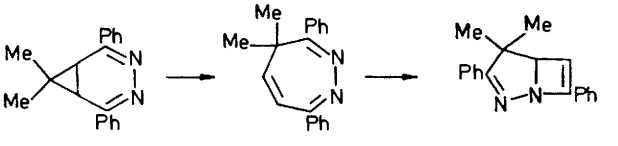
Many ring closures of 1,3-diene units in cycloheptatriene and its heterocyclic analogues have been reported, *e.g.* (17) [8] and (18),[9] but none before which involve the participation of an azo-group. The conversion (1)⟶(7) thus represents the first example of the preparation of an isolable 1,2-diazetine by this method, the only analogous reaction being Closs's irradiation of 3*H*-pyrazoles at low temperature [10] (−50 °C), which gave highly unstable products formulated as (19), which reverted to their pyrazole precursors on warming to room temperature. A report [11] that compound (20; R = Ph) was converted by heat into (21) has been shown to be incorrect.[12] *X*-Ray [12] and ^{1}H n.m.r. studies [13] have shown that the 5*H*-diazepine–diazanorcaradiene system (20)—(22) exists entirely in the bicyclic form, with the diazepine undetectable at any temperature. The true



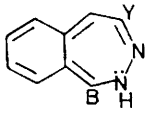
(20) (21)



(22)



(23) (24) (25)



(26)

structure of the thermal product of (20; R = Ph) is not certain but it has been suggested [12] that it is an isomer produced by a hydrogen shift, which seems probable in

[6] Y. L. Chow, J. Streith, and G. Taurand, *Org. Magnetic Resonance*, 1973, **5**, 155.

[7] W. Metlesics, T. Anton, and L. H. Sternbach, *J. Org. Chem.*, 1967, **32**, 2185; J. T. Gerig, *Tetrahedron Letters*, 1967, **46**, 4625.

[8] J. L. Derocque, W. T. Theuer, and J. A. Moore, *J. Org. Chem.*, 1968, **33**, 4381.

[9] G. Kan and V. Snieckus, *Chem. Comm.*, 1970, 1208; 1971, 1022.

[10] G. L. Closs, W. A. Böll, H. Heyn, and V. Dev., *J. Amer. Chem. Soc.*, 1968, **90**, 173.

[11] M. A. Battiste and T. J. Barton, *Tetrahedron Letters*, 1967, 1227.

[12] G. Heinrichs, H. Krapf, B. Schröder, A. Steigel, T. Troll, and J. Sauer, *Tetrahedron Letters*, 1970, 1617.

[13] A. Steigel, J. Sauer, D. A. Kleier, and G. Binsch, *J. Amer. Chem. Soc.*, 1972, **94**, 2770.

the light of our observation that pyrolysis of (1) gives 5*H*-2,3-benzodiazepines as well as products of nitrogen extrusion.[4] Zimmerman has recently shown that the photolysis of the diazanorcaradiene [14] (23) proceeds *via* a 'walk' process of the isopropylidene unit and ring opening to give (24), which can cyclize to (25); these reactions are thermally reversible.

Quantum yields for the photoisomerisation (1) ⟶ (7) have not been measured but it is clearly an easy process, the conversions being effected cleanly by a few minutes irradiation with a Pyrex-filtered 100 W medium-pressure lamp. It is interesting that the reaction path for the 1*H*-2,3-benzodiazepines (1) is quite different from that of their carbocyclic analogues [(2) ⟶ (3)[2]] and also that there is no effective competition from nitrogen extrusion which might be expected to proceed readily by primary cleavage of the benzyl–azo bond in (1). This high selectivity favouring the [$_{\pi}2_s + {}_{\pi}2_s$] reaction is probably due in part to the effect of the azo-group in reducing the stability of the 1,3-diene unit, *e.g.* (5), relative to that of the cyclised product (6), and the consequent increase in the driving force for the cyclisation in comparison with that for the all-carbon case ($\Delta\Delta H$ *ca.* 40 kJ mol^{-1}, assuming the same change in strain energy *). A reaction of structure (1) analogous to that of (2) is also likely to be discouraged by the potentially antiaromatic nature of the first-stage product (26) which would be formed by a [1,7] hydrogen shift to nitrogen. In this context it is notable that when the methylene hydrogen atoms in (2) are replaced by cyano-groups,[15] which have lower mobility in sigmatropic shifts, the molecule adopts a mode of photoreaction analogous to that of (1).

EXPERIMENTAL

^{1}H N.m.r. spectra were obtained with a Varian HA 100 spectrometer and ^{13}C n.m.r. spectra with a Varian XL100 or CFT20 spectrometer. Mass spectra were obtained with an A.E.I. MS902 instrument (70 eV) by use of a direct insertion probe, and g.l.c.-coupled mass spectrometry was carried out with a Micromass 12 instrument. Solvents for the photochemical reactions were dried (1,2-dimethoxyethane and cyclohexane over calcium hydride, ether over sodium, and chloroform and methylene chloride over phosphorus pentaoxide) and distilled under nitrogen immediately before use. The photochemical reactions were carried out at 0 °C or room temperature with a Hanovia 100 W medium-pressure lamp.

1H-2,3-*Benzodiazepines* (1).—These (1a—g) were prepared as already described.[16] 1-*Benzyl*-4-*phenyl*-1H-2,3-*benzodiazepine* (1h) (with E. Stefaniuk), similarly prepared (65%) from *trans*-2-phenylacetylstilbene, had m.p. 126—127° (Found: C, 84.9; H, 5.8; N, 9.0. $C_{22}H_{18}N_2$ requires C, 85.1; H, 5.85; N, 9.0%).

Photolysis of 1H-2,3-*Benzodiazepines*.—Dilute solutions (*ca.* 0.01—0.02M) in 1,2-dimethoxyethane were irradiated through Pyrex until the yellow colour was discharged (*ca.* 5—20 min) and t.l.c. showed that all the starting material had been consumed. Reaction solvents also used were ether, chloroform, methylene chloride, and cyclohexane; however some of the diazepines were insufficiently soluble in the last. The products (7) were isolated as white solids (Table 1), usually in an analytically pure state, by evaporation of solvent below 40 °C. T.l.c. and n.m.r. showed that the conversion into the 2a,7-dihydro[1,2]diazeto[4,1-*a*]isoindoles was virtually quantitative in all cases. The unsubstituted compound (7a) sublimed unchanged (85—90° and 0.2 mmHg) to give colourless crystals (83%), but higher molecular weight compounds, *e.g.* (7e), partly decomposed on sublimation (0.05 mmHg) to give coloured (red or blue) sublimates. Crystallisation of some of the products, *e.g.* (7a and b), resulted in partial decomposition,

TABLE 1

2a,7-Dihydro[1,2]diazeto[4,1-*a*]isoindoles

Compd.	Formula	C (%) Found	C (%) Reqd.	H (%) Found	H (%) Reqd.	N (%) Found	N (%) Reqd.	M.p. (°C)
(7a)	$C_9H_8N_2$	75.05	75.0	5.55	5.6	19.4	19.4	62—64
(7b)	$C_{11}H_{12}N_2O_2$	64.7	64.7	5.7	5.9	13.5	13.7	119—122
(7c)	$C_{12}H_{14}N_2O_2$	65.9	66.0	6.5	6.5	12.4	12.8	116—119
(7d)	$C_{16}H_{10}N_2$	76.1	75.9	6.7	6.4	17.6	17.7	77—81
(7e)	$C_{16}H_{14}N_2$	82.0	82.0	5.8	6.0	11.7	12.0	97—100
(7f)	$C_{15}H_{12}N_2$	82.1	81.8	5.6	5.5	12.4	12.7	94—97
(7g)	$C_{15}H_{12}N_2$	81.7	81.8	5.7	5.5	12.3	12.7	77—83
(7h)	$C_{22}H_{18}N_2$	85.4	85.1	5.9	5.85	8.9	9.0	122—123

TABLE 2

Mass spectra of 2a,7-dihydro[1,2]diazeto[4,1-*a*]isoindoles

Compd.	*m/e* (%)
(7a)	57 (3), 58(7), 62 (3), 63 (10), 64 (3), 89 (27), 90 (43), 91 (3), 115 (40), 116 (47), 117 (100), 118 (10), 144 (13)
(7b)	45 (53), 63 (18), 64 (13), 77 (11), 89 (12), 90 (15), 91 (13), 119 (16), 132 (12), 133 (15), 134 (26), 161 (15), 162 (18), 177 (100), 204 (28)
(7c)	51 (33), 77 (42), 78 (22), 89 (22), 90 (16), 91 (27), 103 (24), 104 (27), 105 (18), 107 (33), 132 (25), 133 (42), 147 (35), 148 (40), 175 (40), 176 (78), 177 (24), 190 (42), 191 (100), 203 (12), 218 (22)
(7d)	89 (11), 90 (16), 115 (20), 116 (19), 129 (18), 130 (60), 131 (100), 143 (10), 158 (26)
(7e)	51 (18), 72 (20), 89 (21), 90 (28), 103 (24), 116 (85), 130 (88), 131 (100), 234 (29)
(7f)	89 (10), 90 (15), 165 (27), 191 (20), 192 (20), 193 (100), 220 (22)
(7h)	78 (14), 91 (50), 103 (50), 116 (90), 117 (10), 206 (43), 207 (29), 219 (100), 220 (19), 310 (14)

but the more highly substituted compounds could be recrystallised, *e.g.* (7h) gave colourless needles (75%) from benzene–petroleum.

Pyrolysis of the Photoproducts.—(i) 7-*Benzyl*-2a,7-*dihydro*-2-*phenyl*[1,2]*diazeto*[4,1-a]*isoindole* (7h). Compound (7h) (0.205 g) and t-butylbenzene (20 ml) were boiled under reflux for 14 h; t.l.c. (alumina; benzene–ether, 1 : 1) then showed that all the photoproduct had decomposed (the mixture was finally deep purple). Analysis was carried out by g.l.c. and the products were identified by their retention times and their mass spectra (g.l.c.–mass spectrometry). Low-temperature analysis (5% Carbowax 20M; 125 °C) with naphthalene as internal standard showed the presence of benzonitrile (30%). High-temperature analysis (1% SE30; 225—250 °C) showed the presence of *cis,trans-o*-distyrylbenzene (23%), *trans,trans-o*-distyrylbenzene (35%), 1-benzyl-4-phenyl-5*H*-2,3-benzodiazepine (2%), and two

* From the following values for bond energies: C=C 607, N=N 382, C=N 602, C–C 345, N–N 166 kJ mol^{-1}.

[14] H. E. Zimmerman and W. Eberbach, *J. Amer. Chem. Soc.*, 1973, **95**, 3970.

[15] E. Ciganek, *J. Amer. Chem. Soc.*, 1967, **89**, 1458.

[16] A. A. Reid, J. T. Sharp, H. R. Sood, and P. B. Thorogood, *J.C.S. Perkin I*, 1973, 2543.

small peaks (*ca.* 6%) which gave mass spectra very similar to those of the *o*-distyrylbenzenes and which are probably the isomeric indenes. A similar pyrolysis of 1-benzyl-4-phenyl-1*H*-2,3-benzodiazepine gave *cis,trans-o*-distyrylbenzene (19%), *trans,trans-o*-distyrylbenzene (47%), the two unidentified isomers as observed in the previous experiment (18%), and 1-benzyl-4-phenyl-5*H*-2,3-benzodiazepine (8%). No *cis,cis-o*-distyrylbenzene was detected in either pyrolysis.

TABLE 3

^{1}H N.m.r. data [τ values; *J* in Hz] of 2a,7-dihydro[1,2]diazeto[4,1-*a*]isoindoles [a]

Compd.	H_X	*B* (*exo*)	H_A (*endo*)	Y	R	Aromatic	Solvent
(7a)	4.52br, s	5.81br, d, J_{AB} 16	5.57dd, J_{AB} 16, J_{AX} 2	2.43d, J_{BY} 1.9		2.8—3.3m	C_6D_6 [b]
(7b)	4.46br, s	5.74br, d, J_{AB} 16	5.54 dd, J_{AB} 16, J_{AX} 2	2.26d, J_{BY} 1.9	6.61s (3 H), 6.68s (3 H)	3.72s (1 H), 3.78s (1 H)	C_6D_6 [b]
(7c)	4.03d, J_{AX} 2	8.63d, J_{AB} 7	5.42qd, J_{AB} 7, J_{AX} 2	1.79s	6.14 (6 H)	3.25s (1 H), 3.31s (1 H)	$CDCl_3$
(7d)	3.95d, J_{AX} 2	8.61d, J_{AB} 7	5.34qd, J_{AB} 7, J_{AX} 2	1.81s		2.5—2.9m (4 H)	$CDCl_3$
(7e)	3.65d, J_{AX} 2.1	8.54d, J_{AB} 7	5.26qd, J_{AB} 7, J_{AX} 2.1			2.25—2.9m (9 H)	$CDCl_3$
(7f)	3.81d, J_{AX} 2		4.34d, J_{AX} 2	1.76s		2.6—3.0m (9 H)	$CDCl_3$
(7g)	3.67br, s	5.44br, s (2 H)				2.2—2.95m (9 H)	$CDCl_3$
	4.02br, s	5.66d, J_{AB} 16	5.39dd, J_{AB} 16, J_{AX} 2			2.3—3.3m (9 H)	C_6D_6
(7h)	3.87d, J_{AX} 2	6.95d (CH_2), J_{AB} 7	5.06br, t, J_{AB} 7			2.35—3.2m (14 H)	$CDCl_3$

[a] Recorded at 100 MHz with field sweep at 28 °C. [b] In $CDCl_3$ the C-7 methylene protons give broad singlets.

TABLE 4

^{13}C N.m.r. data (p.p.m. from Me_4Si) of 2a,7-dihydro-[1,2]diazeto[4,1-*a*]isoindoles *

Compd.	
(7a)	C-2, 174.2; C-7, 55.9; C-3—6, 128.9, 127.3, 124.6, 123.6, C-6a and -2b, 140.5, 136.1; C-2a, 84.0
(7e)	C-2, 179.1; C-7, 63.1; C-2a, 80.3; CH_3, 23.4; aromatic, 146.3 (tert.), 136.4 (tert.), 129.6 (tert.), 130.7, 128.9, 128.8, 127.5, 125.0, 124.3, 123.7
(7h)	C-2, 179.3; C-7, 68.2; C-2a, 80.4; CH_2, 43.5; aromatic, 143.8 (tert.), 137.9 (tert.), 137.4 (tert.), 129.6 (tert.), 130.7, 129.8, 128.8, 128.7. 128.2, 127.7, 126.3, 125.6, 124.3, 123.7

* Deuteriochloroform as solvent.

(ii) 2a,7-*Dihydro*-7-*phenyl*[1,2]*diazeto*[4,1-a]*isoindole* (7f). Compound (7f) (0.1 g) was sublimed (sample temperature *ca.* 60 °C) over 2 days into the reaction tube of a vacuum pyrolysis apparatus (500 °C and 0.005 mmHg). The total product was examined by ^{1}H n.m.r. and mass spectrometry [τ ($CDCl_3$) 2.3—3.0 (14 H, m), 3.52 (1 H, t, *J* 2 Hz), and 6.60 (2 H, d, *J* 2 Hz); the last two multiplets were identical with those in the spectrum of authentic 3-phenylindene.*] The yield of 3-phenylindene, based on n.m.r. integrals, was 65%. The mass spectrum showed *m/e* 193.089 285 (calc. for $C_{14}H_{11}N$: 193.089 145), indicating the presence of 1-phenylisoindole or an isomer.

o-*Distyrylbenzenes*.—The Wittig reaction of *o*-xylylenebis-(triphenylphosphonium bromide) (15.6 g) and benzaldehyde did not, in our hands, give a high yield of *trans,trans-o*-distyrylbenzene by the work-up method described.[17] Chromatography of the crude product gave a yellow oil (6.7 g) not containing triphenylphosphine oxide (t.l.c.); g.l.c. (1% SE30; 240 °C) showed three peaks with relative retention times (*a*) 1, (*b*) 1.4, (*c*) 2.7 and areas 29, 58, and 13%, respectively. G.l.c.–mass spectrometry showed that these were isomers with virtually identical mass spectra [*m/e* 282 (60%), 205 (14), 204 (12), 203 (13), 202 (12), 192 (16), 191 (100), 189 (10), and 91 (9)]. A sample (3.5 g) of the oil was distilled (Buchi Kugelrohr) to give a colourless semi-solid (2.4 g), b.p. 140—155° at 0.1 mmHg. This mixture (1.0 g), iodine (0.1 g), and n-heptane (50 ml) were boiled under reflux under nitrogen and the isomer ratios were monitored by g.l.c.; peak (*a*) disappeared rapidly and peak (*b*) first increased and then decreased until after 36 h the ratios were (*a*) 0, (*b*) 4, (*c*) 96%. The solvent was removed by evaporation under reduced pressure, the residue was dissolved in benzene, and the solution was washed with sodium thiosulphate solution, then water, dried ($MgSO_4$), and evaporated. Recrystallisation from heptane gave *trans,trans-o*-distyrylbenzene (*c*) (0.80 g), m.p. 118.5—119.5° (lit.,[17] 117.5—119°); τ ($CDCl_3$) 2.4—2.9 (16 H, m) and 3.07 (2 H, d, *J* 16 Hz). Thus (*a*) and (*b*) are formulated as the *cis,cis-* and the *cis,trans-o*-distyrylbenzenes, respectively.

1-*Benzyl*-4-*phenyl*-5H-2,3-*benzodiazepine* (with E. STEFANIUK).—The 1*H*-isomer (0.78 g, 2.53 mmol) was isomerised with sodium ethoxide (5 mmol) in ethanol (50 ml); recrystallisation of the product from ethanol gave the 5H-*isomer* (0.65 g, 83%), m.p. 148—149: (Found: C, 84.9; H, 5.8; N, 8.9. $C_{22}H_{18}N_2$ requires C, 85.1; H, 5.85; N, 9.0%).

We thank the Wellcome Foundation Ltd. and the S.R.C. for a C.A.P.S. studentship (to A. A. R.), the latter for financial support (to H. R. S.), and Mr. T. Naisby for assistance in the preparation of the benzodiazepines.

[5/1224 *Received*, 23*rd June*, 1975]

* We thank Dr. I. H. Sadler for the sample of 3-phenylindene.

[17] C. E. Griffin, K. R. Martin, and B. E. Douglas, *J. Org. Chem.*, 1962, **27**, 1627.