

## Regioselective Intramolecular Rearrangements in 1,2-Bis(areneazo)cycloalkenes *via* Triazolium Imide 1,3-Dipoles: Examples of a New Fischer Indole-type Rearrangement. Azolium 1,3-Dipoles. Part 2.†

Richard N. Butler,\* Ann M. Gillan, John P. James, and (in part) Ann M. Evans  
Chemistry Department, University College, Galway, Ireland

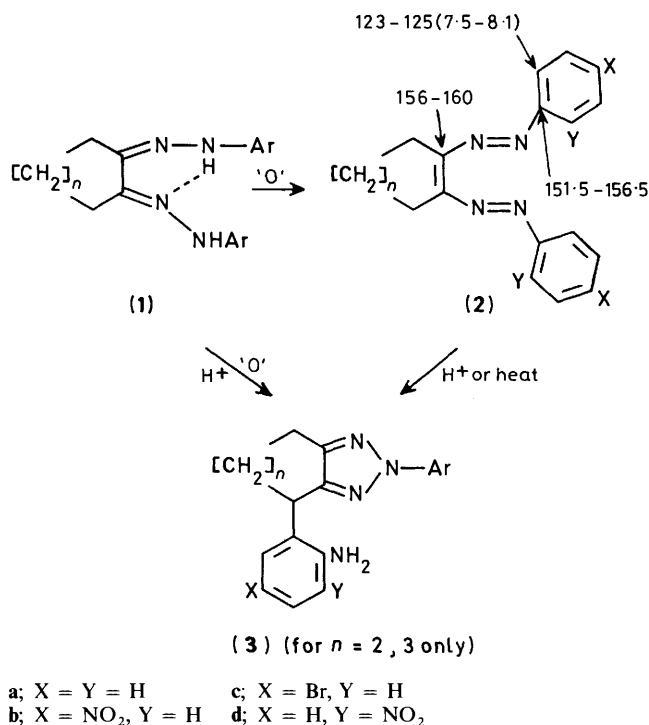
1,2-Bis(areneazo)cycloalkenes (**2**) (6 carbons and higher) when heated or treated with acid rearrange to hydro derivatives of fused 2,4-diarylcyclopolyeno[*d*][1,2,3]triazoles (**3**). The rearrangement, which was regioselective and intramolecular, occurred through a 1,2,3-triazolium imide 1,3-dipole form of the substrates (**2**). Synthesis, structural effects, a variable-temperature 270 MHz n.m.r. search for intermediates, and some kinetic studies are reported. The reaction is a new variation of the Fischer indole reaction.

Few reactions have received as much study as the Fischer indole reaction.<sup>1</sup> When the volume of published work is combined with that on the related benzidine rearrangement, it must be concluded that these types of reactions have occupied a primary place in the interests of organic chemists. Herein we report<sup>2</sup> a new intramolecular rearrangement in 1,2-bis(areneazo)cycloalkenes which we classify as an example of a Fischer indole-type rearrangement.

### Results and Discussion

(i) *Rearrangement*.—Oxidation of cycloalkane-1,2-dione bis(arylhydrazones) (**1**;  $n = 2$ ) with non-protonic oxidizing systems such as  $\text{NiO}_2$  in benzene or  $\text{PbO}_2$  in dichloromethane gives high yields of 1,2-bis(areneazo)cycloalkenes (**2**) (Table, Part III). If the oxidation is carried out using a protonic oxidizing system such as  $\text{Pb}(\text{OAc})_4$  which generates acid the products are the rearranged compounds (**3**) (Table, Part I). These arise from the action of acid on the bis-azo compounds (**2**). Thus when the compounds (**2**) are separately treated with acetic acid in dichloromethane or subjected to prolonged heating they readily rearrange to compounds (**3**) (Table, Part II). The rearrangement was regioselective to the *ortho* position. No *para* products were encountered and even when one of the *ortho* positions was occupied the reaction occurred at the other *ortho* site. No crossover products were encountered and the reaction was exclusively intramolecular. The rearrangement was controlled by the size of the cycloalkene ring and occurred only for six- or higher-membered-ring cycloalkene derivatives (**1**) or (**2**) ( $n = 2, 3$ ). With smaller rings ( $n = 0, 1$ ) neither acidic oxidation of the hydrazones (**1**) (Table, part III), nor heating, nor acid treatment of the compounds (**2**) gave a trace of the rearrangement products, and indeed extensive attempts to induce rearrangement of the series (**2**;  $n = 1$ ) with active Fischer indole reagents such as  $\text{ZnCl}_2\text{-HCl}$  all failed to produce a trace of the rearrangement.

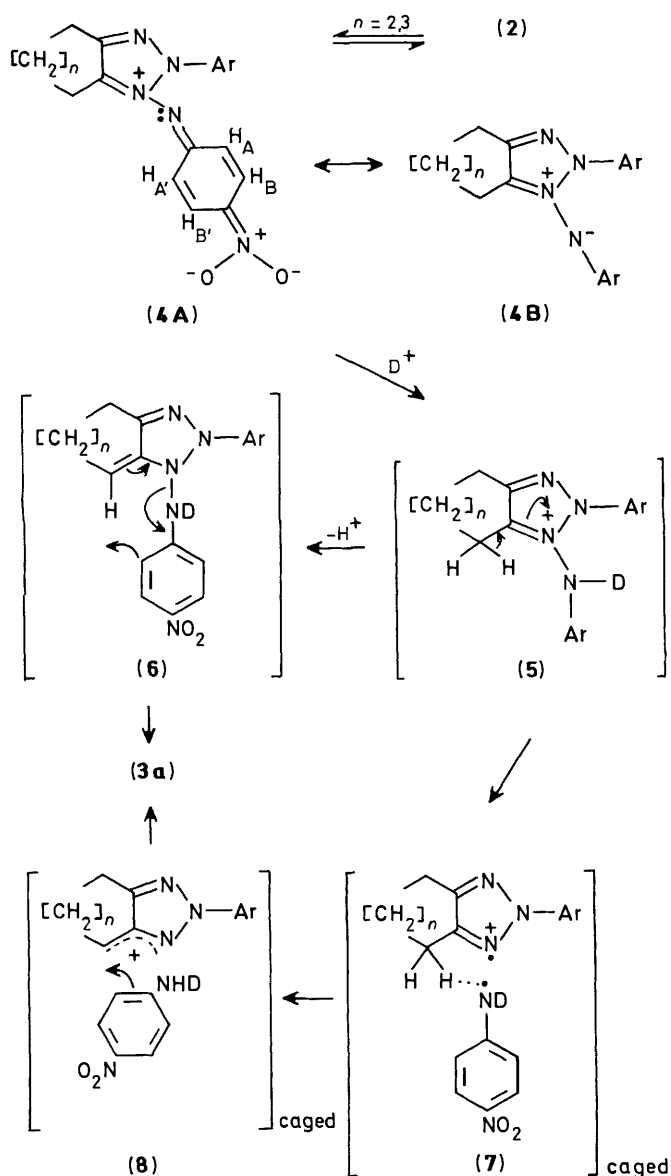
(ii) *Mechanism*.—1,2-Bis(azo)alkenes exist in a cyclic 1,2,3-triazolium imide 1,3-dipole form (**4**) if the azo substituent is strongly deactivating such as  $\text{CN}$ .<sup>3</sup> For 1,2-bis(arylazo)cycloalkenes the compounds exist preferentially in the acyclic form (**2**) as indicated by their  $^1\text{H}$  and  $^{13}\text{C}$  n.m.r. spectra which show characteristic arylazoalkene shifts (Scheme 1). However, for compounds (**2**;  $n = 2$  and  $3$ ) these solutions probably contain a small concentration of the cyclic form (**4**) because when a *p*- $\text{NO}_2$  substituent is present in the aryl ring the cyclic form (**4**), a resonance hybrid of forms (**4A**) and (**4B**), becomes the



Scheme 1. Some n.m.r. shift ranges are shown for series Y = H

dominant form and it only is detected by n.m.r. We have reported<sup>4</sup> a detailed variable-temperature 270 MHz  $^1\text{H}$  n.m.r. analysis of the structure and dynamic effects of the system (**2**)  $\rightleftharpoons$  (**4**). This showed that the cyclic form (**4**) was dominant at all temperatures between 120 and  $-90^\circ\text{C}$  for *p*-nitro derivatives of cycloheptene and cyclohexene ring systems ( $n = 2, 3$ ) but for cyclopentene and cyclobutene rings the bis(arylazo) compounds did not cyclize due to excessive strain in the fused ring system.<sup>4</sup> Since no rearrangements were observed with any derivatives of these smaller ring systems we conclude that the rearrangement occurs through the cyclic form (**4**) (Scheme 2) and that it can only be observed with systems where this cyclic form can exist. The 270 MHz  $^1\text{H}$  n.m.r. spectrum of compound (**4**;  $n = 2$ ) at  $-83^\circ\text{C}$  in  $\text{CD}_2\text{Cl}_2$  is shown [Figure (a)]. Restricted rotation around the imide-aryl bond as in structure (**4A**) is clearly observable,<sup>4</sup> with separate signals for the  $\text{H}_A$  and  $\text{H}_{A'}$  protons at the rearrangement site. The influence of the introduction of a drop of deuterioacetic acid to the n.m.r. sample tube at  $-83^\circ\text{C}$  is shown in the Figure (b). This results in

† Part 1 is ref. 4.



Scheme 2.

a collapse of the sharp H<sub>A</sub> and H<sub>A'</sub> signals due to restoration of the imide-aryl bond rotation arising from protonation of the exocyclic imide nitrogen, giving the species (5). Thereafter as the temperature was raised carefully to 20 °C no further intermediates were detected. At 20 °C the signals of the rearranged product (3a; n = 2) appeared and grew to completion after 32 min [Figure (c)]. No polarization effects (c.i.d.n.p.), which might indicate radicals, were observed in any proton spectra of these rearrangements and no deuterium-hydrogen exchange occurred in the cycloalkane moiety during the rearrangement.

The intermediate (5) may proceed to the products (3) via a 3,3-sigmatropic migration in the ene-hydrazine intermediate (6) or via a caged cation radical (7) with *ortho* substitution, (8), within the cage (Scheme 2).<sup>\*</sup> A rigorous experimental distinction between these possibilities will be difficult and has not been achieved here. The absence of c.i.d.n.p. effects in the n.m.r. spectra does not rule out the radical mechanism. However, we tentatively favour the mechanism shown in structure (6). The exocyclic imide nitrogen is probably a highly active basic centre

thereby facilitating the formation of (6) by thermal proton transfer in the absence of acid. This basicity was confirmed by the n.m.r. spectra (Figure) and also by the introduction of 1 mol equiv. of acetic anhydride to the system. This resulted in acetylation at the imide nitrogen to give (9) and inhibition of the rearrangement giving instead fragmentation to *p*-nitroacetanilide (13) (25%) along with compounds (11) (67%) and (12) (25%) as well as some resins (Scheme 3). In this case fragmentation to the cation (10) [analogous to that in the cage (8)] resulted in competitive external nucleophilic attack. This suggests that a caged species of type (8), although possible, may not be a suitable intermediate to explain an intramolecular rearrangement. The low-temperature n.m.r. data suggest that protonation of the imide nitrogen to give the species (5) occurred rapidly and thereafter the rate-determining step was probably the CH bond cleavage with proton loss to give the ene-hydrazine moiety (6). We have previously directly detected<sup>5</sup> ene-hydrazine tautomers of bis(arylhydrazones) of cyclohexane-1,3-dione. Kinetic evidence for ene-hydrazine tautomerism in the Fischer indole reaction has been reviewed.<sup>1a,6</sup> In a kinetic study of the present reaction by following the disappearance of the substrate (2) at a chosen  $\lambda$  value in its u.v. spectrum in chloroform containing acetic acid it was found that the reaction of the phenyl compound (2a; n = 2) was too rapid for measurement but the *p*-NO<sub>2</sub> substituent slowed the reaction sufficiently for rate measurements giving  $k \times 10^2$  values for compound (2b; n = 2) of 2.0, 7.25, and 25.25 s<sup>-1</sup> at 298, 308, and 318 K respectively. These data correspond to Arrhenius activation parameters of  $\Delta E^{\text{act}}$  24.2,  $\Delta H^{\text{act}}$  23.6 kcal mol<sup>-1</sup>, and  $\Delta S^{\text{act}}$  4.7 cal K<sup>-1</sup> mol<sup>-1</sup>.<sup>†</sup> Electron-withdrawing groups are well known to inhibit the Fischer indole reaction<sup>7,8</sup> and are considered to do so by inhibiting the ene-hydrazine tautomerism. The low activation energy is consistent with the observed ease of reaction and the low positive entropy suggests that the step being monitored is not the intramolecular rearrangement but rather the ene-hydrazine formation. While these kinetic data do not provide a conclusive distinction concerning the mechanism they agree with the other observations and support the classification of the rearrangement as a version of the Fischer indole reaction.

### Experimental

M.p.s were measured on an Electrothermal apparatus. I.r. spectra were measured with a Perkin-Elmer 983G spectrophotometer. N.m.r. spectra were measured on JEOL JNM-GX-270 and MH-100 instruments with tetramethylsilane as internal reference and deuteriochloroform or hexadeuteriodimethyl sulphoxide as solvents. U.v.-visible adsorption spectra were measured with a Shimadzu U.V.-260 Spectrophotometer. The

<sup>\*</sup> A possible alternative mechanism is analogous to the Hoffmann-Martius rearrangement (M. J. S. Dewar, *J. Chem. Soc.*, 1949, 463). This would involve an initial 1,3-N → C rearrangement of the imido moiety giving the *N*-cycloalkylaniline (14). This, under acidic conditions, could undergo another 1,3-N → C rearrangement. This latter known reaction-type, although acid catalysed, usually involves high temperatures and the alkyl groups mainly enter the *para* positions (R. Reilly and W. J. Hickinbottom, *J. Chem. Soc.*, 1920, 117, 103; M. J. S. Dewar, 'Molecular Rearrangements,' ed. P. De Mayo, Interscience, New York, 1963, pp. 323-344). Compound (14), obtained by deacetylation of compound (11), was found to be inert under the conditions of the present rearrangement and even under the most rigorous conditions it could not be rearranged to compound (3b). Neither could compound (11) be rearranged to the *N*-acetyl derivative of compound (3b) (prepared separately) although tertiary alkyl arylamines are known to display this alkyl migration more readily. Hence we rule out a possible Hoffmann-Martius-type mechanism.

<sup>†</sup> 4.184 cal = 1 J.

**Table.** Rearrangements and oxidations

## I Rearrangements from bis(hydrazono) oxidations

Substrate			Conditions			Product		
Compd.	<i>n</i>	Oxidizing agent	Solvent	Temp (°C)	Time (h)	Compd.	Yield (%)	M.p. (°C)
(1b)	2	Pb(OAc) <sub>4</sub>	HOAc	25	2	(3b)	80	285—287 <sup>d</sup>
(1b)	2	Pb(OAc) <sub>4</sub>	CH <sub>2</sub> Cl <sub>2</sub>	reflux	24	(3b)	70	285—287 <sup>d</sup>
(1b)	2	Na <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	HOAc	60	0.5	(3b)	42	285—287 <sup>d</sup>
(1b)	2	Tl(OAc) <sub>3</sub>	HOAc	25	2	(3b)	53	285—287 <sup>d</sup>
(1b)	2	NiO <sub>2</sub>	C <sub>6</sub> H <sub>6</sub>	reflux	2	(3b)	65	285—287 <sup>d</sup>
(1a)	2	Pb(OAc) <sub>4</sub>	CH <sub>2</sub> Cl <sub>2</sub>	25	18	(3a)	68	130—132 <sup>e</sup>
(1c)	2	Pb(OAc) <sub>4</sub>	CH <sub>2</sub> Cl <sub>2</sub>	25	18	(3c)	81	196—198 <sup>d</sup>
(1d)	2	Pb(OAc) <sub>4</sub>	CH <sub>2</sub> Cl <sub>2</sub>	25	18	(3d)	47 <sup>b</sup>	136—138 <sup>d</sup>

## II Rearrangements from bis(azo) compounds (2) ⇌ (4)

(2a)	2	None	CH <sub>2</sub> Cl <sub>2</sub> -HOAc <sup>a</sup>	25	18	(3a)	77	130—132 <sup>d</sup>
(4b)	2	None	CH <sub>2</sub> Cl <sub>2</sub> -HOAc <sup>a</sup>	25	18	(3b)	85	285—287 <sup>d</sup>
(4b)	2	None	HOAc	25	0.25	(3b)	82	285—287 <sup>d</sup>
(4b)	3	None	CH <sub>2</sub> Cl <sub>2</sub> -HOAc <sup>a</sup>	25	0.17	(3b)	78	280—281 <sup>d</sup>
(4b)	2	None	HOAc-Ac <sub>2</sub> O	25	0.25	(11)	67 <sup>c</sup>	284—286 <sup>f</sup>

## Oxidations not involving rearrangements

(1a)	2	NiO <sub>2</sub>	C <sub>6</sub> H <sub>6</sub>	25	3	(2a)	87	134—135 <sup>d</sup>
(1b)	2	PbO <sub>2</sub>	CH <sub>2</sub> Cl <sub>2</sub>	25	18	(4b)	89	176—177 <sup>g</sup>
(1c)	2	PbO <sub>2</sub>	CH <sub>2</sub> Cl <sub>2</sub>	25	18	(2c)	72	205 <sup>g</sup>
(1b)	3	PbO <sub>2</sub>	CH <sub>2</sub> Cl <sub>2</sub>	25	19	(4b)	80	209—210 <sup>g</sup>
(1a)	1	Pb(OAc) <sub>4</sub>	CH <sub>2</sub> Cl <sub>2</sub>	25	2	(2a)	75	129—130 <sup>h</sup>
(1b)	1	Pb(OAc) <sub>4</sub>	CH <sub>2</sub> Cl <sub>2</sub>	25	2	(2b)	96	212 <sup>i</sup>
(1b)	0	Pb(OAc) <sub>4</sub>	CH <sub>2</sub> Cl <sub>2</sub>	25	18	(2b)	52	175 <sup>j</sup>

<sup>a</sup> Substrate (500 mg) in CH<sub>2</sub>Cl<sub>2</sub> (30 cm<sup>3</sup>) containing HOAc (0.5 cm<sup>3</sup>). <sup>b</sup> Starting material recovered (25%). <sup>c</sup> Compounds (12) (25%) and (13) (25%) were also isolated. <sup>d</sup> From ethanol. <sup>e</sup> From light petroleum (b.p. 40—60 °C). <sup>f</sup> From aq. DMSO. <sup>g</sup> From benzene. <sup>h</sup> From aqueous ethanol. <sup>i</sup> From dichloromethane. <sup>j</sup> From chloroform.

bishydrazones (1; *n* = 2) were prepared as previously described.<sup>9</sup> The bishydrazones (1; *n* = 0, 1, 3) were prepared by treating ethanolic or acetic acid solutions of the corresponding cycloalkene-1,2-diyl bistrimethylsilyl ethers (which were generated by literature<sup>10,11</sup> procedures) with the substituted phenylhydrazine (4 mol equiv.). They all exhibited the *E-Z* structure (1), showing n.m.r. characteristics which we have previously analysed.<sup>9</sup> All of the compounds reported gave satisfactory CHN microanalyses and the structures were confirmed by <sup>1</sup>H and <sup>13</sup>C n.m.r. spectroscopy. These spectral data with full assignments are provided as supplementary material.\* Some key n.m.r. data are summarized in the text, Schemes and Figure. All <sup>13</sup>C n.m.r. assignments were confirmed by off-resonance and selective proton decoupling.

(I) *Rearrangements by Oxidations of Bishydrazones (1)*.—The following are typical examples. (a) A mixture of cyclohexane-1,2-dione bis(4-nitrophenylhydrazono) (1b; *n* = 2) (1.0 g) in acetic acid (30 ml) was treated with lead tetra-acetate (1.5 g), stirred at ambient temperature for 2 h, and filtered to collect the product, 4-(2-amino-5-nitrophenyl)-2-(4-nitrophenyl)-4,5,6,7-tetrahydro-2H-1,2,3-benzotriazole (3b; *n* = 2) (0.803 g, 80%), m.p. 285—287 °C (from EtOH) (Found: C, 56.5; H, 4.3; N, 22.15. C<sub>18</sub>H<sub>16</sub>N<sub>6</sub>O<sub>4</sub> requires C, 56.8; H, 4.2; N, 22.1%). <sup>v</sup><sub>max</sub>(KBr) 3 380 and 3 480 cm<sup>-1</sup> (NH<sub>2</sub> doublet); <sup>δ</sup><sub>H</sub>[(CD<sub>3</sub>)<sub>2</sub>SO] 1.8—2.9 (6 H, m, [CH<sub>2</sub>]<sub>3</sub>), 4.53 (1 H, t, cyclohexyl 4-H), 6.6 (2 H, br s, NH<sub>2</sub>),

6.86 (1 H, d, *J*<sub>MX</sub> 9.1 Hz), 7.61 (1 H, d, *J*<sub>AM</sub> 2.5 Hz), 7.97 (1 H, dd, *J*<sub>MX</sub> 9.1, *J*<sub>AM</sub> 2.5 Hz), and 8.22 and 8.45 (4 H, AA' and BB', *J*<sub>AB</sub> 9.3 Hz) [an example of the overlapping AMX and AA'BB' pattern is shown in the Figure (c)]; <sup>δ</sup><sub>C</sub> [(CD<sub>3</sub>)<sub>2</sub>SO] 19.89, 20.63, 28.5, and 32.54 (cyclohexane C-4, C-5, C-6, C-7), 113—120; 117.63, 123.77, 124.06, 124.48, 124.93, 135.13, 142.48, 144.71, 148.29, 148.32, and 152.43 (ArC).

(b) A mixture of cyclohexane-1,2-dione bis(phenylhydrazono) (1a; *n* = 2) (1.0 g) in dichloromethane (50 ml) was treated with lead tetra-acetate (1.6 g), then stirred at ambient temperature for 18 h; the insoluble lead salts were removed and the solvent was evaporated off to give a viscous residue, which was crystallized from light petroleum (b.p. 40—60 °C) to give 4-(2-aminophenyl)-2-phenyl-4,5,6,7-tetrahydro-2H-1,2,3-benzotriazole (3a; *n* = 2), m.p. 130—132 °C (from light petroleum, b.p. 40—60 °C) (68%) (Found: C, 74.5; H, 6.0; N, 19.5. C<sub>18</sub>H<sub>18</sub>N<sub>4</sub> requires C, 74.5; H, 6.2; N, 19.3%). <sup>v</sup><sub>max</sub>(KBr) 3 318 and 3 445 cm<sup>-1</sup> (NH<sub>2</sub>); <sup>δ</sup><sub>H</sub>(CDCl<sub>3</sub>) 1.87—2.95 (6 H, m, [CH<sub>2</sub>]<sub>3</sub>), 4.22 (1 H, t, cyclohexyl 4-H), 3.73 (2 H, br s, NH<sub>2</sub>), 6.68—7.42 (7 H, m, ArH), and 7.84 (2 H, m, ArH); <sup>δ</sup><sub>C</sub> (CDCl<sub>3</sub>) 21.40, 21.95, 29.3, and 34.82 (cyclohexane C-4, C-5, C-6, C-7), 117.45, 118.41, 119.53, 126.88, 127.82, 128.45, 129.22, 140.19, 143.55, 146.32, and 147.65 (ArC).

(II) *Rearrangements of 1,2-Bis(areneazo)cycloalkenes (2) ⇌ (4)*.—The following are typical examples. (a) A solution of compound (4b; *n* = 3) (500 mg, 1.3 mmol) in dichloromethane (30 ml) was treated with glacial acetic acid (0.5 ml) and stirred at ambient temperature for 10 min during which time yellow crystals of 4-(2-amino-5-nitrophenyl)-2-(4-nitrophenyl)-2,4,5,6,7,8-hexahydrocyclohepta[d][1,2,3]triazole (3b; *n* = 3) separated; m.p. 280—281 °C (from EtOH) (78%) (Found: C,

\* Supplementary material. These spectral data have been deposited as Supplementary Publication SUP 56732 (7 pp.). See section 4.0 of Instructions for Authors, January issue.

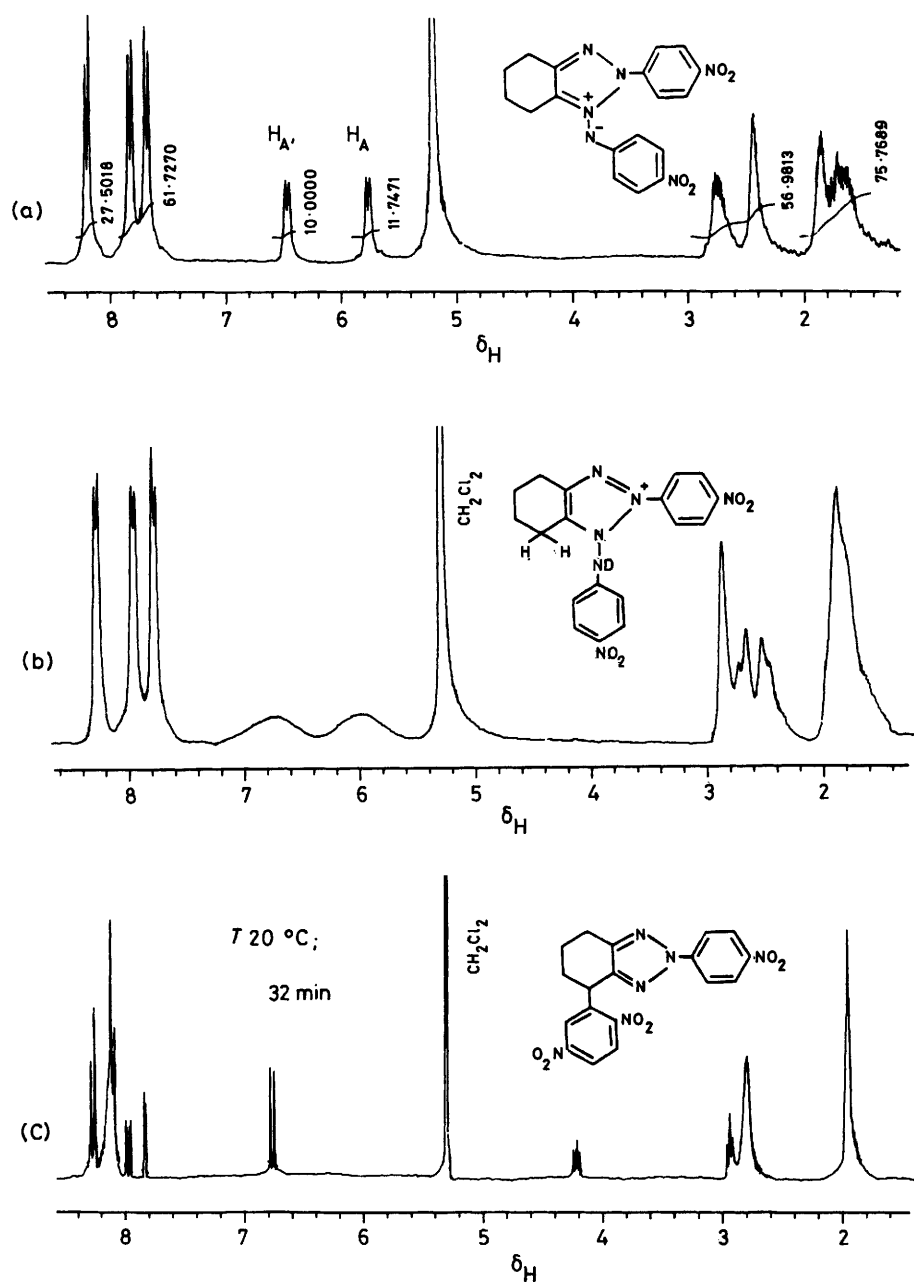


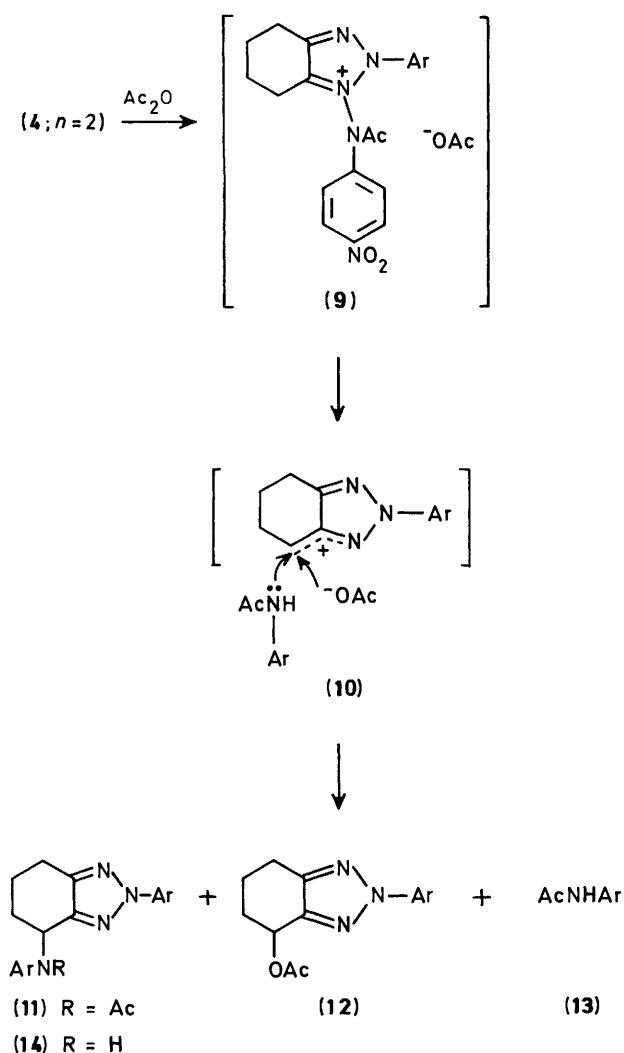
Figure. 270 MHz  $^1\text{H}$  n.m.r. spectra of form (4) of compound (2b;  $n = 2$ ) in  $\text{CD}_2\text{Cl}_2$ . (a) at  $-83^\circ\text{C}$ ; (b) at  $-83^\circ\text{C}$  with one drop of  $\text{CD}_3\text{CO}_2\text{D}$  added; (c) after warming to  $20^\circ\text{C}$ , showing presence of the product (3b;  $n = 2$ )

57.6; H, 4.4; N, 21.3.  $\text{C}_{19}\text{H}_{18}\text{N}_6\text{O}_4$  requires, C, 57.9; H, 4.6; N, 21.3%;  $\nu_{\text{max}}$  (KBr) 3362 and  $3453\text{ cm}^{-1}$  ( $\text{NH}_2$ );  $\delta_{\text{H}}$  [ $(\text{CD}_3)_2\text{SO}$ ] 1.97–3.10 (8 H, m,  $[\text{CH}_2]_4$ ), 4.56 (t, cycloheptyl 4-H), 6.78 (2 H, br, s,  $\text{NH}_2$ ), 6.84 (1 H, d,  $J_{\text{MX}}$  9.1 Hz), 7.82 (1 H, d,  $J_{\text{AM}}$  2.5 Hz), 8.02 (1 H, dd,  $J_{\text{MX}}$  9.1,  $J_{\text{AM}}$  2.5 Hz), and 8.09 and 8.44 (4 H, AA', BB',  $J_{\text{AB}}$  9.2 Hz);  $\delta_{\text{C}}$  [ $(\text{CD}_3)_2\text{SO}$ ] 26.88, 27.04, 28.37, 32.48, and 37.32 (cycloheptane, C-4–C-8), 114.44, 118.49, 124.64, 124.93, 125.56, 126.16, 143.46, 145.69, 152.35, 152.86, and 153.57 (ArC). Similar and more vigorous attempts to rearrange the compounds (2b;  $n = 0, 1$ ) resulted in quantitative recovery of starting material.

(b) A solution of 1,2-bis(phenylazo)cyclohexene (2a;  $n = 2$ ) (500 mg) in dichloromethane (30 ml) was treated with glacial acetic acid (0.5 ml) and stirred at  $25^\circ\text{C}$  for 18 h. Removal of the solvent and crystallization of the residue from light petroleum

(b.p.  $40\text{--}60^\circ\text{C}$ ) gave compound (3a;  $n = 2$ ), m.p.  $130\text{--}132^\circ\text{C}$  (77%).

When 1,2-bis(*p*-nitrophenylazo)cyclohexene (2b/4b;  $n = 2$ ) (500 mg) was treated with  $\text{Ac}_2\text{O}$  (0.5 ml) in acetic acid and stirred at ambient temperatures for 15 min, compound (11) (0.373 g, 67%), m.p.  $284\text{--}286^\circ\text{C}$  (lit.,<sup>9</sup>  $284\text{--}286^\circ\text{C}$ ) was isolated after the solution had been kept in an ice-bath, along with compounds (12) and (13) on further work-up of the filtrate. The same compounds were obtained on oxidation of the bishydrazone (1b;  $n = 2$ ) with  $\text{Pb}(\text{OAc})_4$  in acetic acid containing acetic anhydride. When compound (11) was stirred in conc. sulphuric acid it was deacetylated to compound (14) (63%), m.p.  $211\text{--}212^\circ\text{C}$ , (Found: C, 56.9; H, 4.4; N, 21.8.  $\text{C}_{18}\text{H}_{16}\text{N}_6\text{O}_4$  requires C, 56.85; H, 4.2; N, 22.1%). Compounds (11) and (14) could not be converted into (3b;  $n = 2$ ).

Scheme 3. Ar =  $-C_6H_4NO_2-p$ 

(III) 1,2-Bis(areneazo)cycloalkenes.—The following are typical preparations. (a) A solution of cyclopentane-1,2-dione bis(phenylhydrazone) (**1a**;  $n = 1$ ) (500 mg, 1.8 mmol) in dichloromethane (20 ml) was treated with lead tetra-acetate (900 mg, 2 mmol), stirred at ambient temperature for 2 h, and, after removal of the lead salts, evaporated under reduced pressure. The residue was crystallized from ethanol to give 1,2-bis(phenylazo)cyclopentene (**2a**;  $n = 1$ ) (0.37 g, 75%), m.p. 129–130 °C (from aqueous EtOH) (Found: C, 73.6; H, 6.0; N, 20.3.  $C_{17}H_{16}N_4$  requires C, 73.9; H, 5.8; N, 20.3%);  $\delta_H(CDCl_3)$  1.96–2.20 (2 H, m, cyclopentene 4-H<sub>2</sub>), 2.94–3.08 (4 H, t,  $J$  7 Hz, cyclopentene 3- and 5-H<sub>2</sub>), and 7.41–8.00 (10 H, m, Ph);  $\delta_C(CDCl_3)$  19.23 and 29.56 (cyclopentene C-3, -4, and -5), 123.32, 129.04, 131.38, and 153.86 (Ph), and 157.69 (cyclopentene C-1 and -2).

(b) A mixture of cyclobutane-1,2-dione bis(*p*-nitrophenylhydrazone) (**1b**;  $n = 0$ ) (500 mg, 1.4 mmol) and lead tetra-acetate (0.62 g, 1.4 mmol) in dichloromethane (40 ml) was stirred vigorously at ambient temperatures for 18 h, and, after removal of insoluble lead salts, evaporated and the oily residue was crystallized with ethanol to give 1,2-bis(*p*-nitrophenylazo)cyclobutene (**2b**;  $n = 0$ ), m.p. 175 °C (from  $CHCl_3$ ) (Found: C, 54.3; H, 3.6; N, 23.9.  $C_{16}H_{12}N_6O_4$  requires C, 54.5; H, 3.4; N, 23.9%);  $\delta_H(CDCl_3)$  2.99 (2 H, s, CH<sub>2</sub>) and 8.09 and 8.37 (4 H, AA' BB'  $J_{AB}$  8.7 Hz, *p*-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>);  $\delta_C$  24.50 (CH<sub>2</sub>), 124.24, 124.80, 149.51, and 151.91 (*p*-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>), and 156.52 (cyclobutene C-1 and -2).

(c) A mixture of cyclohexane-1,2-dione bis(*p*-nitrophenylhydrazone) (**1b**;  $n = 2$ ) (1.5 g, 3.9 mmol) and PbO<sub>2</sub> (6.0 g) in  $CH_2Cl_2$  (20 ml) was stirred vigorously at ambient temperature for 24 h. The salts were removed, the solution was evaporated under reduced pressure, and the residue was crystallized from ethanol to give the triazolium imide form (**4**) of 1,2-bis(*p*-nitrophenylazo)cyclohexene (**2b**;  $n = 2$ ) (1.33 g, 89%), m.p. 176–177 °C (from benzene) (Found: C, 57.1; H, 4.2; N, 21.8.  $C_{18}H_{16}N_6O_4$  requires C, 56.8; H, 4.2; N, 22.1%); for a 270 MHz variable-temperature n.m.r. study, see ref. 4. Compounds with the acyclic bisarylozo structure (**2**) were dark brown and showed u.v.–vis. spectra in acetonitrile:  $\lambda_{max}$  at  $370 \pm 10$  (log  $\epsilon \sim 3.5$ –4.3) and  $290 \pm 10$  nm (log  $\epsilon \sim 3.3$ –4.3), and a shoulder at 220 nm, before the cut-off. *p*-Nitro compounds (**2**) which existed predominantly in the cyclic structure (**4**) were deep red and showed two u.v.–vis. bands at  $\lambda_{max}$   $420 \pm 10$  (log  $\epsilon \sim 3.7$ –4.3) and  $290 \pm 5$  nm (log  $\epsilon \sim 3.9$ –4.3).

**Kinetics.**—In a typical experiment a catalytic amount of acetic acid was added to a temperature-pre-equilibrated chloroform solution of compound (**2b/4b**;  $n = 2$ ) which was then rapidly shaken and transferred to the sample cell of a temperature-controlled u.v. system with chloroform in the reference cell. The optical density ( $A$ ) was followed to  $A_\infty$  with time and plots of  $\ln(A_t - A_\infty)$  versus  $t$  were linear with slope  $-k$ . Arrhenius data were obtained at the temperatures quoted. Temperatures were maintained within  $\pm 0.5$  °C.

## References

- B. Robinson, 'The Fischer Indole Synthesis,' Wiley, Chichester, 1982, lists more than 3 000 references on the reaction; (a), pp. 88–90.
- Part of this work has been published in preliminary communication form, R. N. Butler and J. P. James, *J. Chem. Soc., Chem. Commun.*, 1983, 627.
- H. Bauer, A. J. Boulton, W. Fedeli, A. R. Katritzky, A. Majid-Hamid, F. Mazza, and A. Vaciago, *J. Chem. Soc., Perkin Trans. 2*, 1972, 662.
- R. N. Butler, A. M. Gillan, S. Collier, and J. P. James, *J. Chem. Res.(S)*, 1987, 332.
- R. N. Butler and J. P. James, *J. Chem. Soc., Perkin Trans. 1*, 1982, 553.
- I. I. Grandberg and V. I. Sorokin, *Russ. Chem. Rev.*, 1974, **43**, 115.
- D. Desaty and D. Keglevic, *Croat. Chem. Acta*, 1964, **36**, 103.
- K. H. Pausacker and C. I. Schubert, *J. Chem. Soc.*, 1950, 1814.
- R. N. Butler and M. G. Cunningham, *J. Chem. Soc., Perkin Trans. 1*, 1980, 744.
- J. J. Bloomfield and J. M. Nelke, *Org. Synth.*, 1977, **57**, 1.
- U. Schapler and K. Ruhlmann, *Chem. Ber.*, 1964, **97**, 1383.

Received 16th May 1988; Paper 8/01911H