

Regioselective Intramolecular Rearrangements in 1,2-Bis(areneazo)-cyclohexenes derived from Oxidations of Cyclohexane-1,2-dione Bis(arylhydrazones)

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1,2-Bis(areneazo)cyclohexenes undergo a regioselective intramolecular rearrangement to *o*-cyclohexylaniline derivatives when heated or treated with acid.

Oxidations of osazones and dihydrazones of 1,2-diketones are of interest¹⁻⁶ because of the range of unexpected structures which are encountered among the products. These usually arise from secondary reactions of the primary oxidation pro-

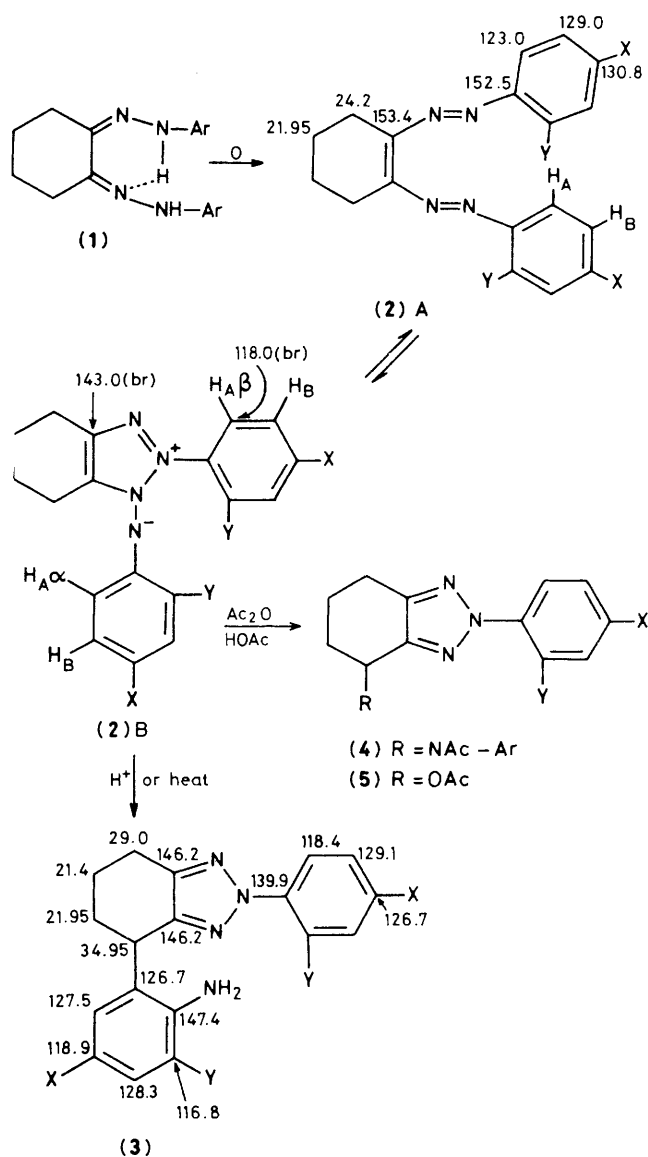
ducts which are 1,2-diazoalkenes.⁴⁻⁶ While many bis(areneazo)alkenes of type (2) have been reported from dihydrazones of acyclic 1,2-diketones there appears to be virtually no reports of such systems derived from cyclic 1,2-diones.

Table 1. Results of the oxidation of (1) to give the rearranged products (3) or (4) and the rearrangements of (2) to (3).

Substrate	Conditions				Product ^d		
	Oxidising agent	Solvent	Temp./°C	Time/h	Compound	Yield, %	M.p./°C
(1b)	Pb(OAc) ₄	HOAc	25	2	(3b)	80	285—287
(1b)		CH ₂ Cl ₂	Reflux	24	(3b)	70	"
(1b)	Tl(OAc) ₃	HOAc	25	2	(3b)	53	"
(1b)	Na ₂ Cr ₂ O ₇	HOAc	60	0.5	(3b)	42	"
(1b)	NiO ₂	C ₆ H ₆	Reflux	2	(3b)	65	"
(1a)	Pb(OAc) ₄	CH ₂ Cl ₂	25	18	(3a)	52	130—132
(1c)	Pb(OAc) ₄	CH ₂ Cl ₂	25	18	(3c)	81	196—198
(1d)	Pb(OAc) ₄	CH ₂ Cl ₂	25	18	(3d)	47 ^e	136—138
(2a)	nil	CH ₂ Cl ₂ -HOAc ^a	25	18	(3a)	77	130—132
(2b)	nil	CH ₂ Cl ₂ -HOAc ^a	25	18	(3b)	85	285—287
(2b)	nil	HOAc	25	0.25	(3b)	82	"
(2b)	nil	HOAc-Ac ₂ O ^b	25	0.25	(4b)	67	284—286
(1b)	Pb(OAc) ₄	HOAc-Ac ₂ O ^{b,c}	25	3	(4b)	30	"

^a Substrate (500 mg) in CH₂Cl₂ (30 ml) containing HOAc (0.5 ml). ^b Substrate (500 mg) in HOAc (30 ml) containing Ac₂O (0.5 ml).

^c Compound (5) (25%) and AcNHAr (25%) were also formed (*cf.* ref. 7). ^d Work-up procedures: for reactions in HOAc and HOAc-Ac₂O the products were crystallised on cooling and standing; for reactions in CH₂Cl₂, C₆H₆, and CH₂Cl₂-Ac₂O the solution was separated from insoluble salts, evaporated, and the residue crystallised from ethanol. ^e Starting material (1d) recovered (25%).



Scheme 1. a, X = Y = H; b, X = NO₂, Y = H; c, X = Br, Y = H; d, X = H, Y = NO₂. ¹³C n.m.r. shifts in CDCl₃ shown for X = Y = H, and for the B form of compound (2b) at 23 °C.

We have found that oxidations of a range of bis(arylhydrazones) of cyclohexane-1,2-diones (1) with a variety of oxidizing agents (Table 1) gave the rearranged products (3). When one, or more, moles of acetic anhydride was present in the medium the main product was the N→C rearranged compound (4). These rearrangements occurred *via* the bis(areneazo)alkenes (2) which were the precursors. Thus compounds (2a) and (2b) (Scheme 1) were separately prepared by oxidation of the corresponding dihydrazones with NiO₂ in benzene at ambient temperatures. These compounds existed in two isomeric forms (2)A and B, both directly observed in dynamic equilibrium for the first time by variable temperature ¹H n.m.r. spectroscopy (Figure 1). Thus for compound (2b) the symmetrical diazo form A was observed at -40 °C with the characteristic shifts of an alkylarylazo moiety [Figure 1(a)]. At 23 °C the compound had cyclised to form B no longer showing symmetry or arylazo proton shifts. The ¹³C n.m.r. spectrum confirmed a triazole structure with the tertiary triazole carbon signals at 143.0 p.p.m. (br.) as against shifts of 153 p.p.m. which are characteristic of the acyclic azo-form

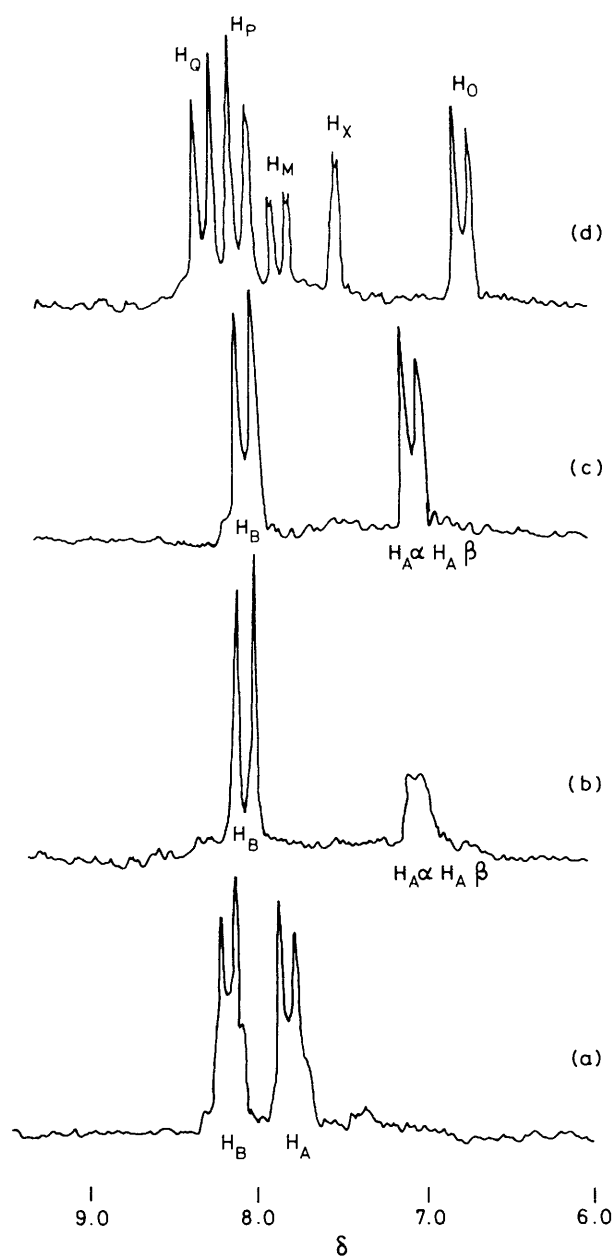


Figure 1. Aromatic region of the ¹H n.m.r. spectra in CDCl₃ of (a) compound (2b) at -40 °C, form A (Scheme 1); (b) compound (2b) at 23 °C, form B (Scheme 1) slow equilibrium exchange of aryl rings (22 s⁻¹); (c) compound (2b) at 40 °C, form B (Scheme 1) fast equilibrium exchange of aryl rings; (d) compound (3b) at 23 °C after addition of HOAc to (b).

(Scheme 1). At 23 °C the compound exhibited a slow equilibrium exchange between the two cyclized forms *via* the azo-form so that the *ortho* H_{Aα} and H_{Aβ} protons appeared as a collapsed exchange broadened peak [Figure 1(b)] and the ¹³C n.m.r. spectrum showed the triazole and C-2' signals also broadened. At 40 °C the exchange rate was sufficiently increased so that the H_{Aα} H_{Aβ} protons appeared as an averaged doublet of the AA'BB' system [Figure 1(c)]. As the temperature was lowered from 23 °C to -40 °C the *ortho* proton signal of the cyclized form broadened and eventually disappeared as the concentration of the cyclized form decreased. At the same time the *ortho* proton signal of the acyclic form appeared first as a broad flattened signal which

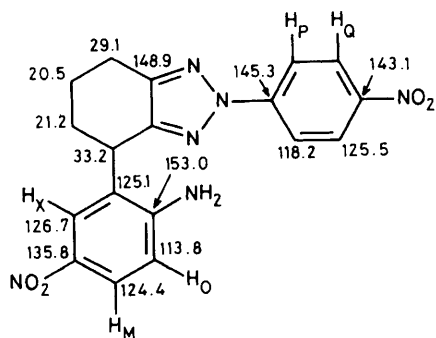
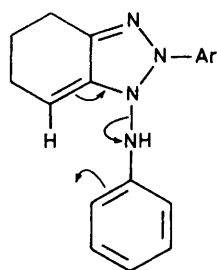
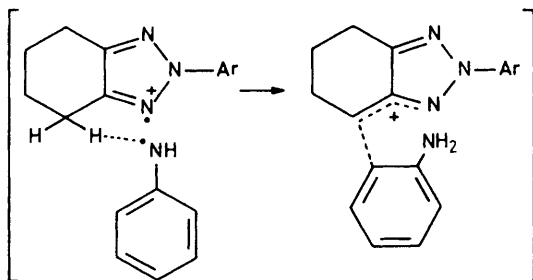


Figure 2. ^{13}C N.m.r. shifts for (3b) in $(\text{CD}_3)_2\text{SO}$.



(6)



(7)

grew and sharpened as the temperature was lowered. The signal for the *meta* protons H_B showed some broadening but remained much the same during these changes since the chemical shift is the same in both forms. When the substrates (2)

were treated with acetic acid or heated they rapidly rearranged to the *ortho*-substituted anilines (3) (Table 1) giving results identical to the oxidations of the compounds (1). The structures of the products (3) were proved by ^1H and ^{13}C n.m.r. spectra which showed all of the expected signals [Figure 1(d) and Figure 2] (Scheme 1) including the characteristic AMX pattern of the 1,2,4-trisubstituted benzene ring in products (3b) and (3c) and the ABCD and ABC patterns in compounds (3a) and (3d), respectively. All of the assignments in the ^1H and ^{13}C n.m.r. spectra of the compounds (3) were confirmed by off-resonance and selective proton decoupling.

The rearrangement (2) \rightarrow (3) was regiospecific *ortho* and intramolecular. No crossover products were encountered and no *para*-substituted products were formed. When one of the *ortho*-positions was blocked as with the substrate (1d) the product (3d) was still formed and there was no *para*-attack. The presence of acetic anhydride changed the reaction to give mainly the products (4) and some (6) by an apparently intermolecular process.

The rearrangement (2) \rightarrow (3) may be viewed as a 3,3-sigmatropic migration (6) (analogous to the Fischer indole reaction⁸) or a possible caged cation radical process (7) with H abstraction from the α -cyclohexyl position, after protonation, followed by electrophilic *ortho*-attack within the cage.

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