Isomerism and Lead(IV) Acetate Oxidation Reactions of *p*-Substituted Phenylosazones of Some Substituted Glyoxals and 1,2-Diketones. Reactions of Metallic Acetates with Nitrogen Compounds. Part 5.†

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The structures of the bis-(*p*-nitrophenyl)hydrazones and some bis-(*p*-bromophenyl)hydrazones of glyoxal, methylglyoxal, phenylglyoxal, butane-2,3-dione, benzil, and cyclohexane-1,2-dione were examined by i.r., ^{1}H n.m.r., and ^{13}C n.m.r. spectroscopy. Generally the *E,E* forms of the osazones were obtained from direct synthesis except for the bis-(*p*-nitrophenyl) hydrazoneof cyclohexane-1,2-dione and phenylglyoxal and the bis-(*p*-bromophenyl)hydrazones of phenylglyoxal, which were obtained as the *E,Z*-chelate forms. Unstable yellow crystalline forms of the bis-(*p*-nitrophenyl)hydrazones of glyoxal, butane-2,3-dione, and benzil containing two molecules of hexamethylphosphoramide (HMPA) of crystallisation, which may contain the *E,Z*-isomers, were isolated from HMPA solutions. Lead tetra-acetate oxidation of a range of *E,E*-osazones gave dehydrogenations to 1,2-bisazoethylenes. Similar oxidations of *E,Z*-osazones gave mainly 2-aryl-1,2,3-triazole type products (osotriazoles) along with lower yields of azoethylenes. Oxidation of cyclohexane-1,2-dione bis-(*p*-nitrophenyl)hydrazone gave a mixture of osotriazoles containing an acetoxy- or *p*-nitroacetanilido-group at the 3-position of the cyclohexyl ring.

INTEREST in the relationship between the isomerism of phenylhydrazones of α-dicarbonyl compounds and their reactions has resulted in some recent structural studies of these systems.[1-9] Our interest in the oxidation reactions of bis(hydrazone) systems [10,11] led us to examine bis-(*p*-nitrophenyl)hydrazones and bis-(*p*-bromophenyl)-hydrazones of some substituted glyoxals. Structural work on the bis-(*p*-nitrophenyl)hydrazones has not been reported previously and, except for compound (10) [1] (Table 1), the isomerism of the *p*-bromophenylosazones has not been reported. The possible isomers of the 1,2-bis(hydrazone) system are the *E,E*, *E,Z*, and the rarer *Z,Z* forms and, although separate *E,E* and *E,Z* isomers were sometimes detected, they were not isolated.[1,4] Remarkably, however, the three isomers of benzil bis-(phenyl)hydrazone have been isolated.[5,12-15] Recently, with benzil bis-(*p*-tolylsulphonyl) hydrazone we detected the *E,E* form only.[10]

TABLE 1

Osazone isomers

Compound	R^1	R^2	X	Structure (A) M.p. (°C) (Colour)	Structure (A) ν(N–H)/ cm^{-1}	Structure (A) ^{1}H N.m.r. (δ) [a] NH	Structure (A) ^{1}H N.m.r. (δ) [a] CH=N	Structure (B) M.p. (°C) (Colour)	Structure (B) ν(N–H)/ cm^{-1}	Structure (B) ^{1}H N.m.r. (δ) [a] NH	Structure (B) ^{1}H N.m.r. (δ) [a] CH=N
(1)	H	H	NO_2	108—110 [b] (yellow)	3 200 3 240			320 (red)	3 250	12.42 [c]	8.02
(2)	Me	H	NO_2					286—290 (red)	3 260 3 320	11.28 [d] 12.34	7.90 [d]
(3)	Ph	H	NO_2	310 (red)	3 260	12.82 [c]	8.56				
(4)	Me	Me	NO_2	173—175 [b] (yellow)	3 180 3 220			311—312 (red)	3 300	10.20 [e,f]	
(5)	Ph	Ph	NO_2	143—153 [b] (yellow)	3 100 3 160			288—289 (red)	3 280	10.50 [e]	
(6)	$[CH_2]_4$		NO_2	274 276 (red)	3 180 3 220	11.12 [g] 13.26					
(7)	H	H	Br					228—229 (pale brown)	3 300	11.36 [h]	7.72
(8)	Me	H	Br					176—178 (yellow)	3 300 3 350	10.40 [i] 11.40	7.76
(9)	Me	Me	Br					218—220 (pale brown)	3 350	10.28 [j]	
(10)	Ph	H	Br	189—190 (yellow)	3 190 3 280	12.2 [k] 13.1	8.4				

[a] ^{1}H N.m.r. δ values are for HMPA solutions unless otherwise stated. [b] Contained 2 molecules HMPA of crystallisation. Structure (A) for these compounds is tentative, *cf.* text. [c] Developed on standing or addition of deuteriochloroform. [d] Spectrum in [$^2H_6$]DMSO was NH, 10.36 and 11.28 δ; CH=N, 7.72 δ; Me–C, 2.22 δ. [e] Values are for [$^2H_6$]DMSO solutions. NH Signals were too broad for observation in HMPA. [f] Me–C, δ 2.22 [$^2H_6$]DMSO. [g] NH, δ 10.38 and 12.9 in [$^2H_6$]DMSO. [h] δ [$^2H_6$]DMSO; NH, 10.44 [i] δ [$^2H_6$]DMSO: NH, 9.44 and 10.48; CH=N, 7.58; Me–C, 2.14. [j] NH, δ 9.40 in [$^2H_6$]DMSO. Me–C, δ 2.16 in [$^2H_6$]DMSO. [k] δ [$^2H_6$]DMSO: NH, 11.80 and 12.36; CH=N, 8.08.

RESULTS AND DISCUSSION

Isomerism.—A series of bis-(*p*-nitrophenyl)hydrazones and bis-(*p*-bromophenyl)hydrazones [Table 1, compounds (1)—(10)] was prepared by normal procedures. The *p*-nitro-osazones were obtained as high-melting red solids which were generally quite insoluble, making satisfactory n.m.r. spectra difficult to obtain.

† Part 4; R. N. Butler and A. M. O'Donohue, *J.C.S. Perkin II*, 1979, 1387.

^{1}H *N.m.r. spectra.* Hexamethylphosphoramide (HMPA) was the only solvent suitable for ^{1}H n.m.r. work on the full series although [$^2H_6$]dimethyl sulphoxide was suitable for most of the compounds. Solutions for compounds (2), (6), (8), and (10) (Table 1), both in HMPA and [$^2H_6$]DMSO, showed two NH signals in the n.m.r. spectrum. For compounds (6) and (10) one of these was a characteristic [1,4,14] low-field signal (Table 1) due to the intramolecular hydrogen bond in the *E,Z* form (A) and the other was at higher field, and due to the intermolecular hydrogen bond [1,4,14] of the second NH–Ar group. As expected, the lower-field signal was insensitive to addition of deuteriochloroform and the higher-field NH signal moved upfield due to cleavage of intermolecular hydrogen bonds. For compounds (2) and (8) dilution with deuteriochloroform resulted in shielding shifts of similar magnitude (0.12—0.16 p.p.m. for a 1 : 1 v/v dilution) in both NH signals confirming an *E,E* structure (B) in which the separate NH signals were due to the different chains. Interestingly, with the osazones (6) and (10) (Table 1), the *E,Z*-chelate isomer (A) was present immediately in the solution and, in agreement with this, the i.r. spectra of the solid bis-(hydrazones) (below) suggested the presence of the *E,Z*-form mainly in the crystals obtained directly from the preparation of the compound.

Solutions of the bis-(*p*-nitrophenyl)hydrazones of glyoxal (1), butane-2,3-dione (4), and benzil (5) (Table 1), and also the bis-(*p*-bromophenyl)hydrazones of glyoxal (7) and butane-2,3-dione (9) (Table 1) in both HMPA and [$^2H_6$]dimethyl sulphoxide showed only the *E,E*-isomers (B). For these compounds only one NH signal, due to intermolecular hydrogen bonding, was encountered. Prolonged standing or addition of deuteriochloroform did not produce any new signals but difficulty was encountered in observing the NH signals in HMPA solutions for compounds (4) and (5) (Table 1). These NH signals were, however, readily detected in [$^2H_6$]-DMSO, in which solvent the shieldings were generally higher than for HMPA (Table 1, footnotes). It did not prove possible to establish unequivocally the configuration of phenylglyoxal bis-(*p*-nitrophenyl)hydrazone (3) due to insolubility and the appearance of only one NH signal in the n.m.r. at low field which grew slowly in HMPA solutions (Table 1). By comparison with compound (10), and also from the oxidation reactions (below), it seems likely that the *E,Z* form is present but the spectroscopic data could be interpreted in terms of an *E,E* or *E,Z* configuration. Attempts to determine whether the NH signal at δ 12.82 was due to an inter- or intra-molecularly hydrogen-bonded species failed owing to immediate precipitation on dilution.

^{13}C *N.m.r. spectra.* The ^{13}C n.m.r. spectra for the *p*-NO_2-series are in Table 2. In general, the ^{13}C n.m.r. spectra were in full agreement with the proton spectra although somewhat less effective for identifying the isomers. For cases where methine substituents R^1 and R^2 were not the same, two α-C signals were observed as expected but these could be due either to the *E,E* or *E,Z* forms, *e.g.* compound (2) (Table 2) and the isomers were therefore not distinguishable from the carbon spectra. For cases where R^1 and R^2 were the same, *e.g.* compounds (1), (4), (5), and (6), the presence of two α-C signals would clearly prove the *E,Z* structure as was the case for compound (6). For the compounds (1), (4), and (5) a single strong α-C signal was observed and, in agreement with the proton n.m.r. data, indicated the presence of the *E,E* form only.

TABLE 2

Carbon-13 n.m.r. spectra of osazones

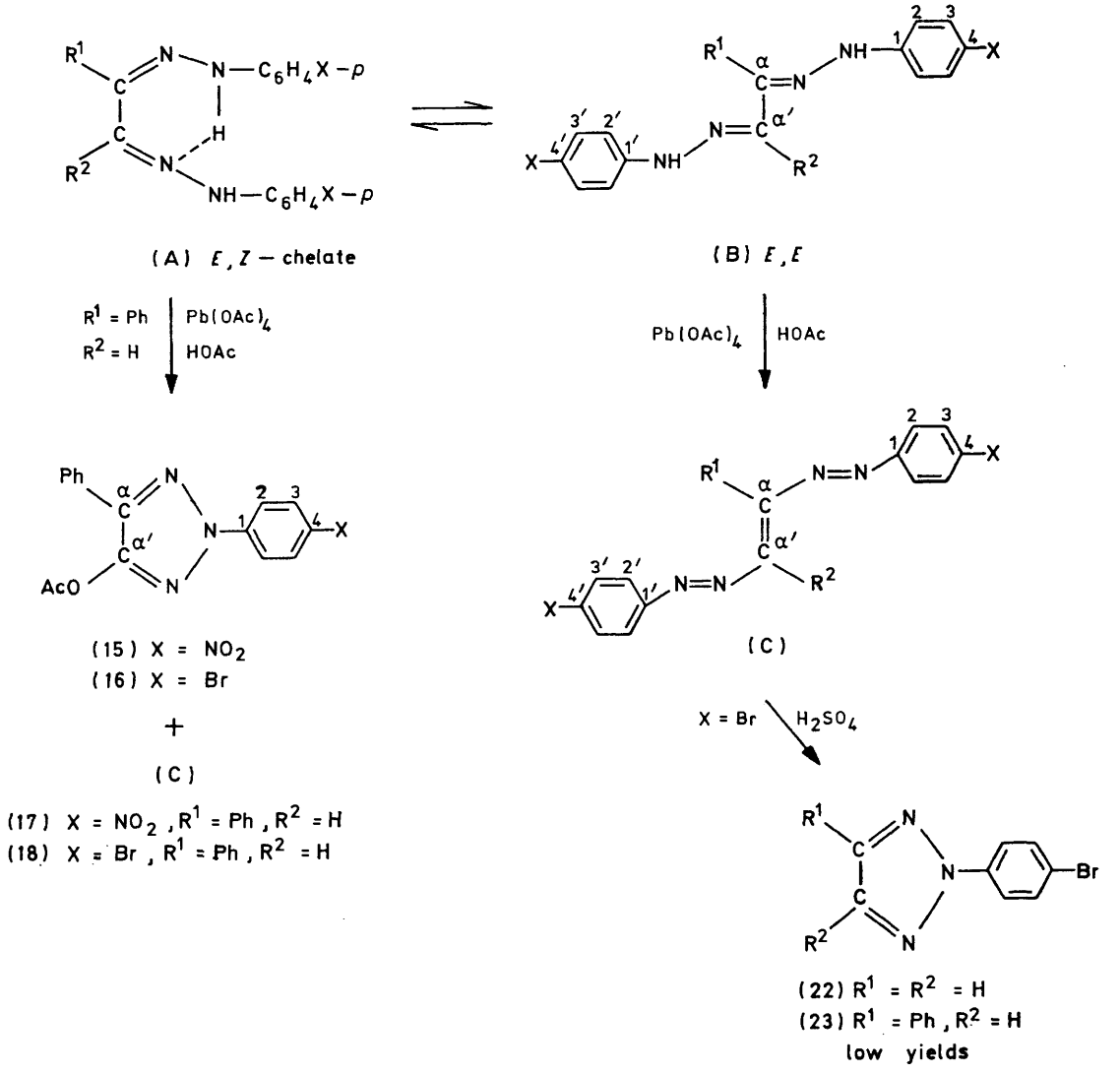
Compound	R^1	R^2	Solvent	Cα,α′	$C^{1,1'}$	$C^{2,2'}$	$C^{3,3'}$	$C^{4,4'}$
(1)	H	H	[$^2H_6$]DMSO	140.5	149.6	111.55	126.0	139.0
(1)	H	H	HMPA–$CDCl_3$ (3 : 1 v/v)	141.25	150.8	111.55	125.85	139.36
(2)	Me [a]	H	[$^2H_6$]DMSO	146.05	150.35	111.43	125.75	139.2
				142.6(CH)	150.15	112.34	126.00	138.8
(3)	Ph	H	[$^2H_6$]DMSO–HMPA (3 : 1 v/v)	*b*	*b*	112.3	126.7	*b*
						113.4	126.0	
(4)	Me [c]	Me	[$^2H_6$]DMSO	146.7	150.8	112.2	125.7	*b*
(5)	Ph	Ph	[$^2H_6$]DMSO	140.3	150.7	113.0	125.5	139.5
(6)	–[CH_2]$_4$–		[$^2H_6$]DMSO	146.3	151.1	112.3	126.05	139.4
				145.4	149.7	112.3	125.7	138.8

[a] δ Me, 10.91. [b] Not detected due to insolubility. [c] δ Me, 11.0.

Solid state. In the solid state a distinction between the *E,Z*-chelate and *E,E* isomers (A) and (B) (where $R^1 = R^2$) can be made from the i.r. N–H stretching bands where a sharp singlet is obtained for the *E,E*-form and a doublet is obtained for the *E,Z*-chelate form due to the two different types of hydrogen bonds. Each of the compounds (1), (4), (5), (7), and (9) (Table 1) were obtained as *E,E* forms (B) in the solid state. Each compound gave a satisfactory microanalysis and showed a single N–H band in the i.r. (Table 1). With the cyclohexane-1,2-dione derivative (6) the *E,Z*-chelate form was strongly present in the solid state. The compound showed i.r. N–H doublets with components of about equal intensities (Table 1). On being dissolved, it showed the n.m.r. signals of both chelate and non-chelate NH moieties immediately, as did the phenylglyoxal derivative (10). Previously, Hooper and Dauphinee [1] have reported the *E,Z*-chelate form of the *p*-bromophenylosazone of phenylglyoxal (10) in HMPA solutions and our results for both DMSO and HMPA solutions are in agreement.

Interestingly, when concentrated HMPA solutions (100—200 mg ml^{-1}) of the symmetrical bis(hydrazones) (1), (4), and (5) were allowed to stand, bright yellow

needles with lower melting points separated (Table 1). These yellow products were unstable and when touched with the solvents benzene, chloroform, carbon tetrachloride, ethanol, acetic acid, or water, they immediately changed to the original high-melting red isomers. The yellow needles, however, could be washed with thoroughly dried pentane or ether without changing them. The n.m.r. spectra of these yellow forms could not be obtained because the compounds changed to the red isomers on being dissolved in normal solvents, and solutions in HMPA gave the same spectra as the original HMPA solutions from which they had separated. However, for each of the yellow forms of compounds (1), (4), and (5) (Table 1) the i.r. spectra showed the characteristic NH doublet of the *E,Z*-chelate form (A) (Table 1). Microanalyses showed the presence of 2 molecules of HMPA per molecule of osazone in these yellow compounds. Comparable yellow forms of the other osazones could not be induced to separate from HMPA solutions, nor could similar HMPA complexes for other representative mono-*p*-nitrophenylhydrazones be obtained. The i.r. results suggest that these yellow crystals may contain the *E,Z*-isomers, stabilized in the solid state by HMPA of crystallization. An *X*-ray crystallographic study will be required to confirm this, and the possibility of HMPA complexes with the *E,E*-isomers cannot be ruled out at present.

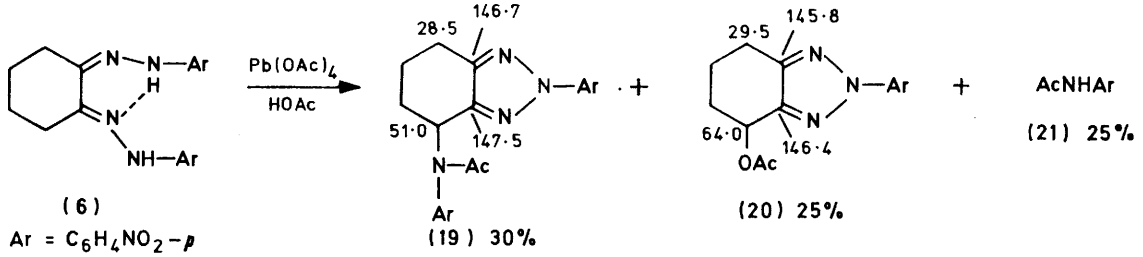


SCHEME 1

The data for the full series suggest that increasing size of R^1 relative to R^2, for $R^2 = H$, facilitates the development of the *E,Z* form (A). This is probably related to the sterically favourable *trans*-orientation of R^1 and the NHAr group of form (A) and the *cis*-orientation of $R^2 = H$ with the second NHAr group. However, the threshold of the balance for the favoured isomer is delicate and, if the methine substituent R^2 is not a hydrogen and the chains may rotate, *e.g.* compounds (4) and (5) *versus* (6), or if the methine substituent R^1 is not as large as a Ph group, *e.g.* compounds (2) and (8), then intermolecular hydrogen-bonding may dominate and favour the *E,E*-isomers.

Lead(IV) *Acetate Oxidations.*—In general, oxidations to sugar osazones gave 2-aryl-1,2,3-triazoles (osotriazoles) in a fragmentative cyclisation involving loss of an aniline molecule.[16] Oxidations of bis(acyl)hydrazones of 1,2-dicarbonyl compounds gave 1-substituted-amino-1,2,3-triazoles [17-19] but these products were originally thought to be dihydro-*v*-tetrazines. Oxidations of bis-(aryl)hydrazones of symmetrical 1,2-dicarbonyl compounds generally gave bisazoethylene products.[17,18] There is a paucity of information on the mechanisms of these oxidations and on the relationship of the products to the stereochemistry of the starting bis(hydrazones).

When the present series of osazones was treated with $Pb(OAc)_4$ in acetic acid, all the compounds with *E,E* structures were relatively cleanly dehydrogenated to the azoethylenes (C) (Scheme 1) (Table 3) and triazoles were not encountered. The structures of the compounds (C) were established by i.r., u.v., and ^1H and ^{13}C n.m.r.



SCHEME 2

TABLE 3

Azoethylenes (C) [a] from oxidation of the corresponding osazones

Compd.	X	R^1	R^2	M.p. (°C)	Yield (%)	$\lambda_{max.}$ ($CHCl_3$) nm	^{13}C N.m.r. ($CDCl_3$) $C_{\alpha,\alpha'}$
(11)	Br	H	H	166—167	90—93	390	155.8
(12)	NO_2	Me	H	187—189	50 [b]	385	162.7; 155.5 (CH)
(13)	NO_2	Me	Me	184—186	50	396	
(14)	NO_2	Ph	Ph	175—176	60	410	165.1
(17)	NO_2	H	Ph	151—153	25 [c]	403	161.8; 147.2 (CH)
(18)	Br	H	Ph	150—151	23	402	160.1; 146.2 (CH)

[a] Compounds (11)—(14) are assigned *trans*-olefin structures due to u.v. similarities with other comparable *trans*-isomers (ref. 17). The olefin stereo-structures of compounds (17) and (18) are not established. No isomeric changes were encountered. [b] Osazone recovered 30%. [c] Osazone recovered 32%.

spectra. The ^{13}C n.m.r. spectra were particularly helpful because the use of azobenzene [20] as a model gave an excellent prediction for the shifts of the aromatic carbons of the compounds (C) wherein the substituent additivity effects [21] were retained. Interestingly, $Pb(OAc)_4$ oxidation of the *E,Z*-osazones gave significant yields of osotriazole-type products. Thus treatment of the osazone (10) (Table 1) with $Pb(OAc)_4$ in acetic acid at 25 °C gave the 2-aryl-4-acetoxy-1,2,3-triazole (16) (60%) along with the bis(azo)ethylene (18) (23%) (*cf.* Table 3) and some deep-brown gums containing *p*-bromoacetanilide. Similar oxidation of the osazone (3) gave the triazole (15) (25%) and the bis(azo)ethylene (17) (23%) (Table 3) along with gums and a 32% recovery of the osazone. Bisazoethylenes of type (C) containing an olefinic CH moiety were unstable in chloroform solution and underwent a decomposition to gums which involved a change at the CH site, possibly an initial tautomerism, since the CH carbon-13 signal could be observed disappearing as the decomposition proceeded. The triazole (15) was also highly labile in $[^2H_6]$dimethyl sulphoxide solution. Independent treatment of the bis(azo)ethylene (17) with $Pb(OAc)_4$ in acetic acid did not give the triazole (15) but rather gave gums and a good recovery of the compound (17), and it is unlikely that the triazoles were formed *via* the bis(azo)ethylenes under the reaction conditions. However, under relatively strong conditions, *i.e.* brief stirring in concentrated sulphuric acid, the bis(azo)ethylenes (11) and (18) (Table 3) were converted in low yields into the corresponding osotriazoles (22) (22%) and (23) (19.5%) (Scheme 1). $Pb(OAc)_4$ Oxidation of the *E,Z*-osazone (6) (Table 1) gave the triazoles (19) and (20) (Scheme 2) (some carbon-13 n.m.r. shifts shown) along with *p*-nitroacetanilide and brown gums. The results suggest that osotriazole formation is more favoured with *E,Z*-osazone isomers and also that for active solvents such as acetic acid the cyclisation may involve solvent participation at an (electrophilic) site near the methine carbon, *e.g.* compounds (15), (16), and (20). Treatment of compound (6) with LTA in dichloromethane containing triethylamine to remove acetic acid did not give the compounds (19) and (20) (but rather a complex mixture involving unidentified gums) confirming acetic acid solvent involvement. The interesting product (19), formation of which involved overall a 1,3-N→C migration of an *N*-aryl moiety, appears to be the first of its kind from an osazone oxidation and could have arisen either intramolecularly or intermolecularly *via* the acetanilide (21). We tentatively suggest that the reaction involved initial electrophilic attack at the free non-hydrogen-bonded amino-NH moiety with a subsequent fragmentation involving activation of the methine region towards nucleophilic attack. It has been established previously that electrophilic acetylation of *E,Z*-osazones occurs at

the free amino-NH moiety.[1,3] Kinetic studies will be carried out to examine the oxidation mechanisms in more detail.

EXPERIMENTAL

M.p.s were measured with an Electrothermal apparatus. I.r. spectra were measured for KBr discs or Nujol mulls with a Perkin-Elmer 377 grating i.r. spectrophotometer. ^1H and ^{13}C N.m.r. spectra were measured at probe temperatures with JEOL JNM-100 and CFT-20 spectrometers using tetramethylsilane as reference. For the ^1H n.m.r. spectra the assigned NH signals were confirmed by deuteriation with [$^2H_4$]methanol, addition of which caused the NH signals to disappear. Blank spectra measured on the HMPA solvent and mixtures of HMPA with $CDCl_3$ showed no signals in the regions where the NH signals from the bis(hydrazones) appeared. Full details of microanalytical data for each compound reported are summarized in SUP 22693 (5 pp.).* All carbon-13 assignments were confirmed by off-resonance proton decoupling which showed the proton splitting pattern of each carbon, and also by using simpler model compounds. The full carbon-13 spectra and assignments for compounds (11), (12), (15), (16), (17), (18), (19), and (20) are given in SUP 22693.

The bis-(*p*-nitrophenyl)hydrazones were prepared by standard procedures,[22] by treating the α-dicarbonyl compound with 2 mol *p*-nitrophenylhydrazine in glacial acetic acid or aqueous alcohol. The yellow forms of compounds (1), (4), and (5) (Table 1) were prepared by allowing HMPA solutions of the compounds to stand for 24 h, during which time the yellow needles separated.

Oxidation Reactions.—The following are typical examples. (i) p-*Bromophenylosazones*. (*a*) A mixture of glyoxal bis-(*p*-bromophenyl)hydrazone (7) (510 mg) in acetic acid (30 ml) containing acetic anhydride (0.5 ml) was treated with $Pb(OAc)_4$ (618.5 mg) and stirred at ambient temperature for 1 h, after which brown 1,2-*bis*-(p-*bromophenylazo*)-*ethylene* (11), m.p. 166—167 °C [from chloroform–light petroleum (40—60 °C)] (473 mg, 93%) was removed; i.r., no NH bands; δ($CDCl_3$) 8.34 (s, 2 H, =CH), and 7.24 and 7.72 (each 4 H, A_2B_2, *p*-bromophenyl-group). Compound (11) (200 mg) was added to concentrated sulphuric acid (10 ml) giving an immediate deep blue colour which changed to brownish white on careful dilution with water (40 ml). The solution was extracted with ether (2 × 50 ml) and the combined ethereal extract was washed with aqueous sodium hydrogencarbonate solution and water, dried, and evaporated to yield a brown gummy residue which on purification with charcoal and hot ethanol gave 2-p-*bromophenyl*-1,2,3-*triazole* (22), m.p. 113—114 °C (from ethanol) (25 mg, 22%); i.r., no NH; $\lambda_{max.}$ (MeOH) 265 nm (log ε 4.21); δ($CDCl_3$) 7.76 (s, =CH), and 7.56 (2 H) and 7.92 (2 H) (A_2B_2, *p*-bromophenyl). A similar sulphuric acid treatment of compound (18) gave the corresponding triazole (23), m.p. 128—129 °C (19.6%); i.r., no NH; $\lambda_{max.}$ (MeOH) 299 nm (log ε 4.37); δ 7.64 (s, =CH), and 7.20—8.08 (m, 9 H, aromatic).

(*b*) A mixture of phenylglyoxal bis-(*p*-bromophenyl)-hydrazone (10) (375 mg) and acetic acid (25 ml) containing acetic anhydride (0.5 ml) was treated with $Pb(OAc)_4$ (382 mg) and stirred at ambient temperature for 1 h, after which brown 1-*phenyl*-1,2-*bis*-(p-*bromophenylazo*)*ethylene* (18), m.p. 150—151 °C [from chloroform–light petroleum (40—60 °C)] (87 mg, 23%) was removed; i.r., no NH; δ($CDCl_3$) 7.96 (s, HC=), and 7.2—7.8 (m, 13 H, aromatic). Treatment of the acetic acid mother-liquor with water gave white 4-*acetoxy*-2-p-*bromophenyl*-5-*phenyl*-1,2,3-*triazole* (16) (filtrate A) (168 mg, 59%), m.p. 145—146 °C [from chloroform–light petroleum (40—60 °C)]; *m/e* 357 and 359 (M^+); i.r., no NH, 1 780 (C=O of OAc), and 1 170—1 185 (ester C–O–C) cm^{-1}; $\lambda_{max.}$ (MeOH) 302 nm (log ε 4.57); δ($CDCl_3$) 2.40 (s, 3 H, Ac) and 7.36—8.04 (m, aromatic). Further work-up, by ethereal extraction, of the filtrate (A) gave gums containing *p*-bromoacetanilide.

(ii) p-*Nitrophenylosazones*. (*a*) A mixture of phenylglyoxal bis-(*p*-nitrophenyl)hydrazone (1 g) in acetic acid (50 ml) containing acetic anhydride (0.5 ml) was treated with $Pb(OAc)_4$ (1.185 g) in acetic acid (30 ml) and stirred at ambient temperatures for 40 h. Solid material was removed (filtrate A) and proved to be a mixture of starting osazone (320 mg, 32%) and 1,2-*bis*-(p-*nitrophenylazo*)-1-*phenylethylene* (17) (250 mg, 25%) which was separated by dissolving compound (17) in chloroform, m.p. 151—153 °C (decomp.); i.r., no NH or C=O; δ($CDCl_3$) 7.52—8.44 (m, overlapping A_2B_2 and Ph) and 8.08 (s, CH=). Treatment of the filtrate (A) with water (2 × 70 ml) gave 4-*acetoxy*-2-p-*nitrophenyl*-5-*phenyl*-1,2,3-*triazole* (15), m.p. 160—162 °C [from chloroform–light petroleum (40—60 °C)] (190 mg, 23%); $M^+ + 1$, 325; i.r., no NH; 1 790 (C=O), and 1 175—1 190 cm^{-1} (ester C–O–C); δ 2.40 (s, 3 H, Ac), 7.36—7.44 (m, 3 H, *m*- and *p*-H of Ph), 7.72—7.88 (2 H, *o*-H of Ph), and 8.08—8.4 (m, 4 H, *p*-$C_6H_4NO_2$). Further work-up of the mother-liquor gave gums containing *p*-nitroacetanilide. In repeated runs of this reaction the yields of compound (17) were erratic and, in general, when these were low, the yield of compound (15) increased correspondingly. However, separate comparable treatment of compound (17) with $Pb(OAc)_4$ in acetic acid gave a 50% recovery along with gums and compound (15) was not encountered.

(*b*) A mixture of cyclohexane-1,2-dione bis-(*p*-nitrophenyl)hydrazone (6) (1 g) in acetic acid (30 ml) containing acetic anhydride (0.5 ml) was treated with $Pb(OAc)_4$ (1.504 g) and the mixture stirred at ambient temperatures for 36 h. A white solid (filtrate A), which separated during the stirring, proved to be 2-(p-*nitrophenyl*)-4-(N-p-*nitrophenyl*-N-*acetyl*)*amino*-4,5,6,7-*tetrahydro*-2H-*benzo*[1,2,3]*triazole* (19), m.p. 284—286 °C (from dimethyl sulphoxide–water) (315 mg, 31%); i.r.; no NH, and 1 650 cm^{-1} (amide C=O); $\lambda_{max.}$ 322 nm (log ε 2.79); δ($CDCl_3$) 1.96 (s, 3 H, NAc), 1.84—2.28 (m, 4 H, cyclohexyl), 2.68 (2 H, cyclohexyl), 7.32 (d, 2 H, A_2B_2, Ar), and 8.04—8.24 (m, 6 H, overlapping A_2B_2, Ar *ortho* to NO_2 and triazole). The filtrate (A) was treated with water (2 × 50 ml) to give a sticky brown solid (filtrate B) (335 mg) from which pale yellow 4-*acetoxy*-2-(p-*nitrophenyl*)-4,5,6,7-*tetrahydro*-2H-*benzo*[1,2,3]*triazole* (20), m.p. 152—154 °C (260 mg, 25%), was extracted by continued leaching with light petroleum (40—60 °C); i.r., no NH and 1 725 cm^{-1} (ester C=O); $\lambda_{max.}$ ($CHCl_3$) 323 nm (log ε 4.29); δ 2.14 (s, 3 H, Ac), 1.80—2.22 (m, 4 H, cyclohexyl), 2.88 (2 H, cyclohexyl), 6.16 (1 H, C*H*OAc), and 8.18 and 8.32 (A_2B_2, *p*-nitrophenyl). Ethereal extraction of the filtrate (B) gave *p*-nitroacetanilide (25%) and a red-brown gum.

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* For details of Supplementary Publications scheme see Notice to Authors No. 7, *J.C.S. Perkin I*, 1979, Index issue.

REFERENCES

[1] D. L. Hooper and G. A. Dauphinee, *J.C.S. Perkin I*, 1974, 14.
[2] C. H. Yoder, S. Kennedy, and F. A. Snavely, *J. Org. Chem.*, 1978, **43**, 1077.
[3] H. S. El Khadem, G. P. Kreishman, and E. H. El-Ashry, *J. Org. Chem.*, 1975, **40**, 3149.
[4] O. L. Chapman, R. W. King, W. J. Welstead, and T. J. Murphy, *J. Amer. Chem. Soc.*, 1964, **86**, 4968.
[5] R. B. Woodward and C. Winter, *Tetrahedron Letters*, 1969, 2697.
[6] O. L. Chapman, *Tetrahedron Letters*, 1966, 2599.
[7] A. D. Mitchell and D. Nonhebel, *Tetrahedron Letters*, 1975, 3859.
[8] A. W. Spasov and N. I. Christova, *Compt. Rend. Acad. Bulg. Sci.*, 1977, **30**, 1717.
[9] N. I. Christova and A. W. Spasov, *Compt. Rend. Acad. Bulg. Sci.*, 1972, **25**, 47.
[10] R. N. Butler, A. B. Hanahoe, and W. B. King, *J.C.S. Perkin I*, 1978, 881.
[11] R. N. Butler, A. B. Hanahoe, and A. M. O'Donohue, *J.C.S. Perkin I*, 1979, 1246.
[12] A. W. Spasov, *Bulgarska Akad. Nauk, Otdel. Geol.-Geograf. Khim. Nauk, Izvest. Khim. Inst.*, 1951, **1**, 217 (*Chem. Abs.*, 1953, **49**, 2153e).
[13] A. W. Spasov and S. Robec, *Bull. Inst. Chim. Acad. Bulg. Sci.*, 1953, **2**, 3 (*Chem. Abs.*, 1953, **49**, 5371).
[14] N. I. Christova and A. W. Spasov, *Z. Chem.*, 1978, **18**, 23.
[15] N. Christova, A. Spasov, R. Radeglia, and W. Altenburg, *Z. Chem.*, 1978, **18**, 102.
[16] H. El Khadem, *Adv. Carbohydrate Chem.*, 1965, **20**, 139.
[17] H. Bauer, A. J. Boulton, W. Fedeli, A. R. Katritzky, A. Majid-Hamid, F. Mazza, and A. Vaciago, *J.C.S. Perkin II*, 1972, 662.
[18] N. E. Alexandrou, *Tetrahedron*, 1966, **22**, 1309.
[19] N. E. Alexandrou and E. D. Micromastoras, *J. Org. Chem.*, 1972, **37**, 2345.
[20] L. F. Johnson and W. C. Jankowski, 'Carbon-13 NMR Spectra,' Wiley–Interscience, J. Wiley and Sons, New York, 1972, spectrum No. 431.
[21] G. C. Levy and G. L. Nelson, 'Carbon-13 Nuclear Magnetic Resonance for Organic Chemists,' Wiley–Interscience, J. Wiley and Sons, New York, 1972, p. 81.
[22] A. I. Vogel, 'Practical Organic Chemistry,' Longmans, London, 1962, p. 722; F. G. Mann and B. C. Saunders, 'Practical Organic Chemistry,' Longmans Green and Co., London, 1956, p. 183.