Synthesis of Some 1,2,4-Triazoles and 1,2,4-Triazolines by Reaction of Oxamidrazone Condensation Products with Acetic Anhydride

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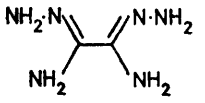
Products of condensation of acetic anhydride with bisalkylideneamino-oxamidines are described. The bis(cyclopentylidene-, cycloheptylidene-, phenylethylidene-, and 1-methyl-2-phenylethylidene-amino)oxamidines gave substituted 5-methyl-1-vinyl-1,2,4-triazoles. Bis(allylidene-, cinnamylidene-, and 1,2-diphenylethylidene-amino)-oxamidines gave substituted 1,4-diacetyl-1,2,4-triazolines. Bis(adamantylidene- and 1,2-diphenylethylidene-amino)oxamidines gave acetylated alkylideneamino-oxamidines. Bis(cyclohexylideneamino)oxamidine was anomalous in that it gave 1,1'-diacetyl-5,5'-dimethyl-3,3'-bi-1,2,4-triazole. Mechanisms of these reactions are discussed.

ALTHOUGH condensation products of amidrazones with aldehydes and ketones have previously been reported,[1] there appear to be few recorded examples of such reactions with oxamidrazone (1). We now find that a



(1)

solution of the acetate of (1) in 1,2-dimethoxyethane condenses rapidly and in high yield with a wide variety of carbonyl compounds to yield products of type (2) (Table).

An attempt to ring-close the cyclopentylidene product (2a) with acetic anhydride to give the imidazoline (3) failed; instead we obtained a product, $C_{16}H_{20}N_6$, showing physical properties expected for the dicyclopentenyltriazole (4). There was no evidence to show that any dicyclopentenyloxamidrazone (5) was present in the condensation product (2a) (n.m.r.; see Experimental section).

The behaviour of other condensation products (2) with acetic anhydride was then investigated. The products obtained are given in the Table.

The possible structures (15) and (16), alternative to the diacetyltriazoline (8) can be rejected on the basis of spectroscopic evidence. The weak C=N i.r. absorption (1 595 cm^{-1}) would be expected to be considerably stronger owing to conjugation in formulae (15) and (16). A singlet band would have been expected in the n.m.r. spectrum ($CDCl_3$) for the equivalent Me groups in (15). In fact we found Me signals at τ 7.7 and 7.85. The signal for the original ' aldehydic ' proton when present occurs at τ *ca.* 3.4 (in 8) but at τ *ca.* 2 in the uncyclised starting compounds (2d and f). Compound (8) showed $\nu_{max.}$ (KBr) 1 710ms (hydrazide CO) and 1 675s cm^{-1} (amide CO). The hydrazide–amide difference is usually *ca.* 20 cm^{-1}. In this case it is increased to 35 cm^{-1} by conjugation.

To account for some of the products we suggest the following mechanism. In the general case (Scheme 1) the condensation product (2) is acylated on NH_2 to give a monoacyl derivative, and additionally is quaternised to give the stable carbocation (17), which is cyclised under the influence of acetate ion to give the bisdiacetyl derivative (18). This would account for the acetyl derivatives (8), (9), and (12) being obtained from the condensation products (2d, e, and h), respectively.

If however the 5-substituent of the Δ^2-1,2,4-triazoline is capable of undergoing β-elimination under the influence of acetate ion, then we envisage two possibilities taking place as outlined in Scheme 2A. Subsequent deacetylation could take place in route *a* by the processes in Scheme 2B, or the two could conceivably be concerted. An analogous scheme is feasible for route *b* leading to (19). This scheme would account for the formation of the substituted methyltriazoles (4), (7), (10), and (11) from the condensation products (2a, c, f, and g), respectively.

The suggested mechanism implies that two isomeric products of the reaction are possible, depending on which C–N bond breaks. In all the cases studied we have obtained one product only, which we consider to be the *N*(1)-substituted 1,2,4-triazole (19). pK_a Determinations on simple substituted 1,2,4-triazoles indicate the 1*H*-triazole to be thermodynamically more stable than the 4*H*-isomer.[2] Additionally we would have expected a 4-substituted 1,2,4-triazole to lose nitrogen in the mass spectrometer.[3] This was never observed.

The influence of the size of the cycloalkylidene ring of the condensation products, *e.g.* (2a and b), on their reaction products [(4) and (6), respectively] is marked, as has been noted by other workers.[4]

The fact that the methyl benzyl ketone condensation product (2g) is converted by acetic anhydride into the 1-substituted triazole (11), whereas the corresponding deoxybenzoin condensation product (2h) gives the 5-substituted triazoline (12) [a shorter reaction time gave the monoacetyl derivative (13)] suggests that the steric effect of the phenyl as compared with the methyl radical renders access to the methylene group by the acetate ion impossible.

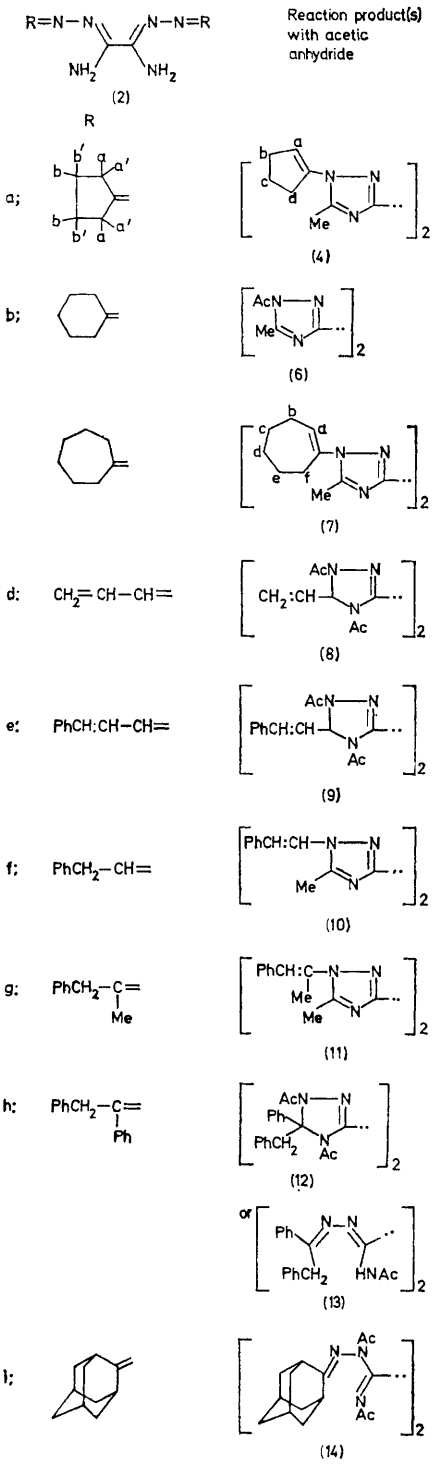
[1] D. G. Neilson, R. Roger, J. W. M. Heatlie, and L. R. Newlands, *Chem. Rev.*, 1970, **70**, 164.

[2] C. F. Kroeger and W. Freiberg, *Chimia* (*Switz.*), 1967, **21**, 161.

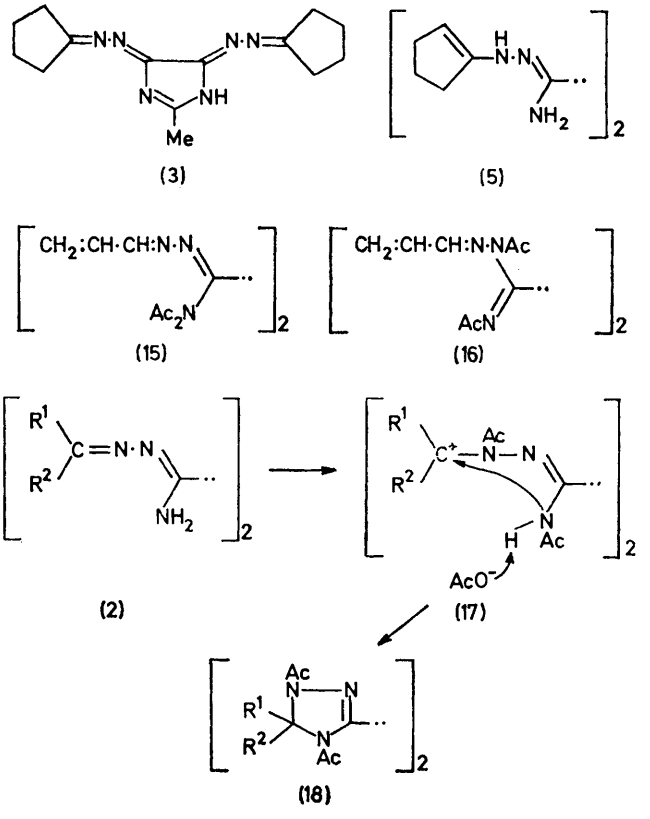
[3] G. Spiteller, in ' Physical Methods in Heterocyclic Chemistry,' ed. A. R. Katritzky, Academic Press, New York and London, 1971, vol. III, p. 259.

[4] G. H. Hitchings, P. B. Russell, and N. Whittaker, *J. Chem. Soc.*, 1956, 1019.

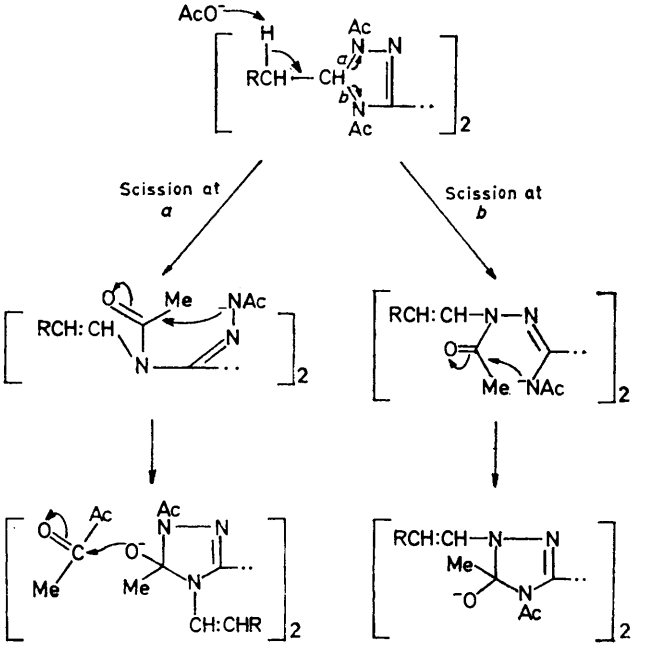
Finally, an attempt was made to prepare the spirotriazoline (20). Compound (2i) was accordingly treated



with acetic anhydride. The product, however, was compound (14). The structure was evident from the i.r. spectrum, which showed $\nu_{max.}$ (Nujol) 1 525 and 1 500s (C:N) and $\nu_{max.}$ ($CHCl_3$) 1 515s and 1 500 cm^{-1} (C:N), suggesting that the C=N system carried an acetyl substituent whose conformation in the solid state was different from that in solution. By analogy with the other diacetyl 1,2,4-triazolines, we would have expected the acetyl n.m.r. singlets to be at τ 7.8 and 7.9, whereas in fact they

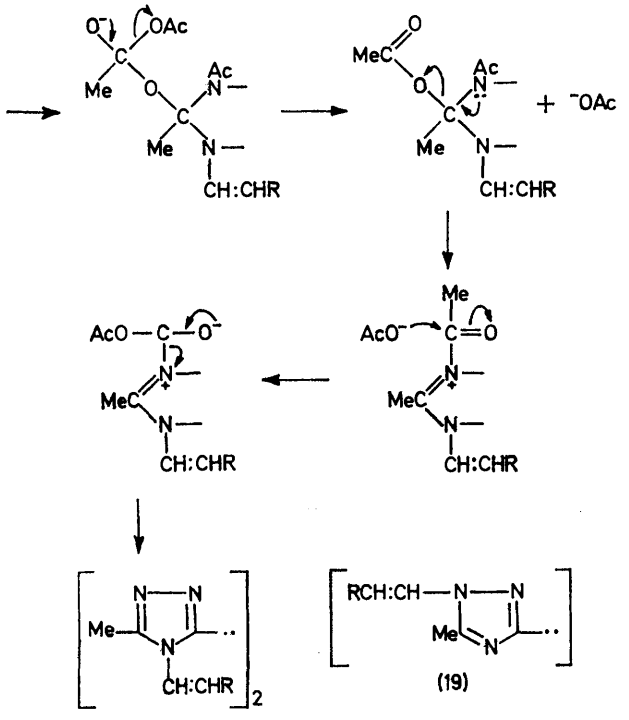


SCHEME 1



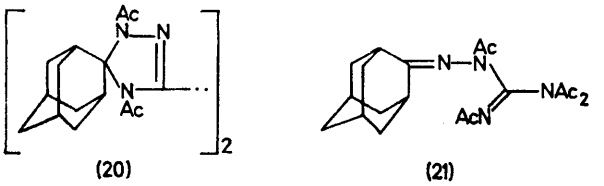
SCHEME 2A

were at τ 7.15 and 8.0, suggesting that they were in different environments.



SCHEME 2B

The fact that we fail to obtain the triazoline (20) could be due to the shielding effect of the three tertiary adamantyl protons, which prevent N(1) from being quaternised [*cf.* (17)]. Probably for similar reasons, we obtained the



(20) (21)

tetra-acetyl compound (21) from the reaction of acetic anhydride with the condensation product of adamantan-2-one and aminoguanidine.

EXPERIMENTAL

Elemental analyses were carried out with a Technicon automatic C, H, and N analyser. I.r. spectra were measured with a Perkin-Elmer 21 or 137 spectrometer, and n.m.r. spectra with a Varian A-60 (60 MHz) or HA-100 (100 MHz) spectrometer.

N^2,N^4-*Bis*(*cyclopentylideneamino*)*oxamidine* (2a).—Cyclopentanone (2 g) in 1,2-dimethoxyethane (DME) (5 ml) was added to a warm solution of oxamidrazone (1.38 g) in 5N-acetic acid (4 ml) and DME (5 ml). Water (50 ml) was then added. The product (2.6 g), m.p. 230° (decomp.), was collected and washed with water. Recrystallisation from toluene gave the *base* as plates, m.p. 233—234° (decomp.) (Found: C, 58.1; H, 8.3; N, 34.3. $C_{12}H_{20}N_6$ requires C, 58.05; H, 8.05; N, 33.9%); $\nu_{max.}$ ($CHCl_3$) 3 500, 3 380 (NH_2), and 1 545 cm^{-1} (NH_2 def.); τ [$(CD_3)_2SO$] 4.18vbr (4H, $2NH_2$), 7.05br (4H, m, H_a or $H_{a'}$), 7.42br (4H, m, H_a or $H_{a'}$), and 8.14br (8h, m, H_b and $H_{b'}$).

1,1′-*Dicyclopent*-1-*enyl*-5,5′-*dimethyl*-3,3′-*bi*-1,2,4-*triazole* (4).—Acetic anhydride (25 ml) was added to N^2,N^4-bis(cyclopentylideneamino)oxamidine (1.5 g) and the mixture was heated under reflux during 7 min. After cooling, an excess of methanol was added and evaporated off under vacuum, and the procedure was repeated thrice. The residue crystallised from ethyl acetate (carbon treatment) to yield the *bitriazole* as rhombs (480 mg), m.p. 193—194° (Found: C, 64.5; H, 6.5; N, 28.3%; M^+, 248. $C_{16}H_{20}N_6$ requires C, 64.85; H, 6.75; N, 28.4%; *M*, 248); τ ($CDCl_3$) 4.2 (2H, m, H_a), 6.05 (4H, m, H_b or H_d), 6.45 (4H, m, H_b or H_d), 6.45 (6H, s, $2CH_3$), and 6.96 (4H, m, H_c).

N^2,N^4-*Bis*(*cyclohexylideneamino*)*oxamidine* (2b).—A warm solution of cyclohexanone (19.6 g) in DME (70 ml) was added to a solution of oxamidrazone (11.6 g) in 5N-acetic acid (70 ml) and DME (100 ml). The *product* (24.5 g), m.p. 238—240°, was collected and washed with water. A sample crystallised from dimethylformamide gave the base as pale yellow needles, m.p. 242—244° (Found: C, 60.5; H, 8.6; N, 30.6. $C_{14}H_{24}N_6$ requires C, 60.9; H, 8.7; N, 30.4%).

1,1′-*Diacetyl*-5,5′-*dimethyl*-3,3′-*bi*-1,2,4-*triazole* (6).—The above condensation product (2 g, 7.0 mmol) and acetic anhydride (14 ml) were heated under reflux during 15 min. After cooling aqueous alcohol was added to destroy the excess of reagent and the product (0.8 g, 32%), m.p. 252—254°, was collected and washed with water. Recrystallisation from ethyl acetate gave the *bisdiacetyltriazole* as needles, m.p. 260—262° (Found: C, 48.2; H, 4.9; N, 34.1. $C_{10}H_{12}N_6O_2$ requires C, 48.4; H, 4.8; N, 33.9%); τ ($CDCl_3$) 7.18 (6H, s, $2CH_3$) and 7.2 (6H, s, $2CH_3$); $\nu_{max.}$ (Nujol) 1 745s cm^{-1} (C=O).

N^2,N^4-*Bis*(*cycloheptylideneamino*)*oxamidine* (2c).—This was prepared in the usual manner from oxamidrazone (3.48 g, 30.0 mmol) in 5N-acetic acid (16 ml) and DME (20 ml), and cycloheptanone (6.72 g, 60.0 mmol) in DME (12 ml). A sample of the *product* (8.6 g, 94%), m.p. 203—205°, crystallised from dimethylformamide as cream plates, m.p. 206—207° (Found: C, 63.2; H, 9.0; N, 27.4. $C_{16}H_{28}N_6$ requires C, 63.2; H, 9.2; N, 27.6%).

1,1′-*Dicyclohept*-1-*enyl*-5,5′-*dimethyl*-3,3′-*bi*-1,2,4-*triazole* (7).—The above condensation product (2 g, 6.6 mmol) and acetic anhydride (12 ml) were heated under reflux during 45 min. The following morning the excess of reagent was removed with methanol. The residue left after evaporation under reduced pressure was triturated with ethyl acetate and the solid (0.9 g, 39%) collected. Two recrystallisations from ethyl acetate gave the *triazole* as prisms, m.p. 186—187.5° (Found: C, 67.9; H, 7.8; N, 23.8%; M^+, 352. $C_{20}H_{28}N_6$ requires C, 68.1; H, 7.95; N, 23.95%; *M*, 352), τ ($CDCl_3$) 4.0 (2H, t, H_a), 7.4 (4H, m, H_f), 7.5 (6H, s, $2CH_3$), 7.74 (4H, m, H_b), and 8.2br (12H, s, H_c, H_d, and H_e).

N^2,N^4-*Bis*(*allylideneamino*)*oxamidine* (2d).—This was prepared in the usual manner from oxamidrazone (4.8 g, 41.0 mmol) in 5N-acetic acid (20 ml) and DME (10 ml), and acrylaldehyde (11.0 ml, 164.0 mmol) in DME (10 ml). The product, after being washed with hot alcohol, crystallised from dimethylformamide as cream *prisms* (2.8 g, 36%), m.p. 208—210° (decomp.) (Found: C, 50.3; H, 6.3; N, 43.6. $C_8H_{12}N_6$ requires C, 50.0; H, 6.25; N, 43.7%); τ [$CDCl_3$–$(CD_3)_2SO$] 1.9 (2H, d, 2CH), 3.7br (6H, s, 2CH and NH_2), and 4.27 (4H, d, $2CH_2$).

1,1′,4,4′-Tetra-acetyl-5,5′-divinyl-3,3′-bi-Δ²-1,2,4-triazoline (8).—N^2,N^4-Bis(allylideneamino)oxamidine (2.0 g, 10 mmol) in acetic anhydride (60 ml) was heated under reflux during 15 min. The excess of reagent was distilled off under reduced pressure, and the last traces were removed by co-evaporation with ethanol. Recrystallisation of the residue from ethanol gave the *product* (0.7 g, 19%) as cream prisms, m.p. 241—243° (Found: C, 53.3; H, 5.8; N, 23.4. $C_{16}H_{20}N_6O_4$ requires C, 53.3; H, 5.55; N, 23.3%); τ ($CDCl_3$) 3.4 (2H, d, 2CH), 3.65—4.5 (6H, m, $2CH_2$:CH), 7.7 (6H, s, $2CH_3$), and 7.85 (6H, s, $2CH_3$); $\nu_{max.}$ (KBr) 1 710, 1 675 (CO), and 1 600s cm^{-1} (CH_2=CH–).

N^2,N^4-*Bis(cinnamylideneamino)oxamidine* (2e).—This was prepared in the usual manner from oxamidrazone (4.8 g, 41.0 mmol) in 5N-acetic acid (20 ml) and DME (10 ml), and cinnamaldehyde (13.2 g, 100.0 mmol) in DME (10 ml). The crude product (12.5 g) after washing with hot alcohol crystallised from dimethylformamide as yellow *plates* (9.0 g, 65%), m.p. 250—252° (Found C, 70.0; H, 5.9; N, 24.3. $C_{20}H_{20}N_6$ requires C, 69.8; H, 5.8; N, 24.4%).

1,1′,4,4′-Tetra-acetyl-5,5′-distyryl-3,3′-bi-Δ²-1,2,4-triazoline (9).—N^2,N^4-Bis(cinnamylideneamino)oxamidine (2.0 g, 6.0 mmol) in acetic anhydride (60 ml) was heated under reflux during 0.25 h. The excess of reagent was removed *in vacuo*, the last traces by co-evaporation with ethanol. The beige-coloured solid was recrystallised twice from dimethylformamide to give *needles* (0.75 g, 24%), m.p. 208—210° (Found: C, 65.1; H, 5.7; N, 16.3. $C_{26}H_{28}N_6O_4$ requires C, 65.7; H, 5.5; N, 16.5%); τ ($CDCl_3$) 2.6 (10H, m, aromatic), 2.92 (2H, d, *J* 16 Hz, β-*trans*-vinyl), 3.28 (2H, d, *J* 7.5 Hz, H-5), 3.54 (2H, q, $J_{\beta,\alpha}$ 16, $J_{5,\alpha}$ 7.5 Hz), 7.72 (6H, s, $2CH_3$), and 7.82 (6H, s, $2CH_3$).

N^2,N^4-*Bis-(2-phenylethylideneamino)oxamidine* (2f).—Freshly distilled phenylacetaldehyde (9.6 ml, 80.0 mmol) in DME (10 ml) was added to oxamidrazone (4.64 g, 40.0 mmol) in 5N-acetic acid (20 ml) and DME (20 ml). After 0.25 h the precipitate was filtered off, washed with alcohol, and dried to yield the *product* (11.9 g, 93%) as cream prismatic needles, m.p. 164—166° (Found: C, 67.6; H, 6.2; N, 26.3. $C_{18}H_{20}N_6$ requires C, 67.5; H, 6.25; N, 26.25%); τ [$(CD_3)_2SO$] 2.14 (2H, t, *J* 6 Hz, 2CH=N), 2.65 (10H, s, aromatic), 3.85br (4H, s, $2NH_2$), and 6.32 (4H, d, *J* 6 Hz, $2ArCH_2$).

5,5′-Dimethyl-1,1′-distyryl-3,3′-bi-1,2,4-triazole (10).—N^2,N^4-Bis-(2-phenylethylideneamino)oxamidine (2.0 g, 6.0 mmol) was heated to reflux in acetic anhydride (50 ml) during 20 min. The excess of reagent was evaporated off, the last traces by co-evaporation with ethanol. The crude product was dissolved in a little chloroform and applied to a silica column (220 g) in chloroform. The column was eluted with chloroform (1 l) and then with 0.5% methanol–chloroform. The product was obtained as a brown oil, homogeneous on t.l.c. The oil was dissolved in a little ethanol from which the trans-*styryltriazole* (0.295 g, 13%) slowly separated as pale cream prismatic needles, m.p. 273—275° (Found: C, 72.1; H, 5.5; N, 22.5. $C_{22}H_{20}N_6$ requires C, 71.8; H, 5.4; N, 22.8%); τ [$(CD_3)_2SO$] 2.01 and 2.15 (2H, d, *J* 14 Hz, 2 *trans*-olefinic), 2.22—2.81 (12H, m, aromatic + olefinic), and 7.36 (6H, s, $2CH_3$). The ethanolic liquors upon evaporation yielded the *cis*-styryltriazole (0.9 g, 41%) as a brown tar, which failed to crystallise and showed t.l.c. behaviour identical with that of the above crystalline material. The n.m.r. spectrum [τ ($CDCl_3$)] showed two *cis*-olefinic doublets at 3.31 (*J* 6 Hz) and 3.40 (*J* 6 Hz).

N^2,N^4-*Bis-(1-methyl-2-phenylethylideneamino)oxamidine* (2g).—Benzyl methyl ketone (10.7 g, 80.0 mmol) in DME (10 ml) was added to a solution of oxamidrazone (4.8 g, 40.0 mmol) in 5N-acetic acid (20 ml) and DME (15 ml). The product was collected and washed with alcohol. Recrystallisation from alcohol gave the *amidrazone* as a microcrystalline powder (11.0 g, 77%), m.p. 145—147° (Found: C, 68.5; H, 6.8; N, 24.4. $C_{20}H_{24}N_6$ requires C, 69.0; H, 6.9; N, 24.1%); τ ($CDCl_3$) 2.7—2.75 (10H, d), 4.25 (4H, s), 6.05—6.3 (4H, d), and 8.05 (6H, s). It was present as the *syn*- and *anti*-isomers.

5,5′-Dimethyl-1,1′-bis-(α-methylstyryl)-3,3′-bi-1,2,4-triazole (11).— N^2,N^4-Bis-(1-methyl-2-phenylethylideneamino)oxamidine (1.5 g, 4.3 mmol) in acetic anhydride (30 ml) was heated to reflux during 2 h. The excess of reagent was removed under vacuum. An excess of ethanol was added and the residue left after evaporation under reduced pressure was triturated with ethyl acetate. The solid (0.65 g) was collected; recrystallisation from ethanol gave the *triazole* (0.55 g, 35%) as plates, m.p. 236—238° (Found: C, 73.0; H, 6.1; N, 21.0. $C_{24}H_{24}N_6$ requires C, 72.25; H, 6.05; N, 21.2%); τ ($CDCl_3$) 2.58 (10H, s, aromatic), 3.3br (2H, s, olefinic), 7.34 (6H, s, 2 triazole Me), and 7.55 (6H, d, 2 C:CMe).

N^2,N^4-*Bis-(1,2-diphenylethylideneamino)oxamidine* (2h).—Deoxybenzoin (4.0 g, 20.0 mmol) in DME (8 ml) was added with vigorous stirring to a solution of oxamidrazone (1.2 g, 10.0 mmol) in 5N-acetic acid (10 ml) and DME (5 ml). The product was collected and washed with alcohol. Recrystallisation from aqueous dimethylformamide gave the *base* (3.7 g, 79%) as yellow plates, m.p. 211—213° (Found: C, 75.9; H, 5.9; N, 18.0. $C_{30}H_{28}N_6$ requires C, 76.2; H, 6.0; N, 17.8%); τ [$(CD_3)_2SO$] 1.85—2.15 (4H, m, aromatic), 2.5—3.0 (16H, m, aromatic), 3.3br (4H, s, $2NH_2$), and 5.48 (4H, s, $2CH_2$).

1,1′,4,4′-Tetra-acetyl-5,5-dibenzyl-5,5′-diphenyl-3,3′-bi-Δ²-1,2,4-triazoline (12).—N^2,N^4-Bis-(1,2-diphenylethylideneamino)oxamidine (1.0 g, 2.0 mmol) and acetic anhydride (50 ml) were heated under reflux during 4 h. The following morning the excess of reagent was evaporated off, the last traces by co-evaporation with ethanol. Addition of ethyl acetate to the residual oil gave the crude *product* (0.4 g), which crystallised from ethyl acetate as microprisms (0.25 g, 20%), m.p. 240—242° (decomp.) (Found: C, 71.2; H, 5.8; N, 12.9. $C_{38}H_{36}N_6O_4$ requires C, 71.3; H, 5.6; N, 13.0%); τ ($CDCl_3$) 2.5—3.1 (16H, m, aromatic), 3.25—3.5 (4H, m, aromatic), 4.8, 5.85, 5.85, and 6.1 (4H, AB doublet, $2CH_2$), and 7.88 and 7.92 (12H, 2s, $4CH_3$).

N^1,N^3-*Diacetyl-N²,N⁴-bis-(1,2-diphenylethylideneamino)-oxamidine* (13).—N^2,N^4-Bis-(diphenylethylideneamino) oxamidine (2.0 g, 4.0 mmol) and acetic anhydride (40 ml) were heated under reflux during 20 min and the product was worked up by the usual procedure. Recrystallisation from alcohol gave pale cream *microprisms* (1.0 g, 45%) m.p. 180—182° (Found: C, 73.6; H, 5.9; N, 15.1. $C_{34}H_{32}N_6O_2$ requires C, 73,3; H, 5.75; N, 15.1%); τ [$(CD_3)_2SO$] 1.9—2.0 and 2.15—2.25 (4H, 2 × m, aromatic), 2.6—3.4 (16H, m, aromatic), 5.34, 5.49, 5.64, 5.78, and 5.92 (4H, q + s, $2CH_2$), and 7.86, 7.89, and 8.0 (6H, d + s, $2CH_3$) (at 160 °C CH_2 and CH_3 signals collapse to single peaks).

N^2,N^4-*Bis(adamantan-2-ylideneamino)oxamidine* (2i)—Adamantan-2-one (6.0 g, 40.0 mmol) in DME (40 ml) was added to oxamidrazone (2.4 g, 20.0 mmol) in 5N-acetic acid (10 ml) and DME (10 ml). The precipitate (7.5 g) was collected and washed with alcohol. Recrystallisation from dimethylformamide gave the *product* (6.0 g, 79%) as microplates, m.p. 268—270° (decomp.) (Found: C, 69.3; H, 8.3;

N, 22.2. $C_{22}H_{32}N_6$ requires C, 69.5; H, 8.4; N, 22.1%); τ ($CDCl_3$) 4.3 (4H, s, NH_2), 6.2 (2H, s, tertiary protons), 7.25 (2H, s, tertiary protons), and 8.0 (24H, s, remainder of adamantanyl protons).

N^1,N^2,N^3,N^4-*Tetra-acetyl*-N^1,N^3-*bis*(*adamantan-2-ylideneamino*)*oxamidine* (14).—N^2,N^4-Bis(adamantan-2-ylideneamino)oxamidine (2.0 g, 5.0 mmol) in acetic anhydride (50 ml) was heated under reflux during 1 h. The mixture was evaporated *in vacuo* and the residue (1.7 g) was triturated with alcohol. Recrystallisation from dimethylformamide gave the *product* (1.6 g, 58%) as prismatic needles, m.p. >325° (Found: C, 65.7; H, 7.2; N, 15.3. $C_{30}H_{40}N_6O_4$ requires C, 65.7; H, 7.3; N, 15.3%); τ ($CDCl_3$) 6.4 (4H, s), 7.15 (6H, s, $2CH_3$), 7.6—8.4 (24H, s, adamantanyl), and 8.0 (6H, s, $2CH_3$); $\nu_{max.}$ (Nujol) 1 750s cm^{-1} (C=O).

1-(*Adamantan-2-ylideneamino*)*guanidinium Formate*.—A suspension of aminoguanidinium hydrogen carbonate (2.7 g, 20.0 mmol) in ethanol (100 ml) and formic acid (0.8 ml, 20.0 mmol) was heated to reflux until a clear solution had formed. Adamantan-2-one (3.0 g, 20.0 mmol) in ethanol (20 ml) was added and the mixture was heated under reflux during 1 h. The crude product, obtained by evaporating off the solvent, crystallised from ethanol in *plates* (2.7 g, 65%), m.p. 188—190° (Found: C, 57.5; H, 8.0; N, 22.3. $C_{12}H_{20}N_4O_2$ requires C, 57.2; H, 7.95; N, 22.3%).

1,1,2,3-*Tetra-acetyl*-3-(*adamantan-2-ylideneamino*)*guanidine* (21).—1-(Adamantan-2-ylideneamino)guanidinium formate (1.0 g, 4.0 mmol) and acetic anhydride (30 ml) were heated under reflux during 1 h. The residue, obtained after evaporation *in vacuo*, was treated with alcohol and the excess of reagent was removed by evaporation. The residue showed two spots on t.l.c. Acetic anhydride (20 ml) was added and the mixture was heated under reflux and worked up by the usual procedure. The residue gave the *tetra-acetylguanidine* (0.5 g, 34%) as microneedles, m.p. 135—137° (from ethyl acetate). A further recrystallisation raised the m.p. to 137—139°. The material was pure by t.l.c. (Found: C, 61.2; H, 7.0; N, 15.1. $C_{19}H_{26}N_4O_4$ requires C, 61.0; H, 6.95; N, 15.0%); $\nu_{max.}$ (Nujol) 1 525mw and 1 500ms (C=NAc), and 1 720br and 1 745br (C=O); $\nu_{max.}$ ($CHCl_3$) 1 730br cm^{-1} (C=O); τ ($CDCl_3$) 6.6—6.8br (2H, s, H-1 and -3 of adamantanyl), 7.3 (3H, s, NAc), 7.65 (6H, s, NAc_2), 7.65—8.4br (12H, s, adamantanyl protons), and 7.9 (3H, s, Ac).

We thank Drs. D. W. van Krevelen, Siggel, and Frank, Akzo Research and Engineering N.V., Arnhem, Holland, for a gift of oxamidrazone, and Dr. P. N. Edwards and Mr. P. J. Taylor for discussions.

[4/2478 *Received*, 27*th November*, 1974]