

STUDIES ON LEAD TETRAACETATE OXIDATION OF α -OXOKETENE S,N- AND N,N-ACETALS¹

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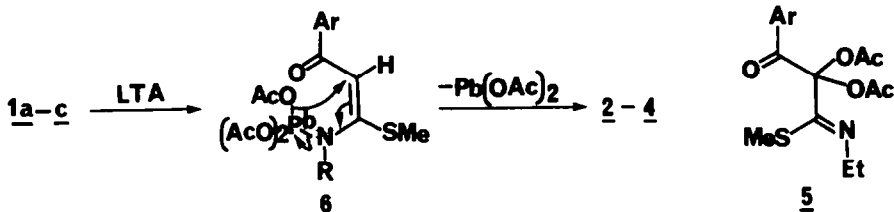
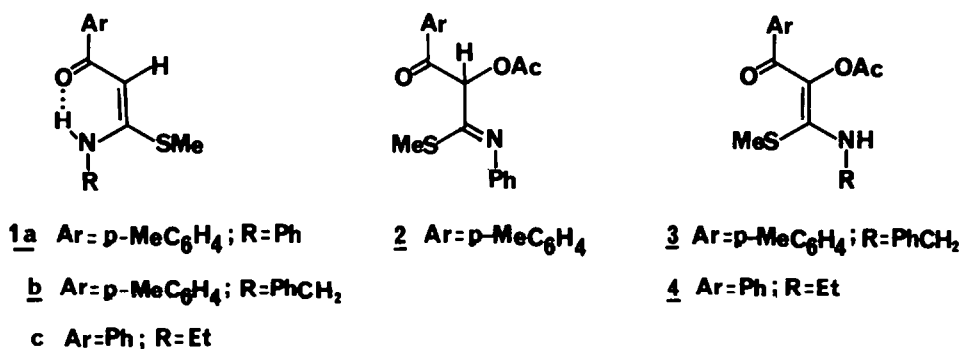
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Lead tetraacetate oxidation of α -oxoketene-S,N-phenyl (1a) and S,N-benzyl (1b) acetals gave the iminoacetate 2 and α -acetoxy-S,N-acetal 3 respectively, while the corresponding S,N-ethylacetal 1c yielded the iminodiacetate 5. The corresponding N,N-arylacetals 7a-d afforded the respective 2-N-aryl-3-(arylimino)-5-aryl-4-isoxazolines 8a-d under similar conditions via oxidative cyclization. The oxidation of N,N-(4-methylphenyl)acetal 7e gave 3-benzoyl-5-methyl-2-(4-methylphenylamino)-indole 9a; iminodiacetate 10 and the dimeric indole 11, besides the corresponding 3-(4-methylphenyl-imino)isoxazoline 8e in varying yields. The N,N-(2-methylphenyl)acetals 7f and 7g afforded under similar conditions the respective 3-(2-methylphenylimino)isoxazolines 8f, 8g and the indoles 9b, 9c in good yields. The structural assignment and the probable mechanism of the formation of all the products have been discussed.

Lead tetraacetate oxidation of compounds capable of imine-enamine tautomerism has been extensively studied.²⁻⁴ The oxidations in these reactions proceed by various pathways leading to different products depending on the nature of the substrates. Vernon and coworkers have studied the lead tetraacetate (LTA) oxidation of N-alkyl/arylaminofumarates⁵⁻⁸ to give a number of five and six membered heterocycles, which are shown to arise from initially formed acyclic oxidative dimers. These studies along with our earlier work⁹ on lead tetraacetate oxidation of S,N-arylacetals derived from arylacetonitriles, prompted further investigation on the oxidation of α -oxoketene-S,N- and N,N-acetals, which represent a novel class of functionalized enamines.¹⁰ The results of these studies are described in this paper.

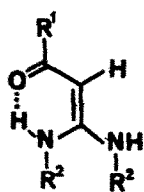
RESULTS AND DISCUSSION

The desired S,N-acetals 1a-c were prepared by the earlier reported procedure,¹¹ while the corresponding N,N-acetals 7a-h were obtained through direct displacement by refluxing the respective oxoketene S,S-acetals and arylamines in acetic acid. These S,N-(1a-c) and N,N-(7a-h) acetals were shown to exist in intramolecular H-bonded form, as displayed by the presence of a low field signal (between δ 12.0-13.50) for NH proton in their ¹H n.m.r. spectra. When 1a was oxidized with LTA in methylene chloride, the product isolated (73%) was characterized as the iminoacetate 2 on the basis of spectral and analytical data (Scheme 1). However, the α -acetoxy product 3 isolated under similar oxidation conditions from the corresponding S,N-benzylacetal 1b was shown to exist in enamino form. No acyclic dimeric or heterocyclic compounds were isolated from the reaction mixture. Oxidation of the corresponding S,N-ethylacetal 1c with either one or two equivalents of LTA under similar conditions gave only the iminodiacetate 5. The products 2, 3 and 5 are apparently formed by α -acetoxylation of the corresponding 1a-c through plumblylated adduct 6 (Scheme 1).¹² The intermediate α -acetoxy compound 4 from 1c however, undergoes further oxidation through plumblylation of more nucleophilic ethylamino nitrogen to give the iminodiacetate 5. The S,N-acetals 1a-c thus behave like enamines, oximes and phenylhydrazones in these oxidations.¹³ Steric hindrance in 1a-c probably impedes the formation of dimeric products.

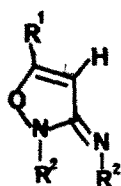


Oxidation of *N,N*-acetals 7a-h was next investigated. When 7a was reacted with equimolar quantity of LTA in CH₂Cl₂, the only product isolated from the reaction mixture along with intractable tar was characterized as 3-(phenylimino)-5-(4-methylphenyl)-4-isoxazoline (8a) (57%). The reaction pathways were not uniform in all the cases. Thus, while 7b-d gave the respective 8b-d as the only isolable products (Scheme 2), the corresponding *N,N*-(4-methylphenyl)acetal 7e afforded three more products besides 8e (29%), along with small amount of unreacted 7e, under similar reaction conditions. These products were characterized as the indole 9a (10%), diacetate (10) (8%) and the dimeric indole 11 (13%) on the basis of spectral and analytical data (Scheme 2). The structure of 11 was supported by its elemental analysis and mass spectral fragmentation (Scheme 3), which exhibited molecular ion peak at *m/z* 678 (28%), besides other peaks at *m/z* 573 (17), 363 (42) and 362 (64). The ¹H and ¹³C n.m.r. spectra of 11 showed it to be a symmetrical dimer. The presence of nine quaternary carbon signals and a peak at δ 170.70 due to anilide carbonyl group in ¹³C n.m.r. spectrum further supported the structure of 11. The oxidation of *N,N*-(2-methylphenyl)acetals 7f and 7g with equimolar quantity of LTA afforded the corresponding 3-(2-methylphenylimino)isoxazolines 8f, 8g and the indoles 9b, 9c in overall higher yields as compared to other *N,N*-acetals. Our attempts to isolate any oxidation product from 7h under varying conditions yielded either inseparable mixture of several products or intractable tar.

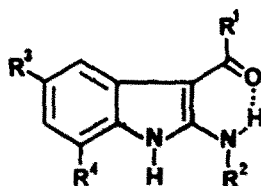
The probable mechanistic pathways for the formation of various products from 7 are shown in the Scheme 4. The initially formed *N*-plumblylated adduct 14 is presumably attacked intramolecularly by carbonyl oxygen assisted by lone pair of arylamino nitrogen leading to 3-aryliminoisoxazolines 8a-g. Alternatively, cyclization could take place on aromatic ring of one of the arylamino groups to give indoles 9a-c. The overall increase in the yields of oxidation products from 7f and 7g is probably due to steric crowding in the plumblylated adducts 14 or 15 thus facilitating their decomposition and cyclization. The dimer 11 appears to be formed either by oxidative dimerization of indole 9a or by nucleophilic attack of 9a on plumblylated adduct 14 followed by oxidative cyclization of 16 to give the intermediate 17. The intermediate 17 undergoes aromatization by intramolecular benzoyl groups migration to give 11. This was supported by oxidation of 7e with two equivalents of LTA which afforded 11 in increased yield (20%) along with 8e, while t.l.c. showed absence of 9a in the reaction mixture.¹⁴ The presence of electron donating 4-methyl group in 7e is probably responsible for its facile oxidation to various products. The iminodiacetate 10 similarly arises as a minor product by α-acetoxylation of 7e.



7



8



9

7, 8a R¹=p-MeC₆H₄; R²=Ph

b R¹=R²=Ph

c R¹=Ph; R²=p-BrC₆H₄

d R¹=Ph; R²=m-MeC₆H₄

e R¹=Ph; R²=p-MeC₆H₄

f R¹=Ph, R²=o-MeC₆H₄

g R¹=p-ClC₆H₄; R²=o-MeC₆H₄

7h R¹=Ph; R²=p-MeOC₆H₄

9a R¹=Ph; R²=p-MeC₆H₄;

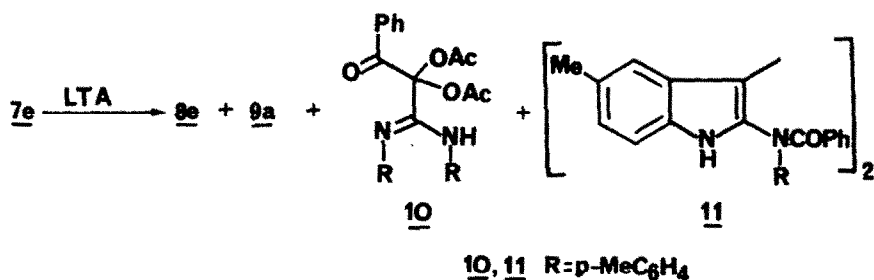
R³=Me; R⁴=H

b R¹=Ph; R²=o-MeC₆H₄;

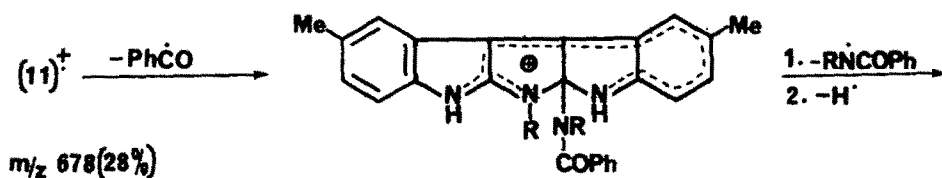
R³=H; R⁴=Me

c R¹=p-ClC₆H₄; R²=o-MeC₆H₄;

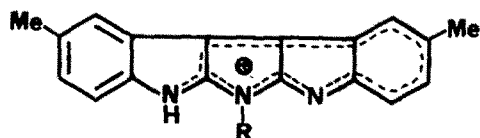
R³=H; R⁴=Me



Scheme 2

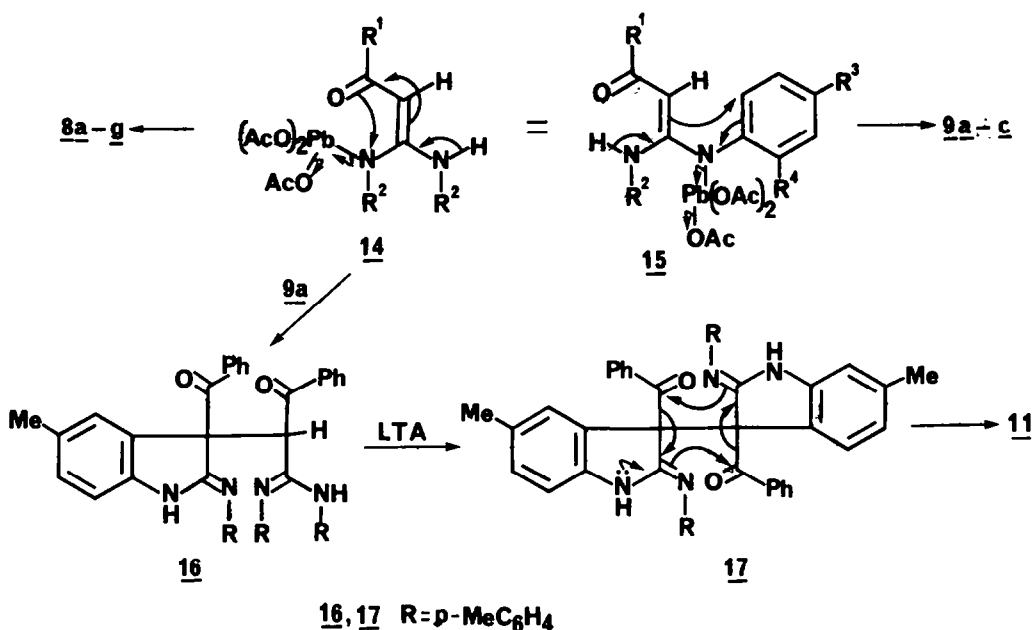


m/z 678(28%)



13 m/z 362(64%); R=p-MeC₆H₄

Scheme 3



Scheme 4

In summary, the oxidation of *S,N*- and *N,N*-acetals with Lead (IV) acetate follows various pathways depending on the nature of amine and substituents on anilino groups.

EXPERIMENTAL SECTION

M.P.s. were determined on a Thomas Hoover Capillary melting point apparatus and are uncorrected. I.r. spectra were recorded on a Perkin-Elmer 297 spectrometer in KBr. ¹H n.m.r. spectra were obtained on Varian EM-390 90 MHz instrument with SiMe₄ as internal standard in deuteriochloroform unless otherwise stated. Mass spectra were recorded on Jeol JMS D-300 spectrometer. ¹³C spectra were obtained on Bruker WM 400 (400 MHz) spectrometer.

Starting Materials:— The known *S,N*-acetals **1a-c** and the *N,N*-acetal **7b** were prepared according to the earlier reported procedure.

General Procedure for *N,N*-acetals 7a-h:— The respective α -oxoketene *S,S*-acetal (10 mmol) and the corresponding aniline (20 mmol) in glacial acetic acid (25 ml) were refluxed for 6–12 h (monitored by t.l.c.). Acetic acid was removed under reduced pressure and the residue dissolved in CHCl₃ (80 ml). The chloroform solution was washed with water, dried (Na₂SO₄) and evaporated to give crude yellow *N,N*-acetals, which were purified by column chromatography over silica gel using hexane-ethylacetate (20:1) as eluent.

3,3-Bis(phenylamino)-1-(4-methylphenyl)-2-propen-1-one (7a).— (72%); m.p. 156–157°C; ν_{\max} 3244–3432, 1629, 1623 cm⁻¹; δ_{H} 2.32(3H, s, CH₃), 5.60(1H, s, =CH), 6.38(1H, brs, NH), 6.62–7.51(12H, m, ArH), 7.52–7.85(2H, d, A, B, ArH), 13.35(1H, brs, NH); ζ_{C} 20.90(CH₃), 78.3(=CH), 123.96, 124.86, 126.00, 126.89, 128.05, 128.90, 129.51, 130.00 (CH, ArH), 136.49, 137.40, 138.08, 139.94 (quaternary C, ArH) 157.97(N, C=), 185.62(CO) (Found: C, 80.71; H, 6.32; N, 8.82. C₂₂H₂₀N₂O requires C, 80.46; H, 6.14; N, 8.53%).

3,3-Bis(4-bromophenylamino)-1-phenyl-2-propen-1-one (7c).— (74%); m.p. 172–173°C; ν_{\max} 3215–3012, 1602 cm⁻¹; δ_{H} 5.55(1H, s, =CH), 6.40(1H, brs, NH), 6.92–7.84(13H, m, ArH), 13.25(1H, brs, NH) (Found: C, 53.67; H, 3.71; N, 6.22. C₂₁H₁₆Br₂N₂O requires C, 53.42; H, 3.42; N, 5.93%).

3,3-Bis(3-methylphenylamino)-1-phenyl-2-propen-1-one (7d).— (70%); m.p. 127–128°C; ν_{\max} 3180, 3030 and 1580 cm⁻¹; δ_{H} 2.33(6H, s, CH₃); 5.53(1H, s, =CH), 6.48(1H, brs, NH), 6.90–7.48(11H, m, ArH), 7.66–7.86(2H, m, ArH); 13.37(1H, brs, NH) (Found: C, 80.41; H, 6.68; N, 8.42. C₂₃H₂₂N₂O requires C, 80.67; H, 6.48; N, 8.18%); m/z 342(19%, M⁺), 236(62).

3,3-Bis(4-methylphenylamino)-1-phenyl-2-propen-1-one (7e).— (76%); m.p. 132–133°C; ν_{\max} 3243–3170, 1610 cm⁻¹; δ_{H} 2.26(3H, s, CH₃); 2.30(3H, s, CH₃), 5.39(1H, s, =CH), 6.36(1H, brs, NH); 6.80–7.39(11H, m, ArH), 7.50–7.71(2H, m, ArH), 13.22(1H, brs, NH) (Found: C, 80.39; H, 6.62; N, 8.40. C₂₃H₂₂N₂O requires: C, 80.67, H, 6.48, N, 8.18%).

3,3-Bis(2-methylphenylamino)-1-phenyl-2-propen-1-one (7f).— (66%); m.p. 131–132°C; ν_{\max} 3434, 3347, 1574 and 1545 cm⁻¹; δ_{H} 2.23(3H, s, CH₃); 2.48(3H, s, CH₃); 5.26(1H, s, =CH), 5.97(1H, s, NH), 7.13–7.40(11H, m, ArH), 7.66–7.84(2H, m, ArH), 13.25(1H, brs, NH) (Found: C, 80.83; H, 6.26; N, 8.39. C₂₃H₂₂N₂O requires: C, 80.67; H, 6.48; N, 8.18%); m/z 342(12%, M⁺), 236(37).

3,3-Bis(2-methylphenylamino)-1-(4-chlorophenyl)-2-propen-1-one (7g).— (68%); m.p. 132–133°C; ν_{\max} 3330–3040 and 1575 cm⁻¹; δ_{H} 2.23(3H, s, CH₃); 2.47(3H, s, CH₃), 5.16(1H, s, =CH), 5.98(1H, brs, NH); 7.10–7.37(11H, m, ArH), 7.55–7.66(2H, m, ArH), 13.18(1H, s, NH) (Found: C, 73.54; H, 5.90; N, 7.71. C₂₃H₂₁ClN₂O requires: C, 73.30; H, 5.62; N, 7.43%); m/z 378(4%), 376(17%, M⁺), 272(11), 270(31).

3,3-Bis(4-methoxyphenylamino)-1-phenyl-2-propen-1-one (7h).— (69%); m.p. 128–129°C; ν_{max} 3310, 3112 and 1592 cm^{-1} ; ν_{H} 3.79(6H, s, OCH_3); 5.34(1H, s, =CH), 6.15(1H, brs, NH), 6.76–7.40(11H, m, ArH), 7.53–7.80(2H, m, ArH), 7.30(1H, brs, NH) (Found: C, 73.51; H, 5.70; N, 7.72. $\text{C}_{23}\text{H}_{22}\text{N}_2\text{O}_3$ requires C, 73.78; H, 5.92; N, 7.48%).

General Procedure for LTA oxidation of S,N-acetals (1a)–(c).— To a stirred and ice-cooled solution of **1** (5 mmol) in CH_2Cl_2 (75 ml), lead (IV) acetate (2.20g, 5 mmol) was added in one portion and the reaction mixture was further stirred for 30 min whilst warming it to room temperature. The precipitated lead (II) acetate was removed by filtration and the filtrate was washed with water (2x200 ml), dried (Na_2SO_4) and evaporated to give crude **2** or **3**, which were crystallized from CH_2Cl_2 -hexane. In the case of oxidation of **1c**, t.l.c. of the reaction mixture showed unreacted starting material along with **5**. Therefore **1c** (5 mmol) was oxidized with 2 eqv. of LTA (4.40g, 10 mmol) following the same procedure.

Methyl 2-acetoxy-3-oxo-3-(4-methylphenyl)-N-phenylthiopropionamide (2).— pale yellow crystals; (73%); m.p. 130–131°C; ν_{max} 1718(ester CO), 1670(ArCO); ν_{H} 1.93(3H, s, SCH_3), 2.03(3H, s, COCH_3); 2.40(3H, s, CH_3), 6.02(1H, s, =CH), 7.19–7.52(7H, m, ArH), 7.85–8.02(2H, d, A, B, ArH) (Found: C, 67.03; H, 5.76; N, 4.41. $\text{C}_{19}\text{H}_{19}\text{NO}_3$ requires C, 66.84; H, 5.61; N, 4.10%; m/z 341(2%, M⁺), 299(4), 294(7), 254(20), 119(100).

2-Acetoxy-3-benzylamino-3-methylthio-1-(4-methylphenyl)-2-propen-1-one (3).— pale yellow crystals; (56%); m.p. 141–142°C; ν_{max} 3270(NH), 1755(ester CO), 1640(ArCO); ν_{H} 1.96(3H, s, SCH_3); 2.19(3H, s, COCH_3), 2.32(3H, s, CH_3), 4.50(2H, d, J=6Hz, ArCH₂), 6.80(1H, brs, NH), 7.06–7.53(9H, m, ArH) (Found: C, 67.82; H, 6.23; N, 4.23. $\text{C}_{20}\text{H}_{21}\text{NO}_3$ requires C, 67.58; H, 5.95; N, 3.94%).

Methyl 2,2-diacetoxy-3-oxo-3-phenyl-N-ethylthiopropionamide (5).— pale yellow crystals; (66%) (with two eqv. LTA); ν_{max} 1756, 1746(ester CO), 1696(ArCO) cm^{-1} ; ν_{H} 1.03(3H, t, J=7Hz, CH_2CH_3); 2.15(3H, s, SCH_3); 2.15(3H, s, COCH_3); 2.18(3H, s, COCH_3), 3.60(2H, q, J=7Hz, CH_2CH_3), 7.25–7.60(3H, m, ArH), 8.01–8.19(2H, m, ArH) (Found: C, 56.68; H, 5.42; N, 4.44. $\text{C}_{16}\text{H}_{19}\text{NO}_5$ requires C, 56.96; H, 5.66; N, 4.15%; m/z 337(2%, M⁺).

General Procedure for LTA oxidation of N,N-acetals (7a)–(g).— To a stirred and cooled (–10° to –15°C) suspension of lead (IV) acetate (2.50g, 5.6 mmol) in CH_2Cl_2 (80 ml), the appropriate N,N-acetal (5 mol) in CH_2Cl_2 (20 ml) was added during 5 min under N_2 atmosphere. The reaction mixture was brought to room temperature with stirring during 0.5 h and further stirred for 2.5 h. The reaction mixture was worked up as described for **1** and the dark brown residue thus obtained was subjected to column chromatography on silica gel using hexane-ethylacetate (20:1) as eluent. Oxidation of N,N-acetals **7a–d** by above general procedure gave **8a–d** respectively.

2-Phenyl-3-(phenylimino)-5-(4-methylphenyl)-4-isoxazoline (8a).— colourless crystals (CH_2Cl_2 -hexane); (57%); m.p. 107°C; ν_{max} 1681, 1588 cm^{-1} ; ν_{H} 2.34(3H, s, CH_3); 6.92(1H, s, H-4); 6.95–7.50(12H, m, ArH); 7.74–7.90(2H, m, ArH); ν_{C} 21.21(Me), 108.68(d, C-4), 121.42, 122.22, 122.76, 123.34, 125.56, 128.64, 129.02, 129.39(CH, ArH); 124.38, 137.76, 137.96, 140.31(C-1' and C-4' of aryl), 146.30(C-4), 147.09(C-3) (Found: C, 81.33; H, 5.84; N, 8.83. $\text{C}_{22}\text{H}_{18}\text{N}_2\text{O}$ requires C, 80.96; H, 5.56; N, 8.58%; m/z 326(100%, M⁺).

2,5-Diphenyl-3-(phenylimino)-4-isoxazoline (8b).— colourless crystals (CH_2Cl_2 -hexane); (31%); m.p. 98°C; ν_{max} 1676, 1595 cm^{-1} ; ν_{H} 7.10(1H, s, H-4); 7.13–7.69(13H, m, ArH); 7.70–8.15(2H, m, ArH); ν_{C} 109.58(d, C-4), 121.66, 122.42, 122.93, 123.47, 125.68, 128.04, 128.82, 128.85, 129.16(CH, aromatic), 127.38, 136.97, 140.25(C-1' of phenyl), 146.56(C-5), 147.13(C-3) (Found: C, 80.47; H, 5.31; N, 9.17. $\text{C}_{21}\text{H}_{16}\text{N}_2\text{O}$ requires: C, 80.75; H, 5.16; N, 8.97%; m/z 312(100%, M⁺).

2-(4-Bromophenyl)-3-(4-bromophenylimino)-5-phenyl-4-isoxazoline (8c).— colourless crystals (CH_2Cl_2 -hexane); (43%); m.p. 189–190°C; ν_{max} 1676, 1602 cm^{-1} ; ν_{H} 7.11(1H, s, H-4), 7.16–7.58(11H, m, ArH); 7.65–7.71(2H, d, A, B, ArH) (Found: C, 53.92; H, 3.21; N, 6.28. $\text{C}_{21}\text{H}_{14}\text{Br}_2\text{N}_2\text{O}$ requires C, 53.65; H, 3.00; N, 5.96%; m/z 472(49%), 470(99%, M⁺).

2-(3-Methylphenyl)-3-(3-methylphenylimino)-5-phenyl-4-isoxazoline (8d).— colourless crystals (CH_2Cl_2 -hexane); (43%); m.p. 129°C; ν_{max} 1670, 1590, 1578 cm^{-1} ; ν_{H} 2.33(3H, s, CH_3); 2.36(3H, s, CH_3); 7.06(1H, s, H-4); 6.73–7.45(11H, m, ArH); ν_{C} 48–7.63(2H, m, ArH) (Found: C, 80.86; H, 6.27; N, 8.51. $\text{C}_{23}\text{H}_{20}\text{N}_2\text{O}$ requires C, 81.15; H, 5.92; N, 8.23%; m/z 340(100%, M⁺).

Oxidation of 7e.— **7e** was oxidized by above general procedure followed by column chromatography over silica gel. Elution with hexane-EtOAc (20:1) gave **2-(4-methylphenyl)-3-(4-methylphenylimino)-5-phenyl-4-isoxazoline (8e)** as colourless crystals (CH_2Cl_2 -hexane); (29%); m.p. 136°C; ν_{max} 1666, 1601 cm^{-1} ; ν_{H} 2.29(6H, s, CH_3); 7.01(1H, s, H-4); 7.06–7.72(13H, m, ArH) (Found: C, 81.33; H, 6.27; N, 8.37. $\text{C}_{23}\text{H}_{20}\text{N}_2\text{O}$ requires C, 81.15; H, 5.92; N, 8.23%; m/z 340(100%, M⁺). Further elution with hexane-ethylacetate (8:1) gave **N,N'-bis(4-methylphenyl)-2,2-diacetoxy-3-oxo-3-phenylpropanamide (10)** as colourless crystals; (8%); m.p. 165–166°C; ν_{max} 3432(br), 1778, 1748(ester CO), 1691(ArCO); ν_{H} 1.46(3H, s, CH_3), 2.13(3H, s, CH_3); 2.29(3H, s, COCH_3), 2.30(3H, s, COCH_3); 6.83(1H, s, NH), 7.01–7.72(13H, m, ArH) (Found: C, 70.98; H, 6.02; N, 6.39. $\text{C}_{27}\text{H}_{26}\text{N}_2\text{O}_6$ requires C, 70.73; H, 5.73; N, 6.11%; **3-benzoyl-5-methyl-2-(4-methylphenylamino)indole (9a)**, as yellow crystals (CH_2Cl_2 -hexane); (10%); m.p. 171–172°C; ν_{max} 3490, 3300, 3160, 1624, 1602 cm^{-1} ; ν_{H} 2.19(3H, s, CH_3); 2.36(3H, s, CH_3); 6.57–7.66(12H, m, ArH); 8.35(1H, s, indole NH), 10.69(1H, s, NH); ν_{C} 21.11(CH_3), 21.28(CH_3); 97.48(s, C-3), 109.82(d, C-7), 119.36, 121.58, 122.27, 122.50, 127.67, 130.12, 130.69(CH, ArH, indole C-4 and C-6); 128.79(s, C-8), 130.78, 130.98, 135.34(s, C-5, C-1' of benzoyl, C-4' of 4- $\text{CH}_2\text{C}_6\text{H}_4\text{NH}$), 135.44(s, C-9); 142.26(s, C-1' of 4- $\text{CH}_2\text{C}_6\text{H}_4\text{NH}$), 152.71(s, C-2), 190.69(s, CO) (Found: C, 81.37; H, 6.28; N, 8.50. $\text{C}_{23}\text{H}_{20}\text{N}_2\text{O}$ requires: C, 81.15; H, 5.92; N, 8.23%; m/z 340(27%, M⁺), 339(100), 338(93) and starting material (**7e**), (8%) (mixed m.p. and superimposable i.r.) followed by **5,5'-dimethyl-2,2'-bis[N-benzoyl-N-(4-methylphenyl)amino]-3,3'-biindole(11)**; colourless crystals; (13%); m.p. 315–316°C (d); ν_{max} 3280(NH), 1642

(anilide CO) cm^{-1} ; δ_{H} 1.97(6H, s, CH_3), 2.12(6H, s, CH_3); 6.25-7.36(22H, m, ArH), 8.44(2H, brs, indole NH); δ_{C} (DMSO- d_6) 20.21, 21.05(CH_3), 101.53(s, C-3), 110.54(d, C-7), 119.20, 122.89, 126.32, 126.64, 127.44, 128.19, 128.47(d, CH, ArH and indole C-4 and C-6), 127.68(s, C-8), 129.49, 131.57, 133.82(s, C-5, C-1' of benzoyl, C-4' of 4- $\text{CH}_2\text{C}_6\text{H}_4\text{NH}$) 134.69(C-1' of 4- $\text{CH}_2\text{C}_6\text{H}_4\text{NH}$), 136.03(C-9), 139.46(C-2), 170.70(NCO) (Found: C, 81.62; H, 5.91; N, 8.53. $\text{C}_{46}\text{H}_{38}\text{N}_2\text{O}_2$ requires C, 81.39; H, 5.64; N, 8.25%).

Oxidation of **7e** (1.70g, 5 mmol) with excess of LTA (4.50g, 10 mmol) under similar conditions and work-up gave **8e** (23%); **10** (5%) and **11** (20%).

Oxidation of 7f.— **7f** was oxidized by general procedure described, followed by column chromatography.

Elution with hexane-ethylacetate (20:1) gave **2-(2-methylphenyl)-3-(2-methylphenylamino)-5-phenyl-4-isoxazoline (8f)** as colourless crystals (CH_2Cl_2 -hexane); (43%); m.p. 130-131°C; ν 1677, 1592 cm^{-1} ; δ_{H} 2.20(3H, s, CH_3); 2.43(3H, s, CH_3), 6.84(1H, s, H-4), 6.88-6.94(1H, m, ArH), 7.11-7.14(12H, m, ArH); δ_{C} 18.18, 18.42(CH_3), 112.13(d, C-4), 122.11, 122.18, 122.59, 125.96, 126.89, 127.46, 127.64, 128.63, 128.72, 130.02, 131.32(CH, ArH), 127.59, 131.38, 135.51(C-1' of phenyl, C-2' of 2- $\text{CH}_2\text{C}_6\text{H}_4\text{NH}$) 135.91, 139.89 (C-1' of 2- $\text{CH}_2\text{C}_6\text{H}_4\text{NH}$), 145.44(C-5), 147.55(C-3) (Found: C, 80.89, H, 6.31, N, 8.49. $\text{C}_{23}\text{H}_{20}\text{N}_2\text{O}$ requires C, 81.15; H, 5.92; N, 8.23%; m/z 340(100%, M^+). Further elution with hexane-ethyl acetate (15:1) gave **3-benzoyl-7-methyl-2-(2-methylphenylamino)indole (9b)** as yellow crystals (CH_2Cl_2 -hexane), (27%), m.p. 179-180°C; ν 3422, 1623, 1593 cm^{-1} ; δ_{H} 2.34(3H, s, CH_3); 2.41(3H, s, CH_3); 6.67-6.83(3H, m, ArH), 7.15-7.54(7H, m, ArH), 7.67-7.72(2H, m, ArH), 8.15(1H, s, indole NH), 10.11(1H, s, NH); δ_{C} 16.35, 17.94(CH_3), 97.86(s, C-3), 116.65(d, CH, ArH), 118.90(s, C-7), 121.69, 121.71, 122.32, 125.75, 127.35, 127.56, 128.19, 130.09, 131.82(d, CH, ArH), 125.85(s, C-8), 131.82, 131.99 (s, C-1' of PhCO and C-2' of 2- $\text{CH}_2\text{C}_6\text{H}_4\text{NH}$), 136.56(s, C-9), 141.83(s, C-1' of 2- $\text{CH}_2\text{C}_6\text{H}_4\text{NH}$), 152.11(s, C-2), 190.93(s, CO) (Found: C, 81.41; H, 6.23; N, 8.51. $\text{C}_{23}\text{H}_{20}\text{N}_2\text{O}$ requires: C, 81.15; H, 5.92; N, 8.23%; m/z 340(28%, M^+); 339(100), 338(92).

Oxidation of 7g.— **7g** was oxidized according to general procedure described, followed by column chromatography. Elution with hexane-ethylacetate (20:1) gave **5-(4-chlorophenyl)-2-(2-methylphenylamino)-4-isoxazoline (8g)** as colourless crystals (CH_2Cl_2 -hexane); (41%); m.p. 120°C; ν 1665, 1590 cm^{-1} ; δ_{H} 2.16(3H, s, CH_3); 2.38(3H, s, CH_3); 6.75(1H, s, H-4), 6.80-7.38(m, 12H, ArH) (Found: C, 73.47; H, 5.27; N, 7.69. $\text{C}_{23}\text{H}_{19}\text{ClN}_2\text{O}$ requires C, 73.69; H, 5.11; N, 7.47%; m/z 376(6%), 374(31%, M^+). Further elution with hexane-ethyl acetate (15:1) gave **3-(4-chlorobenzoyl-7-methyl-2-(2-methylphenylamino)indole (9c)** as yellow crystals (CH_2Cl_2 -hexane); (30%), m.p. 200-201°C; ν 3420, 1620, 1590 cm^{-1} ; δ_{H} 2.30(3H, s, CH_3); 2.37(3H, s, CH_3); 6.60-6.90(3H, m, ArH), 7.12-7.73(8H, m, ArH), 8.20(1H, s, indole NH), 10.75(s, 1H, NH) (Found: C, 73.87; H, 5.32; N, 7.79. $\text{C}_{23}\text{H}_{19}\text{ClN}_2\text{O}$ requires C, 73.69; H, 5.11; N, 7.47%; m/z 376(23%), 374(100%, M^+), 375(48), 373(74).

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