

Structures and Chromotropic Properties of Imidazole Derivatives Produced from 3,6-Bis(4,5-diphenyl-2*H*-imidazol-2-ylidene)cyclohexa-1,4-diene

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Addition of acetic acid to 3,6-bis(4,5-diphenyl-2*H*-imidazol-2-ylidene)cyclohexa-1,4-diene (1) afforded 2-[4-(4-acetoxy-4,5-diphenyl-4*H*-imidazol-2-yl)phenyl]-4,5-diphenyl-1*H*-imidazole (2). Lead dioxide oxidation of (2) in acetic acid yielded 1,4-bis(4-acetoxy-4,5-diphenyl-4*H*-imidazol-2-yl)-benzene (13) but hexacyanoferrate(III) oxidation in alkaline solution gave a 2,2'-imidazolyl dimer (7) derived *via* 2-[4-(5-oxo-4,4-diphenyl-4,5-dihydro-1*H*-imidazol-2-yl)phenyl]-4,5-diphenyl-1*H*-imidazole (4).

Irradiation of compounds (2) and (13) with u.v. light resulted in the formation of the starting quinonoid compound (1) as indicated by its deep blue colour. However, the dimeric compound (7) shows chromotropism caused by radical dissociation of the dimer during irradiation, heating, or grinding. Particularly rapid reversible photochromic behaviour was observed for (7).

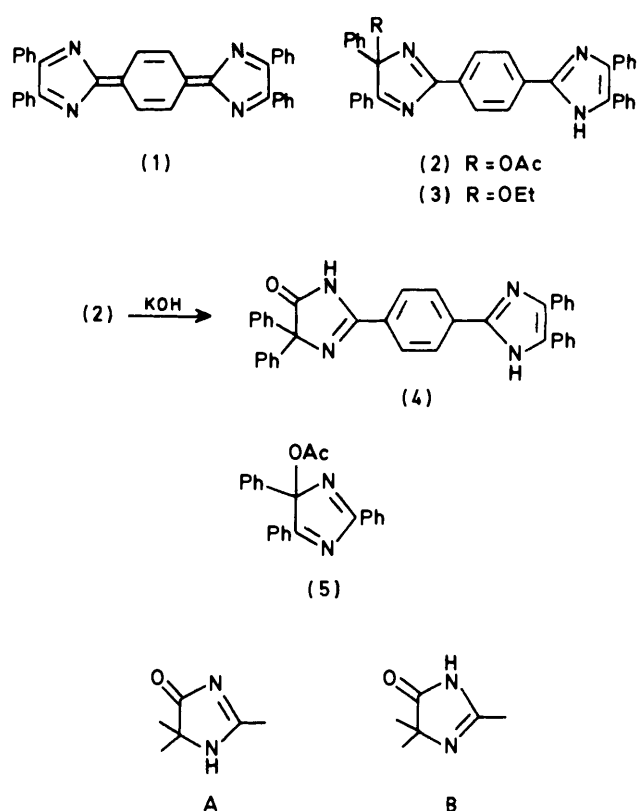
In the course of our studies on photochromic compounds, 3,6-bis(4,5-diphenyl-2*H*-imidazol-2-ylidene)cyclohexa-1,4-diene (1) was found to react with acetic acid to give the mono-acetoxy compound (2). Hexacyanoferrate(III) oxidation of this acetoxy compound in alkaline media afforded a photochromic dimer of a 2-*p*-substituted 4,5-diphenylimidazolyl radical in which the *p*-substituent is a 4,4-diphenylimidazol-5-one group. Photochromism of this dimer was reversible and rapid.

Photochromism of 2,4,5-triaryl imidazolyl dimers is well known.¹⁻⁶ When light irradiation to the dimer is cut off compounds in which the aryl group has an *ortho*-substituent show rapid fading of the photochromic colour because of destabilization of the chromophore, *i.e.* the 2,4,5-triaryl imidazolyl radical, while *para*-substituted compounds show slow fading of the photochromic colour because of the extended resonance effect of the chromophore. Rapidly reversible photochromic imidazolyl dimers, having *para*-substituents in the aryl group, are very rare. We are interested in studying such photochromic compounds, and we report here the structures and properties of some chromotropic compounds prepared from (2).

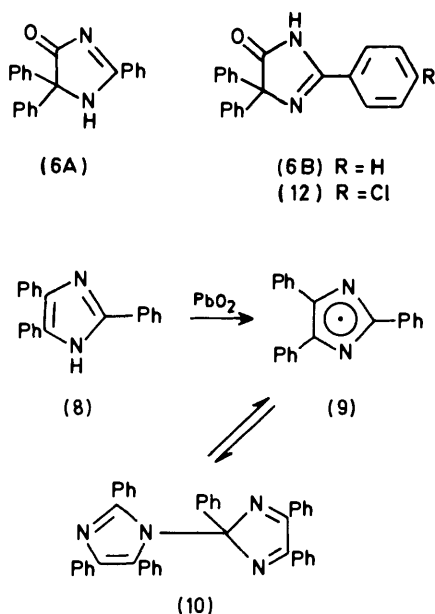
Results and Discussion

When acetic acid was added to a deep blue benzene solution of the quinonoid compound (1), the colour readily disappeared and a yellow compound (2) was formed. The ¹H n.m.r. spectrum of (2) (in C₆D₆-CDCl₃, 3:1) showed a singlet at δ 1.75 for the acetoxy group, a characteristic A₂B₂ pattern at δ 7.8 and 8.6 (*J* 9 Hz) for four protons of the central phenylene group and a multiplet centred at δ 8.05 (2 H) for the *ortho*-protons of the phenyl group at position 5 of the 4*H*-imidazole ring. In its i.r. spectrum (KBr), absorptions at 3 400 cm⁻¹ due to the imino group and at 1 760 cm⁻¹ due to the acetoxy group were observed. The u.v. absorptions [λ_{max.} (EtOH) 225sh, 244sh, 282 (ε 31 400), and 385 nm (24 100)] were similar to those of the ethoxy compound and, as for (3),⁷ the absorption at 385 nm was dependent on the temperature of the solution. Thus the acetoxy compound was assigned the structure (2). On treatment with base, this compound (2) was readily converted into the imidazolone derivative (4) with concomitant rearrangement of a phenyl group.

† This benzilic acid type rearrangement was also observed in the reaction of 4-acetoxy-2,4,5-triphenyl-4*H*-imidazole (5) with base and could easily be used to obtain many imidazolone derivatives.



Schipper and Chinnery⁸ found that the non-conjugated imidazolone (type B) showed a signal in its i.r. spectrum (KBr disk) at 1 740—1 725 cm⁻¹ while the conjugated imidazolone (type A) absorbed at 1 710—1 695 cm⁻¹. The results of J. T. Edward and I. Lantos,⁹ and of T. Sakaguchi and S. Tanabe¹⁰ are consistent with these, but they report a wider range of absorptions. The i.r. spectrum of imidazolone (4) in KBr showed absorptions at 3 450 (NH) and 1 730 cm⁻¹ (CO), and therefore may exist as the non-conjugated imidazolone in the solid state. The ¹H n.m.r. spectrum (CD₃-COCD₃) showed δ 10.7 (br, 1 H) for the imino proton of the imidazolone ring, δ 8.31 (s, 4 H) for the central phenylene group, and δ 7.60 (m, 8 H) and 7.35 (m, 12 H) for the other aromatic protons. The assignment of the imino protons of (4) was made by analogy with that of 1*H*-imidazole-5-one (6B).

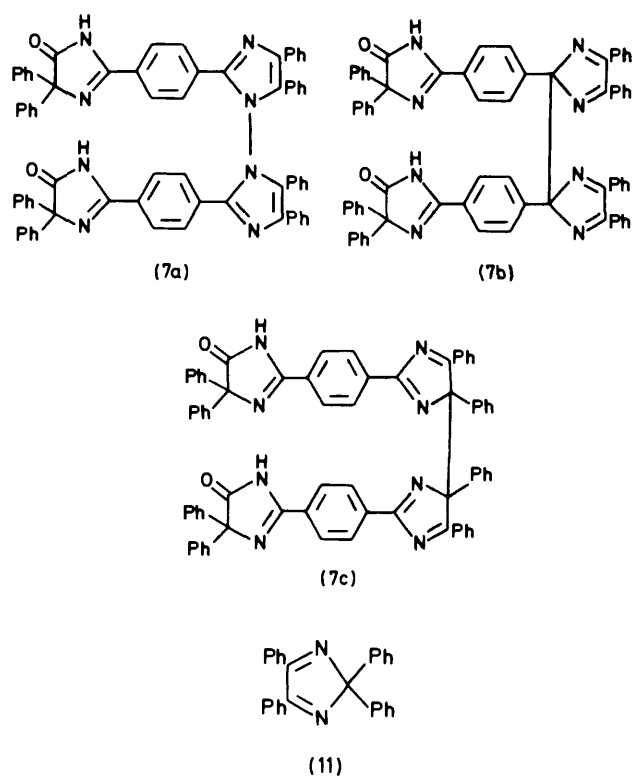


Scheme 1.

The imidazolone derivative (4) was oxidized by lead dioxide in benzene to give a dimer (7); the imidazolone (6) did not undergo oxidation, but lophine (8) was oxidized by lead dioxide to yield a dimer (10). Although compound (4) has two imino protons, only the imino proton of the imidazole group was oxidized to give the dimer. The i.r. spectrum of (7) in KBr showed ν_{NH} at 3450 cm^{-1} , ν_{CO} at 1745 and no absorption at around 1700 cm^{-1} . The ν_{CO} band suggests that the imidazolone group in (7) may exist as the non-conjugated form in the solid. The ^1H n.m.r. spectrum (CD_3COCD_3 - C_6D_6 , 3:1) of (7) exhibited a signal at δ 10.55 (br, 1 H) for the imino protons of the imidazolone rings, and an A_2B_2 signal at δ 8.02 and 7.7 (J 7 Hz) for the central phenylene protons. Other signals at δ 7.85–7.6 and 7.4–7.2 were assigned to the remaining aromatic protons. An upfield part of the A_2B_2 signal at δ 7.7 overlapped the signal of the other aromatic protons. The intensities of the signal at δ 8.02 and 7.85–7.2 were found to be in the ratio 4:44, and this was unchanged when the n.m.r. solvent was varied (CD_3COCD_3 or CD_3COCD_3 - CDCl_3). The results show that the two A_2B_2 signals are completely coincident. If the dimer had an unsymmetrical structure such as (17), two A_2B_2 signals would be expected¹¹ together with a proton ratio of 2:46. Thus, the presence of a single A_2B_2 signal for the phenylene groups and one signal for the imino protons show that the compound (7) must have a symmetrical structure such as (7a), (7b), or (7c).

The structure (7c) was excluded by analysis of the ^1H n.m.r. patterns of the phenylene group. The central phenylene groups in (7c) bear 4-substituted imidazolyl groups and as observed for compounds (2) and (3),¹¹ the *ortho*-protons of the aromatic group bonded to the 2-position of the 4-substituted imidazole rings were found to be strongly deshielded and appeared at δ 8.5 or further downfield.^{6a}

The u.v. spectrum of (4) gave signals at 238sh (ϵ 44 000), 295sh (ϵ 24 000) and 352 nm (ϵ 49 000) in ethanol at 22 °C. However, the absorption spectrum of (7) did not show well-defined absorptions in ethanol and the absorption maxima appeared at wavelengths shorter than 266 nm. Thus structure (7a) was also excluded and (7b) was left as the only possible structure for the compound (7). In the case of imidazolone (6), the conjugated tautomer (6A) was obtained by recrystalliz-

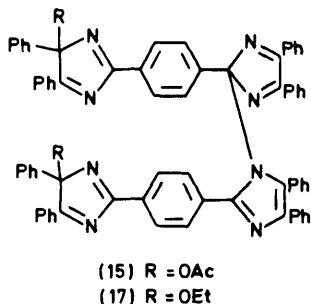
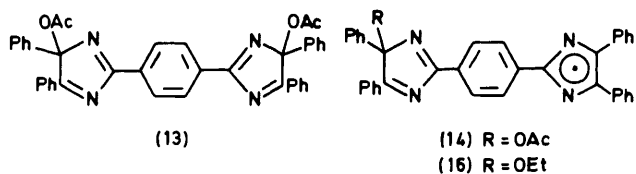
Scheme 2. i, $-\text{e} [\text{K}_3\text{Fe}(\text{CN})_6]$; ii, dimerization

ation from ethanol, and the non-conjugated tautomer (6B) from chloroform. This suggests that the non-conjugated tautomer predominates in chloroform, but that the proportion of conjugated tautomer is increased in ethanol. We could not obtain the conjugated tautomer in the pure state, but the indistinct absorption of (7) in ethanol may be due to the existence of a small amount of conjugated tautomer. The u.v. spectrum of (7) in chloroform showed absorptions at λ_{max} 261 (ϵ 44 444) and 267sh nm (44 017), coincident with the u.v. spectrum of a 1:1 mixture of (11) and (12).

When an aqueous solution of potassium ferricyanide was added to the acetoxy compound (2) in dioxan containing potassium hydroxide at 5 °C, a greenish yellow precipitate gradually separated. The precipitate showed many spots on t.l.c., but compound (7b) was obtained as the major product in this reaction and other minor products were considered to be its isomers. Formation of the dimer (7b) in this oxidation reaction was considered to take place as shown in Scheme 2.

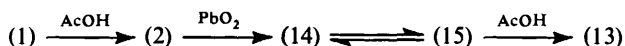
When acetic acid was added to a benzene solution of the quinonoid compound (1) in the presence of lead dioxide, the colourless compound (13) was produced as the main product in addition to small amounts of the 1,2'-dimer (15).[†] The elemental analysis of (13) gave the formula $\text{C}_{40}\text{H}_{30}\text{N}_4\text{O}_4$ which indicated the incorporation of two acetoxy groups. Its i.r.

[†] The 1,2'-dimer (15) was obtained as minor product. We have attempted another method for preparing (15) which will be reported in a later paper.



spectrum exhibited absorption due to the acetoxy group at 1750 cm^{-1} , but no absorption for an imino group. $^1\text{H N.m.r.}$ (CDCl_3) signals from these two acetoxy groups appeared coincidentally at δ 2.2 (s, 6 H) and the aromatic protons of the central phenylene group were found downfield at δ 8.55 as a singlet. The coincidence of the two acetoxy groups and the equivalence of the four aromatic protons were also observed in other solvents, and compound (13) therefore has a symmetrical structure. The downfield resonance of the four aromatic protons of the central phenylene group show that the acetoxy groups were incorporated at C-4 of the imidazolyl groups, consistent with the structure (13).

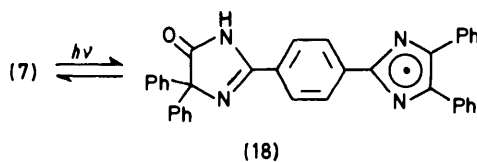
The diacetoxy compound (13) is considered to be produced by heterolytic substitution of acetic acid on to the dimer (15). The reaction was considered to take place as follows:



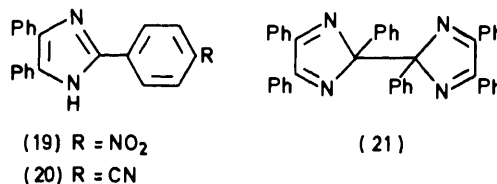
On exposure to irradiation from the sun or a mercury lamp, a light yellow benzene solution of (2) readily turned blue. The blue benzene solution showed the characteristic absorption spectrum of the quinonoid compound (1).¹² The i.r. spectrum of a photoirradiated KBr disk prepared from (2) showed an absorption at 2350 cm^{-1} , attributable to carbon dioxide, and a weakened absorption at 1760 cm^{-1} (CO), and thus the colouration of (2) may be due to the formation of (1).

Upon exposure to radiation from the sun or a xenon lamp, a light yellow benzene solution of the dimer (7) turned to green, and the colour quickly reverted to the original when placed in the dark at room temperature. This light yellow benzene solution of (7) showed no e.s.r. signals and no absorptions in the visible region, but the green solution showed strong e.s.r. signals, the intensity of which decreased on standing in the dark, and new absorptions in the visible at 360sh, 394, 410sh, 550sh, 592, and 640sh nm; the absorbance of the dimer at around 280 nm was decreased. The absorbance of these bands in the visible region decreased in the dark, with recovered absorbance at around 280 nm. An isosbestic point was observed at 327 nm. The new absorption bands in the visible region were assigned to the radical (18).

The rate of decrease of absorption of the long wavelength bands obeyed the second-order rate law, so the mechanism for the photochromism of the dimer (7) was considered to be a reversible dissociation of the dimer to the radical (18) (Scheme 3). The degree of photodissociation of the dimer (7) in benzene (ϵ $1.89 \times 10^{-5}\text{ mol dm}^{-3}$) at 22°C was estimated to be *ca.*



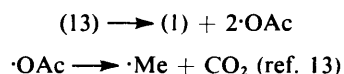
Scheme 3.



0.26 from the change of absorbance at 280 nm (ϵ $33\,100$) measured before and after irradiation for 3 min (thickness of the solution layer, 1 cm; illumination intensity $4.2 \times 10^{-4}\text{ W cm}^{-2}$). The rate constant for recombination of the radical was estimated to be $174\text{ dm}^3\text{ mol}^{-1}\text{ s}^{-1}$ at 25°C by using a second-order equation determined by the rate of decreasing absorbance at 394 nm, and the activation energy, 20.5 kJ mol^{-1} . The rate constants for the lophyl radical (9) and the alkoxy radical (16) are 66 and $23\text{ dm}^3\text{ mol}^{-1}\text{ s}^{-1}$ at 25°C , and their activation energies^{4,11} are 31 and 34 kJ mol^{-1} , respectively. In spite of the extended conjugation of the radical (18), the higher recombination constant and lower activation energy for the dimerization of (18) than for that of the lophyl radical (9) are due to the electron-withdrawing ability of the substituents in the former; it is known that electron-withdrawing substituents accelerate the rate of radical dimerization. Lophine derivatives carrying electron-withdrawing substituents such as (19) or (20) do not undergo hexacyano-ferrate(III) oxidation because of the stability of their anion.^{3b}

In contrast to the 2,2'-dimer (7), the corresponding 2,2'-lophyl dimer (21) does not show photochromic behaviour.⁶ Compound (7) in naphthalene turned green above 80°C and the colour deepened with the rise of temperature. On cooling in darkness the colour reverted to its initial light green. This phenomenon showed that (7) is a thermo-chromic compound. The light yellow colour of (7) in the solid state changed to green on grinding in a mortar, and the colour gradually reverted to the original in the dark, thus showing that compound (7) is also a tribochromic compound.

The colourless benzene solution of the diacetoxy compound (13) also turned blue on photoirradiation. The rate of colouration was slower than that of (2). A decrease in the intensity of the absorption at 1750 cm^{-1} (CO), together with an increase in carbon dioxide and the characteristic absorption of (1),¹² were observed by i.r. and u.v. measurement of the photoirradiated compound (13). Thus the colouration of (13) is due to the formation of (1) as follows:



Experimental

Spectral data were recorded on the following instruments: $^1\text{H n.m.r.}$ on a Hitachi R-24B, i.r. on a Hitachi EPI-S₂, and u.v. on a Hitachi EPS-3T spectrophotometer equipped with a cell compartment with circulating thermostatted water. Elemental analyses and the molecular weight determination were performed in the Institute of Physical and Chemical

Research, Wako-shi, Saitama, Japan, and mass spectra were measured in the Institute of Kawamura Physical and Chemical Research, Kamikizaki, Saitama, Japan.

1,4-Bis(4,5-diphenylimidazol-2-yl)benzene and 3,6-bis(4,5-diphenylimidazol-2-ylidene)cyclohexa-2,5-diene (1) were prepared by the method previously reported.¹¹

2-[4-(4-Acetoxy-4,5-diphenyl-4H-imidazol-2-yl)phenyl]-4,5-diphenyl-1H-imidazole (2).—To a solution of (1) (2 g) in benzene (300 cm³), acetic acid (1 cm³) was added and the mixture was stirred for 15 min until the deep blue colour changed to yellow. The solution was washed with water and was evaporated under reduced pressure. The residue was subjected to silica-gel t.l.c. (chloroform–acetone, 10 : 1). A main yellow band was eluted by acetone to yield the compound (2) (1.8 g) which was recrystallized from ethanol–water. It formed yellow prisms, m.p. (decomp.) > 300 °C (Found: C, 74.95; H, 5.3; N, 9.25. Calc. for C₃₈H₂₇N₄O₂·2H₂O: C, 74.96; H, 5.30; N, 9.20%).

2-[5-Oxo-4,4-diphenyl-4,5-dihydro-1H-imidazol-2-yl)-phenyl]-4,5-diphenyl-1H-imidazole (4).—To a solution of (2) (1.2 g) in dichloromethane (50 cm³), ethanolic potassium hydroxide (1M; 50 cm³) was added. The mixture was left overnight in a refrigerator and then neutralized with dilute hydrochloric acid. The precipitate of potassium chloride was filtered off. The filtrate was evaporated, and the residue was recrystallized from ethanol to give (4) (0.6 g, 60%) as light yellow prisms, m.p. > 300 °C (Found: C, 80.95; H, 5.0; N, 10.55; M⁺, 530.211. Calc. for C₃₆H₂₆N₄O·1/4C₂H₅OH: C, 80.85; H, 5.12; N, 10.34%; M, 530.211).

4-Acetoxy-2,4,5-triphenyl-4H-imidazole (5).—A mixture of 2,4,5-triphenyl-1-(2,4,5-triphenyl-2H-imidazol-2-yl)imidazole (4 g), acetic acid (10 cm³), lead dioxide (20 g), and sodium sulphate (10 g) in dichloromethane (100 cm³) was refluxed for 3 h with stirring under a nitrogen stream. After being cooled, the reaction mixture was filtered and the filtrate was washed with water then evaporated under reduced pressure. The residue was subjected to silica-gel t.l.c. (benzene–ethyl acetate, 20 : 1). The product was recrystallized from methanol to give colourless prisms of (5) (2.6 g, 62%), m.p. 164 °C; ν_{max} (KBr) 1765 cm⁻¹ (CO); λ_{max} (in ethanol) 225 (ϵ 25 000), 232 (24 000), 260sh, and 286 (32 000); δ (CDCl₃) 2.1 (s, 3 H), 7.1–7.6 (m, 11 H), 8.0 (m, 2 H), and 8.4 (m, 2 H) (Found: C, 77.85; H, 5.25; N, 7.95. Calc. for C₂₃H₁₈N₂O₂: C, 77.94; H, 5.13; N, 7.90%).

2,5,5-Triphenyl-1,5-dihydroimidazol-4-one (6).—This compound was prepared from the acetoxy compound (5) by the same method as that used for the preparation of (4). The crude product obtained was a mixture of conjugated form A and non-conjugated form B. The crude product was recrystallized from chloroform to give (6B) (73%) as colourless prisms, m.p. 220 °C (lit.,¹⁴ m.p. 220–222 °C).

Bis[2-[4-(5-oxo-4,4-diphenyl-4,5-dihydro-1H-imidazol-2-yl)-phenyl]-4,5-diphenylimidazolyl] (7).—(a) Oxidation of (4) with lead dioxide. A mixture of (4) (500 mg), lead dioxide (5 g), and sodium sulphate (5 g) in benzene–acetone (6 : 1 v/v; 200 cm³) was stirred overnight in the dark at room temperature, then filtered. The filtrate was evaporated and the residue was subjected to preparative t.l.c. (chloroform–ethanol, 25 : 1) to obtain compound (7) (300 mg). Recrystallization from ethanol–water afforded light yellow prisms, m.p. 210–212 °C (Found: C, 80.75; H, 4.7; N, 10.45; M, 1145. Calc. for C₃₆H₂₅N₄O₂·1/2H₂O: C, 80.98; H, 4.73; N, 10.50%; M, 1058).

(b) Hexacyanoferrate(III) oxidation of compound (2). To a solution of (2) (1 g) in dioxan (50 cm³) containing aqueous potassium hydroxide (1M; 50 cm³), was added dropwise aqueous potassium ferricyanide (20%; 400 cm³) under ice-cooling at ca. 5 °C during 2 h. After addition of cold water (400 cm³) the mixture was stirred for an additional 1 h. A greenish yellow precipitate separated. The precipitate was filtered off, washed with water, and dried *in vacuo* to yield crude product (0.65 g). The product was purified by preparative t.l.c. (chloroform–acetone, 10 : 1) to give compound (7) (0.2 g).

2,2,4,5-Tetraphenyl-2H-imidazole (11).—This compound was prepared by the method of M. Weiss,¹⁵ m.p. 200 °C (lit., 199–201 °C).

2-(4-Chlorophenyl)-4,4-diphenyl-1,4-dihydroimidazol-5-one (12).—This compound was prepared from 4-acetoxy-2-(4-chlorophenyl)-4,5-diphenyl-4H-imidazole (m.p. 204 °C) by the same method as used for (6), colourless prisms, m.p. 277–278 °C (Found: C, 72.65; H, 4.4; Cl, 10.3; N, 8.05. Calc. for C₂₁H₁₅ClN₂O: C, 72.72; H, 4.37; Cl, 10.22; N, 8.07%).

1,4-Bis(4-acetoxy-4,5-diphenyl-4H-imidazol-2-yl)benzene (13).—A mixture of (1) (1.8 g), acetic acid (5 cm³), lead dioxide (10 g), and sodium sulphate (10 g) in benzene (300 cm³) was stirred overnight and then filtered. The filtrate was evaporated and the residue was chromatographed on silica gel with chloroform as eluant to give compound (13). This was further recrystallized from chloroform–hexane to give colourless prisms (1 g), m.p. 255–256 °C (Found: C, 76.2; H, 4.8; N, 8.7. Calc. for C₄₀H₃₀N₄O₄: C, 76.16; H, 4.80; N, 8.88%).

Acknowledgements

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