of *trans*-cinnamamide. The several fractions preceding *trans*-cinnamamide were rich in an unidentified product as shown by t.l.c. Preparative t.l.c. (0.50 mm Silica Gel GF-254, 5% methanol in chloroform) of a portion of the combined fractions afforded an 8 mg sample of t.l.c. homogeneous (R_f 0.25, 5% methanol in chloroform) *cis*-cinnamamide: i.r. ($CHCl_3$) 3570 (m), 3460 (m), 1680 (s), 1630 (m), and 1590 cm^{-1} (m).

Hydrolysis of β*-Truxinimide*

An 89 mg sample of pure β-truxinimide (0.3 mmole) was dissolved in 30 ml of Claisen's alkali and the reaction mixture was refluxed, under nitrogen, for 24 h. Concentrated hydrochloric acid was added to bring the mixture to pH 2, and the aqueous phase was extracted continuously with ether. The ether extract was dried over anhydrous magnesium sulfate and the solvent evaporated under vacuum to afford 129 mg of a residue. Two recrystallizations from benzene–acetic acid afforded 40 mg (45% yield) of pure β-truxinic acid: m.p. 190–202°. No melting point depression was observed when mixed with an authentic sample of β-truxinic acid[4]: i.r. (KBr) 3000 (very broad), 2300 (broad) and 1700 cm^{-1}; n.m.r. (acetone-d_6) 6.09 τ (cyclobutane methine multiplet, 2H, B_2 of A_2B_2), 5.58 τ (cyclobutane methine multiplet, 2H, A_2 of A_2B_2) and 2.95 τ (aromatic hydrogen singlet, 10H).

A 40 mg sample of β-truxinic acid (0.13 mmoles) was treated with diazomethane. The white crystalline solid was recrystallized to a constant melting point from hexane. An authentic sample of dimethyl β-truxinate was prepared from a sample of the authentic β-truxinic acid. The i.r. spectra of both esters were identical. Dimethyl β-truxinate: m.p. 69–70°; i.r. 1730 cm^{-1} (strong); n.m.r. 6.28 τ (methoxyl singlet, 6H), 6.05 τ (cyclobutane methine multiplet, 2H, B_2 of A_2B_2), 5.63 τ (cylcobutane methine multiplet, 2H, A_2 of A_2B_2) and 2.92 τ (aromatic hydrogen singlet, 10H).

Synthesis of cis-Cinnamamide

Phenylpropiolic acid (m.p. 132–136°) was prepared by the method of Reimer (8) and converted to phenylpropiolyl chloride (b.p. 63–66° at 0.6 mm) through a 2 h treatment with a threefold excess of thionyl chloride at room temperature. A 6.5 g sample of phenylpropiolyl chloride was dissolved in 50 ml of anhydrous ether and excess ammonia gas was bubbled into the solution. The solvent was evaporated from the heterogeneous reaction mixture and the solid washed with 25 ml of water and extracted with chloroform (3 × 30 ml). The chloroform extracts were combined and dried over anhydrous magnesium sulfate. When the solvent was removed on the rotary evaporator, phenylpropiolamide (m.p. 108–109°) was afforded in nearly quantitative yield.

A 1.53 g sample of phenylpropiolamide (0.01 moles), dissolved in 50 ml of methanol, was shaken in an atmosphere of hydrogen at standard pressure along with 2% palladium on barium sulfate catalyst, poisoned with 170 mg of reagent grade quinoline. A total of 259 ml of hydrogen was absorbed over 2.7 h (258 ml calculated for 0.01 mole). No further hydrogen uptake was observed after an additional 30 min of hydrogenation. Removal of the catalyst by filtration, and the solvent on a rotary evaporator produced a residue which was then redissolved in chloroform. The resulting solution was washed consecutively with 30 ml of 1 *N* hydrochloric acid, water and dried over anhydrous magnesium sulfate. Removal of the solvent at the rotary evaporator gave the crude product. One recrystallization from cyclohexane afforded 1.0 g (70% yield) of analytically pure *cis*-cinnamamide: m.p. 83–87°; u.v. λ_{max}(EtOH) 255 mμ, ε = 10 600; i.r. ($CHCl_3$) 3570, 3460, 1680, 1630, and 1590 cm^{-1}; n.m.r. 4.07 τ (vinyl hydrogen doublet, J = 12 Hz, 1H), 3.23 τ (vinyl hydrogen doublet, J = 12 Hz, 1H) and 2.6 τ (aromatic hydrogen multiplet, 5H).

Anal. Calcd. for C_9H_9NO: C, 73.46; H, 6.12; N, 9.53. Found: C, 73.38; H, 6.36; N, 9.24.

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1,2,3,4,5-Pentaphenylimidazolium benzoate

James G. Smith and Hazem M. H. Ghonima
University of Waterloo, Department of Chemistry, Waterloo, Ontario

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The compound reported to be *N*,*N*′-dibenzoyl-*N*,*N*′-diphenylstilbene-α,α′-diamine is shown to be 1,2,3,4,5-pentaphenylimidazolium benzoate.

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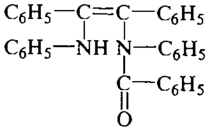
In connection with other work (1) the synthesis of *N*-benzoyl-*N*,*N*′-diphenylstilbene-α,α′-diamine (1), reported by Everest and McCombie (2), was repeated. The synthesis proceeds by the initial preparation and subsequent alkaline hydrolysis of a compound whose structure was considered



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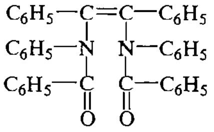

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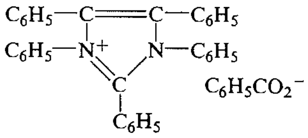

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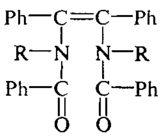
to be *N*,*N*′-dibenzoyl-*N*,*N*′-diphenylstilbene-α,α′-diamine (**2**). This structure (**2**) was indicated by the conversion of the compound with aqueous alkali to **1** plus benzoic acid.

It has been found that the infrared (i.r.) spectrum (Fig. 2) of the compound is incompatible with structure **2** since no amide carbonyl band appears in the 1630–1650 cm^{-1} region. Furthermore, the remarkably easy hydrolysis of one *N*-benzoyl group appears unlikely for a compound of structure **2**. Structure **3** was felt to be compatible with the i.r. spectrum, with the ready formation of **1** by alkaline hydrolysis (6), and with the fact that both **1** and **3** gave the same picrate; however, at the time, no convenient way of firmly establishing this structure was available.

Recently, the synthesis of a related compound, 1,2,3,4,5-pentaphenylimidazolium chloride (**4**), has been described (3). With this as a starting point, the proposed structure **3** has been confirmed. The imidazolium chloride (**4**) underwent facile hydrolysis to **1** in alcoholic alkali. Treatment of the chloride (**4**) with silver benzoate produced the benzoate (**3**) and treatment of the benzoate with excess lithium chloride in *N*,*N*-dimethylacetamide produced the chloride (**4**). Thionyl chloride also effected this last conversion, although the conversion of **1** to **4** by this means was not successful.

In view of the above results, the structure **5** assigned by McCombie to products from similar reactions are suspect. While a detailed structure proof has not been performed, the fact that both these compounds lack carbonyl bands in their i.r. spectra and both are obtained under reaction conditions similar to those producing **3**, strongly indicates that their true structure is **6**. McCombie's reaction conditions thus provide a convenient, although inefficient, means of preparing these pentaarylimidazolium salts.



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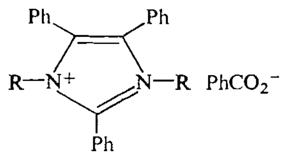

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R = *m*–tolyl or *m*–chlorophenyl

Experimental

Infrared spectra were recorded on a Beckmann IR-10 spectrophotometer using Nujol mulls. The spectra reported in Fig. 1 and 2 were recorded on a Beckmann IR-9 spectrophotometer using either a Nujol mull (Fig. 1) or a split Fluorolube–Nujol mull (Fig. 2).

1,2,3,4,5-Pentaphenylimidazolium Benzoate (3)

The compound was prepared according to McCombie's directions (2) in 11% crude yield. In accordance with these directions, purification was effected by a lengthy extraction with diethyl ether. A simpler purification method was recrystallization from *N*,*N*-dimethylacetamide (27 ml/g). Infrared spectra of both samples were identical and the absence of a carbonyl absorption band is evident from Fig. 2.

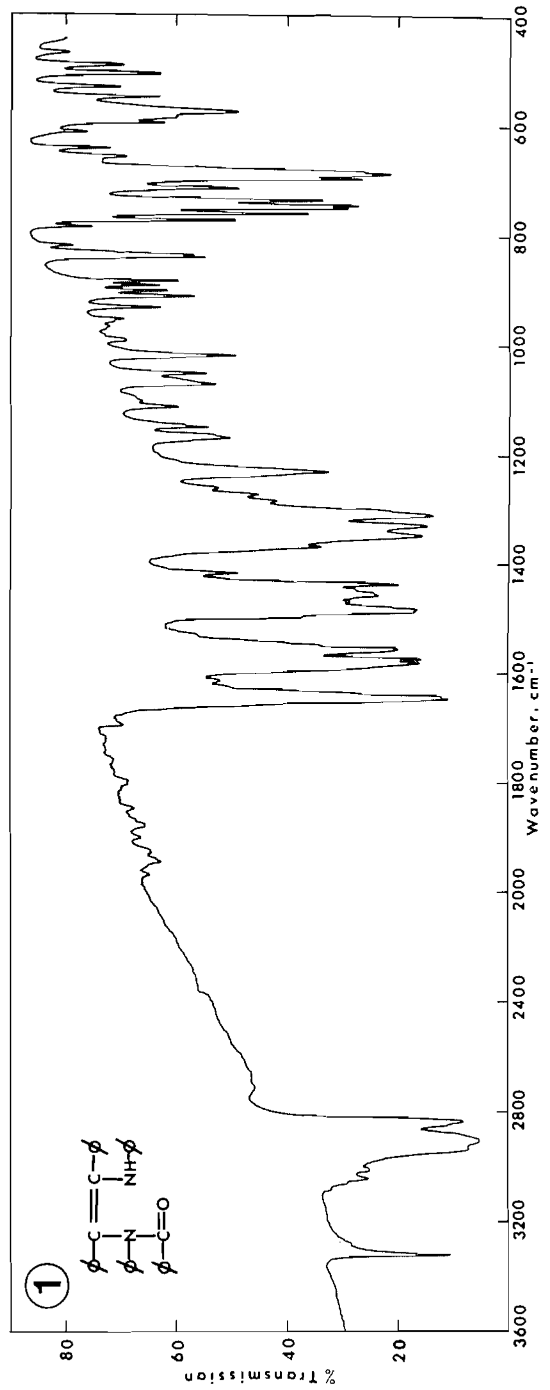
Alternatively, the benzoate (**3**) can be prepared from the chloride (**4**). The chloride (**4**) (0.400 g, 0.00083 moles) was dissolved in a boiling mixture of 15 ml of *N*,*N*-dimethylacetamide and 4 ml of water. Silver benzoate (**5**) (0.195 g, 0.00085 moles) dissolved in 10 ml of hot *N*,*N*-dimethylacetamide was then added. After boiling briefly, the mixture was filtered, the filtrate was evaporated, and the brownish crystalline residue (0.415 g, 86% crude yield) recrystallized from 15 ml of *N*,*N*-dimethylacetamide to give 0.262 g of 1,2,3,4,5-pentaphenylimidazolium benzoate (**3**). The infrared spectra of the crude and the purified benzoate (**3**) were identical with that of the material prepared using McCombie's method.

1,2,3,4,5-Pentaphenylimidazolium Chloride (4)

A reference sample was prepared according to the published procedure (3). Purification was effected by recrystallization from ethanol or from *N*,*N*-dimethylacetamide containing 20% water (26 ml/g).

Alternatively, 0.570 g (.001 mole) of the benzoate (**3**) and 0.212 g (.005 mole) of lithium chloride were heated in 10 ml of *N*,*N*-dimethylacetamide to reflux for 5 min. The mixture was cooled and filtered to give 0.472 g (97% yield) of the chloride (**4**). Recrystallization was effected from 15 ml of *N*,*N*-dimethylformamide containing 10% water. The i.r. spectra of both the crude and recrystallized material were identical with that of the reference sample (**4**).

The benzoate (**3**) (0.150 g, 0.00026 moles) was refluxed



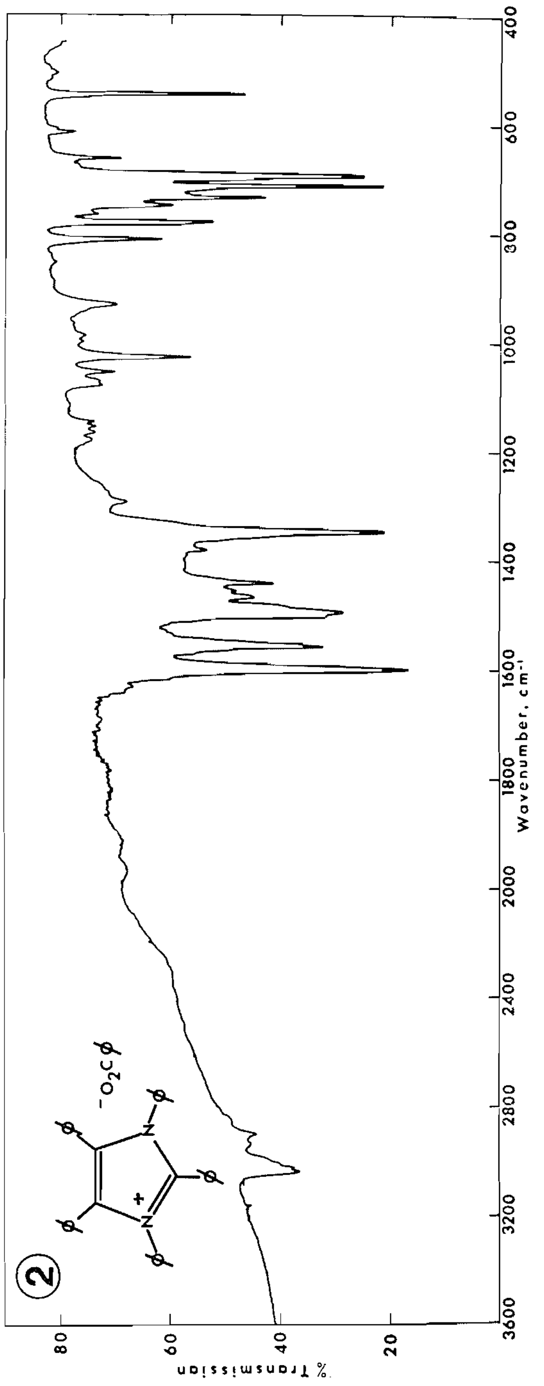


FIG. 1. Infrared spectrum of *N*-benzoyl-*N*,*N'*-diphenylstilbene-α,α'-diamene (**1**).
FIG. 2. Infrared spectrum of 1,2,3,4,5-pentaphenylimidazolium benzoate (3).

with 6 ml of thionyl chloride for 45 min. The clear solution was poured onto ice and the precipitate which separated was filtered, washed with water, and dried; weight: 0.097 g (76% yield). This material was recrystallized from 6 ml of *N*,*N*-dimethylacetamide containing 10% water to give 0.034 g of solid having an i.r. spectrum identical with that of the chloride (**4**). The i.r. spectrum of the crude material contained a strong band in the 1200–1300 cm^{-1} region which was attributed to sulfate or sulfite impurities.

Hydrolysis of 1,2,3,4,5-Pentaphenylimidazolium Chloride

The chloride (**4**) (0.25 g, 0.00056 moles) was dissolved in 20 ml of hot ethanol and 0.25 g of sodium hydroxide in 10 ml of ethanol was added. A yellow color developed and after boiling for 5 min the solution was treated with 50 ml of water. A yellow solid separated and was filtered, washed with water, and dried; weight 0.183 g (70% yield). This solid had a m.p. of 210–215° (with decomposition) and an i.r. spectrum identical to *N*-benzoyl-*N*,*N*′-diphenylstilbene-α,α′-diamine (**1**) prepared by a similar hydrolysis (2) of 1,2,3,4,5-pentaphenylimidazolium benzoate (**3**).

1,3-Diaryl-2,4,5-triphenylimidazolium Benzoate

These were prepared by the method described by Bailey and McCombie (4) in rather poor yields: 1,3-di-*m*-tolyl-, 0.7% yield, m.p. 370–375°, 1,3-di-*m*-chlorophenyl-, 4% yield. Both were purified by dissolving in boiling benzene containing sufficient methanol to solubilize the compound, filtering with decolorizing charcoal, and boiling the filtrate so as to distill off the methanol and precipitate the imidazolium salt. Neither the crude nor the purified products showed a carbonyl band in their i.r. spectra.

Acknowledgment

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Azaindoles. Part II. The proton magnetic resonance spectra of 5-azaindoles[1]

P. G. Riley and B. Robinson

Department of Pharmacy, University of Manchester, Manchester 13, England

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The proton magnetic resonance (p.m.r.) spectra of 5-azaindole and 5-aza-1- and 3-methylindoles have been recorded and analyzed. It has been shown that in the spectrum of 5-azaindole, 3,7- coupling occurs but 1,3- coupling is not observed. In none of the spectra were any 2,6- or 4,6- couplings observed.

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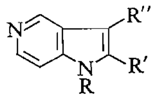
The p.m.r. spectra of 5-aza-2,3-dimethylindole (**1**; R = H, R′ = R″ = Me) (1) and 5-azaindole (**1**; R = R′ = R″ = H) (2) have been reported.



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The doublet of doublets centered at 3.30 τ in the spectrum of 5-azaindole has been assigned (2) to the 3-proton (H-3) which, it is suggested (2), is coupled with H-2 ($J_{2,3}$ = 3.2 Hz) and the *N*-proton ($J_{1,3}$ = 1.0 Hz). The possibility that this latter fine coupling was not caused by 1,3- but by 3,7- coupling was not considered, probably because the H-7 signal was detected (2) only as a doublet of doublets centered at 2.61 τ ($J_{7,4}$ = 1.0 Hz, $J_{7,6}$ = 5.6 Hz). However, such 3,7- coupling or its equivalent is well-established in indole and many other polynuclear aromatic systems (3, 4). Also, the spectrum of 5-azaindole in DCl/D_2O (in which the *N*-proton will be completely exchanged for deuterium) still shows such coupling (2), and in the spectrum of 7-azaindole such coupling is absent (2, 5). We have now reinvestigated the p.m.r. spectrum of 5-azaindole (6) and have also analyzed the p.m.r. spectrum of its 1- and 3-methyl derivatives (**1**; R = Me, R′ = R″ = H and R = R′ = H, R″ = Me, respectively). The results of these studies have established that in the 5-azaindole

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[1] For Part I, see reference 8.