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Synthesis of Desyl Esters by the Application of Phase Transfer Catalysis and a Study of the Fluorescent Properties of 2-Substituted 4,5-Diphenyloxazoles Derived from Desyl Esters

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ABSTRACT

Desyl alcohol was converted to desyl chloride by the application of phase-transfer catalysis using triethyl benzyl ammonium chloride (TEBA) in aqueous sodium hydroxide and chloroform at 0–5°C. The desyl chloride thus obtained was condensed with the potassium salts of various carboxylic acids under phase-transfer catalysis using PEG-400 to give the desyl esters in excellent yields. These were cyclized to 2-substituted 4,5-diphenyloxazoles. 2-(4-Nitrophenyl)-4,5-diphenyloxazole was reduced to the 2-(4-aminophenyl) derivative, which upon acetylation yielded 2-(4-acetamidophenyl)-4,5-diphenyloxazole. The fluorescent properties of the 2-substituted 4,5-diphenyloxazoles were studied.

1 INTRODUCTION

Among heterocyclic fluorophoric systems employed in the synthesis of fluorescent brightening agents applicable to polyester fibres, the oxazole ring system has been extensively used.[1–5] This small five-membered heterocycle constitutes a very good fluorophoric system with its compactness and extension of conjugation, especially when substituted with aromatic or heterocyclic substituents in 2- and 5-positions.

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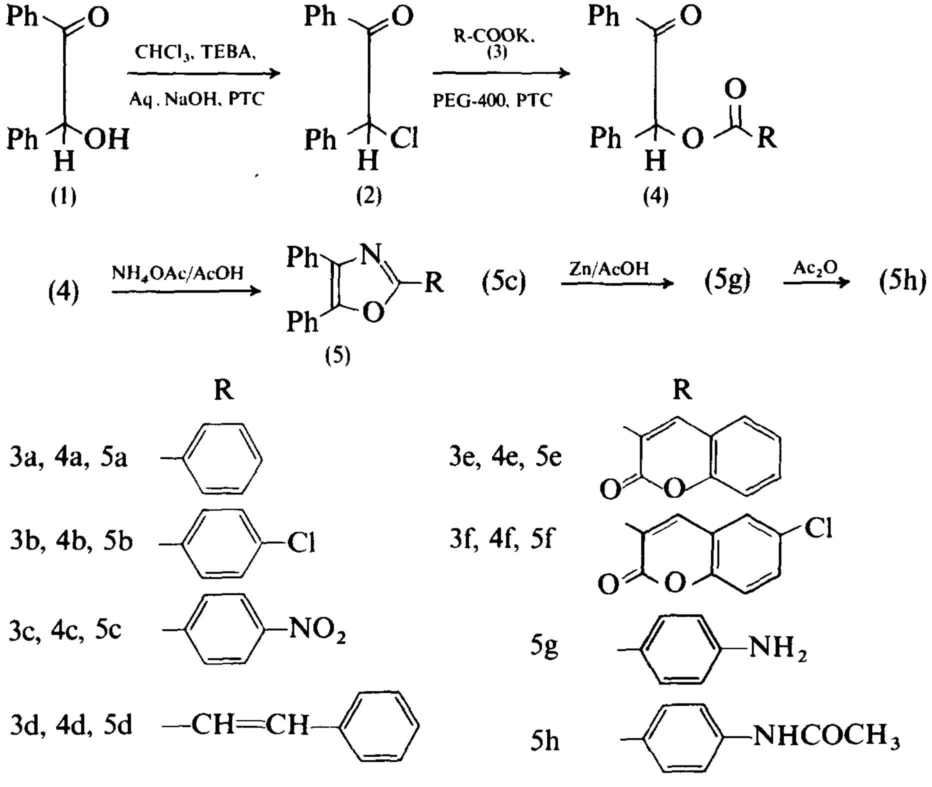
The present work describes a novel synthetic approach to desyl esters, their conversion to 2-substituted 4,5-diphenyloxazoles, and a study of the fluorescent properties of the oxazoles.

2 RESULTS AND DISCUSSION

The synthesis of desyl esters (**4a–4f**) involved a two-step reaction from desyl alcohol (**1**) following phase-transfer catalysis at each step (Scheme 1). Thus, in the first step desyl alcohol (**1**) was converted to desyl chloride (**2**) in good yields (72%) using a phase-transfer catalyst, TEBA (triethylbenzylammonium chloride), in aqueous sodium hydroxide (50% solution) and chloroform at 0–5°C. The desyl chloride thus prepared was confirmed from its elemental analyses, mixed m.p. and superimposable IR spectrum with an authentic sample prepared by the known method.[6] The main advantages of this new preparation of compound **2** were in avoiding the use of pyridine and



Scheme 1.

thionyl chloride and in enabling the reaction to be effected at lower temperatures.

The desyl chloride thus prepared was reacted with the potassium salts of a variety of carboxylic acids (**3a–3f**) under phase-transfer catalysis using acetonitrile as solvent to give the desyl esters (**4a–4f**). The sodium salts of the carboxylic acids, when used under identical reaction conditions failed to give the desyl esters. The phase-transfer catalysts used were TEBA and polyethylene glycols with molecular weights 200, 400, 600 and 1000 and the best results were obtained when polyethylene glycol of molecular weight 400 (PEG-400) was employed. The yields of the desyl esters obtained when using PEG-400 were in the range 82–95%. The general work-up to isolate the desyl esters was simple as PEG-400 is water-soluble whereas the desyl esters are insoluble. The desyl esters were extracted in suitable organic solvents and isolated in excellent yields. The various desyl esters (**4a–4f**) thus prepared were confirmed from their elemental analyses, mixed m.p. and superimposable IR spectra with the authentic samples prepared following the conventional method.[7]

2-Substituted 4,5-diphenyloxazoles (**5a–5f**) were synthesized from the desyl esters using Davidson's method,[8] involving treatment with ammonium acetate in boiling glacial acetic acid.

The elemental analyses and IR spectra of **5a–5h** were in agreement with their assigned structures.

The absorption and fluorescence emission maxima of compounds **5a–5h**

TABLE 1

Absorption and Fluorescence Emission Spectra of Oxazole Derivatives

Compound	*Absorption maximum in DMF (nm)*	*Fluorescence emission maximum in DMF (nm)*	*log E*	*Q (mg)*
5a	340	433	4·40	0·76
5b	318	400	4·24	3·60
5c	365	390	4·08	10·01
5d	334	416	4·42	0·85
5e	376	510	4·17	2·73
5f	380	518	4·18	2·78
5g	327	400	4·28	3·70
5*h*	323	406	4·07	3·50
Standard[a]	376	458	4·40	1·68

Q is the quantity of the compound, in miligrams, dissolved in 100 ml of solvent which is required for the 100 units of intensity.

[a] 7-Diethylamino-4-methylcoumarin was used as standard fluorescent compound.

in DMF solution are given in Table 1. The absorption maxima and fluorescence emission maxima of **5a**–**5h** were in the ranges 318–380 nm and 390–518 nm, respectively. Thus, the fluorescence emission maximum of **5a** was in the blue region (433 nm), those of **5b**, **5d**, **5g** and **5h** in the violet region and those of **5e** and **5f** were in the green region. When applied on polyester fibres as fluorescent brightening agents, **5a** and **5d** showed excellent properties with grade 3 and **5d**, **5g** and **5h** showed moderate properties with grade 1. The coumarin derivatives **5e** and **5f** when applied to polyester fibres as fluorescent dyes gave brilliant greenish-yellow hues with poor pick-up (1) and excellent sublimation fastness (4 to 5). The lightfastness of dyes **5e** and **5f** was 1–2 and 3, respectively.

3 EXPERIMENTAL

All the melting points are uncorrected and are in °C. Visible and emission spectra in DMF were recorded on a Beckman Model 25 spectrophotometer and Aminco Bowman Spectrophotofluorimeter, respectively. Infrared spectra were recorded on a Perkin–Elmer Model 397 spectrometer.

3.1 Preparation of starting materials

Commercially available benzoin (desyl alcohol) (**1**), m.p. 137°C, and salicylaldehyde, m.p. 196–197°C, were used. 5-Chloro-2-hydroxybenzaldehyde,[9] coumarin-3-carboxylic acid[10,11] and 6-chlorocoumarin-3-carboxylic acid[12] were prepared by reported methods.

3.2 α-Chlorobenzyl phenyl ketone (desyl chloride) (2)

To a well-stirred mixture of desyl alcohol (**1**; 21·2 g, 0·1 mol), TEBA (3·4 g, 0·015 mol) and aqueous sodium hydroxide solution (50%, 25 ml) was added chloroform (16 ml) at the rate of 1 to 2 drops min^{-1} at 0–5°C in about 0·5 h. The reaction mixture was further stirred at 0–5°C for 4–5 h. After completion of reaction (monitored by TLC) chloroform was distilled, the reaction mixture was diluted with excess of cold water (about 100 ml) and slowly added to a mixture of hydrochloric acid (30%), water and ice (1:1:1 by weight) to bring the pH to 7–8. The thick oily product that separated was triturated and allowed to solidify by keeping in a deep-freeze for about 12 h. The solid obtained was filtered, and repeatedly recrystallized from 95% ethanol to yield desyl chloride (16·3 g; 71%), m.p. 65–66°C (lit.[6] m.p. 65°C).

3.3 α-Benzoyl benzyl phenyl ketone (desyl benzoate) (4a)

The potassium salt of benzoic acid (1·76 g, 0·011 mol) and PEG-400 (2 ml) were stirred in acetonitrile (20 ml) at 70°C for 0·5 h. To this mixture desyl chloride (2·31 g, 0·01 mol) was added and stirring was continued at reflux until the reaction was complete (4 h, monitored by TLC). Acetonitrile was distilled and the residue was taken in ice-cold water (50 ml). The oily substance which separated was triturated in ice-cold water to obtain a solid. This was filtered, washed with water and dried in a vacuum desiccator. Recrystallization from 95% ethanol gave colourless needles of **4a**, 2·97 g, 94%, m.p. 122–123°C (lit.[13] m.p. 122°C). Calculated for $C_{21}H_{16}O_3$: C, 79·75; H, 5·1. Found: C, 79·7; H, 5·1%.

The other desyl esters (**4b–4f**) were prepared in the same manner as described above.

3.4 α-(4-Chlorobenzoyl)benzyl phenyl ketone (desyl 4-chlorobenzoate) (4b)

Recrystallized from 95% ethanol as colourless needles (93%). Calculated for $C_{21}H_{15}ClO_3$: C, 71·9; H, 4·3; Cl, 10·1. Found: C, 71·9; H, 4·3; Cl, 10·0%.

3.5 α-(4-Nitrobenzoyl)benzyl phenyl ketone (desyl 4-nitrobenzoate) (4c)

Recrystallized from 95% ethanol as colourless needles (95%), m.p. 84–85°C (lit.[13] m.p. 84–85°C). Calculated for $C_{21}H_{15}NO_5$: C, 69·8; H, 4·15; N, 3·9. Found: C, 69·8; H, 4·1; N, 3·9%.

3.6 α-Cinnamoylbenzyl phenyl ketone (desyl cinnamate) (4d)

Recrystallized from 95% ethanol as colourless needles (91%), m.p. 97–98°C. Calculated for $C_{23}H_{18}O_3$: C, 80·7; H, 5·3. Found: C, 80·6; H, 5·3%.

3.7 α-(Coumarin-3-carboxyl)benzyl phenyl ketone (desyl coumarin-3-carboxylate) (4e)

Recrystallized from 95% ethanol as pale yellow crystals (82%), m.p. 127–128°C (lit.[12] m.p. 128°C). Calculated for $C_{24}H_{16}O_5$: C, 75·0; H, 4·2. Found: C, 75·0; H, 4·1%.

3.8 α-(6-Chlorocoumarin-3-carboxyl)benzyl phenyl ketone (desyl 6-chlorocoumarin-3-carboxylate) (4f)

Recrystallized from 95% ethanol as pale yellow crystals (83%), m.p. 142°C (lit.[12] m.p. 143°C). Calculated for $C_{24}H_{15}ClO_5$: C, 68·8; H, 3·6; Cl, 8·5. Found: C, 68·8; H, 3·6; Cl, 8·3%.

3.9 α-(4-Aminobenzoyl)benzyl phenyl ketone (desyl 4-aminobenzoate) (5g)

Recrystallized from 95% ethanol as pale yellow needles (87%), m.p. 113–115°C. Calculated for $C_{21}H_{17}NO_3$: C, 76·1; H, 5·1; N, 4·2. Found: C, 76·0; H, 5·0; N, 4·3%.

3.10 2,4,5-Triphenyloxazole (5a)

A mixture of desyl benzoate (**4a**) (1·58 g, 0·005 mol) and ammonium acetate (2·31 g, 0·03 mol) was refluxed for 4 h in glacial acetic acid (10 ml). The mixture was poured onto crushed ice (about 100 g) and the separated solid was filtered, washed with water until acid-free and dried. The crude product was purified by column chromatography over neutral silica using *n*-hexane as eluent. The solid obtained was recrystallized from DMF as pale yellow needles, 1·26 g (85%), m.p. 114–115°C (lit.[13] m.p. 114°C). Calculated for $C_{21}H_{15}NO$: C, 84·8; H, 5·05; N, 4·7. Found: C, 84·70; H, 5·1; N, 4·6%.

The other 2,4,5-trisubstituted oxazoles (**5b–5f**) were prepared by following the procedure given for **5a**.

3.11 2-(4-Chlorophenyl)-4,5-diphenyloxazole (5b)

Crystallized from DMF as pale yellow needles (73%), m.p. 135–136°C. Calculated for $C_{21}H_{14}ClNO$: C, 76·0; H, 4·2; N, 4·2; Cl, 10·7. Found: C, 76·1; H, 4·2; N, 4·1; Cl, 10·6%.

3.12 2-(4-Nitrophenyl)-4,5-diphenyloxazole (5c)

Crystallized from DMF as yellow needles (81%), m.p. 138–140°C. Calculated for $C_{21}H_{14}N_2O_3$: C, 73·7; H, 4·1; N, 8·2. Found: C, 73·8; H, 4·05; N, 8·2%.

3.13 2-(2-Styryl)-4,5-diphenyloxazole (5d)

Crystallized from DMF as pale yellow needles (60%), m.p. 118–119°C (lit.[14,15] m.p. 118°C). Calculated for $C_{23}H_{17}NO$: C, 85·45; H, 5·3; N, 4·3. Found: C, 85·4; H, 5·2; N, 4·25%.

3.14 2-(3-Coumaryl)-4,5-diphenyloxazole (5e)

Crystallized from DMF as yellow needles (59%), m.p. 199·5°C (lit.[12] 200°C). Calculated for $C_{24}H_{15}NO_3$: C, 78·9; H, 4·1; N, 3·8. Found: C, 78·8; H, 4·1; N, 3·8%.

3.15 2-(6-Chloro-3-coumaryl)-4,5-diphenyloxazole (5f)

Crystallized from DMF as yellow needles (52%), m.p. 194°C (lit.[12] 194°C). Calculated for $C_{24}H_{14}ClNO_3$: C, 72·1; H, 3·5; N, 3·5; Cl, 8·9. Found: C, 72·2; H, 3·6; N, 3·4; Cl, 8·7%.

3.16 2-(4-Aminophenyl)-4,5-diphenyloxazole (5g)

Crystallized from DMF as pale yellow needles (69%), m.p. 210–212°C. Calculated for $C_{21}H_{16}N_2O$: C, 80·8; H, 5·1; N, 9·0. Found: C, 80·6; H, 5·0; N, 8·8%. (IR: νNH at 3350 cm^{-1} and 3450 cm^{-1}.)

3.17 2-(4-Acetamidophenyl)-4,5-diphenyloxazole (5h)

The amino oxazole derivative **5g** (1·56 g, 0·005 mol) was refluxed with acetic anhydride (5 ml) and acetic acid (5 ml) for 4 h. The mixture was poured over crushed ice (50 g), the precipitated solid filtered, washed with water and dried. Crystallization from DMF gave pale yellow crystals (68%), m.p. 222–223°C. Calculated for $C_{23}H_{18}N_2O_2$: C, 81·7; H, 5·3; N, 8·3. Found: C, 81·7; H, 5·3; N, 8·3%. (IR: νCO at 1680 cm^{-1}; νNH at 3260 cm^{-1}.)

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REFERENCES

1. Mitsui Chemical Industry Co. Ltd, French Patent 1 336 949 (1963); *Chem. Abstr.*, **60** (1964) 5682.
2. Ciba Ltd, Belgian Patent 661360 (1965); *Chem. Abstr.*, **64** (1966) 852.
3. Farbenfabriken Bayer AG, Dutch Patent, 6517273 (1966), *Chem. Abstr.*, **66** (1967) 19849.
4. Farbwerke Hoechst AG, Dutch Patent, 6 611 004 (1966); *Chem. Abstr.*, **67** (1967) 33840.
5. Ciba–Geigy AG, Swiss Patent 499 533 (1971); *Chem. Abstr.*, **74** (1971) 100616.
6. Ward, A. M. In *Org. Synth. Coll. Vol.* **2**, ed. A. H. Blatt, (1942) 159.
7. Brenster, J. H. & Ciotti, C. J., Jr, *J. Amer. Chem. Soc.*, **77** (1955) 6214.
8. Davidson, D., Weiss, M. & Jelling, M., *J. Org. Chem.*, **2** (1937) 328.
9. Schueler, F. W. & Honna, C., *J. Amer. Chem. Soc.*, **73** (1951) 3529.
10. Cijar, H., *Ber.*, **31** (1898) 2809.

11. Khan, A. I., Kurien, P. N. & Pandya, K. C., *Proc. Ind. Acad. Sci.*, **1A** (1935) 440; *Chem. Abstr.*, **29** (1935) 3325.
12. Chodankar, N. K., PhD (Tech.) Thesis, University of Bombay, India, 1978.
13. Lora-Tomayo, M., Madronero, R. & Lipprand, H., *Ber.*, **97** (1964) 2230.
14. Walker, D. & Waugh, T. D., *J. Heterocycl. Chem.*, **1** (1964) 72; Arapahoe Chemicals Inc., US Patent 3 148 194 (1964); *Chem. Abstr.*, **61** (1964) 14677.