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ATOMIC ENERGY COMMISSION

**SYNTHESIS OF A NEW SCINTILLATOR 2- PHENYL-
5- (4-p-TERPHENYLYL) - OXAZOLE**

by

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Chemical Engineering Division

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BHABHA ATOMIC RESEARCH CENTRE

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INIS Subject Category: B24

Descriptors:

OXAZOLES

LIQUID SCINTILLATORS

CHEMICAL PREPARATION

FRIEDEL-CRAFTS REACTION

FLUORESCENCE

EMISSION SPECTRA

ULTRAVIOLET SPECTRA

INFRARED SPECTRA

A B S T R A C T

Friedel-Crafts reaction between hippuryl chloride and p-terphenyl gave benzoylaminoethyl-(4-p-terphenyl) ketone (II) which on cyclodehydration gave hitherto unreported 2-phenyl-5-(4-p-terphenyl) oxazole (I). IR, UV absorption and fluorescence spectra of I have been recorded. The performance of I as a scintillator solute has been tested.

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It is well known that the fluorescent organic compounds 2, 5-diphenyloxazole (PPO) and p-terphenyl (TP) are used as primary scintillators¹ in liquid scintillation counting. As TP cannot attain optimum concentration in the counting solution at the operational freezing temperature of many organic counters, it is less suitable for liquid scintillation counting. Both have their mean emission wavelengths which do not match with the maximum of spectral response curve of the cathodes of the photomultipliers. Hence they need secondary scintillators¹ such as 1, 4-bis-[2-(5-phenyl oxazolyl)]-benzene (POPOP) to act as a wavelength shifter to increase the spectral matching factor towards unity and efficiency of the scintillator formulation.

These considerations have prompted us to synthesise hitherto unreported 2-phenyl-5-(4-p-terphenyl) oxazole(I) to be abbreviated as PTPO according to commonly used abbreviation system in the organic

scintillator field. Presently I has been prepared by a reaction scheme indicated in Fig.1 which is an elaboration of our earlier work².

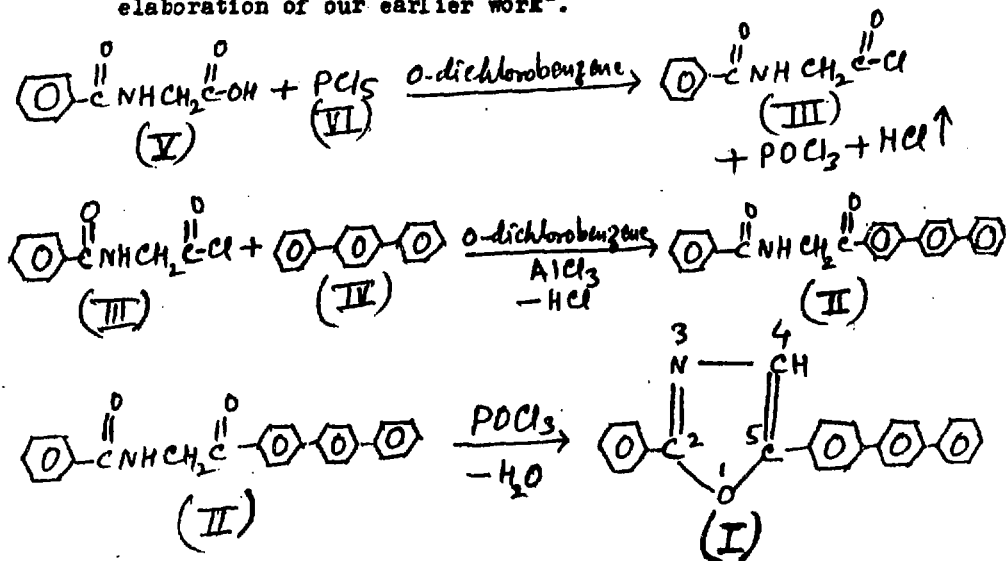


Fig. 1. Reaction scheme for the synthesis of (I)

This involves Friedel-Crafts reaction using acylating agent hippuryl chloride (III) prepared in situ from hippuric acid (V) and phosphorus pentachloride (VI), hydrocarbon TP (IV), catalyst anhydrous aluminium chloride and solvent *o*-dichlorobenzene to yield the intermediate benzoylamino-methyl-(4-p-terphenyl) ketone (II). The introduction of

hippuryl group into the 4-position of IV was established by the oxidation product p-terphenyl-4-carboxylic acid of II with alkaline potassium permanganate. The structure II was further confirmed by its elemental analysis and IR spectrum. II on cyclodehydration with phosphorus oxychloride gave oxazole I. Elemental analysis and IR spectrum³ supports structure I.

UV absorption and fluorescence spectra of I have been recorded (Fig.2). I has a maximum emission wavelength of 396 nm. TP and PPO have their emission maxima around 340 nm and 360 nm respectively⁴. As expected compared to them, PTPO(I) exhibits the bathochromic displacement in the emission spectrum due to the extension of conjugation by the linear chain of aromatic rings. The absorption and emission spectra have minimum overlap. Thus I meets the scintillation property of less self-absorption.

The performance of I as a scintillation solute was tested. The scintillation data (Table 1) using dioxane based scintillator formulations with aqueous source has been collected. It shows, as a primary solute with a saturated solution of 0.5 gm/l, efficiency of I is 13.72 % and that of PPO whose concn.

concentration is 14-fold higher, is 32.58 %. But it's efficiency as a secondary solute is comparable to POPOP.

Table 1. Scintillation Data*

Obs. no.	Scintillator	Counting efficiency(%)
1.	7.0 gms/l PPO +100 gms/l naphthalene in dioxane	32.58
2.	0.5 gms/l PTPO +100 gms/l naphthalene in dioxane	13.72
3.	7.0 gms/l PPO + 0.3 gms/l POPOP +100 gms/l naphthalene in dioxane	36.89
4.	7.0 gms/l PPO + 0.3 gms/l PTPO + 100 gms/l naphthalene in dioxane	36.29

* Tritiated water 1.0 ml with 23641 dpm/ml was added to each counting vial and Liquid scintillation Spectrometer of Packard Instrument Co. Model 3255 was used.

Melting points were determined in open glass capillaries on W. Buchi's apparatus and are uncorrected. The IR spectra(\checkmark max cm^{-1}) were recorded in KBr on Perkin Elmer Infracord 137 model. For UV absorption spectrum, Karl Zeiss spectrophotometer and fluorescence spectrum Aminco Bowman spectro-photofluorometer was used.

benzoylaminomethyl-(4-p-terphenyl) ketone (II):

In a three necked round bottom flask hippuric acid 80 gms (0.44 mole) and dry o- dichlorobenzene 1200 ml ~~was~~ ^{were} taken . Phosphorus pentachloride 120 gms(0.57 mole) was slowly added and stirred for 40 minutes. To the light red coloured reaction mixture p-terphenyl 92 gms (0.4 mole) was added and reaction flask was cooled in ice cold water. Then anhydrous aluminium chloride 320 gms (2.4 mole) was added in small portions to control the reaction. After the addition, the dark reaction mixture was stirred at room temperature for five hours. It was hydrolyzed by slowly pouring into the well stirred ice water mixture. The solid was filtered. The organic layer filtrate after washing with water, was distilled under reduced pressure. The solid thus obtained alongwith the earlier one was stirred with aqueous sodium carbonate. It was filtered,

washed with water, dried in air. Recrystallised from benzene using soxhlet extractor to yield 84 gms (53.5 % based on p-terphenyl) of II, m.p. 240°C, IR(KBr) 3572, 3448 (NH stretching); 1724 (C=O stretching of ketone); 1666 (C=O stretching of amide), 1618, 1592 (NH bending). (Found: C, 82.51, H, 5.40, N, 3.78 $C_{27} H_{21} NO_2$ requires C, 82.86; H 5.37; N, 3.58%.)

2-Phenyl-5(4-p-terphenyl)-oxazole (I) - 40 gms of II and one liter of phosphorus oxychloride were heated under reflux for 14 hours, when most of the solid dissolved. After cooling it, the reaction mixture was added dropwise to the well stirred ice water mixture. The solid was filtered, washed with water, dried in air, and recrystallised through chlorobenzene. It was further purified by column chromatography (neutral alumina). The solvent benzene was removed by distillation under reduced pressure to yield 32 gms (83% of theoretical) of I, m.p. 244°C; IR³ (KBr) 3059 (CH stretching of oxazole ring); 1492 (N-C-O stretching), 1143 (C-O-C stretching). (Found C, 86.35; H, 5.72; N, 3.38; $C_{27} H_{19} NO$ requires C, 86.86; H, 5.09, N, 3.75; %)

Our thanks are due to Shri R.K. Garg, Head, Chemical Engineering Group and Shri S. Sen, Head, Chemical Engg. Division for their encouragement throughout work.

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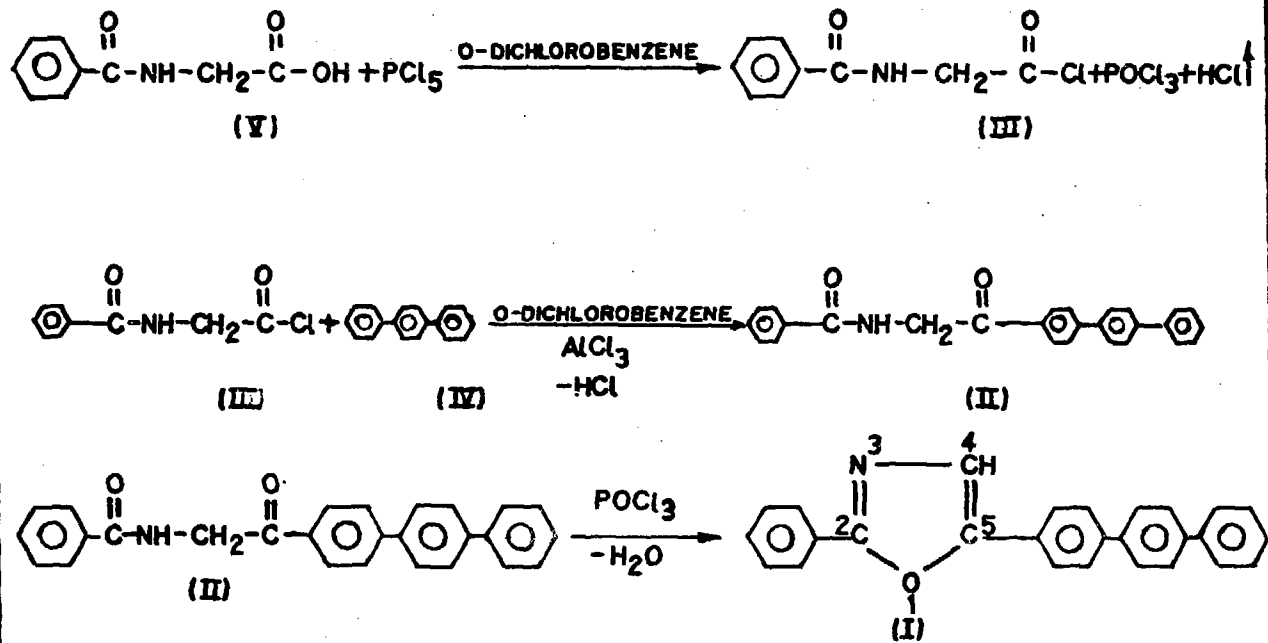


FIG. 1. REACTION SCHEME FOR THE SYNTHESIS OF PTP OII.

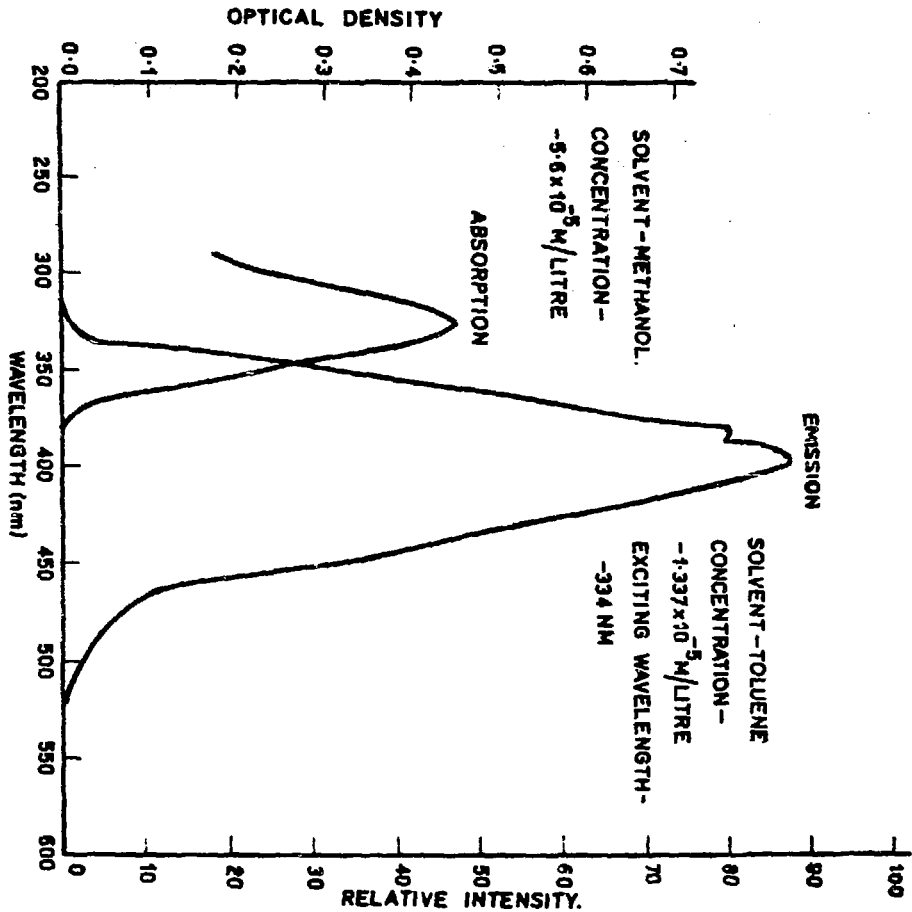


FIG. 2. UV ABSORPTION AND FLUORESCENCE SPECTRA OF PTPOL.

