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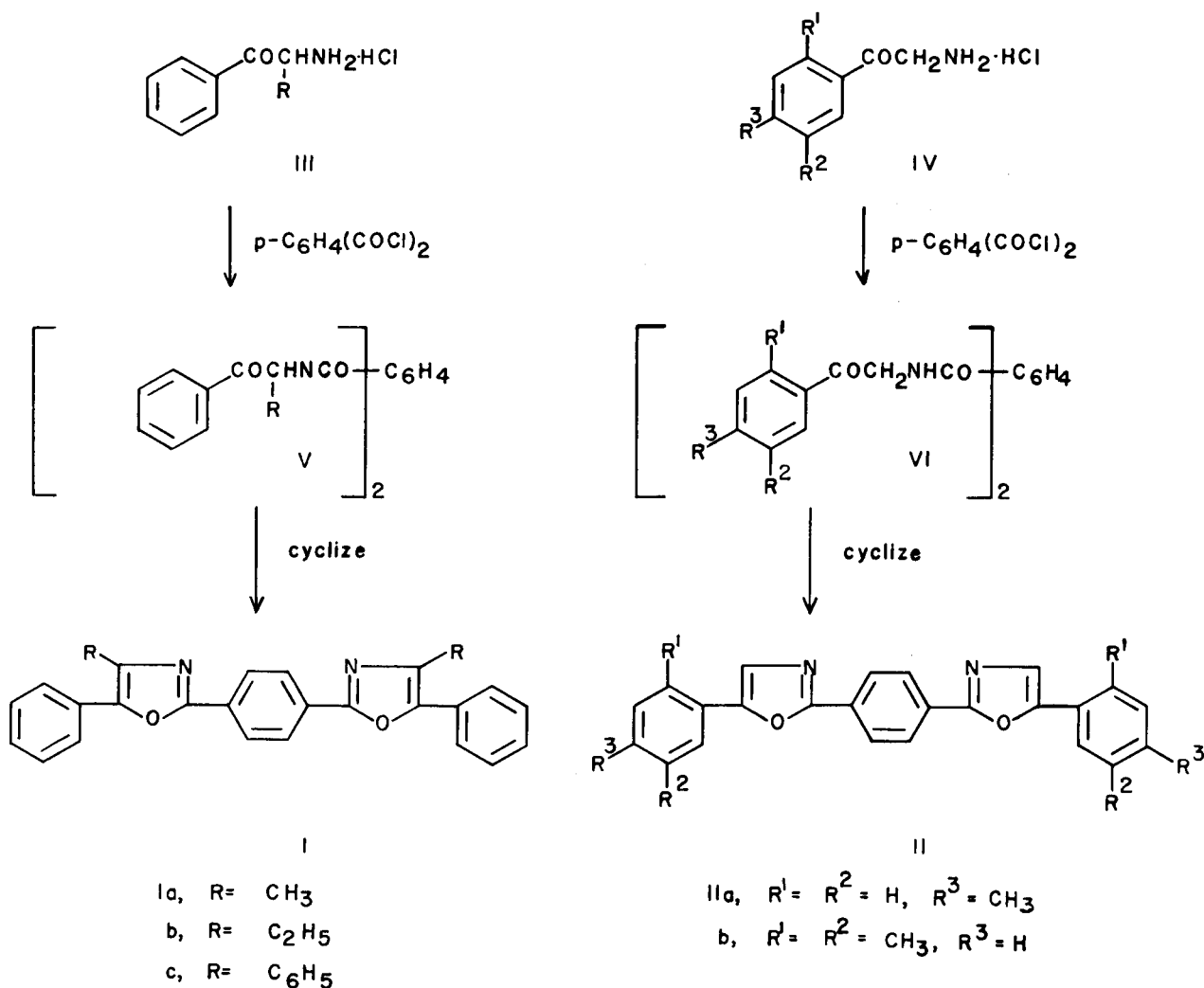
2,2'-*p*-Phenylenebis(4-methyl-5-phenyloxazole) and other Solutes for Scintillation Counting(1)

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The advent of large liquid scintillation counters has created a need for a secondary solute which is more soluble in organic solvents than is 2,2'-*p*-phenylenebis(5-phenyloxazole) (POPOP, I or II, R-substituents = H), the preferred secondary solute for small-scale work.

Recently Wirth (2) showed that substitution of methyl groups into quaterphenyl gave derivatives of markedly improved solubility in organic solvents. Furthermore, methyl substitution did not destroy the efficiency of the

quaterphenyl ring system as a scintillator. This work encouraged us to synthesize a number of alkyl and aryl derivatives of 2,2'-*p*-phenylenebis(5-phenyloxazole) in the hope of improving its solubility.



We found that those derivatives containing one or two methyl groups in each of the terminal benzene rings (IIa and IIb) had about the same solubility as 2,2'-*p*-phenylenebis(5-phenyloxazole). On the other hand those derivatives containing alkyl substituents in the oxazole rings (Ia and Ib) were considerably more soluble than the parent compound. 2,2'-*p*-Phenylenebis(4,5-diphenyloxazole) (Ic), however, was only about as soluble as 2,2'-*p*-phenylenebis(5-phenyloxazole) (see Table I).

The fluorescence maxima of the alkyl derivatives of 2,2'-*p*-phenylenebis(5-phenyloxazole) are shifted to longer wavelengths with respect to 2,2'-*p*-phenylenebis(5-phenyloxazole) itself, the effect being most pronounced in those derivatives containing substituents in the oxazole rings. This observation is surprising since it is known that 2,5-diphenyloxazoles containing alkyl substituents in the benzene rings possess fluorescence maxima little different from 2,5-diphenyloxazole (3). The longer wavelength of the fluorescence spectra of the new derivatives (I and II) is advantageous in that a scintillator containing any of them will be more transparent to its internally emitted light and that a better match is afforded with the peak response (440 m μ) of S-11 photomultiplier tubes, the tubes most widely used in scintillation counting.

The phenacylammonium chlorides III and IV are the key intermediates to the synthesis of I and II.

Reaction of III and IV with terephthaloyl chloride gave, respectively, the amides V and VI, which upon cyclization (4) gave I and II as shown below.

The phenacylammonium chlorides (III and IV) were prepared by several methods. The phenacylammonium chlorides required for the synthesis of Ic, IIa, and IIb were prepared from the hexamine salts (8) of 2-bromo-2-phenylacetophenone, 4-methylphenacyl bromide and 2,5-dimethylphenacyl chloride, respectively. For the synthesis of Ia the intermediate III (R = CH₃) was prepared by hydrolyzing the product from the action of potassium phthalimide on 2-bromopropiophenone (5). A simple synthesis of the III required for the preparation of Ib was achieved by the Friedel-Crafts acylation of benzene with 2-aminobutyryl chloride hydrochloride.

EXPERIMENTAL (6)

2,2'-*p*-Phenylenebis(4,5-diphenyloxazole). Ic.

2-Bromo-2-phenylacetophenone (27.5 g., 0.1 mole) and hexamine (14 g., 0.1 mole) were stirred in chloroform (90 ml.) for 24 hrs. at room temperature. At the end of this time acetone (100 ml.) was added, the suspension cooled to 5° and the hexamine salt filtered. Yield: 31.6 g., m.p. 186-190°. This salt, in ethanol (250 ml.), was treated with concentrated hydrochloric acid (31 ml.) and stirred at room temperature for 60 hrs. After filtering the ammonium chloride the filtrate was diluted with water (500 ml.) and adjusted to pH 8 with aqueous sodium bicarbonate. Free 2-amino-2-phenylacetophenone was extracted with chloroform (4 x 100 ml.) and precipitated as the hydrochloride (III, R = C₆H₅), yield, 7.1 g., 38%.

2-Amino-2-phenylacetophenone hydrochloride was converted, in 59% yield, to Ic, m.p. 259-261°, by a previously described method (4).

Anal. Calcd. for C₂₈H₂₄O₂N₂: C, 83.7; H, 4.68; N, 5.43. Found: C, 83.64; H, 4.70; N, 5.48.

2,2'-*p*-Phenylenebis[5-(2,5-dimethylphenyl)oxazole]. IIb.

2,5-Dimethylphenacyl chloride was converted to the hexamine salt in 64% yield. This salt with hydrochloric acid in ethanol gave 2,5-dimethylphenacylammonium chloride (25%), which with terephthaloyl chloride gave VIb (81%). Cyclization of VIb by a known method (4) led to IIb in 58% yield, m.p. 231-233°.

Anal. Calcd. for C₂₈H₂₄O₂N₂: C, 79.65; H, 5.75; N, 6.67. Found: C, 80.41; H, 5.95; N, 6.30.

2,2'-*p*-Phenylenebis[5-(4-methylphenyl)oxazole]. IIa.

This compound was prepared from 4-methylphenacyl bromide according to the above scheme. Yields of the intermediates were as follows: hexamine salt (55%), IVa from hexamine salt (32%), VIa from IVa (90%), IIa, m.p. 259-260°, from VIa (57%).

Anal. Calcd. for C₂₈H₂₀O₂N₂: C, 79.6; H, 5.14; N, 7.14. Found: C, 79.78; H, 5.27; N, 7.00.

2,2'-*p*-Phenylenebis(4-methyl-5-phenyloxazole). Ia.

Propiophenone (22.1 g., 0.165 mole) was treated with bromine (26.4 g., 0.165 mole) over 1.5 hrs., a temperature of 20-25° being maintained. After the last of the hydrogen bromide produced in this reaction had been removed (vacuum) the resulting oil was taken up in dimethylformamide (130 ml.). Potassium phthalimide (32 g., 0.173 mole) was then added to this dimethylformamide solution over five min.

After the initial exothermic reaction (temperature controlled at 50°) the mixture was stirred for 1 hr. and poured into ice water (500 ml.). A sticky solid was obtained which after two crystallizations from methanol gave pure 2-methyl-2-phthalimidoacetophenone, m.p. 87-88°, in a yield of 17.8 g. (64%). This solid was hydrolyzed by refluxing in a solution of concentrated hydrochloric acid (42 ml.) and water (33.5 ml.) for 48 hrs. The resulting solution was cooled to 0° and the mixture of phthalic acid and III (R = CH₃) was filtered, yield, 11.8 g.

The mixture of phthalic acid and III was not separated. Reaction of this mixture with terephthaloyl chloride gave Va in 19% yield (based on 2-methyl-2-phthalimidoacetophenone.) Cyclization (4) of Va led to Ia (63%), m.p. 232-233°.

Anal. Calcd. for C₂₈H₂₀O₂N₂: C, 79.6; H, 5.14; N, 7.14. Found: C, 79.62; H, 5.18; N, 7.14.

2,2'-*p*-Phenylenebis(4-ethyl-5-phenyloxazole). Ib.

A suspension of aluminum chloride (24 g., 0.18 mole) in a mixture of carbon disulfide (150 ml.) and benzene (150 ml.) was treated with 2-aminobutyryl chloride hydrochloride (7) (14.2 g., 0.09 mole) over one hour at 45°. The mixture was stirred for 4 hrs., cooled to 0°, and poured onto ice (450 g.) and concentrated hydrochloric acid (30 ml.). After separating the layers the aqueous portion was evaporated to 50 ml. and treated with concentrated hydrochloric acid (120 ml.). The solution was cooled to 0° and the product (III, R = C₂H₅) was filtered, yield, 10.6 g., (59.1%). This product was converted by the standard method to 2,2'-*p*-phenylenebis(4-ethyl-5-phenyloxazole), (I, R = C₂H₅) m.p. 214-215°. The overall yield of 2,2'-*p*-phenylenebis(4-ethyl-5-phenyloxazole) based on 2-aminobutyryl chloride hydrochloride was 32%.

Anal. Calcd. for C₂₈H₂₄O₂N₂: C, 79.65; H, 5.75; N, 6.67. Found: C, 80.09; H, 5.78; N, 6.61.

REFERENCES

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- (3) D. G. Ott, F. N. Hayes, E. Hansbury and V. N. Kerr, *J. Am. Chem. Soc.*, **79**, 5448 (1957). Further to this reference we found that the previously undetermined fluorescence maximum of 4-methyl-2,5-diphenyloxazole was 376 m μ . This represents a marked shift to longer wavelength since 2,5-diphenyloxazole possesses a fluorescence maximum of 365 m μ .
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TABLE I

Some Properties of 2,2'-*p*-Phenylenebis(5-phenyloxazole) and Derivatives

| Compound | M.P., °C | Toluene at 25°C (g/l) | Fluorescence Max. (m μ) |
|-------------------------------|----------|-----------------------|------------------------------|
| (I or II, R-substituents = H) | 242-244 | 0.95 | 418 |
| (Ia) | 231-233 | 3.1 | 430 |
| (Ib) | 214-215 | 4.0 | 430 |
| (Ic) | 260-261 | 0.99 | 428 |
| (IIa) | 259-260 | 1.04 | 425 |
| (IIb) | 231-233 | 1.1 | 423 |