effective stabilization. Measurements in the polymer which consider both excited carbonyl and singlet oxygen quenching are now needed to completely characterize the behavior of stabilizers.

**Acknowledgment.** We wish to thank R. P. Hendrix for performing many of the quenching experiments and Professor R. S. Becker of the University of Houston for many helpful suggestions.

---

# 2,4,6-Trisubstituted Pyridines. Synthesis, Fluorescence, and Scintillator Properties[1a]

**Maria del Carmen G. Barrio, Jorge R. Barrio, Graham Walker, Armando Novelli,[1b] and Nelson J. Leonard***

*Contribution from the Facultad de Farmacia y Bioquímica,*
*Universidad de Buenos Aires, Buenos Aires, Argentina, and the*
*Roger Adams Laboratory, School of Chemical Sciences,*
*University of Illinois, Urbana, Illinois 61801.* *Received December 9, 1972*

**Abstract:** The synthesis of 2,4,6-trisubstituted pyridines from chalcones and formamide, under the conditions of the Leuckart reaction, is described. In contrast to 2,4,6-triphenylpyridine, which yields 2,4,6-tricyclohexylpiperidine on catalytic hydrogenation with platinum in acetic acid, 2,6-diphenyl-4-(*p*-methoxyphenyl)pyridine and 2,6-di(*p*-methoxyphenyl)-4-phenylpyridine yield 2,6-dicyclohexyl-4-(*p*-methoxyphenyl)pyridine and 4-cyclohexyl-2,6-di(*p*-methoxyphenyl)pyridine, respectively. Physical and chemical evidence firmly established the proposed structures. The ultraviolet absorption and fluorescence excitation and emission spectra of the substituted pyridines synthesized showed structure and pH dependence. Most of the compounds showed extremely high fluorescence intensity, being readily visible at concentrations even below $1 \times 10^{-9}$ *M*. Initial studies have demonstrated that certain 2,4,6-triaryl substituted pyridines show promising potential as scintillators that will allow liquid scintillation counting to be carried out at high efficiency in strongly acidic solution.

A convenient and relatively simple procedure for the preparation of 2,4,6-triarylpyridines has been developed during the course of attempts to synthesize 1,3-diarylallylamines. The starting materials for this synthesis are the commercially available or easily accessible chalcones (**1**). The reaction of chalcones (**1**) with formamide under conditions of the Leuckart reaction[2] (Scheme I) yielded 2,4,6-triarylpyridines (**2**) as the major products. The overall yields, in the range of 30–33%, were good compared with those obtained by other routes. The spectroscopic properties of certain of the 2,4,6-trisubstituted pyridines are of interest, particularly the high degree of fluorescence and the efficiency of liquid scintillation counting in strongly acidic solution.

Previously, 2,4,6-triarylpyridines have been prepared by the condensation of 1,5-diketones with formamide–formic acid[3] and by other synthetic procedures including the Chichibabin method.[4–7] Following this procedure, the yields of single products are low because of the formation of mixtures of pyridines and various by-products.[7] Formamide has proved to be a versatile agent in heterocyclic syntheses,[8–10] in the Leuckart reaction with aldehydes and ketones,[11–17] and in addition reactions to olefins in the presence of ultraviolet light[18–24] or peroxides.[25,26] The course of the reaction of the chalcones (**1**) with the product mixture resulting from heating ammonium carbonate and formic acid in *ca.* 1:2 molar proportion, or with excess formamide–ammonium formate, is complicated because of the combined functionality in **1**. Formamide alone during 6 hr at 180–190° did not produce appreciable triarylpyridine from chalcone **1c**. The structures of the products formed in the general condensation reaction, **1** → **2** (Scheme I), were established by elemental analysis, nmr spectra, and positive compari-

---

(1) (a) The synthetic methodology described in this article was initiated at the University of Buenos Aires under the guidance of Professor Armando Novelli. (b) Deceased.

(2) M. L. Moore, *Org. React.*, **5**, 301 (1949).

(3) F. Chubb, A. S. Hay, and R. B. Sandin, *J. Amer. Chem. Soc.*, **75**, 6042 (1953).

(4) W. Dilthey, *J. Prakt. Chem.*, **102**, 209 (1921).

(5) R. Lombard and J. P. Stephan, *Bull. Soc. Chim. Fr.*, 1458 (1958).

(6) W. Zecher and F. Kröhnke, *Chem. Ber.*, **94**, 690 (1961).

(7) R. L. Frank and R. P. Seven, *J. Amer. Chem. Soc.*, **71**, 2629 (1949), and references therein.

(8) H. Bredereck, R. Gompper, H. G. v. Schuh, and G. Theilig, *Angew. Chem.*, **71**, 753 (1959).

(9) H. Bredereck, R. Gompper, H. G. v. Schuh, and G. Theilig, *Newer Methods Prep. Org. Chem.*, **3**, 241 (1964).

(10) H. W. Gibson, *Chem. Rev.*, **69**, 673 (1969).

(11) P. A. S. Smith and A. J. Macdonald, *J. Amer. Chem. Soc.*, **72**, 1037 (1950).

(12) W. H. Davies and M. A. T. Rogers, *J. Chem. Soc.*, 126 (1944).

(13) M. Mousseron, R. Jacquier, and R. Zagdoun, *Bull. Soc. Chim. Fr.*, 197 (1952).

(14) V. Komarov, E. A. Chernikova, and G. V. Komarov, *Zh. Fiz. Khim.*, **36**, 540 (1962); *Chem. Abstr.*, **57**, 1605 (1962).

(15) A. N. Kost and I. I. Grandberg, *Zh. Obshch. Khim.*, **25**, 1432 (1955); *Chem. Abstr.*, **50**, 4800 (1956).

(16) D. S. Noyce and F. W. Bachelor, *J. Amer. Chem. Soc.*, **74**, 4577 (1952).

(17) A. Chatterjee and R. Raychaudhuri, *J. Org. Chem.*, **33**, 2546 (1968).

(18) D. Elad, *Proc. Chem. Soc., London*, 225 (1962).

(19) D. Elad, *Chem. Ind.* (*London*), 362 (1962).

(20) D. Elad and J. Rokach, *J. Org. Chem.*, **29**, 1855 (1964).

(21) D. Elad and J. Rokach, *ibid.*, **30**, 3361 (1965).

(22) D. Elad and J. Rokach, *J. Chem. Soc.*, 800 (1965).

(23) D. Elad, *Angew. Chem., Int. Ed. Engl.*, **5**, 255 (1966).

(24) M. Fish and G. Ourisson, *Bull. Soc. Chim. Fr.*, 1325 (1966).

(25) A. Rieche, E. Schmitz, and E. Gruendemann, *Z. Chem.*, **4**, 177 (1964).

(26) A. Rieche, E. Schmitz, and E. Gruendemann, *Angew. Chem.*, **73**, 621 (1961).

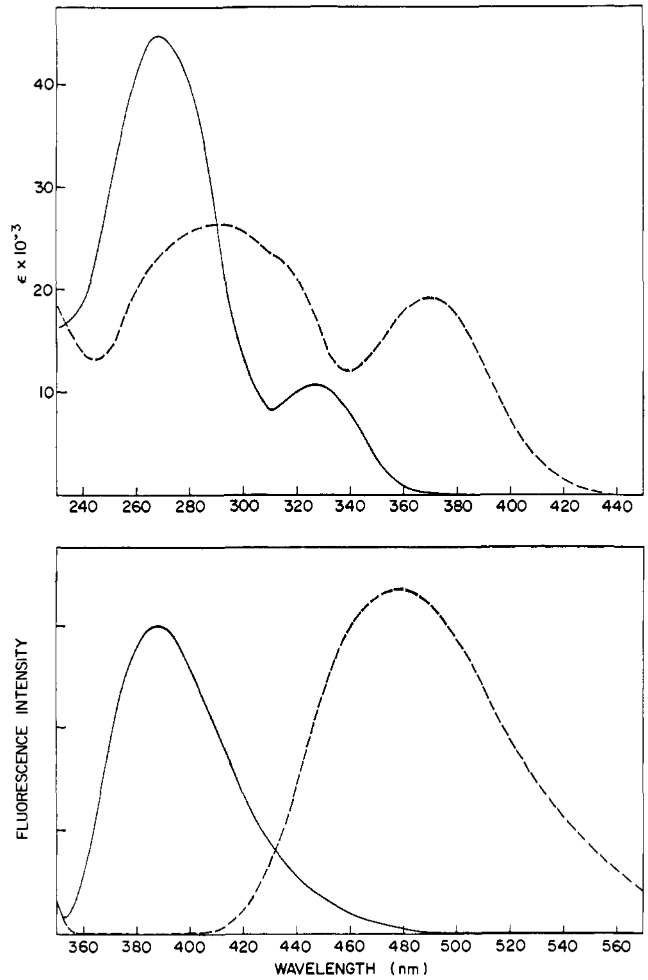
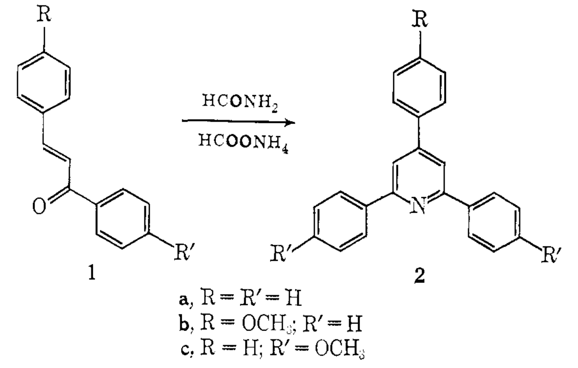


Figure 1. Top panel: electronic absorption spectra (230–440 nm) of **2c** in ethanol (——) and in 0.05 *N* HCl in 50% ethanol (------). Bottom panel: molecular fluorescence emission spectra of **2c** in the same solvents.

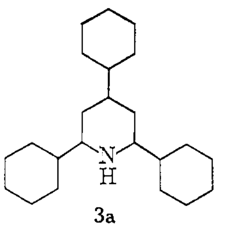
**Scheme I**



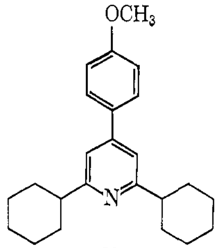
a, R = R′ = H
b, R = OCH$_3$; R′ = H
c, R = H; R′ = OCH$_3$

son of the physical properties with those previously described for the particular 2,4,6-triarylpyridines. The positions of the substituents in **2b** and **2c** define the precursor units: an intact chalcone accounting for the 2, 3, and 4 carbons of the pyridine and the acetophenone moiety of another chalcone accounting for the 5 and 6 carbons. The formal rationalization of the product formation involves a reverse aldol reaction of the $\alpha,\beta$-unsaturated ketone, a Michael-type addition, condensation with formamide,[3] and dehydrogenation by hydrogen transfer[27] or disproportionation.[28] The addition of ferric chloride or sparging the reaction mixture with air was without apparent effect on the yield. No evidence of pyridine mixtures was detected in the isolated product, suggesting that the most useful aspect of the present method is that competitive reactions can be avoided.

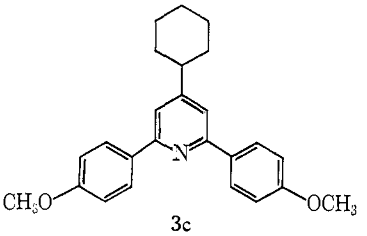
The structures of the catalytic reduction products **3a–c** formed from **2a–c** by the action of hydrogen and platinum oxide in acetic acid solution were established by analyses, ultraviolet, infrared, nmr, and mass spectra. For example, the catalytic hydrogenation of 2,6-di(*p*-methoxyphenyl)-4-phenylpyridine (**2c**) resulted in the absorption of 3 mol equiv of hydrogen. The ir spectrum showed the disappearance of bands at 698, 763, and 775 cm$^{-1}$, corresponding to the monosubstituted benzene ring. No change was observed in the aromatic band at 833 cm$^{-1}$, characteristic of disubstitution.[29] The nmr spectrum of **2c** in CDCl$_3$ included a multiplet centered at $\delta$ 7.50 that was replaced by a new, broad resonance (11 H) centered at $\delta$ 1.60 for **3c**. The $\beta$-pyridine hydrogens appeared as a sharp singlet at $\delta$ 7.74 in **2c**, shifted to $\delta$ 7.10 in **3c**, and the AB pattern of doublets at $\delta$ 7.15 and 8.16, $J$ = 9.0 Hz, indicative of the meta and ortho hydrogens of the *p*-methoxyphenyl rings, respectively, was shifted to $\delta$ 6.70 and 7.75 in the conversion. The molecular ion peak at *m/e* 373 confirmed the extent of the reduction process and the assignment of the product as 4-cyclohexyl-2,6-di(*p*-methoxyphenyl)pyridine. Similarly, 2,6-diphenyl-4-(*p*-methoxyphenyl)pyridine (**2b**) underwent reduction in the rings lacking methoxyl to give 2,6-dicyclohexyl-4-(*p*-methoxyphenyl)pyridine (**3b**). 2,4,6-Triphenylpyridine (**2a**) underwent complete reduction to 2,4,6-tricyclohexylpiperidine (**3a**), mp 153°, under our conditions, whereas Overhoff and Wibaut[30] observed the formation of 2,4,6-tricyclohexylpyridine, mp 47°, by catalytic reduction in ethanol and HCl. The spectral evidence which established structure **3a** included an ultraviolet spectrum devoid of maxima between 210 and 360 nm, an ir spectrum indicating the



3a



3b



3c

---

[27] M. Weiss [*J. Amer. Chem. Soc.*, **74**, 200 (1952)] isolated 2,4,6-triphenylpyridine and benzylacetophenone (low yield) from the reaction between benzaldehyde and acetophenone in ammonium acetate and glacial acetic acid.

[28] Dihydropyridines are known to disproportionate to form pyridine and piperidine derivatives; see M. Scholtz, *Ber.*, **30**, 2295 (1897); K. W. Merz and H. Richter, *Arch. Pharm.*, **275**, 294 (1937).

[29] D. H. Hey, C. J. M. Stirling, and G. H. Williams, *J. Chem. Soc.*, 3963 (1955).

[30] J. Overhoff and J. P. Wibaut, *Recl. Trav. Chim. Pays-Bas*, **50**, 957 (1931).

**Table I.** Ultraviolet Absorption and Fluorescence Excitation and Emission Data[a]

| Compd | | Ultraviolet absorption<br>$\lambda_{max}$, nm | $\epsilon \times 10^{-3}$ | Fluorescence emission,[b] nm<br>$\lambda_{max}$ | $\lambda_{+1/2}$ | $\lambda_{-1/2}$ | Fluorescence excitation,[c] nm<br>$\lambda_{max}$ | $Q^d$ | $\tau^e$ |
|---|---|---|---|---|---|---|---|---|---|
| **2a** | EtOH | 253 | 48.4 | 360 | 384 | 341 | 264, 310 | 0.30 | 2.2 |
| | | 310 | 9.8 | | | | | | |
| | Acid | 257 | 22.2 | 404 | 441 | 383 | 314 | 0.37 | 1.0 |
| | | 307 | 22.1 | | | | | | |
| **2b** | EtOH | 266 | 37.8 | 350 | 379 | 338 | 285 | 0.29 | 1.6 |
| | | 287 sh | 29.6 | | | | | | |
| | Acid | 257 | 17.4 | 460 | 513 | 428 | 264, 343 | 0.29 | 1.3 |
| | | 338 | 34.3 | | | | | | |
| **2c** | EtOH | 268 | 44.4 | 388 | 417 | 367 | 280, 328 | 0.47 | 2.7 |
| | | 328 | 10.7 | | | | | | |
| | Acid | 292 | 26.1 | 480 | 525 | 443 | 318, 376 | 0.86 | 4.2 |
| | | 370 | 19.1 | | | | | | |
| **3b** | EtOH | 275 | 21.9 | 340 | 366 | 318 | 286 | 0.17 | 1.2 |
| | Acid | 283 | 12.2 | 408 | 440 | 386 | 285, 330 | 0.99 | 2.4 |
| | | 326 | 24.0 | | | | | | |
| **3c** | EtOH | 270 | 32.1 | 364 | 388 | 342 | 284, 316 | 0.39 | 1.8 |
| | | 313 sh | 13.4 | | | | | | |
| | Acid | 287 | 16.5 | 446 | 491 | 417 | 294, 356 | 0.94 | 2.9 |
| | | 350 | 23.3 | | | | | | |

[a] The spectra are for ethanol solutions and 0.05 *N* HCl, ethanol–water, 1:1 by vol (acid). [b] Corrected spectra. [c] Fluorescence excitation spectra (uncorrected) were taken by fixing on the fluorescence emission maximum. [d] Quantum yield of PPO is 1.00, based on 1,10-diphenylanthracene as 1.00: M. P. Neary and A. L. Budd, "The Current Status of Liquid Scintillation Counting," E. D. Bransome, Ed., Grune and Stratton, New York, N. Y., 1970. [e] Fluorescence lifetime by phase, in nanoseconds. Decay time of PPO in cyclohexane is 1.4 nsec: I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules," Academic Press, New York, N. Y., 1965.

lack of aromatic and olefinic bonds, an nmr spectrum indicative of only aliphatic protons (broad signals centered at $\delta$ 1.40), and a mass spectrum exhibiting a molecular ion peak at *m*/*e* 331.

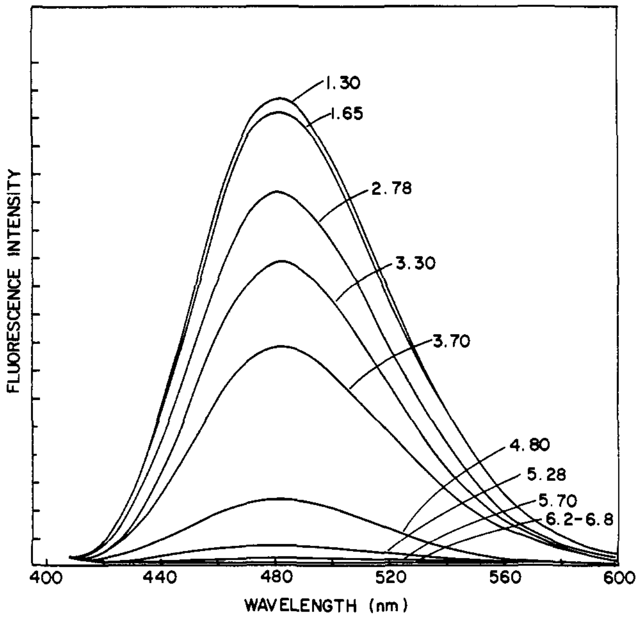


Figure 2. Variation in fluorescence emission intensity of **2c** (at a concentration of $10^{-7}$ *M*) with pH in phosphate buffers. Excitation at 370 nm.

The ultraviolet absorption spectra recorded for **2a–c**, **3b**, and **3c** (Table I, see also Figure 1) had certain features worthy of consideration. A phenylpyridine is an absorbing unit similar to a biphenyl, with uv spectra indicative of appreciable orbital overlap between the two rings[31] and differing with the position of pyridine substitution; *e.g.*, 2-phenylpyridine shows two maxima, at 245 and 275 nm;[31] 4-phenylpyridine, one maximum at 257 nm ($\epsilon$ 16,000);[32] 4-phenyl-2,6-lutidine, one at 254 nm ($\epsilon$ 14,100).[33] Comparison of the spectrum of **3b** with either of the last two indicates extended resonance conjugation through the 4-(*p*-methoxyphenyl)pyridine unit. The spectra of the other bases, **2a–c** and **3c**, with aromatic rings in the 2 and 6 positions of the pyridine unit, consist essentially of two bands, displaced toward longer wavelength from those of 2-phenylpyridine.[34] The probabilities of the two electronic transitions, as observed in solution and expressed by the molar extinction coefficients (Table I), are consistent with the position and degree of substitution in the two series (**2** and **3**). The most striking feature of the ultraviolet spectra of the substituted pyridines **2b**, **2c**, **3b**, and **3c** is their long wavelength ultraviolet maxima in acidic medium. These occur at longer wavelengths (up to 50 nm) and at higher $\epsilon$ values than for the same compounds in ethanol alone, while the intensity of the shorter wavelength band is greatly diminished. In all the compounds, with the exception of **3a**, the shifts to longer wavelength also occur in the fluorescence emission maxima on protonation, and the unusually large Stokes shift may be due to relocation of the proton in the equilibrium excited state. At intermediate acidity, both cationic and neutral species are present.[35] Indeed, the remarkably wide pH range over which both protonated and unprotonated forms are present, as shown in several cases by the fluorescence spectra, can be interpreted as evidence of incomplete ionization equilibrium being established during

---

(31) A. E. Gillam, D. H. Hey, and A. Lambert, *J. Chem. Soc.*, 364 (1941).

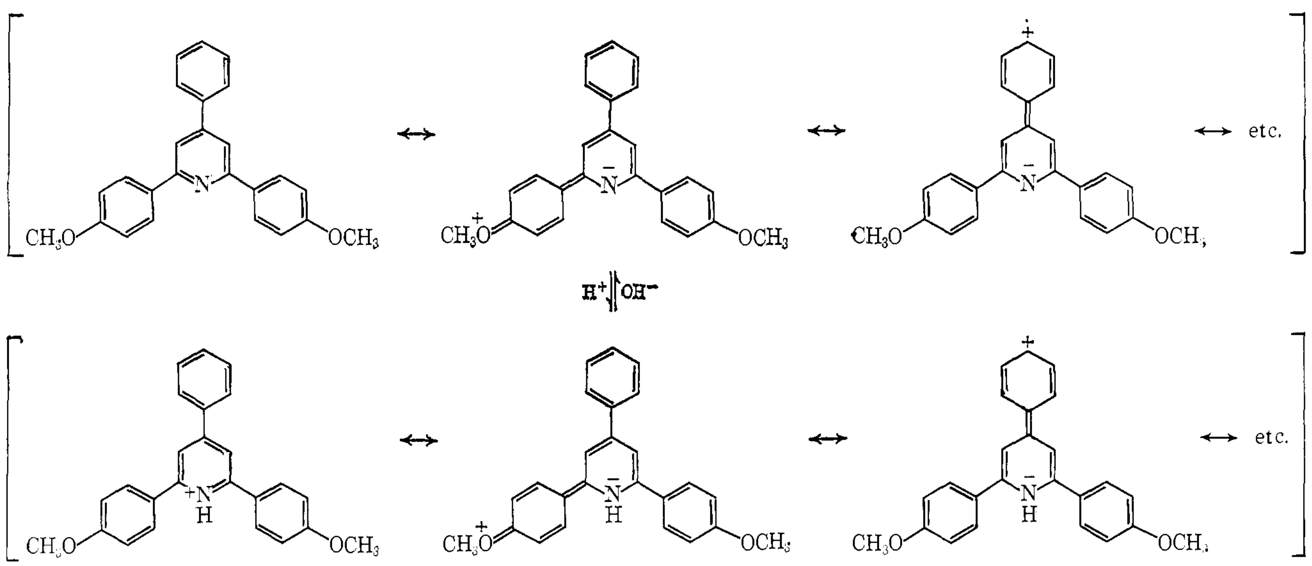
(32) P. Krumholz, *J. Amer. Chem. Soc.*, **73**, 3487 (1951).

(33) A. P. Phillips and P. L. Graham, *ibid.*, **74**, 1552 (1952).

(34) L. Sobczyk, *Bull. Acad. Pol. Sci.*, **9**, 237 (1961).

(35) Studies on the dissociation constants of phenylpyridines[32] showed 2-phenylpyridine to be a very weak base. Earlier work [W. Dilthey, H. Nusslein, H. Meyer, and H. Kaffer, *J. Prakt. Chem.*, **104**, 28 (1922)] demonstrated that 2,4,6-triphenylpyridine was also a very weak base. Upon excitation they can be expected to become more basic: A. Weller, *Progr. React. Kinet.*, **1**, 189 (1961).

**Scheme II**



the lifetime of the excited state.[36,37] Figure 2 shows the variation in the intensity of fluorescence emission of compound **2c** with pH in serial phosphate buffers, upon excitation at 370 nm, and illustrates the points of (a) great intensity at extremely acid pH and (b) strong fluorescence response over a broad pH range. Both acid–base and tautomeric equilibria may cause difficulty in the interpretation of the solution uv absorption and emission spectra of substituted nitrogen heterocycles. The formulas shown in Scheme II convey the idea that the transition involves an electronic demand from the pyridine nitrogen[38] and that this electronic demand should be greater in the cationic form. Possible steric effects may alter the spectra,[39] but analysis of the spectra of the compounds in these terms is complicated by the fact that comparison cannot be made with appropriate unhindered models.

The details of the maxima and half bandwidths of the corrected emission spectra of the substituted pyridines, in alcohol and in 0.05 *N* HCl in alcohol–water, 1:1 by volume, are presented in Table I. Most of the compounds show extremely high fluorescence intensity, being *readily visible at concentrations even below 1* $\times$ $10^{-9}$ *M*. The absolute quantum yields were determined using quinine sulfate as the reference compound. These values are highly dependent on the protonation. Thus, whereas **3b** in ethanol presents a quantum yield of 0.17, in acid this value is very close to 1.00. Using the equation that has been proposed by Stickler and Berg,[40] it is possible to estimate the emissive lifetimes. The observed values (Table I) showed relative short fluorescence lifetimes that are in agreement with the expected values.

Liquid scintillation counting with conventional scintillation solutes such as PPO (2,5-diphenyloxazole) is susceptible to acid quenching. This quenching is thought to be due to protonation of the scintillator solute which causes a change in its permitted excited states. The resulting energy mismatch between the energy levels of the solvent and the fluorophor reduces the efficiency of the energy transfer and causes quenching.[41] This can be particularly troublesome when counting thin layer chromatograms which have been sprayed with visualizing agents such as $H_2SO_4$.[42] As most of the compounds discussed in this paper were highly fluorescent in both neutral and acidic conditions and had emission maxima close to the maximum sensitivity of the bialkali photomultiplier tubes, their possible use as scintillator solutes in both neutral and acidic conditions was explored.

In toluene under neutral conditions $^{14}C$ could be counted at an efficiency of 88% with compound **2c** although a slightly higher instrumental gain was necessary than for PPO. In the dioxane-based solvent A compounds **2b**, **2c**, and **3c** allowed $^{14}C$ to be counted at efficiencies greater than 70% (Figure 3). In solvent A, the addition of 40 $\mu$l of 6 *N* HCl to each vial decreased the efficiency attainable with each compound tested, and it was noted that the addition of more acid further decreased the efficiencies attainable for each compound except **3c**. By the time 240 $\mu$l of 6 *N* HCl had been added, $^{14}C$ could be counted with a greater efficiency with compound **3c** than with PPO, as indicated in Figure 3, panel B. The increases in $^{14}C$ counting efficiency observed with compounds **3b** and **3c** in solvent B (Table II) upon the addition of acid indicate that compounds with this basic structural skeleton have promising potential as scintillators that will allow liquid scintillation counting to be carried out at high efficiency in strongly acidic solutions. It should also be possible to utilize the fluorescence capability on the acid side in binding studies with certain proteins.

## Experimental Section[43]

**Spectra.** The nmr spectra were obtained on a Varian A-60 spectrometer using $CHCl_3$ as solvent and $Si(CH_3)_4$ as an internal

---

(36) T. Förster, *Z. Elektrochem.*, **54**, 531 (1950).

(37) D. M. Hercules and L. B. Rogers, *Spectrochim. Acta*, **14**, 393 (1959).

(38) It has been shown, for example, that the transition in the *p*-haloanisoles requires electron acceptance by the halogen: W. M. Schubert, J. M. Craven, and H. Steadly, *J. Amer. Chem. Soc.*, **81**, 2695 (1959).

(39) H. H. Jaffé and M. Orchin, "Theory and Application of Ultraviolet Spectroscopy," Wiley, New York, N. Y., 1966.

(40) S. J. Strickler and R. Berg, *J. Chem. Phys.*, **37**, 814 (1962).

(41) M. P. Neary and A. L. Budd, "The Current Status of Liquid Scintillation Counting," E. D. Bransome, Ed., Grune and Stratton, New York, N. Y., 1970, p 273.

(42) F. Snyder, ref 41, p 248.

(43) Melting points were determined on a Thomas-Hoover apparatus (capillary method) and are uncorrected.

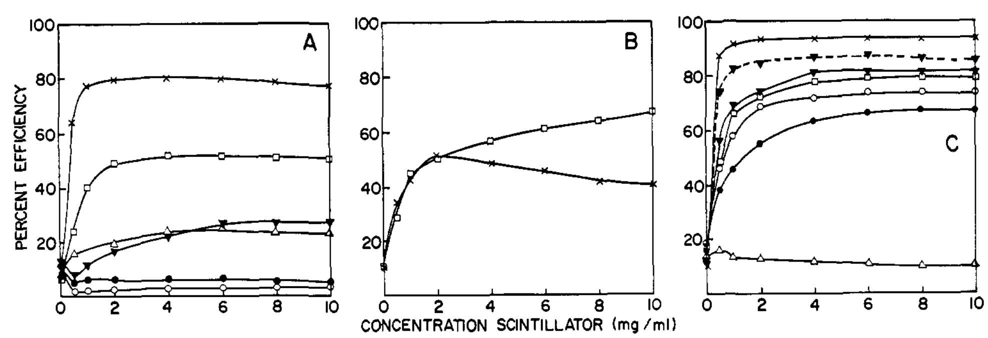


Figure 3. Selective scintillation efficiency *vs.* concentration of scintillator for compounds **2a** (●), **2b** (○), **2c** (▼), **3b** (△), **3c** (□), and PPO (×). A, in solvent A, upon addition of 40 μl of 6 *N* HCl; B, in solvent A, upon addition of 240 μl of 6 *N* HCl; C, in solvent A, under neutral conditions. In this panel, **2c** in toluene is shown as --▼--.

**Table II.** $^{14}$C Counting Efficiencies in Toluene–Methyl Cellosolve[a]

| Scintillation solute | % $^{14}$C counting efficiency<br>Neutral | Acid[b] |
|---|---|---|
| **2a** | 60 | 14 |
| **2b** | 62 | 34 |
| **2c** | 78 | 59 |
| **3b** | 2 | 84 |
| **3c** | 71 | 84 |
| PPO | 93 | 91 |

[a] Proportion 7:3, at a solute concentration of 4 mg/ml. [b] After addition of 40 μl of 6 *N* HCl to 10 ml of solution.

standard. Chemical shifts are reported in parts per million (δ) and signals are described as br (broad), s (singlet), d (doublet), or m (complex multiplet). Microanalyses were performed by Mr. Josef Nemeth and his staff at the University of Illinois, who also weighed samples for the quantitative ultraviolet spectra. All infrared spectra were taken on a Perkin-Elmer 237 spectrophotometer by the normal Nujol mull technique. The ultraviolet spectra were recorded on a Cary Model 15 spectrophotometer. Technical fluorescence emission and fluorescence excitation spectra were measured on a Hitachi-Perkin-Elmer MPF-2A spectrophotometer. Molecular fluorescence emission spectra were determined on a sophisticated digital spectrophotometer. In this instrument, the ratio of the fluorescence intensity to the exciting light intensity was measured by a Dana ratio digital voltmeter and values were averaged. The final molecular spectra were produced by correcting the technical spectra for photomultiplier and optical responses as a function of wavelength. Fluorescence lifetimes were determined by phase using the cross-correlation fluorometer reported by Spencer and Weber.[44] For quantum yield determinations, quinine sulfate in 0.1 *N* $H_2SO_4$ was used as a reference compound assuming a quantum yield value of 0.70.[45] Mass spectra were recorded on a Varian-MAT CH-5 mass spectrometer. All scintillation counting was performed using a Packard Tricarb liquid scintillation spectrometer Model 2003. The compounds were tested as scintillation solutes in two different solvents: solvent A, 50 g of naphthalene and 100 ml of methyl cellosolve, diluted to 1 l. with dioxane; and solvent B, toluene–methyl cellosolve, 7:3 (compound **2c** was also tested in toluene, see Figure 3, panel C). For each sample the correct amount of scintillator was weighed into a standard glass scintillation vial and 10 ml of solvent and $1.72 \times 10^4$ dpm of a 1-butanol-*1*-$^{14}$*C* standard were added. After thorough mixing the instrument gain was optimized for a wide discriminator window setting and the sample was counted. The procedure was repeated after the addition of the 6 *N* HCl.

**2,4,6-Triphenylpyridines (General Procedure).** A mixture of 10 g of ammonium carbonate and 10 g of formic acid was heated cautiously and then distilled slowly until the temperature was about 160°.[2] To the hot residual mixture was added 0.024 mol of the appropriate chalcone and the temperature was raised to 185–190° during 3 hr. After cooling, the reaction mixture was poured into 30 ml of 50% ethanol and allowed to stand. The crude product crystallized and was collected, washed with 50% ethanol, dried, and recrystallized from ethanol.

When the chalcone **1c** was treated with commercial ammonium formate or a mixture of $HCOONH_4$ and $HCONH_2$ (1:1, w/w), the triarylpyridine **2c** was obtained in similar yield to that under the Leuckart conditions. When **1c** was heated at 180–190° for 3 hr with formamide or with $HCONH_2 + H_2O$ (1:1, w/w), no triarylpyridine was obtained and most of the chalcone was recovered.

**2,4,6-Triphenylpyridine (2a):** yield 30% based on chalcone; mp 138° (lit.[6] mp 138°).

**2,6-Diphenyl-4-(*p*-methoxyphenyl)pyridine (2b):** yield 32%; mp 102° (lit.[4] mp 100–101°).

**2,6-Di(*p*-methoxyphenyl)-4-phenylpyridine (2c):** yield 33%; mp 135° (lit.[4] mp 133–134°).

**Catalytic Hydrogenation (General Procedure).** A solution of 4.0 mmol of the appropriate triphenylpyridine in 20 ml of acetic acid was hydrogenated using 0.2 g of $PtO_2$ under 3 atm of hydrogen. The catalyst and solvent were removed and the residue was crystallized.

**2,4,6-Tricyclohexylpiperidine (3a):** yield 78%; mp 153° (acetone); ir (Nujol) no aromatic absorption; nmr ($CDCl_3$) δ 1.40 (br m, $CH_2$ and CH); *m/e* 331 ($M^+$).

*Anal.* Calcd for $C_{23}H_{41}N$: C, 83.38; H, 12.38; N, 4.22. Found: C, 83.30; H, 12.31; N, 4.17.

**2,6-Dicyclohexyl-4-(*p*-methoxyphenyl)pyridine (3b):** yield 81%; mp 117° (ethanol); ir (Nujol) 1610 (C=C), 830 (benzene *p*-disubstituted), 1250, 1170, 1030 $cm^{-1}$ ($OCH_3$); nmr ($CDCl_3$) δ 7.23 (d, 2, $J$ = 9 Hz, meta hydrogens), 6.80 (s, 2, β-pyridine protons), 6.60 (d, 2, $J$ = 9 Hz, ortho hydrogens), 3.64 (s, 3, $OCH_3$), 1.50 (br m, 22, $CH_2$ and CH); *m/e* 349 ($M^+$).

*Anal.* Calcd for $C_{24}H_{31}NO$: C, 82.52; H, 8.88; N, 4.01. Found: C, 82.10; H, 8.87; N, 4.18.

**4-Cyclohexyl-2,6-di(*p*-methoxyphenyl)pyridine (3c):** yield 81%; mp 127° (ethanol); ir (Nujol) 1610 (C=C), 833 (benzene *p*-disubstituted), 1242, 1170, 1030 $cm^{-1}$ ($OCH_3$); nmr ($CDCl_3$) δ 7.70 (d, 4, $J$ = 9 Hz, meta hydrogens), 7.10 (s, 2, β-pyridine protons), 6.65 (d, 4, $J$ = 9 Hz, ortho hydrogens), 3.70 (s, 6, $OCH_3$), 1.60 (br m, 11, $CH_2$ and CH); *m/e* 373 ($M^+$).

*Anal.* Calcd for $C_{25}H_{27}NO_2$: C, 80.42; H, 7.23; N, 3.75. Found: C, 79.83; H, 7.25; N, 3.80.

**Acknowledgment.** We wish to thank Professor Gregorio Weber for helpful discussions and for providing the necessary facilities for the fluorescence determinations. This work was supported by Research Grant GP-8407X from the National Science Foundation and in its earlier stages by the Consejo Nacional de Investigaciones Científicas y Técnicas, Argentina. M. C. G. B. was on leave of absence from the Facultad de Farmacia y Bioquímica, Universidad de Buenos Aires, Buenos Aires, Argentina. J. R. B. was a fellow, 1970–1972, of the Consejo Nacional de Investigaciones Científicas y Técnicas, Argentina. G. W. held an Eli Lilly fellowship during 1971–1972 at the University of Illinois.

---

(44) R. D. Spencer and G. Weber, *Ann. N. Y. Acad. Sci.*, **158**, 361 (1969).

(45) T. G. Scott, R. D. Spencer, N. J. Leonard, and G. Weber, *J. Amer. Chem. Soc.*, **92**, 687 (1970).