ORGANIC SECTION

Scintillation Properties of Alkyl and Alkoxy Derivatives of 5,5′-Diphenyl-2,2′-bioxazole

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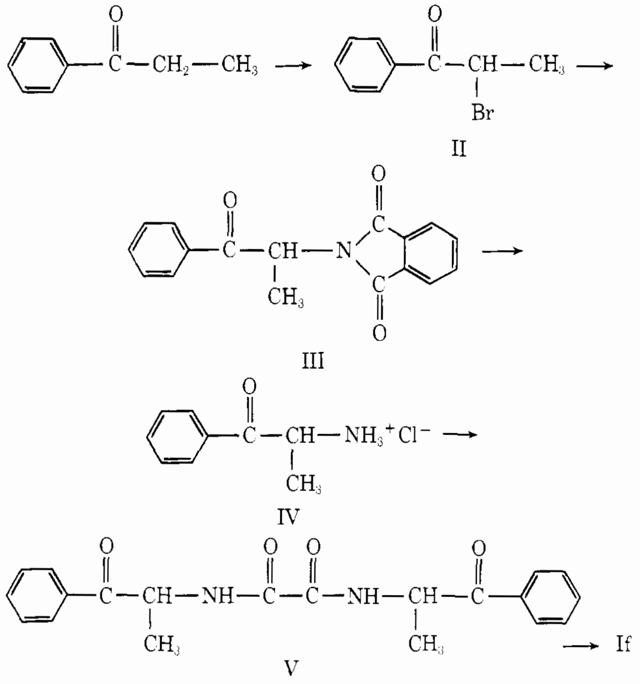
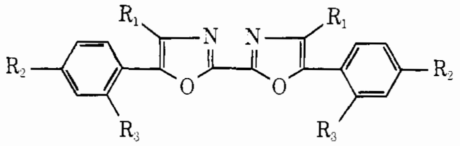
Several alkyl and alkoxy derivatives of the 5,5′-diphenyl-2,2′-bioxazole (POOP) system were synthesized and were good primary liquid scintillation solutes. The absorption and fluorescence characteristics are reported and discussed.

Previous investigations by Hayes and his coworkers (*5, 6*) of compounds which might prove suitable as primary and secondary liquid scintillation solutes indicated that 5,5′-diphenyl-2,2′-bioxazole (POOP) (Ia) was a good scintillator, but its performance was hampered by its limited solubility in the solvent employed, toluene. Compound Ia, at a concentration of just 1.0 g/l., was reported to have a maximum pulse height of 0.76 relative to a 3.0 g/l. solution of PPO in toulene. In view of this excellent scintillation performance at relatively low concentration, we decided to synthesize a number of alkyl and alkoxy derivatives of POOP in an attempt to improve the solubility and thus the scintillation performance of this compound. Those compounds prepared and evaluated in this study are listed in Table I.



The synthesis of each of the compounds was accomplished by first brominating the appropriate substituted acetophenone or propiophenone followed by a Gabriel synthesis to the amine salt (IV) and a reaction of IV with oxalyl chloride in pyridine to give the amide V. Cyclization of V to the POOP derivatives Ib–If was accomplished with phosphorous oxychloride as described by Walker and Waugh (*10*).



Ia, $R_1 = R_2 = R_3 = H$
b, $R_1 = R_3 = H$, $R_2 = -OCH_3$
c, $R_1 = R_3 = H$, $R_2 = -OCH_2CH_3$
d, $R_1 = R_3 = H$, $R_2 = -CH_2CH_3$
e, $R_1 = H$, $R_2 = R_3 = -CH_3$
f, $R_1 = CH_3$, $R_2 = R_3 = H$

All the bioxazole derivatives were extensively purified by repeated recrystallizations and chromatography through alumina in cyclohexane. Solutions left standing in the light and air began decomposition in a few days. All compounds were checked for purity by thin-layer chromatography on Mallinckrodt SILICAR TLC-7GF with a 10–90 mixture by volume of diethyl ether–methylene chloride as a developing solvent. Impurities appeared as dark or fluorescence spots under a short wavelength ultraviolet light.

Evaluation of the compounds as primary liquid scintillation solutes was carried out as previously described (2).

Four derivatives (Ic–If) were excellent primary liquid scintillation solutes. Compound If, 5,5′-diphenyl-2,2′-bi(4-methyloxazole), was the best primary solute, with a maximum relative pulse height of 0.98 under air-equilibrated conditions at a concentration of 5.6 g/l., which was the maximum concentration obtainable in toluene for If. This RPH value probably is close to the maximum obtainable for If, even at higher concentrations, in view of the value of 0.94 for Id, which was obtained at a concentration of 10.8 g/l. Although placing an alkyl group in the 4-position of the oxazole ring can bring about a bathochromic shift in the emission spectrum, it does not appear to markedly improve the scintillation performance (*10*).

The bioxazoles were subject to severe quenching of the luminescence by dissolved oxygen (Table II). Maximum relative pulse heights under deaerated conditions

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Table I. Physical Data for 5,5′-Diphenyl-2,2′-bioxazole Derivatives[a]

Compound	MP, °C	Solubility in toluene at 25°C, g/l.	Formula
5,5′-Di(4-methoxyphenyl)-2,2′-bioxazole (Ib)	226.5–227	1.3	$C_{20}H_{16}N_2O_4$
5,5′-Di(4-ethoxyphenyl)-2,2′-bioxazole (Ic)	193.5–194	42.3	$C_{22}H_{20}N_2O_4$
5,5′-Di(4-ethylphenyl)-2,2′-bioxazole (Id)	209–210	13.2	$C_{22}H_{20}N_2O_2$
5,5′-Di(2,4-dimethylphenyl)-2,2′-bioxazole (Ie)	176.5–177	4.6	$C_{22}H_{20}N_2O_2$
5,5′-Diphenyl-2,2′-bi(4-methyloxazole) (If)	219.5–220	5.1	$C_{20}H_{16}N_2O_2$

[a] Elemental analyses (C and H) in agreement with theoretical values were obtained and submitted for review.

resulted in a 20% increase over those obtained under air-equilibrated conditions.

The solubility of POOP is increased only slightly by substituting alkyl or alkoxy groups into the 4-position of the benzene ring, unless the group is quite large. Compound Ib, for example, which has a methoxy substituent in the 4-position in the benzene ring, is soluble only to the extent of 1.3 g/l. in toluene, too low for suitable evaluation of the compound as a primary liquid scintillation solute. The introduction of the relatively small methyl group into the 4-position of the oxazole ring markedly increases the solubility, however, an observation also made by Walker and Waugh for other oxazole compounds (*10*).

There has been considerable interest in recent years with the formation of excimers in luminescent compounds, particularly those used as organic scintillators (*9*). In view of this interest, we also screened compounds Id, Ie, and If for the formation of excimers, by concentration dependence and temperature dependence emission techniques as described by Horrocks (*8*). Within the limits of solubility, the POOP derivatives investigated do not show excimer formation between 0° and 90°C which is in contrast to the one oxazole system, 2,5-diphenyloxazole, which has been previously investigated for excimer formation (*1*).

Walker and Waugh also observed in a study on 2,2′-*p*-phenylenebis(4-methyl-5-phenyloxazole) (dimethyl POPOP) that substitution of a methyl group into the 4-position of the oxazole ring caused a bathochromic shift of 5 nm for the fluorescence maximum when compared with the unsubstituted POPOP. Also, they reported an 11-nm bathochromic shift in the fluorescence maximum for 4-methyl-2,5-diphenyloxazole (376 nm) when compared to 2,5-diphenyloxazole (365 nm) (*10*). Compound If, which has a methyl substituent in the 4-position of the oxazole ring, likewise shows a bathochromic shift of 9 nm of the fluorescence maximum when compared to the value of 401 nm reported for Ia by Hansbury et al. (*4*).

Experimental

Melting points are uncorrected and were determined in capillary tubes with a Thomas Hoover apparatus. Ultraviolet spectra were determined in spectrograde cyclohexane at concentrations of approximately 10^{-5} M in 1-cm quartz cuvettes with a Beckman DU-2 spectrophotometer. Fluorescence measurements were made with a Farrand MK-1 spectrofluorimeter in scintillation grade toluene by using slits with an 0.5-nm bandpass. Solutions were saturated with nitrogen. A quartz triangular cell was used to minimize self-absorption at shorter wavelengths, and spectra were corrected for the response of the phototube. Microanalyses were performed by Huffman Laboratories, Wheat Ridge, Colo., or the Heterocyclic Chemical Corp., Harrisonville, Mo.

All the POOP derivatives were prepared by the same general procedure outlined for compound If.

Table II. Scintillation and Spectral Data for 5,5′-Diphenyl-2,2′-bioxazoles

Compound	RPH_{ox}[a]	RPH_{deox}[b]	Fluorescence max, nm	Absorption max, nm	log ε	C_{max},[c] g/l.
Ic	0.90	1.17	408	337	4.50	2.35
Id	0.94	1.13	408	336	4.57	10.4
Ie	0.88	1.11	408	334	4.50	4.7
If	0.98	1.20	410	339	4.52	5.6

[a] Aerated solution in toluene, relative to a 3.0 g/l. solution of 2,5-diphenyloxazole in toluene. [b] Toluene solution saturated with air, relative to a 3.0 g/l. solution of 2,5′-diphenyloxazole in toluene. [c] Concentration at which maximum relative pulse height reached.

α-Bromopropiophenone (II). A solution of 200 grams (1.48 moles) of propiophenone (Aldrich Chemical Co., cat. no. P5160-5) in 100 ml of dry ether was placed in a dry three-necked flask fitted with a separatory funnel, mechanical stirrer, and reflux condenser. The solution was cooled in an ice-bath, 1.5 grams of anhydrous aluminum chloride introduced, and 237 grams (1.48 moles) of bromine was added dropwise with stirring. After addition was complete, the ether and dissolved hydrogen bromide were removed under vacuum, and the resulting liquid was distilled under reduced pressure through a 6-in. Vigreux column, collecting the fraction boiling at 125–135°C/12 mm, reported (*7*) 110–112°C at 4 mm. Yield, 230 grams (73%). The compound is a severe lachrymator and was not purified further before use.

α-Phthalidimopropiophenone (III). The preparation of α-phthalidimopropiophenone (III) was accomplished by stirring 20 grams (0.094 mole) of II and 17.4 grams (0.094 mole) of potassium phthalimide at 50°C for 1.5 hr in 200 ml of dimethylformamide. The reaction mixture was poured over ice, filtered, and dried under vacuum at 40°C. Recrystallization from methanol gave 19.0 grams (64%) of III, mp 87–88°C, reported (*3*), 87–88°C.

N,N′-(2-methylphenacyl) oxamide (V). A solution of 86 grams (0.27 mole) of α-phthalidimopropiophenone (III) in 350 ml glacial acetic acid and 250 ml of concentrated hydrochloric acid was stirred at 80°C for 5 hr and then poured into an ice water mixture. The resulting precipitate was filtered, dried, and found to consist mostly of phthalic acid and unhydrolyzed III. The filtrate was concentrated to about 200 ml and filtered to give fairly pure phthalic acid as a precipitate. The filtrate was then concentrated to dryness to give 19 grams of crude α-aminopropiophenone hydrochloride (IV), mp 160–175°C. Purification of samples of the crude amine salt IV resulted in decomposition; therefore, the crude material was converted directly to the oxamide V.

Nineteen grams of the crude IV was added with stirring over a period of 1 hr to 17.1 grams (0.135 mole) of oxalyl chloride dissolved in 100 ml of dry pyridine. The reaction mixture was stirred at room temperature for 2 hr and then refluxed for an additional hour. After cooling in an ice bath, the reaction mixture was poured into water and allowed to stand overnight. The precipitate was filtered, dried, and recrystallized from ethyl acetate. The semipurified material was then taken up in methylene chloride and chromatographed through alumina. Recrystallization of this material from ethanol gave 9.0 grams of *N,N'*-(2-methylphenacyl) oxamide (V), mp 153–157°C in 19% overall yield from III. Repeated chromatography of V through alumina in methylene chloride followed by recrystallizations from ethanol gave a more pure product, mp 162–162.5°C.

5,5'-Diphenyl-2,2'-bi(4-methyloxazole)(If). One and three-tenths grams (0.0037 mole) of *N,N'*-(2-methylphenacyl) oxamide (V), mp 156–158°C, was heated at 80°C with stirring in 60 ml of phosphoryl chloride for 48 hr. Upon cooling, the reaction mixture was poured into water, and the resulting precipitate filtered. Recrystallization of the crude precipitate from ethyl acetate, followed by chromatography through alumina in benzene and another recrystallization from ethyl acetate, gave 0.72 gram (62%) of If as pale green crystals, mp 218–219.5°C. Shorter reaction times gave substantially lower yields. Repeated recrystallization from ethyl acetate gave an analytical sample, mp 219.5–220°C.

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Literature Cited

(1) Berlman, I. B., *J. Chem. Phys.*, **34**, 1083 (1961).
(2) Daub, G. H., Hayes, F. N., Lehman, R. B., Yguerabide, J., in "Organic Scintillators and Liquid Scintillation Counting," D. L. Horrocks and C. T. Peng, Eds., p 441, Academic Press, New York, N.Y., 1971.
(3) Gabriel, S., *Chem. Ber.*, **41**, 242 (1908).
(4) Hansbury, E., Hayes, F. N., Kerr, V. N., Ott, D. G., *J. Amer. Chem. Soc.*, **79**, 5448 (1957).
(5) Hayes, F. N., Kerr, V. N., Ott, D. G., *Nucleonics*, **14** (12), 42 (1956).
(6) Hayes, F. N., Kerr, V. N., Ott, D. G., Rogers, B. S., *ibid.*, 38 (1956).
(7) Higginbotham, L., Lapworth, A., Simpson, C., *J. Chem. Soc.*, **125**, 2343 (1924).
(8) Horrocks, D. L., in "Organic Scintillators and Liquid Scintillation Counting," D. L. Horrocks and C. T. Peng, Eds., p 75, Academic Press, New York, N.Y., 1971.
(9) Parker, C. A., "Photoluminescence of Solutions," p 344, Elsevier, New York, N.Y., 1968.
(10) Walker, D., Waugh, T. D., *J. Heterocyclic Chem.*, **1**, 72 (1964).

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Mass Spectra of Isomers of Trinitrotoluene

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The mass spectra of the six isomers of trinitrotoluene are presented. The fragmentation pathways leading to the major fragment ions are outlined.

Detection of explosives by sensing associated vapors has been under investigation in this and other laboratories for some time (*1, 2, 5, 9*). During a study to define the composition of vapor emitted by production grade TNT, a requirement developed for accurate mass spectra of the individual isomers of trinitrotoluene. Since these data were not available in the literature, it was necessary to make these determinations.

Table I is a compilation of the mass spectra of the six isomers of trinitrotoluene at 75 eV. Mass spectra were also taken (*8*) at ionizing energies intermediate between this value and the ionization potential of the molecules, but no anomalous behavior was observed; therefore, these spectra are not presented here. Mass spectra were similarly obtained (*8*) for the isomers of DNT and were consistent with earlier published results (*7*).

Discussion

The major route of decomposition, for all isomers except 3, 4, 5, originates with a loss of the hydroxyl radical (OH) from the molecular ions. This fragmentation is important in cases where a methyl group is located ortho to an aromatic nitro substituent (*4, 8*). This path leads to a rearranged species of mass 210 which subsequently loses NO and NO_2, giving ions of mass 180 and 134, respectively. Prevalent lower mass ions generally are formed from further decomposition of these species, although a portion of the mass 30 ion may originate from primary fragmentation of the molecular ion.

In contrast, the mass spectrum of the 3, 4, 5 isomer is dominated by a large mass 30 ion (NO^+) accounting for more than 25% of the total ion current. This ion is formed at least in part from the molecular ion as confirmed by the presence of a metastable at $m/e = 4.0$. The remaining ions are generally the result of successive loss of NO_2 molecules followed by normal hydrocarbon fragmentation. The total absence of a mass 210 ion for this compound is to be expected, since it is the only isomer without an ortho methyl group.

Experimental

The mass spectra reported in Table I were obtained on a Perkin-Elmer 270B mass spectrometer operated at 75 eV with the ion source temperature maintained at 150°C. The samples were introduced via a quartz capillary from the standard solids probe inlet system. The probe was not intentionally heated, although a thermocouple within the solid probe indicated a temperature of 70°C. The purity of the individual isomers was established (*6*) by melt-

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