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SYNTHESIS OF 2,5-DIARYLOXAZOLES THROUGH FRIEDEL-CRAFTS REACTION OF AZLACTONES WITH AROMATIC HYDROCARBONS*

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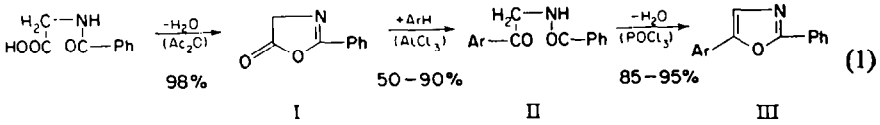
Abstract—2-Phenyl-5-oxazolone (hippuric acid azlactone, I) gives good yields of benzoylaminoketones(II) in the Friedel–Crafts benzoylaminoacetylation of aromatic hydrocarbons. On this basis a new synthesis of 2,5-diaryloxazoles was devised, resulting in the simplest preparation of several 2-phenyl-5-aryl-oxazoles (III), which are good scintillator solutes. Ultra-violet absorption spectra are described and discussed.

IT was recently shown that α-acylaminoketones may be obtained by the reaction of azlactones with aromatic nuclei in the presence of aluminium chloride; the reaction may proceed either intermolecularly[1] or intramolecularly.[2] The present paper describes the condensation of hippuric acid azlactone (2-phenyl-5-oxazolone, I) with several aromatic hydrocarbons ArH; the benzoylaminoketones (II) thus obtained being subsequently converted into 2-phenyl-5-aryl-oxazoles (III):



(1)

The reaction was applied to the following hydrocarbons: benzene, toluene, *m*-xylene, phenylcyclohexane, biphenyl, naphthalene, fluorene, acenaphthene and phenanthrene. A series of nine 2-phenyl-5-aryl-oxazoles was obtained for the purpose of studying their use as scintillator solutes. Some of the compounds are not yet recorded in the literature.

The Friedel–Crafts reaction of aminoacid chlorides[3,4] or phthalylaminoacid chlorides[5] yields aminoketones, but the use of azlactones instead of aminoacid chlorides is a substantial simplification; the proof that azlactones are effective Friedel–Crafts acylating agents extends the convertion of aminoacids into alkyl-substituted oxazoles[6] to the aromatic series.

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Benzoylaminoacetylation of aromatic hydrocarbons

Reaction conditions and yields are presented in Table 1. In all cases aluminium chloride was added to the hydrocarbon–azlactone solution (eventually in carbon disulphide as solvent). Benzoylaminomethyl aryl ketones (II) were isolated by

TABLE 1. REACTION CONDITIONS FOR THE SYNTHESIS OF BENZOYLAMINOMETHYL KETONES (II)

	Hydrocarbon		Azlactone	Catalyst	Solvent	Temp	Yield
		m moles	m moles	m moles	ml	°C	%
a	Benzene	141	38·5	105	50	46	55
		950	38·5	120	—	20	55
		3500	280	845	—	80	55·2
b	Toluene	980	120	376	—	20	59·5
c	*m*-Xylene	1100	168	502	—	20	78
d	Naphthalene	164	38·5	105	150	20	39·5
e	Acenaphthene	390	123	376	200	20	90
f	Biphenyl	335	81	248	150	46	70·6
g	Phenylcyclohexane	56	55	203	100	20	34·5
h	Fluorene	379	155	470	150	20	97
i	Phenanthrene	297	103	309	150	20	27·5

filtration and washing with ether. The melting point of the crude products increased on subsequent purification by less than 8° in all cases, indicating that the crude product was a single compound and fairly pure. This standard procedure gives good results in the case of higher hydrocarbons, but for benzene and toluene it is unsatisfactory since a substantial part of the product dissolves in the aromatic hydrocarbon; evaporation of the organic layer from the filtrate shows that in these cases the real yield is of over 80 per cent.[1] In a few cases (phenylcyclohexane, naphthalene and phenanthrene), benzene was tried as solvent; the reaction proceeds normally but lower yields (20–30%) are secured. Owing to its low solubility, anthracene does not react under these conditions. The reaction with 2,5-diphenyloxazole in place of the aromatic hydrocarbon gives an unidentified product.

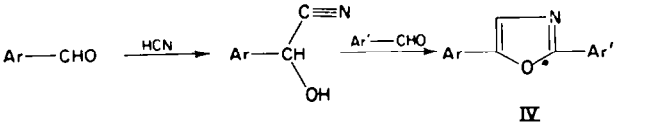
The structure of the reaction products is based on data from the literature for cases *a*, *b*, *c*, and *f*. It may be seen that the orientation in the benzoylaminoacetylation reaction obeys the usual substitution rules. It must be borne in mind that the benzoylaminomethyl aryl ketones obtained are the major reaction products and that minor reaction products escaped observation, as when excess of hydrocarbon was removed in ether, minor reaction products could also be carried away. The compound obtained with naphthalene is the 1-acylation product, as shown by its UV

spectrum (see last section). By analogy with the usual orientation in acylations it was assumed that phenylcyclohexane is substituted in the 4-position, phenanthrene in the 3-position,[7] acenaphthene in the 4-position,[8] and fluorene in the 2-position.[8]

Preparation of 2-phenyl-5-aryl-oxazoles

The crude benzoylaminoketones (II) were converted into oxazoles (III) by dehydration. In order to develop a standard procedure, phosphorus oxychloride was employed, as sulphuric acid is not always successful in bringing about this conversion, and under more drastic conditions has a sulphonating action. Melting points of oxazoles (III) with polynuclear aryl groups are about 155°, and for better characterization, picrates were also prepared. It was observed that owing to the reduced basicity of the oxazole nucleus, picrates underwent slight decomposition during recrystallization from ethanol; this decomposition was more pronounced for polynuclear aryl groups, and in the case of *f* (2-phenyl-5-biphenylyl-oxazole) the picrate decomposed completely on recrystallization; it had to be recrystallized from ethanol saturated in the cold with picric acid and followed by rapid washing with ethanol.

By the method described in the present paper, 2-phenyl-5-aryl-oxazoles (III) are obtained in fewer stages and with better overall yields than by any other method,[9] especially when the aryl group is derived from a polynuclear aromatic hydrocarbon. Reactions (2)[10–13] and (3)[14–24] which are most generally applied, start with benzaldehyde and acetophenone respectively and lead to isomeric 2-aryl-5-phenyl-oxazoles (IV, Ar=Ph).



(2)

IV

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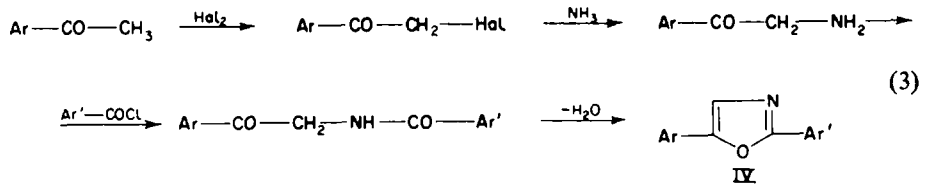
TABLE 2. ULTRA-VIOLET ABSORPTION DATA OF 2-PHENYL-5-ARYL-OXAZOLES [a]

	Aryl	Found					Literature[16]			
		C	B	A	A′	A″	C	B	A	Code[b]
a	Phenyl	224 20500	—	302 28100	318 26400	333*s* 13000	223 20400	—	303 30400	aa
b	4-Methylphenyl	224 23000	—	306 30400	320 28600	340*s* 14000	—	—	—	—
c	2,5-Dimethylphenyl	225 18500	—	307 25100	321*s* 21000	338*s* 9000	225*s* 14500	—	306 22400	ae
d	1-Naphtyl	229 41200	279 14400	323 23300	—	—	229 ε_2	—	323 ε_1	bn[c]
e	4-Acenaphtyl	237 43600	286 14400	337 28300	—	—	—	—	—	—
f	4-Biphenylyl	220 32100	259 13600	322 41500	328*s* 41000	- -	—	260*s* 6700	323 39000	bi
g	4-Cyclohexylphenyl	224 26500	—	307 39700	322 37300	337*s* 18500	—	—	—	—
h	2-Fluorenyl	221 28600	273 9400	335*s* 48000	341 53200	357*s* 30600	—	—	—	—
i	3-Phenanthryl	252 40800	280 25300	325 36000	339 40500	353*s* 24600	—	—	—	—

[a] Absorption maxima $\left\{\begin{matrix}\lambda(\mathrm{m}\mu)\\ \varepsilon\end{matrix}\right\}$ are given; *s* indicates a shoulder.

[b] Notation in Table 2 from ref. 16.

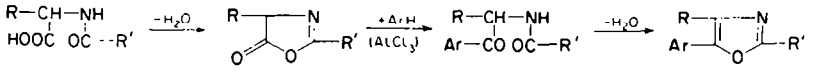
[c] A ratio $\varepsilon^1/\varepsilon_2 = 0{\cdot}51$ is reported;[16] our values yield a ratio 0·56.



(3)

IV

Although only the azlactone of hippuric acid was studied, it should be possible to start from other acylated aminoacids:



(4)

For instance, by employing other aroylglycines, Ar'—CO—NH—CH_2—COOH, oxazoles of the general formula IV may be prepared.

Ultra-violet absorption spectra

It is known, that 2,5-diaryloxazoles as a class of scintillator solutes possess the best scintillation characteristics.[25] Some clinical applications of oxazole derivatives are also known.[21,26]

Fluorescence and absorption spectra are both important for scintillators. Ultraviolet absorption spectra of the 2-phenyl-5-aryl-oxazoles were determined in cyclohexane. The results are presented in Figs. 1 and 2.

The agreement with available data[16] (for III*a*, *c*, *d* and *f*) is very good.

On the basis of the absorption spectra, an unequivocal structure determination can be made for compound III*d*: all data for 2- (and 5-) phenyl-5-(and 2-) (1- and 2-naphthyl)-oxazoles are available[16] (the 2-naphtyl derivatives have only a shoulder in the 230 mμ region); direct comparison reveals that only 5-(1-naphthyl)-2-phenyl-oxazole has similar spectral data with compound III*d* (only the intensity ratio $\varepsilon_1/\varepsilon_2$ was previously reported because of insufficient material available.)[16]

The bands are labelled with capital letters in the decreasing wavelength order (cf.[27]). Two main bands, namely A (300–340 mμ) and C (220–225 mμ), are apparent in the spectrum of 2-phenyl-5-(alkylphenyl)-oxazoles (III*a–c*, *g*). The longer wavelength band is a system of several distinct vibrational peaks: A at ca. 305 mμ, A' at ca. 320 mμ, and a shoulder A'' at ca. 335 mμ (for compounds III*a* and III*c*, another small shoulder is apparent in the 290 mμ region). The remaining oxazoles with larger aryl groups in the 5-position have, besides these two band systems, an intermediate band, B, at ca. 270 mμ which is possibly due to the isolated aryl chromophore. In these cases, the A band system either loses its fine structure (III*d–f*), or is displaced at ca. 340–360 mμ (III*h*, *i*). A remarkable shift towards longer wavelengths is observed in passing from the naphthyl-derivative III*d* to the acenaphthyl-derivative III*e*. The largest bathchromic shifts are observed in the spectra of the fluorenyl-(III*h*) and phenanthryl-derivatives (III*i*); the fine structure in the latter spectrum is very pronounced in all three bands. From the point of view of application as scintillators,

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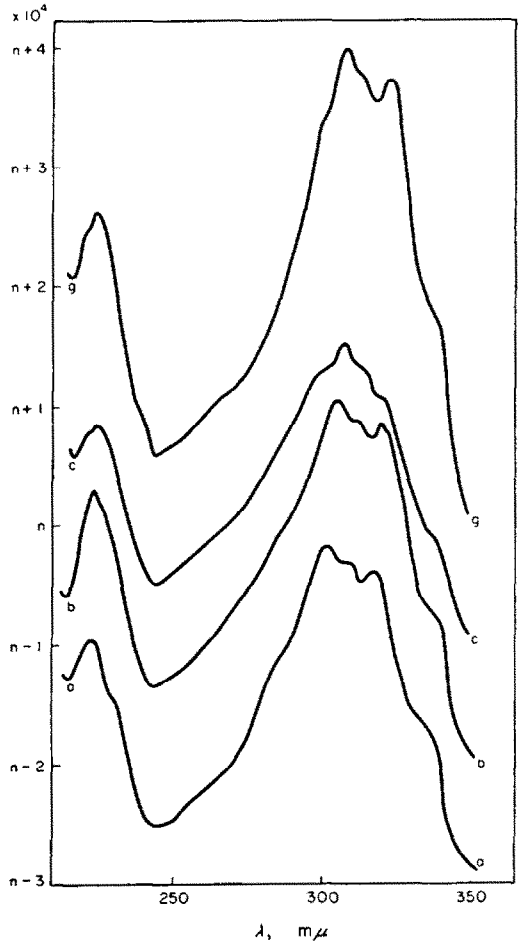

FIG. 1. U.V. absorption spectra of oxazoles in cyclohexane:
III*a*, n = 3; III*b*, n = 2; III*c*, n = 1; III*g*, n = 0.

5-(2-fluorenyl)-2-phenyl-oxazole (III*h*) appears the most promising, both for spectral and preparative reasons (for the isomeric 2-(2-fluorenyl)-5-phenyl-oxazole, cf.[18]).

The similarity in spectral characteristics of the oxazole and benzene rings has already been mentioned.[16,28] It should be emphasized that the oxazole ring system has a greater polarizability, since larger bathchromic shifts result on substitution with conjugative substituents.

Fluorescence spectra and scintillation characteristics will be reported later.

EXPERIMENTAL

2-Phenyl-5-oxazolone (I).[29] In order to obtain in good yield a pure product, the following conditions have to be observed. Recrystallized and dried hippuric acid, in a fivefold amount of acetic anhydride, is heated with stirring on a water bath previously brought to boiling, until all hippuric

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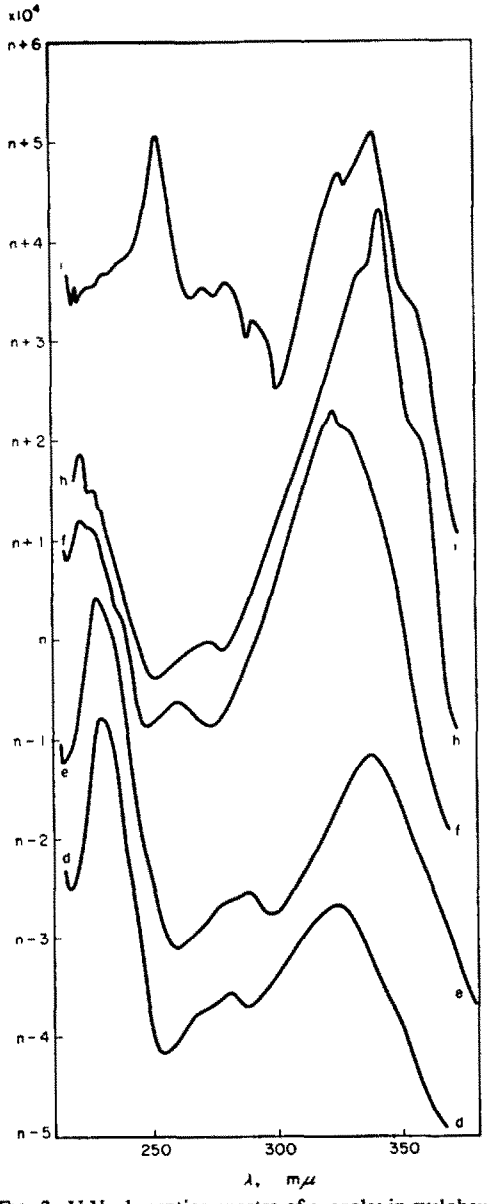

FIG. 2. U.V. absorption spectra of oxazoles in cyclohexane:
III*d*, n = 5 .; III*e*, n = 4; III*f*, n = 2; III*h*, n = 1; III*i*, n = −1.

acid is dissolved. The operation must be conducted as rapidly as possible (ca. 10 min) in order to obtain a pure and nearly colourless product. The flask is then chilled and the Ac_2O–AcOH mixture completely evaporated at 3–5 Torr on a bath (below 55°). The product, a straw-coloured oil, crystallizes on cooling, and consists of nearly pure azlactone (97–99% yield). If during evaporation the azlactone crystallizes, acetic anhydride is retained in the product, which has to be absorbed on porous plate, and the product recrystallized from absolute ethanol or cyclohexane, resulting in smaller yields.

Benzoylaminomethyl aryl ketones (II) are prepared by gradual addition of anhydrous aluminium chloride, at 0–10°, to a mixture of azlactone (I) and aromatic hydrocarbon. The solvent is either the

aromatic hydrocarbon itself, or carbon disulphide. The mixture is stirred for 5 hr at the temp indicated in Table 1 and then left overnight. After hydrolysis with ice and hydrochloric acid, the mixture is filtered and the product (II) washed with water and ether (compound II*i* crystallizes in the carbon disulphide layer only after several hours).

Benzoylaminomethyl phenyl ketone (IIa), m.p. 124° from ethanol, Lit. m.p. 122,[22] 123,[30] 124.[31]

Benzoylaminomethyl p-*tolyl ketone* (IIb), m.p. 114° from ethanol Lit.[32] m.p. 118–119°, sinter. 113°. (Found: C, 75·94; H, 6·12; N, 5·77. Calc. for $C_{16}H_{15}NO_3$: C, 75·87; H, 5·97; N, 5·53%).

Benzoylaminomethyl 2,4-*xylyl ketone* (IIc), m.p. 130° from ethanol, Lit.[16] m.p. 107–108°. (Found: C, 76·36; H, 6·42; N, 5·45. Calc. for $C_{17}H_{17}NO_2$: C, 76·38; H, 6·41; N, 5·24%).

Benzoylaminomethyl 1-*naphthyl ketone* (IId), m.p. 148° from ethanol, Lit.[33] m.p. 150°. (Found: C, 78·78; H, 5·31; N, 5·11. Calc. for $C_{19}H_{15}NO_2$: C, 78·87; H, 5·23; N, 4·84%).

Benzoylaminomethyl 4(?)-*acenaphthyl ketone* (IIe), m.p. 160–161° from ethanol–benzene. (Found: C, 80·40; H, 5·63; N, 4·48. $C_{21}H_{17}NO_2$ requires: C, 79·98; H, 5·43; N, 4·44%).

Benzoylaminomethyl 4-*biphenylyl ketone* (IIf), m.p. 185–186° from ethanol, Lit.[14] m.p. 182–183°. (Found: C, 80·07; H, 5·45; N, 4·70. Calc. for $C_{21}H_{17}NO_2$: C, 79·98; H, 5·43; N, 4·44%).

Benzoylaminomethyl 4-*cyclohexylphenyl ketone* (IIg), m.p. 146° from ethanol–benzene. (Found: C, 78·30; H, 7·34; N, 4·48. $C_{21}H_{23}NO_2$ requires: C, 78·47; H, 7·21; N, 4·36%).

Benzoylaminomethyl 2(?)-*fluorenyl ketone* (IIh), m.p. 194° from ethanol–benzene. (Found: C, 80·81; H, 5·25; N, 4·07. $C_{22}H_{17}NO_2$ requires: C, 80·71; H 5·24; N, 4·28%).

Benzoylaminomethyl 3(?)-*phenanthryl ketone* (IIi), m.p. 166° from ethanol–benzene. (Found: C, 81·75; H, 5·08; N, 3·96. $C_{23}H_{17}NO_2$ requires: C, 81·37; H, 5·05; N, 4·13%).

2-*Phenyl*-5-*aryl-oxazoles* (III). Dehydration of benzoylaminomethyl aryl ketones may be effected either by heating with conc sulphuric acid[22,30,32] or by refluxing with 3–5 moles of phosphorus oxychloride. Since the former method is unsuccessful when larger aryl groups are present,[14,15] the latter method was followed, and yields of over 80% were secured. After 4 hr refluxing, the mixture was hydrolysed and the product recrystallized from ethanol or aqueous ethanol in the presence of carbon black. One recrystallization was sufficient for analytical purity but for spectral determination two recrystallizations were made. All oxazoles present a violet fluorescence whose intensity increases in the order a ≃ b ≃ c ≃ g < d ≃ i < e ≃ f ≃ h.

2,5-*Diphenyloxazole* (IIIa), m.p. 71–72°. Lit. m.p. 70–71,[31] 73,[30] 71–72,[22], 74.[10]. *Picrate*, m.p. 176° from ethanol, Lit. m.p. 172–173.[34] (Found: N, 12·18. Calc. for $C_{21}H_{14}N_4O_8$: N, 12·44%).

2-*Phenyl*-5-p-*tolyl-oxazole* (IIIb), m.p. 75°. Lit. m.p. 81–82,[32] 81.[12] (Found: C, 81·47; H, 5·75; N, 6·02. Calc. for $C_{16}H_{13}NO$: C, 81·68; H, 5·56; N, 5·95%). *Picrate*, m.p. 190° from ethanol, Lit.[32] m.p. 189–190°. (Found: N, 11·95. Calc. for $C_{22}H_{16}N_4O_8$: N, 12·01%).

2-*Phenyl*-5-(2,4-*xylyl*)-*oxazoles* (IIIc), m.p. 86–87°. Lit.[16] m.p. 80–81°. (Found: C, 81·77; H, 5·83; N, 5·97. Calc. for $C_{17}H_{15}NO$: C, 81·90; H, 6·07; N, 5·62%). *Picrate*, m.p. 151° from ethanol. (Found: N, 11·42. $C_{23}H_{18}N_4O_8$ requires: N; 11·71%).

2-*Phenyl*-5-(1-*naphthyl*)-*oxazole* (IIId), m.p. 112°. Lit.[33] m.p. 116–117°. (Found: C, 81·47; H, 5·75; N, 5·37. Calc. for $C_{19}H_{13}NO$: C, 81·68; H, 5·56; N, 5·16%). *Picrate*, m.p. 140–141° from ethanol, Lit.[33] m.p. 142–144°. (Found: N, 11·12. Calc. for $C_{25}H_{16}N_4O_8$: N, 11·20%).

2-*Phenyl*-5-(4-*acenaphthyl*)-*oxazole* (IIIe), m.p. 155–156°. (Found: C, 84·63; H, 5·19; N, 4·81. $C_{21}H_{15}NO$ requires: C, 84·82; H, 5·09; N, 4·71%). *Picrate*, m.p. 169–170° from ethanol. (Found: N, 10·71. $C_{27}H_{18}N_4O_8$ requires: N, 10·64%).

2-*Phenyl*-5-(4-*biphenylyl*)-*oxazole* (IIIf), m.p. 157°. Lit.[14] m.p. 158°. (Found: C, 84·57; H, 5·22; N, 4·56. Calc. for $C_{21}H_{15}NO$: C, 84·82; H, 5·09; N, 4·71%). *Picrate*, m.p. 163° from ethanol saturated in the cold with picric acid. (Found: N, 10·57. $C_{27}H_{18}N_4O_8$ requires: N, 10·64%).

2-*Phenyl*-5-(4-*cyclohexylphenyl*)-*oxazole* (IIIg), m.p. 113°, (Found: C, 83·18; H, 7·04; N, 4·48. $C_{21}H_{19}NO$ requires: C, 83·13; H, 6·98; N, 4·62%). *Picrate*, m.p. 163–164° from ethanol. (Found: N, 10·39. $C_{27}H_{24}N_4O_8$ requires: (N, 10·52%).

2-*Phenyl*-5-(2-*fluorenyl*)-*oxazole* (IIIh), m.p. 157°. (Found: C, 85·34; H, 4·88; N, 4·52. $C_{22}H_{15}NO$ requires: C, 85·41; H, 4·89; N, 4·54%). *Picrate*, m.p. 199° from ethanol. (Found: N, 10·17. $C_{28}H_{18}N_4O_8$ requires: N, 10·40%).

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2-*Phenyl*-5-(3-*phenanthryl*)-*oxazole* (IIIi), m.p. 155–156°. (Found: C, 86·07; H, 4·77; N, 4·33. $C_{23}H_{15}NO$ requires: C, 85·96; H, 4·70; N, 4·36%). *Picrate*, m.p. 178° from ethanol. (Found: N, 9·93. $C_{29}H_{18}N_4O_8$ requires: N, 10·18%).

Ultra-violet absorption spectra were recorded in $5 \cdot 10^{-5}$ molar solutions in cyclohexane (the oxazoles III*e* and III*h* were dissolved in cyclohexane by leaving for 24 hr at room temp) with a VS1 Zeiss spectrophotometer.

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