

## PREPARATION AND SPECTRA OF *para*-SUBSTITUTED 2,5-DIPHENYLOXAZOLES\*

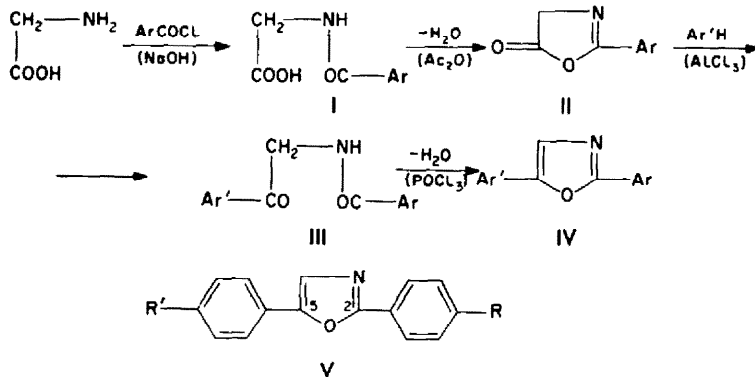
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**Abstract**—2,5-Diaryloxazoles, with the 2- and 5-aryl groups, substituted in the *para* position by halo, methyl, methoxy or nitro groups were obtained by the Friedel-Crafts reaction of *p*-substituted hippuric acid azlactones with benzene, or the hippuric acid azlactone with halobenzenes, toluene, and anisole, followed by treatment with phosphorus oxychloride. Grignard and Ullmann reactions of *p*-halo-substituted 2,5-diaryloxazoles are described. Absorption spectra of these compounds are discussed and the pronounced bathochromic effect of coupled donor and acceptor groups in both *para* positions is accounted for by a simple MO treatment.

IN PARTS III,<sup>2</sup> IV,<sup>3</sup> and V,<sup>1</sup> the preparation of 2-phenyl-5-aryloxazoles, 2-(1-naphthyl)-5-aryloxazoles and 2-(*p*-biphenyl)-5-aryloxazoles by the Friedel-Crafts aroyl-amination of aromatic hydrocarbons with azlactones were described. The present paper reports the reaction of *p*-substituted hippuric acid azlactones with benzene, toluene, halobenzenes and anisole, and the preparation of 2,5-diaryloxazoles in which one or both aryl groups have a *para*-substituent. Only two non-hydrocarbon aromatics have previously been treated with azlactones under Friedel-Crafts conditions, namely anisole<sup>4</sup> and chlorobenzene.<sup>5</sup> The reactions involved are depicted in the following sequence



\* Aminoketone Syntheses. Part VI.<sup>1</sup>

<sup>1</sup> Part V, A. T. Balaban, I. Bally, P. T. Frangopol, M. Băcescu, E. Ciorănescu and L. Bîrlădeanu, *Tetrahedron* **19**, 169 (1963).

<sup>2</sup> P. T. Frangopol, A. T. Balaban, L. Bîrlădeanu and E. Ciorănescu, *Tetrahedron* **16**, 59 (1961).

<sup>3</sup> E. Ciorănescu, L. Bîrlădeanu, P. T. Frangopol and A. T. Balaban, *Revue de Chimie, Acad. R.P.R.* **7**, 41 (1962).

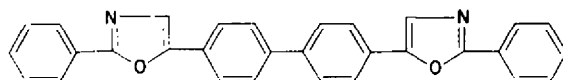
<sup>4</sup> E. Ciorănescu, L. Bîrlădeanu and R. Sternberg, *Izv. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* **144** (1961).

<sup>5</sup> W. I. Awad and M. S. Hafez, *J. Org. Chem.* **26**, 2055 (1961).

The reactions performed may be divided into three groups: (i) reaction of hippuric acid azlactone (Ar = Ph) with substituted aromatics resulting in the following compounds: Table 1, *b*, *d*, *f*, *h*, *j*,<sup>2</sup> and *l*,<sup>4</sup> the yield decreasing in the substituent series F, Cl, Br, I; (ii) reactions of *p*-substituted hippuric acid azlactones with benzene (Ar' = Ph) resulting in the compounds *c*, *e*, *g*, *i*, *k*, *m*, and *n*, the yield markedly increasing in the series F, Cl, Br, I; (iii) reactions of *p*-substituted hippuric acid azlactones with substituted aromatics—only one of the many possible combinations pertaining to this group has as yet been tested—resulting in the compound *q*(2-*p*-nitrophenyl-5-*p*-methoxyphenyl-oxazole). *p*-Phenyl-substituted oxazoles (R = H, R' = Ph, or R = Ph, R' = H, or R = R' = Ph) obtained previously<sup>2,4</sup> are not included in the Table, but compounds *Va*, *Vj* and *Vi* are included so as to allow a comparison with the related compounds prepared in the present work.

The yields of the Friedel-Crafts stage are usually 50–70% while in the dehydration stage to oxazoles they are always over 80%. This reaction provides a convenient route to mono- or disubstituted 2,5-diaryloxazoles (V).

Starting from the readily accessible 2-phenyl-5-*p*-halo-phenyloxazoles obtained from hippuric acid azlactone and halo-benzenes, one can obtain additional oxazole derivatives by means of Grignard and Ullmann reactions. The organomagnesium derivatives obtained from the bromo-oxazoles (*Vf* and *Vg*) by entrainment with methyl iodide in ether yielded on carbonation the carboxylic acids (*Vo* and *Vp*). By heating the iodo-derivative with copper powder (*Vh*, R = H, R' = I), the yellow *p,p'*-bis-(2-phenyl-5-oxazolyl)-biphenyl (VI) was obtained in ca. 25% yield. Such analogs of sexiphenyl could be used as secondary scintillator solutes.



VI

#### Ultra-violet absorption spectra

Table 1 contains absorption data for cyclohexane solutions of the non-substituted 2,5-diphenyloxazole (*Va*), the mono-substituted compounds *Vb*–*Vp*, and the disubstituted 2,5-diaryloxazole (*Vq*). As in the previous papers, bands are denoted by letters A, B, etc. in the order of increasing frequencies, while individual vibrational peaks due to transitions from the fundamental state to vibrational sublevels of the same electronically excited state are indicated by A, A', A'', A'''. Absorption curves are presented in Figs. 1–4.

Considering first the monosubstituted 2,5-diaryloxazoles, it may be seen that with one and the same substituent in the *para* position of the 2-phenyl or 5-phenyl group (*b* and *c*, *d* and *e*, . . . , *l* and *m*), the spectra are nearly identical. This supports the idea that in a spectral classification as proposed in the previous paper,<sup>1</sup> the 2- and 5-positions of the oxazole nucleus should be considered as practically equivalent. The slight differences between such pairs are: (i) small shifts of peaks A and A'': 1–2  $m\mu$  for halo-substituted oxazoles,  $\lambda_{\max}$  being higher when the substituted phenyl is bound to the 2-position of the oxazole nucleus; 1–4  $m\mu$  for the methyl- or methoxy-substituted oxazoles,  $\lambda_{\max}$  being lower when the substituted phenyl is in the 2-position; (ii) slight differences between the extinction coefficients: in the series F, Cl, Br, I,

TABLE I. ABSORPTION MAXIMA OF OXAZOLES V IN CYCLOHEXANE

Groups in V		Absorption bands <sup>a</sup>										Peak A' (cm <sup>-1</sup> )		
V	2-R	5-R'	C	C'	B	B'	A	A'	A''	A'''	Literature <sup>b</sup>	Code <sup>b</sup>	Experimental	Calc.
	H	H	2.05	—	230s	—	302	310s	318	333s	C	A	$\bar{\nu}$	$\delta_{calc}$
a <sup>b</sup>	H	H	2.05	—	230s	—	302	310s	318	333s	223	303	31400	0
b	H	F	1.50	219	238s	—	302	307s	315	331s	—	—	31800	+400
c	F	H	1.65	230s	239s	—	302	308	315	331s	223	303	31800	+400
d	H	Cl	1.69	230s	243s	—	2.77	2.71	2.60	1.20	1.65	2.90	31200	-200
e	Cl	H	2.24	231s	243	—	308	313	322	337s	—	—	31000	-400
f	H	Br	1.59	230s	243s	—	2.95	2.88	2.86	1.35	1.98	4.10	31200	-200
g	Br	H	1.45	230s	244	—	308	314s	321	337s	—	—	31100	-300
h	H	I	1.63	231s	246	251	310	315	324	338s	226	307	30850	-550
i	I	H	1.48	—	247s	253	312	317s	325	341s	221	312	30750	-650
j <sup>c</sup>	H	Me	2.30	—	0.68	0.88	3.34	3.27	3.32	1.68	1.58	3.94	31200	-200
k	Me	H	1.72	230s	240s	—	305	311	318	333s	225	304	31400	0
l <sup>c</sup>	H	MeO	1.33	1.25	0.95	0.73	2.84	2.72	2.71	1.30	1.76	3.11	30750	-650
m	MeO	H	1.37	1.40	0.65	0.72	3.16	3.17	3.07	1.40	223	308	31100	-300
n	NO <sub>2</sub>	H	1.47	1.23	1.06	1.22	2.58	—	362	382	218	347	27600	-3800
o <sup>d</sup>	H	CO <sub>2</sub> H	2.33	—	240s	—	318	322	330	345s	—	—	30300	-1100
p <sup>d</sup>	CO <sub>2</sub> H	H	—	—	240s	—	322	325	335	350s	—	—	29800	-1600
q	NO <sub>2</sub>	MeO	—	—	1.35	0.56	2.17	—	2.17	1.23	—	—	26400	-5000

<sup>a</sup> Values of  $\lambda_{max}$  in  $m\mu$  (upper row) and  $\epsilon \cdot 10^{-4}$  (lower row) are given; s denotes shoulder.  
<sup>b</sup> Lit. ref.<sup>2</sup>  
<sup>c</sup> Lit. ref.<sup>4</sup>  
<sup>d</sup> Owing to the slight solubility in cyclohexane, no extinction coefficients may be given.

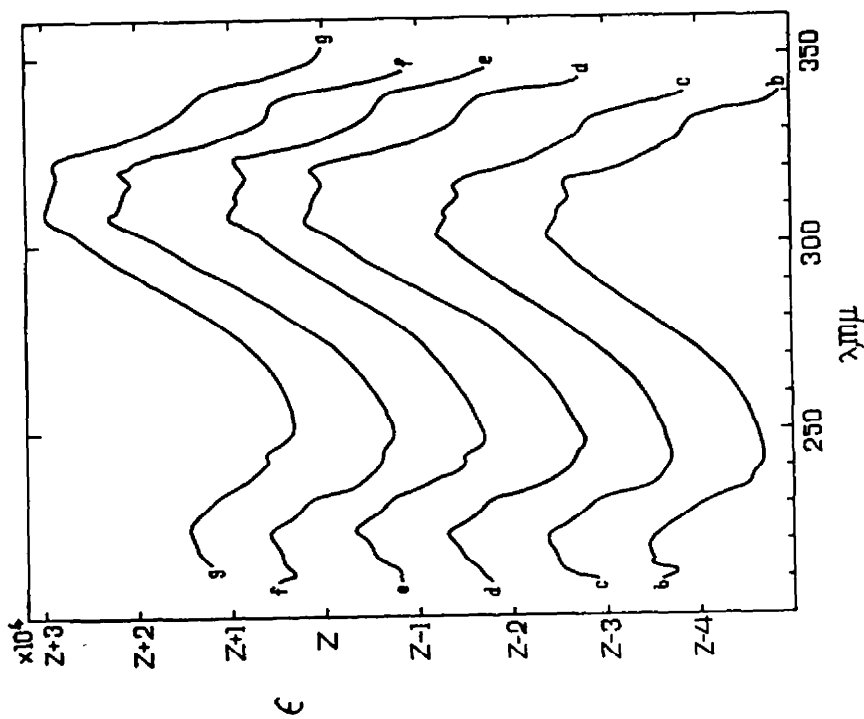


FIG. 1. Absorption spectra of oxazoles Vb ( $z = 5$ ); Vc ( $z = 4$ ); Vd ( $z = 3$ ); Ve ( $z = 2$ ); Vf ( $z = 1$ ); and Vg ( $z = 0$ ) in cyclohexane.

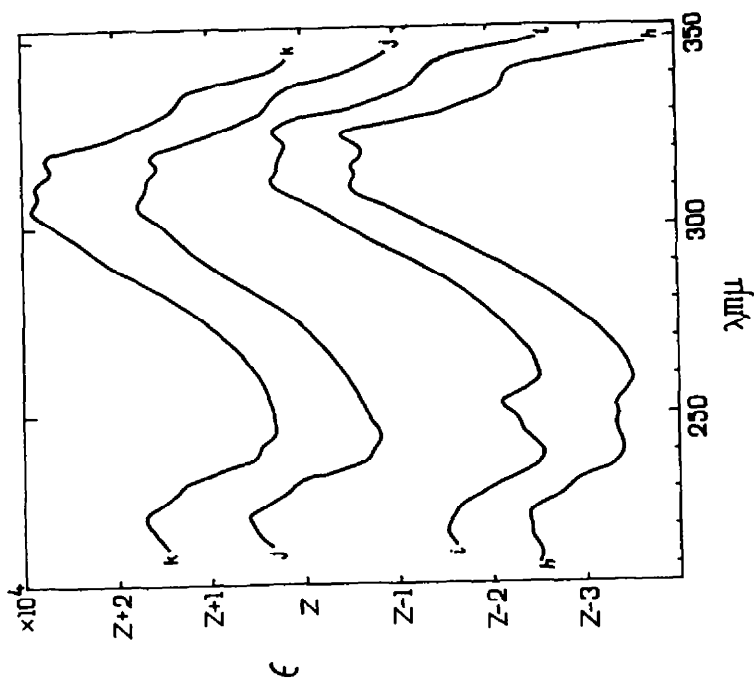


FIG. 2. Absorption spectra of oxazoles Vh ( $z = 4$ ); Vi ( $z = 3$ ); Vj ( $z = 1$ ); and Vk ( $z = 0$ ) in cyclohexane.

the intensity of peak A' relatively to the other vibrational peaks is decreasing in the 2-substituted oxazoles and increasing in the 5-substituted oxazoles, so that this peak appears only as a shoulder in the 5-substituted fluoro- and chloro-derivatives *b* and *d* and in the 2-substituted iodo-derivative *i*; in the same series, band B is only a shoulder in the 5-substituted oxazoles, but a peak in the 2-substituted oxazoles *e* and *g*.

Since the 2,5-diphenyloxazole group is both a good electron donor and a fairly

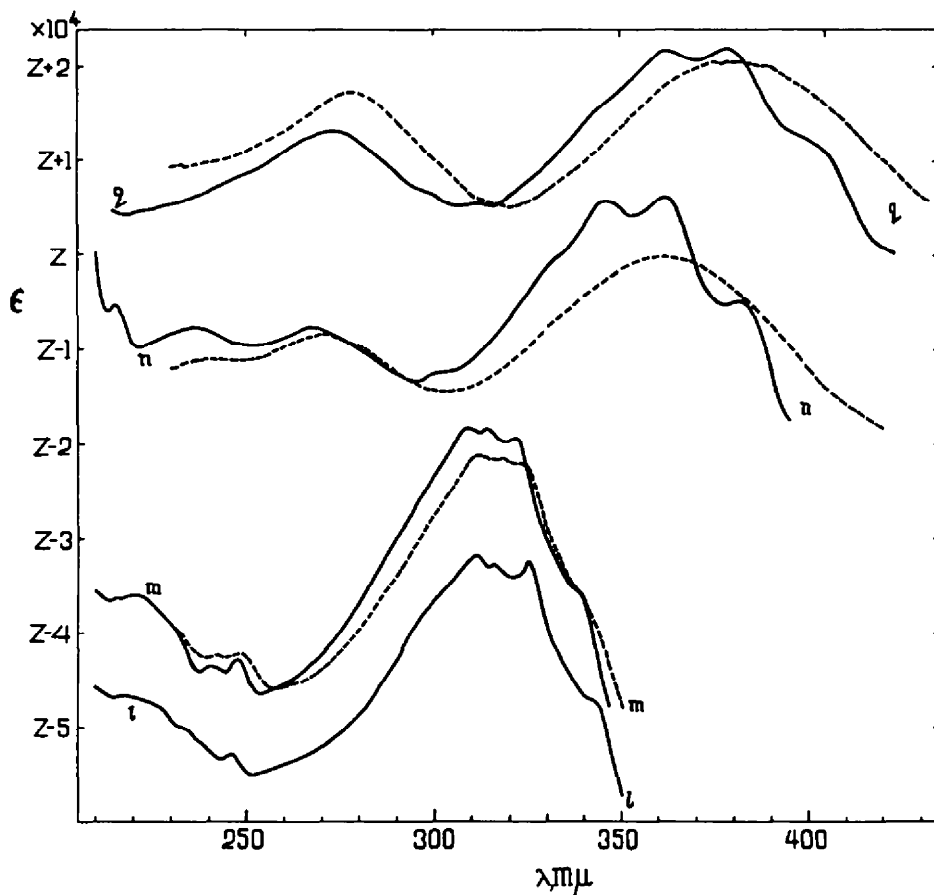


FIG. 3. Absorption spectra of oxazoles VI ( $z = 6$ ); Vm ( $z = 5$ ); Vn ( $z = 2$ ) and Vg ( $z = 0$ ) in cyclohexane (full line) and in dichloroethane (dashed line).

good electron acceptor, the A bands of *p*-substituted oxazoles Vb — Vo are all bathochromically shifted relative to the unsubstituted 2,5-diphenyloxazole Va, irrespective whether the substituent is electron-attracting or repelling, and whether it acts by inductive or conjugative effects. Thus no single correlation between the position of band A and Hammett's sigma constants of the substituents may be made. However, it may be seen that electron-attracting substituents cause larger bathochromic effects than donor substituents. Thus the methoxy group causes a shift of 6–9  $\mu\mu$  of peak A and of 3–7  $\mu\mu$  of peak A' (these are the two main peaks of band A, common to all oxazoles), while the shifts for the carboxy group are respectively 16–20 and 12–17  $\mu\mu$ , and those for the nitro group 43 and 44  $\mu\mu$ .

In the nitro-substituted oxazoles  $n$  and  $q$  no trace of  $A'$  is visible but in exchange  $A''$  is a peak, not a shoulder as in all other oxazoles. This gives the spectra of these oxazoles a characteristic aspect (a shoulder at  $300\text{ m}\mu$  of both these oxazoles is not included in Table 1).

A bathochromic effect of both A and B bands is observed in the series F, Cl, Br, I,

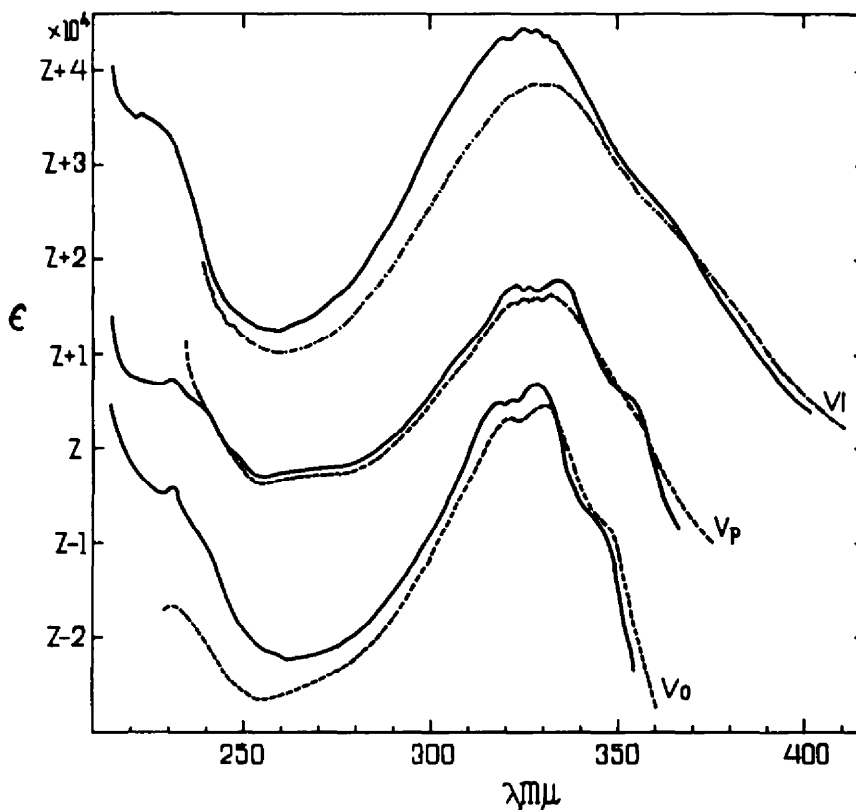


FIG. 4. Absorption spectra of oxazoles  $V_0$  ( $z = 3$ );  $V_p$  ( $z = 1$ ); and  $V_i$  ( $z = 0$ ) in cyclohexane (full line, arbitrary extinction units), in dichloroethane (dashed line) and in chloroform (dashed-dotted line).

while band C remains unaffected (in fact, band B is in  $V_a$ - $V_g$ ,  $V_i$  and  $V_j$  merely a structure detail on band C, but in the above series it emerges gradually till in the iodo-derivatives it is a clearly recognizable band).

The most marked bathochromic effect is observed in the nitro-methoxy-substituted oxazole V where peaks A and  $A''$  are shifted by  $60\text{ m}\mu$  (a hypochromic effect is also apparent). In this compound a push-pull is exerted on the  $\pi$ -electrons so that band A, which is the through-conjugation (internal charge-transfer) band, is much displaced towards longer wavelengths. This fact could be applied, with suitable donor and acceptor substituents (nitro-groups completely quench fluorescence<sup>6</sup>), to the

\* D. G. Ott, F. N. Hayes, E. Hansbury and V. N. Kerr, *J. Amer. Chem. Soc.* **79**, 5448 (1957).

preparation of better primary or secondary scintillator solutes, without having recourse to substituents with condensed aromatic nuclei that considerably lower the solubility.

A perturbational computation in the first and second approximation within the Hückel MO method was applied to the highest occupied molecular orbital (HOMO;  $e_+$ ) and to the lowest empty molecular orbital (LEMO;  $e_-$ ) of 2,5-diphenyloxazole. For this parent compound the energies  $\epsilon$  and the coefficients of the atomic orbitals in both *para* positions ( $c$  and  $c'$ ) are:<sup>7</sup>

$$\begin{array}{lll} \epsilon_-^\circ = \alpha - 0.583\beta & c_- = +0.443 & c_-' = +0.300 \\ \epsilon_+^\circ = \alpha + 0.503\beta & c_+ = +0.376 & c_+' = -0.299 \end{array}$$

For various substituents the following values of  $h_X$ , respectively  $k_{CX}$ , were used<sup>8</sup> in order to obtain  $\alpha_X = \alpha + h_X\beta$  and  $\beta_{C-X} = k_{CX}\beta$ : F (3; 0.7); Cl (2; 0.4); Br (1.5; 0.3); I (1; 0.25); CH<sub>3</sub> (2; 0.7); CH<sub>3</sub>O (2; 0.8). By treating the COOH and NO<sub>2</sub> substituents as three-atom systems with 4 $\pi$ -electrons, two occupied orbitals with very low energy and one empty orbital with low energy are obtained, therefore these substituents may be considered as atoms with one empty orbital; the following values for  $h_X$  and  $k_{CX}$  were used: NO<sub>2</sub> (-0.4; 0.7); COOH (-0.9; 0.8). The inductive effect on the neighbouring carbon atom is  $h_{C\alpha} = 1/20 h_X$  (in the case of the methyl group, however,  $h_{C\alpha} = -0.20$ ).

The shift of the A band caused by monosubstitution will thus be given by  $\delta$

$$\delta = (\epsilon_- - \epsilon_+) - (\epsilon_-^\circ - \epsilon_+^\circ) = (c_-^2 - c_+^2)h_{C\alpha}\beta + \left( \frac{c_-^2}{\epsilon_- - h_X} - \frac{c_+^2}{\epsilon_+ - h_X} \right) k_{CX}^2\beta$$

By employing a value<sup>7</sup>  $\beta = 30,000 \text{ cm}^{-1}$ , the values  $\delta_{\text{calc}}$  included in Table 1 were obtained. An inspection of the experimental and calculated values of  $\delta$  reveals that the effect of substitution is qualitatively well accounted for. The differences between the 2- and 5-positions, and the opposite effect of halogen substituents and of methyl groups is explained (theory predicts, and compounds *Vo* and *Vp* confirm, that electron-attracting substituents *para* to the 2-phenyl group should exert a stronger bathochromic effect than in the case of a 5-phenyl group), as is the generality of the bathochromic effect and the fact that nitro and carboxy groups exert by far the most pronounced influence.

In the case of the less soluble oxazoles, besides the spectra of cyclohexane solutions, spectra of dichloroethane solutions were also recorded (cf. Figs. 3 and 4). Bathochromic and hypochromic effects, and the loss of fine structure were noted in passing from the former to the latter solvent. In the case of the carboxylic acids (*Vo* and *Vp*) and of the product of the Ullman reaction (VI), the slight solubility in cyclohexane allowed no computation of the extinction coefficients in this solvent, therefore the only extinction coefficients available for these three compounds refer to dichloroethane or chloroform solution.

<sup>7</sup> Z. Simon and A. T. Balaban, *Studii si Cercetări Chim. Acad. R.P.R.* 11, 63 (1963); *Revue de Chimie Acad. R.P.R.* 7 (1962) in press.

<sup>8</sup> A. Streitwieser Jr., *Molecular Orbital Theory for Organic Chemists* Chaps. 5 and 8. J. Wiley, New York (1961).

## EXPERIMENTAL

Aroylation of glycine was effected<sup>1,2</sup> by making use of Steiger's procedure.<sup>3</sup> A solution of 1 mole aroyl chloride in dioxan was run simultaneously with 1 mole NaOH aq into a solution of glycine (2 moles in water-dioxan) and NaOH (1 mole) at 0°, then stirred for 1 hr longer and acidified (HCl). The *p*-substituted hippuric acid (I) was converted into an azlactone (II)<sup>10</sup> by dissolving it in hot acetic anhydride and evaporating at low pressure the acetic acid and excess acetic anhydride. Yields varied between 80–95% and the azlactones were used without further purification (but for the m.p. determination they were recrystallized from benzene).

Friedel-Crafts aroylaminoacetylations were performed by adding powdered anhydrous AlCl<sub>3</sub> gradually to a stirred mixture of azlactone and aromatic compound at 0–10°. The molar ratio azlactone: AlCl<sub>3</sub> was 1 : 3 except where specified. Benzene, bromobenzene, and iodobenzene were employed in excess (3–10 moles), but with fluorobenzene and chlorobenzene (3 moles) 1,2-dichloroethane was used as solvent. After 5 hr stirring at room temp, the mixture was hydrolysed. With benzene, the upper layer was washed (water and Na<sub>2</sub>CO<sub>3</sub> aq), then evaporated to dryness; with the other aromatics, ether was added and the precipitated ketone (III) was filtered off and washed with ether. For analysis the ketone was recrystallized.

*p*-Methylbenzoyl-aminomethyl phenyl ketone (IIIk) was obtained from the unstable 2-(*p*-tolyl)-5-oxazolone and benzene in 70% yield; m.p. 125° (from ethanol). Lit.<sup>11</sup> m.p. 125°.

*p*-Methoxybenzoyl-aminomethyl phenyl ketone (III<sub>l</sub>m) was obtained from 1 mole 2-(*p*-anisyl)-5-oxazolone m.p. 117° and excess benzene in the presence of 5 moles AlCl<sub>3</sub> in 80% yield; m.p. 140–141° (from ethanol). Lit.<sup>11</sup> m.p. 141°.

*p*-Fluorobenzoyl-aminomethyl phenyl ketone (IIIc) was prepared in 45% yield from 2-(*p*-fluorophenyl)-5-oxazolone, m.p. 118°, and benzene; m.p. 135–136° (from ethanol). Lit.<sup>12</sup> m.p. 134–135°.

*p*-Chlorobenzoyl-aminomethyl phenyl ketone (IIIe) was obtained in 54% yield from 2-(*p*-chlorophenyl)-5-oxazolone, m.p. 103°, and benzene; m.p. 152–153° (from ethanol). Lit.<sup>12</sup> m.p. 148°.

*p*-Bromobenzoyl-aminomethyl phenyl ketone (IIIg) was obtained in 59% yield from 2-(*p*-bromophenyl)-5-oxazolone, m.p. 121°, and benzene; m.p. 162° (from ethanol). Lit.<sup>12</sup> m.p. 164–165°.

*p*-Iodobenzoyl-aminomethyl phenyl ketone (IIIi) was prepared in 70% yield from 2-(*p*-iodophenyl)-5-oxazolone, m.p. 153°, and benzene; m.p. 165° (from ethanol). Lit.<sup>12</sup> m.p. 163–165°.

*p*-Nitrobenzoyl-aminomethyl phenyl ketone (III<sub>l</sub>n) was obtained in 42% yield from 1 mole 2-(*p*-nitrophenyl)-5-oxazolone, m.p. 119–120°, 4.5 moles AlCl<sub>3</sub> and excess benzene; m.p. 194° (from ethanol). Lit.<sup>11</sup> m.p. 197°.

*Benzoylaminomethyl p*-fluorophenyl ketone (IIIb) was prepared in 51% yield from 2-phenyl-5-oxazolone and fluorobenzene in dichloroethane; m.p. 151–152° (from ethanol). (Found: C, 70.37; H, 5.11; N, 5.32. C<sub>15</sub>H<sub>13</sub>FNO<sub>2</sub> requires: C, 70.03; H, 4.70; N, 5.45%).

*Benzoylaminomethyl p*-chlorophenyl ketone (III<sub>l</sub>d) was prepared in 52% yield from 2-phenyl-5-oxazolone and chlorobenzene in dichloroethane; m.p. 158–159° (from benzene). Lit.<sup>5</sup> m.p. 160°. (Found: C, 66.13; H, 4.44; Cl, 12.60; N, 4.84. Calc. for C<sub>15</sub>H<sub>11</sub>ClNO<sub>2</sub>: C, 65.82; H, 4.42; Cl, 12.95; N, 5.25%).

*Benzoylaminomethyl p*-bromophenyl ketone (III<sub>l</sub>f) was obtained in 50% yield from 2-phenyl-5-oxazolone and bromobenzene without solvent; m.p. 148–149° (from benzene). (Found: C, 56.76; H, 3.87; Br, 25.96; N, 4.69. C<sub>15</sub>H<sub>13</sub>BrNO<sub>2</sub> requires: C, 56.62; H, 3.80; Br, 25.11; N, 4.40%).

*Benzoylaminomethyl p*-iodophenyl ketone (III<sub>l</sub>h) was prepared in 22% yield from 2-phenyl-5-oxazolone and iodobenzene without solvent; m.p. 159° (from ethanol). (Found: C, 49.39; H, 3.44; I, 34.65; N, 3.62. C<sub>15</sub>H<sub>11</sub>INO<sub>2</sub> requires: C, 49.33; H, 3.31; I, 34.76; N, 3.84%).

*p*-Nitrobenzoyl-aminomethyl *p*-methoxyphenyl ketone (IIIq) was prepared in 15% yield from 1 mole 2-(*p*-nitrophenyl)-5-oxazolone in 4 moles anisole with 4 moles AlCl<sub>3</sub> at 50° for 1 hr; m.p. 168° (from ethanol). (Found: C, 61.42; H, 4.70; N, 9.00. C<sub>18</sub>H<sub>14</sub>N<sub>2</sub>O<sub>6</sub> requires: C, 61.14; H, 4.49; N, 8.91%).

<sup>3</sup> R. E. Steiger, *J. Org. Chem.* **9**, 396 (1944).

<sup>10</sup> E. Mohr and T. Geis, *Ber. Dtsch. Chem. Ges.* **41**, 478 (1908); E. Mohr and F. Stroschein, *Ibid.* **42**, 2521 (1909); E. Mohr, *J. Prakt. Chem.* **82**, 322 (1910).

<sup>11</sup> J. Lister and R. Robinson, *J. Chem Soc.* **101**, 1297 (1912).

<sup>12</sup> F. N. Hayes, B. S. Rogers and D. G. Ott, *J. Amer. Chem. Soc.* **77**, 1850 (1955).



The conversion of ketones (III) into oxazoles (IV) was performed by refluxing the crude dry ketones with 5 moles phosphorous oxychloride on the steam bath for 2 hr, and then pouring into water and filtering off the oxazole formed in 80–90% yield.

- 2-*p*-Fluorophenyl-5-phenyloxazole (IVc), m.p. 81° (from ethanol). Lit.<sup>18</sup> m.p. 81–82°.  
 2-*p*-Chlorophenyl-5-phenyloxazole (IVe), m.p. 116–117° (from ethanol). Lit.<sup>18</sup> m.p. 115–116°.  
 2-*p*-Bromophenyl-5-phenyloxazole (IVg), m.p. 165° (from ethanol). Lit.<sup>12</sup> m.p. 164–165°.  
 2-*p*-Iodophenyl-5-phenyloxazole (IVi), m.p. 131° (from ethanol). Lit.<sup>12</sup> m.p. 130–131°.  
 2-*p*-Tolyl-5-phenyloxazole (IVk), m.p. 75° (from pet. ether). Lit.<sup>11</sup> m.p. 77°.  
 2-*p*-Anisyl-5-phenyloxazole (IVm), m.p. 99–100° (from 80% ethanol). Lit.<sup>11</sup> m.p. 99°.  
 2-Phenyl-5-*p*-fluorophenyloxazole (IVb), m.p. 96–97° (from ethanol). (Found: C, 75.58; H, 4.75; N, 6.10. C<sub>15</sub>H<sub>10</sub>FNO requires: C, 75.48; H, 4.21; N, 5.85%),  
 2-Phenyl-5-*p*-chlorophenyloxazole (IVd), m.p. 105–106° (from ethanol). (Found: C, 70.54; H, 3.96; Cl, 13.89; N, 5.72. C<sub>15</sub>H<sub>10</sub>ClNO requires: C, 70.46; H, 3.94; Cl, 13.80; N, 5.48%).  
 2-Phenyl-5-*p*-bromophenyloxazole (IVf), m.p. 103–104° (from ethanol). (Found: C, 60.13; H, 3.58; Br, 26.21; N, 4.74. C<sub>15</sub>H<sub>10</sub>BrNO requires: C, 60.02; H, 3.35; Br, 26.22; N, 4.67%).  
 2-Phenyl-5-*p*-iodophenyloxazole (IVh), m.p. 110° (from ethanol). (Found: C, 52.02; H, 3.20; I, 37.63; N, 4.27. C<sub>15</sub>H<sub>10</sub>I NO requires: C, 51.90; H, 2.94; I, 36.55; N, 4.02%).  
 2-Phenyl-5-*p*-anisylloxazole (IVI), m.p. 79–80° (from ethanol) was prepared from the previously described\* benzoylaminomethyl *p*-anisyl ketone. (Found: C, 75.69; H, 5.58; N, 5.63. C<sub>16</sub>H<sub>13</sub>NO<sub>2</sub> requires: C, 75.29; H, 5.48; N, 5.57%).  
 2-*p*-Nitrophenyl-5-phenyloxazole (IVn), m.p. 202° (from ethanol). Lit.<sup>11</sup> m.p. 202–204°.  
 2-*p*-Nitrophenyl-5-*p*-anisyl-oxazole (IVq), m.p. 162° (from ethanol). (Found: C, 64.95; H, 4.28; N, 9.76. C<sub>16</sub>H<sub>12</sub>N<sub>2</sub>O<sub>4</sub> requires: C, 64.86; H, 4.08; N, 9.96%).

*Preparation of 2-phenyl-5-oxazolylcarboxylic acid (Vo) and 5-phenyl-2-oxazolylcarboxylic acid (Vp) by Grignard reaction.* Mg turnings (1.8 g, 0.08 g-atoms) activated by heating to 500° in the presence of iodine, 6 g (20 mmoles) bromo-oxazole (Vf, respectively Vg) and 40 ml abs. ether were slowly treated during 8 hr with a solution of 7.8 g (60 mmoles) methyl iodide in 40 ml anhydrous ether at reflux temp with stirring. As the reaction proceeded, the difficultly soluble oxazolylmagnesium bromide separating as a brownish oil, and was kept in solution by the addition of 30 ml tetrahydrofuran. After completion of the reaction, dry CO<sub>2</sub> was added with stirring and cooling. After hydrolysis with dil H<sub>2</sub>SO<sub>4</sub>, the filtered organic layer was extracted with 5% NaOH aq, the alkaline extract filtered and acidified yielding the acids: (Vo), white-yellow powder m.p. (crude) 242°, and after recrystallization from acetone-water m.p. 244–245°. (Found: C, 71.98; H, 3.76; N, 5.59. C<sub>16</sub>H<sub>11</sub>NO<sub>2</sub> requires: C, 72.44; H, 4.18; N, 5.28%); yield about 25%; and (Vp), m.p. 248° (from dil ethanol) is pale yellow (Found: C, 71.84; H, 4.48; N, 5.50. C<sub>16</sub>H<sub>11</sub>NO<sub>2</sub> requires: C, 72.44; H, 4.18; N, 5.28%).

*Preparation of p,p'-bis-(2-phenyl-5-oxazolyl)-biphenyl (VI) by Ullmann reaction.* The iodo-oxazole (Vh) was mixed thoroughly with Cu powder and heated on a Wood metal bath at 120° for 1 hr. The melt soon resolidified and was then heated at ca. 250° for 2 hr. After grinding, the product was extracted with hot benzene, and ethanol was added to the concentrated extract. The yellow precipitate was recrystallized from benzene-ethanol, m.p. 312°. The compound is very slightly soluble in ethanol or cyclohexane; in benzene it presents a strong fluorescence. The Ullmann reaction was also attempted in dimethylformamide but the results were not satisfactory. (Found: N, 12.01; C<sub>16</sub>H<sub>11</sub>NO<sub>2</sub> requires: N, 12.49%).