In order to determine the possible effects of adventitious oxygen on the rate of decomposition, a benzene solution of *cis*-$Et(CH_3)_2AuPPh_3$ containing *tert*-butylbenzene as an internal standard was placed in an nmr tube, rigorously degassed three times using freeze–pump–thaw cycle, and then sealed. The rates of decomposition were followed by nmr and shown to be the same within ±10% of comparable reactions carried out in air. The rates of thermal decomposition carried out in decalin solutions were difficult to reproduce even after careful purification and manipulation of the solvent in the absence of air. The formation of propane and ethane, however, showed little variation. The effect of peroxidic contaminants was examined by the deliberate addition of *tert*-butyl hydroperoxide or *tert*-butyl peroxyoxalate and will be reported separately at a later time. Water at low concentrations had no noticeable effect on the rate. The addition of up to equimolar amounts of CH_3AuPPh_3 also exerted a minimal effect on the rate of decomposition of *cis*-$Et(CH_3)_2AuPPh_3$.

Analysis. The gold content was determined gravimetrically by digesting the sample in concentrated sulfuric acid.[20] Other methods involving iodometry or complete thermolysis followed by gravimetry did not afford accurate analyses.

The hydrocarbon gases were analyzed by gas chromatography (hydrogen flame, Aerograph 500, 50 cm Porapak Q column at 90° or a 20 ft ODPN column). Quantitative analysis was effected by the internal standard method after careful calibration under reaction conditions. The latter was especially important when solvent was present due to differential solubility of gases. The analyses were reproducible to ±2%.

The molecular weights in benzene solutions were carried out with a Mechrochrom 301A vapor pressure osmometer at 37° using benzil or benzophenone as calibrant. The pmr spectra were obtained on a Varian HA 100 spectrometer with variable temperature control or routinely on a Varian EM-360 spectrometer. All chemical shifts were measured (±0.05 ppm) relative to external TMS. Phosphorus nmr spectra were taken on a Varian XL-100 Fourier transform spectrometer using H_3PO_4 as an external reference.

(20) C. L. Wilson and D. W. Wilson, "Comprehensive Analytical Chemistry," Vol. IC, Elsevier, Amsterdam, 1961, p 390.

Acknowledgment. We wish to thank the National Science Foundation for their financial support of this work and Dr. R. S. Tobias for generously providing us with a sample of pure $(CD_3)_3AuPPh_3$.

The Cornforth Rearrangement

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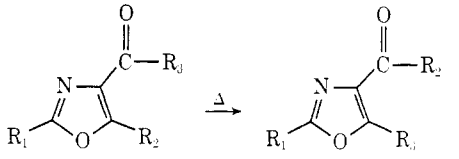
Contribution from the Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712. *Received March 12, 1974*

Abstract: The rates of Cornforth rearrangements of 2-aryl-5-methoxyoxazole-4-carboxylic amides have been studied. Variation of substituents in the 2-phenyl group indicates that a small positive charge develops at the adjacent carbon on passing to the transition state. Similar variation of substituents in a phenyl group attached to the amide nitrogen indicates that a similar small negative charge develops in the amide moiety. The effect of changes in the solvent also indicates that the transition state is not strongly polar. Either the transition state must occur early in the reaction or the open chain intermediate must be less polar than a classical zwitterionic structure would suggest.

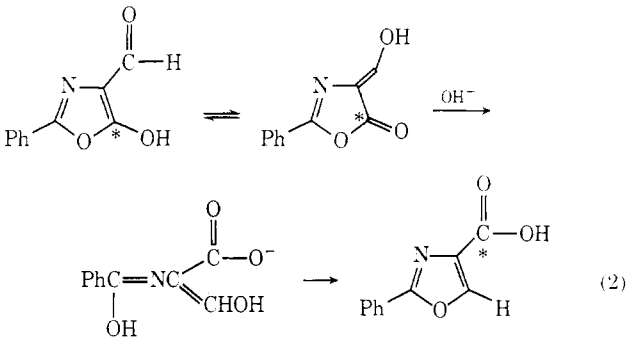
The thermal rearrangement of 4-carbonyl substituted oxazoles was first observed by Cornforth.[1] The general reaction is given in eq 1.



(1)

1 2

An analogous reaction, the base-induced rearrangement of 4-hydroxymethylene-5-oxazolones (*i.e.*, **1**, R_2 = OH; R_3 = H) to oxazole-4-carboxylic acids, has been investigated by isotopic labeling experiments.[2] When the carbonyl carbon of the oxazolone ring was labeled with carbon-14 and the compound was subjected to treatment with base, the rearranged oxazole-4-carboxylic acid was labeled only at the carboxyl carbon atom. The authors propose initial attack of hydroxide ion at the 2-position of the oxazolone ring with subsequent ring opening to **3** and ring closure to yield the ^{14}C labeled acid (eq 2).



(2)

3

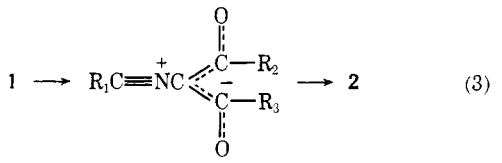
* = carbon-14

The thermal rearrangement of 4-carbonyl substituted 5-oxazolones to oxazoles has been studied for its synthetic utility since the oxazoles produced are intermediates in the synthesis of substituted amino acids.[3]

The mechanisms which have been proposed[2,3c,4] are interrelated in that they involve the ring opening of the oxazole or oxazolone derivative to a zwitterionic inter-

(1) J. W. Cornforth in "The Chemistry of Penicillin," Princeton University Press, Princeton, N. J., 1949, p 700.
(2) C. G. Stuckwisch and D. D. Powers, *J. Org. Chem.*, **25**, 1819 (1960).
(3) (a) W. Steglich and G. Hofle, *Chem. Ber.*, **102**, 883, 899 (1969); (b) *Tetrahedron Lett.*, 4727 (1970); (c) *Chem. Ber.*, **104**, 1408 (1971).
(4) M. J. S. Dewar, "Electronic Theory of Organic Chemistry," Oxford University Press, Oxford, 1949.

mediate **3** or **4** with subsequent ring closure to the rearranged product **2** (eq 3). Intermediate **4** can be con-



(3)

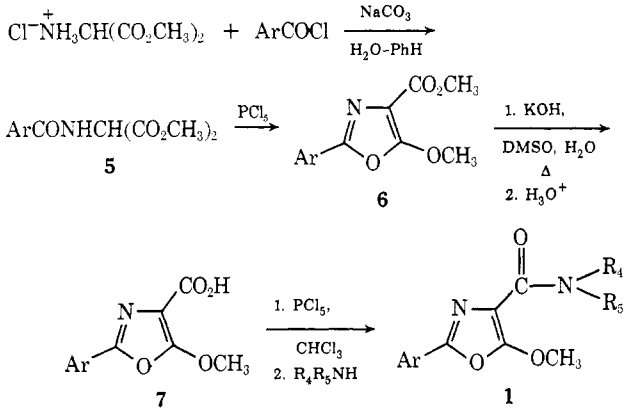
4

sidered to be a stabilized nitrile ylide. Experimental[5] and theoretical[6] studies concerning this rearrangement have provided us with an insight into the nature of the mechanism and the intermediate **4**.

Results and Discussion

This paper is concerned with the effects of various solvents and substituents on the rate of the rearrangement of the oxazoles **1** (R_1 = Ar–, R_2 = $-OCH_3$, R_3 = $-NR_{4,5}$; R_4 and R_5 are various alkyl and aryl groups (see Table II)). The synthesis of the oxazole-4-carboxamides (**1**) is outlined in Scheme I.[8] All of the steps in

Scheme I



5–7, a, Ar = *p*-CH_3OPh e, Ar = *p*-FPh
b, Ar = *p*-CH_3Ph f, Ar = *p*-BrPh
c, Ar = *p*-*t*-BuPh g, Ar = *m*-BrPh
d, Ar = Ph h, Ar = *p*-CF_3Ph

the above sequence are straightforward with the exception of the hydrolysis of the ester **6** to the acid **7**. The usual methods for hydrolyzing esters (*e.g.*, aqueous KOH, KOH in CH_3OH, toluenesulfonic acid in benzene, CH_3SO_3H–HCO_2H, etc.) were unsuccessful in our hands, only unidentified products being formed. When the ester **6** reacted with 3 equiv of KOH in ethanol an oxazole-4-carboxylic acid salt separated from the solution. Treatment of this with acid gave in 80% yield an analog of **7** in which the 5-methoxy function had been replaced by an ethoxy group. This presumably occurs by a Michael-type addition of ethoxide ion or ethanol to the 5-position of the oxazole ring with subsequent expulsion of methoxide or methanol. This unusual reaction of **6** is now being examined with other nucleophiles.

(5) For a preliminary report of this work see M. J. S. Dewar, P. A. Spanninger, and I. J. Turchi, *J. Chem. Soc., Chem. Commun.*, 925 (1973).

(6) Theoretical studies of the Cornforth rearrangement by the MINDO/3 method[7] are in progress.

(7) R. Bingham, M. J. S. Dewar, and D. H. Lo, to be submitted for publication.

(8) For the synthesis of dimethyl aminomalonate hydrochloride see "Organic Syntheses," Collect. Vol. V, Wiley, New York, N. Y., 1973, p 376.

The hydrolysis of **6** to **7** was finally achieved using aqueous potassium hydroxide in the presence of DMSO (see the Experimental Section).

In a preliminary communication[5] we reported the changes in rate of rearrangement of **1** → **2** with changes in the solvent and in the substituent, Ar, in **1** (R_2 = Ar, R_2 = OCH_3, R_3 = $-N(Ph)CH_3$). These results are shown in Tables I and II. It will be seen that in aprotic

Table I. Rate Constants for the Disappearance of **1** (R_1 = Ph, R_2 = OCH_3, R_3 = $N(Ph)CH_3$) in Various Solvents at 95.3 ± 0.1°

Solvent	Dielectric constant (25°)	10^5k, sec^{-1}
Dimethyl sulfoxide	46.60	9.04 ± 0.12
Nitrobenzene	34.82	6.59 ± 0.07
o-Dichlorobenzene	9.93	6.30 ± 0.07
Chlorobenzene	5.62	5.92 ± 0.04

Table II. Rate Constants for the Disappearance of 2-Aryl-5-methoxyoxazole-4-carboxamides (**1**) in Nitrobenzene at 95.3 ± 0.1°

	R_1	R_2	R_3	10^5k, sec^{-1}
1a	*p*-CH_3OPh–	$-OCH_3$	$-N(Ph)CH_3$	34.80 ± 0.5
b	*p*-CH_3Ph–	$-OCH_3$	$-N(Ph)CH_3$	13.40 ± 0.2
c	*p*-*t*-BuPh–	$-OCH_3$	$-N(Ph)CH_3$	13.40 ± 0.2
d	Ph–	$-OCH_3$	$-N(Ph)CH_3$	6.59 ± 0.07
e	*p*-FPh–	$-OCH_3$	$-N(Ph)CH_3$	4.12 ± 0.03
f	*p*-BrPh–	$-OCH_3$	$-N(Ph)CH_3$	2.54 ± 0.03
g	*m*-BrPh–	$-OCH_3$	$-N(Ph)CH_3$	1.63 ± 0.03
h	*p*-CF_3Ph–	$-OCH_3$	$-N(Ph)CH_3$	1.07 ± 0.01
i	Ph–	$-OCH_3$	$-NHPh$-*p*-CF_3	24.90 ± 0.2
j	Ph–	$-OCH_3$	$-NHPh$-*m*-CF_3	22.70 ± 0.2
k	Ph–	$-OCH_3$	$-NHPh$-*m*-Cl	21.60 ± 0.3
l	Ph–	$-OCH_3$	$-NHPh$	15.70 ± 0.2
m	Ph–	$-OCH_3$	$-NHPh$-*p*-CH_3	13.80 ± 0.1
n	Ph–	$-OCH_3$	$-NHPh$-*p*-OCH_3	13.40 ± 0.3
o	Ph–	$-OCH_3$	$-NHCH_3$	7.86 ± 0.10
p	Ph–	$-OCH_3$	$-NH$-*t*-Bu	5.34 ± 0.08
q	Ph–	$-OCH_3$	$-N(CH_3)_2$	1.07 ± 0.02

solvents the rate changes little with the polarity of the solvent, suggesting that the transition state is not much more polar than the ground state. However, when **1** (R_1 = *p*-CF_3Ph–, R_2 = $-OCH_3$, R_3 = $-N(Ph)CH_3$) is isomerized to **2** (R_1 = *p*-CF_3Ph–, R_2 = $-N(Ph)CH_3$, R_3 = $-OCH_3$) in the protic solvent, benzyl alcohol, the rate (2.11×10^{-5} sec^{-1}) is double that for the same reaction in nitrobenzene (1.07×10^{-5} sec^{-1}) even though the dielectric constant for benzyl alcohol (ϵ 13.4) is only one-third that of nitrobenzene (ϵ 34.8). The rate increase in the protic solvent suggests that a developing negative charge in the transition state is stabilized by hydrogen bonding to the solvent.

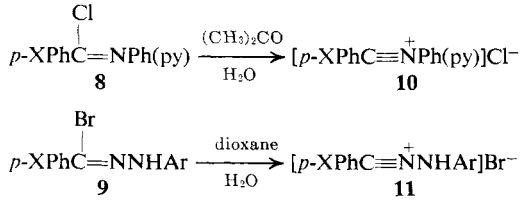
The effect of substituents on the rate of the rearrangement of **1** to **2** is shown in Table II. We have now extended the kinetic study to nine additional substituted oxazole-4-amides **1i–q**.

Each reaction was followed for at least two half-lives of the starting material and obeyed first-order kinetics throughout. All the reactions are irreversible.

As previously reported,[5] a plot of log *k* *vs.* σ^+ for the rearrangement of compounds **1a–h** was linear (r = 0.976) with $\rho^+ = -1.16 \pm 0.11$.

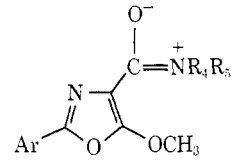
The negative value of ρ^+ implies that some electron deficiency develops at the 2-position in the oxazole ring in passing from **1** to the transition state. At the same time the rather small magnitude of ρ^+ implies that no strong positive charge can develop at this position in the transition state. Preliminary results of our theoretical studies support this conclusion.[6]

This small negative value for the reaction constant is, however, not at variance with the results of Ugi, *et al.*,[9] and Scott and Butler[10] in their study of the kinetics of the solvolysis of diarylimidic halides (**8**) and *N*-arylhydrazidic halides (**9**), respectively. For the solvolysis of **8** in aqueous acetone, $\rho = -1.2 \pm 0.1$, while for the solvolysis of **9** in aqueous dioxane $\rho = -0.93$ for variation in the substituent X. Despite the small magnitude of the reaction constant, nitrilium ions seem to be intermediates in these solvolyses. The small magnitude of ρ is probably due to delocalization of the positive charge in the transition state leading to **10** or **11**.



The rates of rearrangement of **1i–n** provide information concerning the effect of the *N*-aryl substituent. Here a plot of log *k* *vs.* σ was linear (r = 0.997) with $\rho = 0.34 \pm 0.01$. The positive value of ρ indicates an increase in negative charge at the amide group in passing from **1** to the transition state. The small magnitude of ρ is probably due to several factors. As is evident from the results above, very little charge separation is present in the transition state. Furthermore, the large distance of the substituent from the charged site would tend to attenuate any interaction between them.

We next studied the effect on the rate of the reaction of varying the alkyl and phenyl groups attached to the amide nitrogen (compounds **1d** and **1o–q**). It can be seen that increasing alkyl substitution decreases the rate of the isomerization of **1** to **2**. The decrease in the rate on passing from electron withdrawing to electron releasing substituents could be due, in part, to a greater importance of the resonance structure **12** in the case of



12

the electron releasing substituents, resulting in a decrease of the ground state energy of **1**. However, it is more likely that electron releasing substituents on the amide nitrogen hinder the development of negative charge in the transition state leading to **4**, by an inductive or field effect.

The results of our kinetic study imply that the transition state leading to the intermediate **4** is not strongly polar. The charge distributions calculated by MINDO/3 for the transition state and for **4** are in complete accord with this conclusion. The carbenoid structure for **4**, which we suggested earlier,[5] must be ruled out on the basis of our calculations. The charge distribution in **4** precludes a satisfactory classical representation of this species. Furthermore, the calculations show that this transition state occurs early in the reaction. These calculations will be reported in full elsewhere.

The effect of temperature on the rate of the rearrangement of **1h** to **2h** was studied in nitrobenzene and *o*-dichlorobenzene. The rate constants gave linear Arrhenius plots. The rate constants and activation parameters are listed in Table III.

Table III. Rate Constants and Activation Parameters for the Disappearance of 2-(*p*-Trifluoromethylphenyl)-5-methoxy-4-(*N*-phenyl-*N*-methyl)oxazolecarboxamide, **1h**, in Nitrobenzene and *o*-Dichlorobenzene

Temp, °C	10^5k, sec^{-1}	$\Delta H^{\pm}$, kcal/mol	$\Delta S^{\pm}$, eu
	In Nitrobenzene		
96.0	1.07 ± 0.01		
108.9	4.11 ± 0.03	28.2	−5.3
116.9	8.79 ± 0.03		
125.4	19.8 ± 0.5		
	In *o*-Dichlorobenzene		
96.0	1.04 ± 0.01		
108.9	3.99 ± 0.04	28.2	−5.4
116.9	8.45 ± 0.03		
125.4	19.3 ± 0.2		

The small negative value for the entropy of activation ($\Delta S^{\pm} = -5.3$ eu) implies that the transition state is slightly more constrained than the reactant. This seems at variance with the proposed mechanism because if ring opening were the rate determining step, a positive $\Delta S^{\pm}$ should be observed. A possible explanation of this unexpected observation is that in the ground state the 2-aryl and the 4-carbonyl substituents can rotate relatively freely while in the transition state some of this rotational freedom is lost due to the tendency of the

(9) I. Ugi, F. Beck, and U. Fetzer, *Chem. Ber.*, **95**, 126 (1962).
(10) F. L. Scott and R. N. Butler in "Carbonium Ions," Vol. IV, G. A. Olah and P. v. R. Schleyer, Ed., Wiley, New York, N. Y., 1973, pp 1680–1686, and references cited therein.

Table IV. Melting Points, Mass Spectral Data, and Elemental Analyses for Compounds **1**, **2**, **5**, and **6**

Compound	Mp, °C	Mass Spectra (relative intensity)	Calcd, % C	Calcd, % H	Found, % C	Found, % H
1a	149–150	338 (67), 204 (40), 173 (100), 146 (47), 77 (24)	67.45	5.36	67.33	5.50
b	160–161	322 (100), 216 (39), 188 (43), 146 (84), 119 (27)	70.79	5.63	70.62	5.72
c	84–85	364 (33), 258 (12), 173 (100), 146 (53), 116 (11)	72.51	6.64	72.79	6.71
d	100–101	308 (100), 277 (14), 202 (70), 174 (73), 146 (45)	70.13	5.19	70.24	4.99
e	138–139	326 (100), 220 (34), 173 (87), 146 (60), 123 (60)	66.25	4.63	66.43	4.69
f	161–162	388 (88), 386 (90), 280 (22), 173 (100), 146 (57)	55.83	3.90	56.08	4.06
g	167–168	388 (92), 386 (92), 280 (11), 173 (100), 146 (34)	55.83	3.90	56.03	3.99
h	120–121	376 (13), 242 (17), 214 (23), 173 (100), 146 (77)	60.64	4.02	60.48	3.94
i	133–135	362 (100), 330 (94), 274 (22), 248 (30), 202 (30)	59.67	3.62	59.89	3.52
j	105–106	362 (100), 330 (71), 274 (27), 248 (32), 202 (25)	59.67	3.62	59.49	3.42
k	112–113	330 (27), 328 (72), 296 (45), 174 (40), 77 (100)	62.11	3.99	62.37	3.83
l	125–126	294 (78), 262 (100), 206 (21), 174 (25), 77 (64)	69.38	4.79	69.24	4.75
m	129–130	308 (100), 277 (17), 276 (18)	70.12	5.23	70.30	5.34
n	115–116	325 (22), 324 (100), 292 (99), 277 (18)	66.66	4.97	66.65	4.82
o	70–71	232 (100), 200 (25), 172 (13.6), 105 (65)	62.06	5.21	62.12	5.13
p	106–107	274 (25), 218 (95), 186 (67), 105 (100), 77 (37)	65.68	6.61	65.70	6.50
q	57–58	246 (100), 202 (18), 174 (22), 105 (68), 77 (60)	63.40	5.73	63.51	5.65
2a	100–101	338 (50), 204 (20), 173 (100), 146 (33), 135 (20)	67.45	5.36	67.61	5.29
b	88–89	322 (100), 216 (17), 188 (17), 173 (60), 146 (33)	70.79	5.63	70.62	5.80
c	49–50	364 (39), 258 (21), 173 (100), 146 (60)	72.51	6.64	72.38	6.49
d	51–52	308 (50), 202 (24), 174 (32), 173 (74), 146 (100)	70.13	5.19	69.92	5.43
e	93–94	326 (48), 192 (39), 173 (80), 146 (70), 123 (100)	66.25	4.63	65.98	4.74
f	114–115	388 (13), 386 (12), 252 (13), 183 (15), 173 (100)	55.83	3.90	55.63	3.70
g	116–117	388 (100), 386 (88), 355 (5), 173 (20), 146 (13)	55.83	3.90	55.62	3.85
h	109–110	376 (79), 270 (26), 242 (23), 146 (76)	60.64	4.02	60.40	4.12
i	162–163	362 (100), 330 (94), 248 (37), 202 (39), 174 (42)	59.67	3.62	59.68	3.53
j	122–123	362 (47), 330 (100), 248 (32), 202 (28), 105 (79)	59.67	3.62	59.40	3.72
k	136–137	330 (37), 328 (100), 296 (77), 261 (53), 202 (40)	62.11	3.99	61.98	3.79
l	105–106	294 (31), 262 (27), 219 (100), 191 (59), 178 (27)	69.38	4.79	69.55	4.90
m	146–147	308 (77), 276 (100), 220 (13), 105 (58)	70.12	5.23	69.93	4.99
n	107–108	324 (60), 293 (28), 292 (100), 277 (19)	66.66	4.97	66.39	5.11
o	139–140	232 (54), 207 (36), 172 (32), 105 (100), 77 (49)	62.06	5.21	61.97	5.15
p	66–67	274 (38), 218 (95), 186 (58), 105 (100), 77 (37)	65.68	6.61	65.80	6.70
q	44–45	246 (70), 202 (20), 174 (33), 105 (100), 77 (47)	63.40	5.73	63.21	5.81
5a	112–113	281 (5), 210 (15), 135 (53), 123 (100), 95 (22)	55.49	5.38	55.61	5.43
b	122–123	265 (9), 206 (10), 119 (100), 91 (26)	58.86	5.70	58.78	5.69
c	67–69	307 (5), 292 (10), 248 (10), 161 (100)	62.53	6.89	62.76	6.91
d	95–96	251 (2), 191 (83), 174 (22), 145 (70), 104 (100)				
e	105–106	269 (2), 210 (25), 123 (100), 95 (26)	53.51	4.50	53.48	4.49
f	157–158	331 (3), 329 (3), 185 (93), 183 (100), 155 (15)	43.66	3.66	43.88	3.59
g	108–109	331 (3), 329 (3), 272 (22), 185 (96), 183 (100)	43.66	3.66	43.52	3.54
h	133–134	319 (0.5), 260 (17), 173 (100), 145 (28)	48.91	3.79	48.72	3.85
6a	119–120	263 (47), 136 (56), 135 (100), 107 (29), 92 (51)	59.31	4.98	59.52	5.02
b	130–131	247 (37), 187 (17), 119 (100), 97 (19), 91 (22)	63.15	5.30	63.08	5.44
c	124–125	289 (29), 274 (10), 173 (15), 161 (100), 146 (21)	66.42	6.62	66.24	6.61
d	98–99	233 (22), 173 (16), 146 (12), 105 (100), 77 (33)				
e	106–107	251 (24), 191 (10), 123 (100), 95 (19)	57.35	4.01	57.31	4.02
f	128–129	313 (23), 311 (23), 251 (11), 185 (96), 183 (100)	46.18	3.23	45.95	3.26
g	133–135	313 (31), 311 (32), 251 (14), 185 (94), 183 (100)	46.18	3.23	46.22	3.34
h	114–115	301 (27), 241 (11), 173 (100), 145 (29)	51.84	3.35	51.75	3.27

substituents to become coplanar with the developing charged centers.

Attempts to trap the intermediate **4** have so far been unsuccessful. When the ester **6a** was refluxed in xylene in the presence of dimethyl acetylenedicarboxylate or diphenylacetylene, none of the expected 1,3 dipolar addition product was observed and the starting material **6a** was recovered almost quantitatively.[11] Similar results were obtained when **6a** was heated in the presence of piperidine, isobutyl alcohol, or benzyl alcohol. It has also been reported that the nitrile ylide intermediate from the rearrangement of 4-carbonyl substituted 5-oxazolones could not be trapped with *tert*-butyl alcohol or maleonitrile.[3c] These unsuccessful experiments suggest that the activation energy for collapse of the intermediate **4** to **2** is small.

(11) To demonstrate the ability of **6** to rearrange, the ester **6** (R_1 = *p*-CF_3Ph–, R_2 = $-OCH_3$, R_3 = $-OCD_3$) was prepared. This compound rearranged to **6** (R_1 = *p*-CF_3Ph–, R_2 = $-OCD_3$, R_3 = $-OCH_3$) at 96.0° in nitrobenzene. The isomerization was reversible with a rate constant $k_f = k_r = 2.5 \times 10^{-5}$ sec^{-1} ($K_{eq} = 1$).

Experimental Section

Melting points are uncorrected. Nmr spectra were recorded on a Varian A-60 instrument using solutions approximately 15% w/v in deuteriochloroform. Ir spectra were determined with a Beckman IR-8 spectrophotometer (KBr disk). Mass spectra were measured with 70 eV electrons. Elemental analysis was carried out by Galbraith Laboratories, Knoxville, Tenn.

General Procedure for the Preparation of the Dimethyl Arylamidomalonates, 5a–h. To a mixture of dimethyl aminomalonate hydrochloride (15.0 g, 0.082 mol), anhydrous sodium carbonate (8.7 g, 0.082 mol), water (30 ml), and benzene (100 ml) at 0°, the corresponding acid chloride (0.082 mol) was added dropwise with stirring. The ice bath was then removed and stirring continued at room temperature for 12 hr. The benzene layer was separated, dried over $MgSO_4$, and evaporated to dryness, and the solid product was recrystallized from methanol. Yields ranged from 85 to 95%. See Table IV. Ir: **5a–h**, 3305–3345 (s), 1640–1660 cm^{-1} (s). Nmr: **5a–h**, τ 1.8–3.3 (m, aromatic and NH), 4.5–4.7 (d, 1 H, CH),

6.1–6.2 (s, 6 H, $-OCH_3$); also **5a**, 6.15 (s, 3 H, *p*-CH_3OPh); **5b**, 7.60 (s, 3 H, *p*-CH_3Ph–); **5c**, 8.65 (s, 9 H, *p*-*t*-BuPh–).

General Procedure for the Preparation of the Methyl 2-Aryl-5-methoxyoxazole-4-carboxylates. A mixture of the dimethyl arylamidomalonate (0.07 mol), phosphorus pentachloride (14.6 g, 0.07 mol), and dry chloroform (50 ml) was refluxed, the reaction time depending on the aryl substituent, (*viz.*, *p*-CH_3OPh–, *p*-CH_3Ph–, *p*-*t*-BuPh, Ph, 30 min; *p*-FPh–, 90 min; *p*-BrPh–, *m*-BrPh–, 24 hr; *p*-CF_3Ph–, 5 days (14 hr in refluxing toluene)). After removal of the solvent *in vacuo* the residue was dissolved in ether (100 ml), poured into water (50 ml), and neutralized with Na_2CO_3. The ether layer was separated and the water layer extracted twice with ether (50 + 50 ml). The combined ether layers were dried ($MgSO_4$). After evaporation to dryness the residue was recrystallized from methanol. Yields ranged from 40 to 60%. Ir: **6a–h**, 1700–1720 (s), 1600–1620 cm^{-1} (s). Nmr: **6a–h**, τ 1.8–3.3 (m, aromatic protons), 5.6–5.8 (s, 3 H, ring methoxyl), 6.0–6.2 (s, 3 H, ester methoxyl); **6a**, 6.10 (s, 3 H, *p*-CH_3OPh); **6b**, 7.62 (s, 3 H, *p*-CH_3Ph–); **6c**, 8.65 (s, 9 H, *p*-*t*-*Bu*Ph–).

General Procedure for the Hydrolysis of the Methyl 2-Aryl-5-methoxyoxazole-4-carboxylates, 6a–h, to the Carboxylic Acids, 7a–h. A slurry of finely pulverized KOH (1.7 g, 0.03 mol) in DMSO (20 ml) was added to the ester (0.02 mol), and the mixture was stirred for 5 min. Water (100 ml) was then added and the mixture then heated on a steam bath until the ester had dissolved (30 min). The solution was cooled and acidified with dilute H_2SO_4, and the precipitated acid was filtered, washed with water, dried, and converted without further purification to the acid chloride. Yields ranged from 50 to 60%. Ir: **7a–h**, 2850–3040 (s, br), 1655–1700 (s), 1590–1620 cm^{-1} (s). Nmr: **7a–h**, τ 1.6–2.3 (m, aromatic), 2.8–2.9 (s, 1 H, carboxylic acid), 5.6–5.8 (s, 3 H, ring methoxyl); **7a**, 6.15 (s, 3 H, *p*-CH_3OPh–); **7b**, 7.60 (s, 3 H, *p*-CH_3-Ph–); **7c**, 8.65 (s, 9 H, *p*-*t*-*Bu*Ph–).

The acid chlorides were prepared by refluxing equimolar amounts of the acids, **7**, and PCl_5 in $CHCl_3$ for 30 min. After removing the $CHCl_3$ and $POCl_3$, the residue was recrystallized from petroleum ether (bp 60–70°). Yields ranged from 35 to 45%. Ir: 1740–1745 (s), 1605–1625 cm^{-1} (s). Nmr: τ 1.8–3.3 (m, aromatic), 6.0–6.3 (s, 3 H, ring methoxyl); *p*-CH_3OPh–, 6.22 (s, 3 H); *p*-CH_3-Ph–, 7.70 (s, 3 H); *p*-*t*-*Bu*Ph–, 8.70 (s, 9 H).

General Procedure for the Preparation of the 2-Aryl-5-methoxyoxazole-4-(N-substituted)carboxamides, 1a–q. A solution of the acid chloride (0.005 mol) in benzene (20 ml) was added to a solution of the corresponding amine (0.005 mol) and triethylamine (0.5 g, 0.005 mol) in benzene at 0°. The mixture was then stirred 3 hr at room temperature, filtered, washed with dilute HCl and then with water, and dried ($MgSO_4$), and the benzene was evaporated. The resulting amide was recrystallized several times from petroleum ether (bp 60–70°). Yields ranged from 80 to 90%. Ir: **1a–h**, 1630–1650 (s), 1585–1610 (s), **1i–p**, 3325–3405 (m), 1645–1680 (s), 1585–1635 (s), **1q**, 1640 (s), 1600 cm^{-1} (s). Nmr: **1a–h**, τ 2.0–3.2 (m, aromatic), 6.0–6.1 (s, 3 H, ring methoxyl), 6.5–6.6 (s, 3 H, *N*-methyl); **1a**, 6.18 (s, 3 H, *p*-CH_3OPh–); **1b**, 7.65 (s, 3 H, *p*-CH_3-Ph–); **1c**, 8.71 (s, 9 H, *p*-*t*-*Bu*Ph–); **1i–n**, 1.8–3.2 (m, aromatic protons), 1.12–1.43 (broad singlet, 1 H, N–H), 5.7–5.8 (s, 3 H, ring methoxyl); **1m**, 7.70 (s, 3 H, NHPh-*p*-CH_3); **1n**, 6.23 (s, 3 H, NH-*p*-*H*-*p*-OCH_3); **1o**, 1.8–2.7 (m, aromatic protons), 3.10 (broad singlet, 1 H, NH), 5.7 (s, 3 H, ring methoxyl), 7.03 (d, J = 5 Hz, 3 H, $NHCH_3$); **1p**, 1.9–2.6 (m, aromatic protons), 3.23 (s, 1 H, NH), 5.74 (s, 3 H, ring methoxyl), 8.53 (s, 9 H, NH-*t*-*Bu*); **1q**, 1.8–2.7 (m, aromatic protons), 5.8 (s, 3 H, ring methoxyl), 6.77 (broad, 6 H, $-N(CH_3)_2$).

The amides **1a–q** were refluxed in toluene (reaction times were dependent upon the rate of the rearrangement), and the solvent was evaporated to yield the methyl 2-aryl-5-(N-substituted amino)oxazole-4-carboxylates (**2a–q**). Yields after recrystallization from pentane or petroleum ether were greater than 95%. Ir: **2a–h**, 1705–1720 (s), 1580–1630 (s); **2i–p**, 3315–3360 (m), 1660–1670 (s), 1600–1650 (s); **2q**, 1660 (s), 1610 cm^{-1} (s). Nmr: **2a–h**, τ 1.8–3.2 (m, aromatic protons), 6.29–6.40 (s, 3 H, carbomethoxy protons), 6.58–6.68 (s, 3 H, N-CH_3); **2a**, 6.13 (s, 3 H, *p*-CH_3OPh); **2b**, 7.68 (s, 3 H, *p*-CH_3Ph–); **2c**, τ 8.70 (s, 9 H, *p*-*t*-*Bu*Ph–); **2i–n**, 1.6–3.0 (m, aromatic protons), 6.16–6.28 (s, 3 H, carbomethoxy protons), 1.3–1.6 (s, 1 H, NH); **2m**, 7.69 (s, 3 H, NHPh-*p*-CH_3); **2n**, 6.23 (s, 3 H, NHPh-*p*-OCH_3); **2o**, 1.8–2.7 (m, aromatic protons), 3.3 (broad singlet, 1 H, NH), 6.16 (s, 3 H, carbomethoxy protons), 6.86 (d, J = 4.5 Hz, N-CH_3); **2p**, 1.9–2.6 (m, aromatic protons), 3.2 (broad singlet, 1 H, NH), 6.20 (s, 3 H, carbomethoxy protons), 8.65 (s, 9 H, N-*t*-*Bu*); **2q**, 1.7–2.7 (m, aromatic protons), 6.16 (s, 3 H, carbomethoxy protons), 6.81 (s, 6 H, $N(CH_3)_2$).

Kinetic Measurements. The reactions were carried out in solutions containing 15% w/v of oxazole. For each run an appropriate sample in an nmr tube was heated in a thermostated bath. At intervals the tube was removed, quenched in ice water, analyzed by nmr with a Varian A-60 spectrometer, and then returned to the bath. The reactions were followed by the disappearance of the 5-methoxy group in **1a–q** and by the appearance of the corresponding carbomethoxy group in **2a–q**. The spectra were calibrated with appropriate internal standards.

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