Anal. Calcd for $C_{12}H_{13}NO$: C, 76.97; H, 7.00; N, 7.48. Found: C, 77.02; H, 7.11; N, 7.48.

Acid-Catalyzed Rearrangement of 5b. Lactone **5b** (1.13 g, 6.4 mmol) was dissolved in 80 ml of 30% sulfuric acid and the reaction mixture was stirred at room temperature for a period of 16 hr. This solution was added to 300 g of ice–water and the solution was basified and extracted with ether (4 × 150 ml). The combined extracts were dried, filtered, and evaporated to give a greenish oil which was chromatographed on Florisil. Elution with petroleum ether–ether (1:1) afforded 0.64 g (58%) of **10**, mp 127–128° (from petroleum ether).

Anal. Calcd for $C_{11}H_{10}O_2$: C, 75.84; H, 5.79. Found: C, 75.82; H, 5.80.

Photorearrangement of 10. A solution of 490 mg (2.7 mmol) of **10** in 450 ml of anhydrous ether was irradiated for 17 hr through quartz with a 450-W Hanovia lamp. The progress of the reaction was followed by periodically removing aliquots and analyzing these by vpc. Evaporation of the ether left a semicrystalline residue which consisted of three products in the ratio of 56:24:20. These substances were separated by preparative vpc at 160° on a 12 ft × 0.25 in. column packed with 5% SE-30.

The first eluate (**14**, retention time 49 min) was recrystallized from petroleum ether to give white crystals, mp 140–141.5°.

Anal. Calcd for $C_{11}H_{10}O_2$: C, 75.84; H, 5.79. Found: C, 75.91; H, 5.84.

The second eluate (**20**, retention time 64 min) was sublimed at 50° and 20 mm and recrystallized from petroleum ether to give white crystals, mp 65.5–67°.

Anal. Calcd for $C_{11}H_{10}O_2$: C, 75.84; H, 5.79. Found: C, 76.11; H, 5.61.

The third eluate (**30**, retention time 72 min) was recrystallized from petroleum ether–ether to afford a white solid, mp 218–219.5°.

Anal. Calcd for $C_{11}H_{10}O_2$: C, 75.84; H, 5.79. Found: C, 75.59; H, 5.89.

Acknowledgment. This work was supported in large part by the National Science Foundaton, Grant No. GP-8678. We wish also to thank the Badische Anilin und Soda Fabrik for the generous gift of cyclooctatetraene which made this work possible.

1,3-Dipolar Cycloaddition Reactions. LIII.[1] The Question of the 1,3-Dipolar Nature of Δ^2-Oxazolin-5-ones

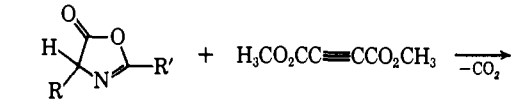
Hans Gotthardt, Rolf Huisgen, and Horst O. Bayer

Contribution from the Institut für Organische Chemie der Universität München, Munich, Germany. *Received December 6, 1969*

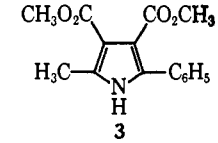
Abstract: Azlactones such as 4-methyl-2-phenyl- (**1**) and 2-methyl-4-phenyl-Δ^2-oxazolin-5-one (**2**) react with dimethyl acetylenedicarboxylate to give dimethyl 2-methyl-5-phenylpyrrole-3,4-dicarboxylate (**3**) and carbon dioxide. These cycloadditions are preceded by a tautomerization of the parent azlactone to a mesoionic oxazolium 5-oxide (**19**) which, as a cyclic azomethine ylide, combines further with the dipolarophile. Ultraviolet and ir spectral studies of 2,4-diphenyloxazolin-5-one (**23**) support the formation of the 2,4-diphenyloxazolium 5-oxide tautomer (**25**). The equilibrium concentration of **25** in turn is highly dependent on the polarity of the solvent employed. 5-Ethoxy-2,4-diphenyloxazole (**13**) reacts with dimethyl acetylenedicarboxylate to give dimethyl 2-ethoxy-5-phenylfuran-3,4-dicarboxylate (**15**) and benzonitrile.

In 1961, when we discovered that azlactones (Δ^2-oxazolin-5-ones) are capable of cycloaddition to acetylene derivatives,[2] an abundance of literature was available on this class of compounds.[3,4] In particular, their relationship to amino acid and peptide chemistry was responsible for the fact that the chemistry of this class of compounds was by no means "underdeveloped." Nevertheless, there had been no previous indications of their utility as partners in cycloaddition reactions.

A. Reactions with Dimethyl Acetylenedicarboxylate. On heating the azlactone of N-benzoylalanine (**1**) with 2 equiv of dimethyl acetylenedicarboxylate in refluxing xylene, carbon dioxide was evolved and a 71% yield of dimethyl 2-methyl-5-phenylpyrrole-3,4-carboxylate (**3**) was obtained. Alkaline hydrolysis to **5** followed by destructive distillation of the calcium salt gave 2-methyl-5-phenylpyrrole (**6**) which was identical with a sample obtained from phenacylacetone.[5]



1, R = CH_3; R′ = C_6H_5
2, R = C_6H_5; R′ = CH_3



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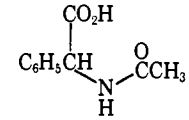

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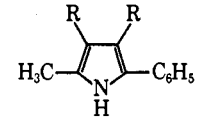


5, R = CO_2H
6, R = H

The positions 2 and 4 of Δ^2-oxazolin-5-one become equivalent in this pyrrole synthesis. To avoid handling

(1) For paper LII in this series, see R. Huisgen and J. Wulff, *Chem. Ber.*, **102**, 1848 (1969).

(2) Preliminary communication: R. Huisgen, H. Gotthardt, and H. O. Bayer, *Angew. Chem. Intern. Ed. Engl.*, **3**, 135 (1964).

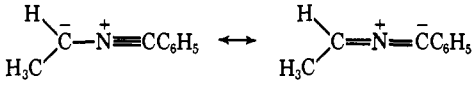
(3) For reviews, see H. E. Carter, *Org. Reactions*, **3**, 198 (1946); J. W. Cornforth in "The Chemistry of Penicillin," H. T. Clarke, J. R. Johnson, and R. Robinson, Ed., Princeton University Press, Princeton, N. J., 1949, p 730; E. Baltazzi, *Quart. Rev.* (London), **9**, 150 (1962); J. W. Cornforth in "Heterocyclic Compounds," Vol. 5, R. C. Elderfield, Ed., John Wiley & Sons, Inc., New York, N. Y., 1957, p 336.

(4) Monographs published since 1961: R. Filler in "Advances in Heterocyclic Chemistry," Vol. 4, Academic Press, New York, N. Y., 1965, p 75; W. Steglich, *Fortschr. Chem. Forsch.*, **12**, 77 (1969).

(5) F. Angelico and E. Calvello, *Gazz. Chim. Ital.*, **31** (II), 4 (1901).

the sensitive 2-methyloxazolin-5-ones—**2** has still not been described to our knowledge—we allowed N-acetylphenylglycine (**4**) to react with dimethyl acetylenedicarboxylate in acetic anhydride at 130°. In this manner compound **2** was formed *in situ* and treated with the acetylenic bond to give a 78% yield of the same tetrasubstituted pyrrole **3**, in a reaction which was complete within a few minutes. N-Acetylation could also be carried out *in situ*, 75% pyrrole **3** being obtained upon heating of C-phenylglycine with the acetylenedicarboxylic ester in acetic anhydride.

In a formal sense, CO_2 from the azlactone ring is exchanged for dimethyl acetylenedicarboxylate. Since **1** is stable in boiling xylene, the possibility of a primary decomposition into carbon dioxide and the nitrile ylide **7** followed by 1,3-dipolar cycloaddition[6] of the latter may be ruled out. However, the Δ^2-oxazolin-5-one structure does not provide any indication of reacting directly as a 1,3-dipole. The fact that the azlactone of α-benzoylamidoisobutyric acid (**8**)—here C-4 is devoid of a hydrogen atom—was found *stable* to dimethyl acetylenedicarboxylate in boiling xylene is also significant.



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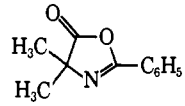
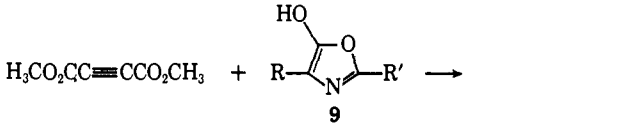


8

It may be assumed that a tautomer formed in equilibrium with the normal Δ^2-oxazolin-5-one enters into the cycloaddition, presumably the 4 H playing a part therein. Which tautomer is involved?

B. Cycloadditions of 5-Ethoxy-2,4-diphenyloxazole. We considered first a modest equilibrium concentration of the aromatic 5-hydroxy-2,4-diphenyloxazole derivative **9**. It is conceivable that **9** undergoes a Diels–Alder reaction to form the bicyclic intermediate **10**. The adduct **10** could rearrange to a 2H-pyrrolecarboxylic acid **11** which, in turn, forms **3** by elimination of CO_2.



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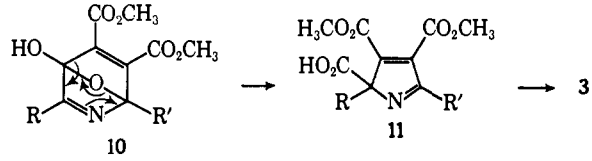
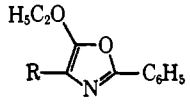
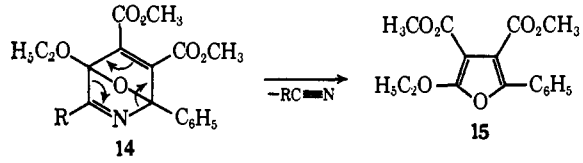


10 11 3

The 5-hydroxy tautomer, however, is fixed in the 5-ethoxy-2,4-diphenyloxazole derivatives **12** and **13**. According to Kondrat'eva,[7] oxazoles indeed undergo Diels–Alder addition reactions; the primary endoxides readily lose water to form pyridine derivatives. The particularly active 5-ethoxy-4-methyloxazole[8] thus permits a simple synthesis of the pyridoxine.[9]

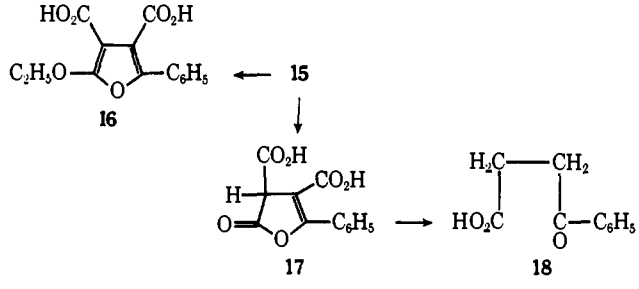


12, R = CH_3
13, R = C_6H_5



14 15

When acetylenic dienophiles are used the primary adducts **14** cannot be isolated. On heating the ethoxyoxazoles **12** and **13** with dimethyl acetylenedicarboxylate to 100°, we isolated in both cases dimethyl 2-ethoxy-5-phenylfuran-3,4-dicarboxylate (**15**) in a 71 and 77% yield, respectively; this is undoubtedly the result of a retro-Diels–Alder reaction. Benzonitrile was identified by gas chromatography for the reaction of **13**. This difference in the reaction course argues against **9** as an intermediate for the pyrrole synthesis.



16 17 18

Vigorous alkaline hydrolysis of **15** gave the dicarboxylic acid **16** along with 3-benzoylpropionic acid (**18**); the latter is probably formed *via* the $\Delta^{\beta,\gamma}$-butenolide **17**. Both the conversion of alkoxyfurans to butenolides[10,11] and their hydrolysis to γ-keto acids[12] are known.

C. Tautomerism of Δ^2-Oxazolin-5-ones with Oxazolium 5-Oxides. Another possible mode of tautomerism is between the azlactone and the **mesoionic oxazolium 5-oxide 19** where the resonance formula **19b** indicates a cyclic, aromatic azomethine ylide.[13] Cycloaddition to give **20** would be followed by evolution of CO_2 and aromatization. Azomethine ylides and their capability to undergo cycloadditions have been described.[14]

(6) Cycloadditions of nitrile ylides: R. Huisgen, H. Stangl, H. J. Sturm, and H. Wagenhofer, *Angew. Chem. Intern. Ed. Engl.*, 1, 50 (1962); R. Huisgen and R. Raab, *Tetrahedron Lett.*, 649 (1966); R. Huisgen, *Helv. Chim. Acta*, 50, 2421 (1967).

(7) G. Ya. Kondrat'eva, *Bull. Acad. Sci. USSR*, 457 (1959); G. Ya. Kondrat'eva and C. Huang, *Dokl. Akad. Nauk SSSR*, 141, 628, 861 (1961); *Chem. Abstr.*, 56, 14229 (1962).

(8) G. Ya. Kondrat'eva and C. H. Huang, *Dokl. Akad. Nauk SSSR*, 142, 593 (1962); *Chem. Abstr.*, 57, 2204 (1962).

(9) R. A. Firestone, E. E. Harris, and W. Reuter, *Tetrahedron*, 23, 943 (1967).

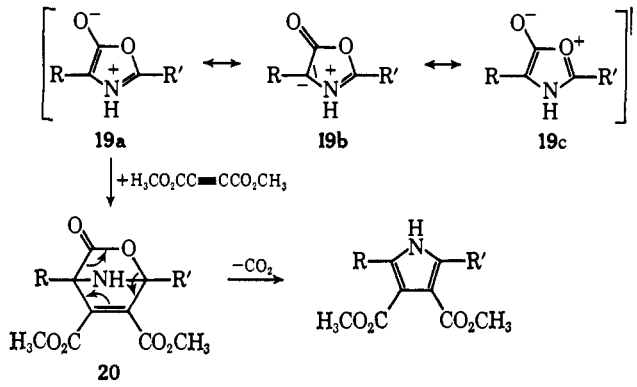
(10) M. I. Ushakov and V. F. Kucherov, *J. Gen. Chem. USSR*, 14, 1073 (1944); *Chem. Abstr.*, 40, 7185 (1946).

(11) E. Winterfeldt and A. Giesler, *Chem. Ber.*, 101, 4022 (1968).

(12) R. C. Elderfield and T. N. Dodd in "Heterocyclic Compounds," Vol. 1, R. C. Elderfield, Ed., John Wiley & Sons, Inc., New York, N. Y., 1950, p 185.

(13) For a classification of 1,3-dipoles, see R. Huisgen, *Angew. Chem. Intern. Ed. Engl.*, 2, 565 (1963).

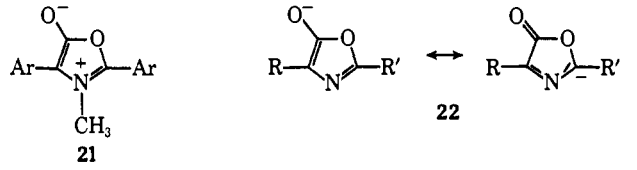
(14) R. Huisgen, R. Grashey, and E. Steingruber, *Tetrahedron Lett.*, 1441 (1963).



19a 19b 19c

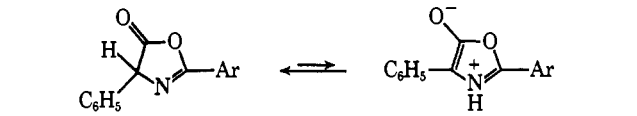
20

It was possible to prepare and characterize structurally the blocked N-methyl tautomers **21** of the azlactone system **19**.[15,16] These mesoionic 3-methyl-2,4-diaryloxazolium 5-oxides (**21**)—referred to in our laboratories as "münchnones" due to their formal similarity to "sydnones"—are extremely reactive toward dimethyl acetylenedicarboxylate, giving N-substituted pyrroles and CO_2 exothermically at 0°.[16,17] Mesoionic oxazolium 5-oxides of type **21** combine with alkenes to give Δ^2-pyrrolines.[18] Further cycloadditions of azlactones *via* mesoionic tautomers **19** with alkynes and alkenes are published elsewhere.[19,20] Also other laboratories have investigated additional examples in recent years.[21]



21 22

The racemization of optically active amino acids during N-acylation, *e.g.*, during peptide synthesis, is attributed to the formation of Δ^2-oxazolin-5-ones as intermediates.[22] Likewise optically active azlactones,[4] obtained with appropriate care, racemize rapidly. This loss of optical activity is usually ascribed to the Δ^2-oxazolinone anion **22** generated by a base.[23–25] Conceivably, the tautomeric equilibrium with the mesoion **19** may also play a deciding role in bringing about such racemizations.



23, Ar = C_6H_5
24, Ar = $C_6H_4NO_2(4)$
25, Ar = C_6H_5
26, Ar = $C_6H_4NO_2(4)$

The colorless crystals of 2,4-diphenyloxazolin-5-one (**23**) produce yellow solutions, particularly in polar solvents. The extinction coefficient of the band at 403–450 mμ, responsible for the color, shows a dramatic dependence on solvent polarity (Table I). For example,

Table I. Solvent Dependence of the Long-Wave Uv Maximum of 2,4-Diphenyloxazolium 5-Oxide (**25**)[a–c]

Solvent	λ_{max}, mμ	ϵ^c	E_T
N-Methylformamide	403	9140	54.1
Acetic acid	408	128	51.9
Acetonitrile	427	42	46.0
Dimethyl sulfoxide	432	6120	45.0
Dimethylformamide	434	9600	43.8
Acetone	438	51	42.2
Chloroform	436	1.4	39.1
Dioxane	450	4	36.0

[a] Compound **25** in equilibrium with **23**. [b] Extinction readings made 2 min following complete solution of **25** at room temperature. [c] ϵ calculated for the sum of **23** and **25**.

a change from chloroform to N-methylformamide increases ϵ from 1.4 to over 9000. An increase in the equilibrium concentration of the yellow mesoionic tautomer **25** offers the simplest explanation.

Assuming that the extinction coefficient of the tautomer **25** approximates that of the N-methyl derivative **21**, Ar = C_6H_5 (ϵ in methylene chloride[15]), it should be possible to calculate the constant of the tautomeric equilibrium from the ϵ values of the table. However, the time dependence of the extinction coefficient of the long-wave absorption band, even in highly purified solvents under nitrogen, introduces an element of uncertainty. For example, ϵ in N-methylformamide decreases by 25% in 6 min. Therefore, the following values for the equilibrium concentration of the mesoionic **25** represent only approximate values: dimethylformamide 49%, dimethyl sulfoxide 32%, acetone 0.26%, chloroform 0.007%.

Inspection of Table I shows that there is no simple relationship between the ϵ values and the solvent polarity parameter E_T,[26] whereas the wave numbers of the absorption maximum exhibit an approximate correlation with E_T (Figure 1).

The tautomeric equilibrium **23** ⇌ **25** is confirmed by ir spectra. The carbonyl absorption is observed at 1825 cm^{-1} in chloroform solution and at 1820 cm^{-1} in KBr, *i.e.*, the range typical for azlactones; the C=N band is observed at 1652 and 1645 cm^{-1}. The CO band of the mesoionic tautomer **25** at 1704 cm^{-1} in dimethyl sulfoxide solution has almost the same extinction coefficient as the azlactone carbonyl at 1821 cm^{-1}. The CO vibration of the N-methyl mesoion **21**, Ar = C_6H_5, is at 1710 cm^{-1} (methylene chloride).

Kille and Fleury[27] recently characterized the cyclization product of N-[4-nitrobenzoyl]phenylglycine as the mesoionic oxazolone **26** on the basis of spectral data. We confirm this finding; the oxazolium 5-oxide **26** is sparingly soluble and separates from solutions as copper-red crystals. This low solubility of the com-

(15) H. O. Bayer, R. Huisgen, R. Knorr, and F. C. Schaefer, *Chem. Ber.*, in press.
(16) Preliminary communication: R. Huisgen, H. Gotthardt, H. O. Bayer, and F. C. Schaefer, *Angew. Chem. Intern. Ed. Engl.*, **3**, 136 (1964).
(17) Paper LVI in this series: R. Huisgen, H. Gotthardt, H. O. Bayer, and F. C. Schaefer, *Chem. Ber.*, in press.
(18) Paper LVII in this series: H. Gotthardt and R. Huisgen, *ibid.*, in press.
(19) Paper LIV in this series: H. O. Bayer, H. Gotthardt, and R. Huisgen, *ibid.*, in press.
(20) Paper LV in this series: H. Huisgen, H. Gotthardt, and H. O. Bayer, *ibid.*, in press.
(21) A. Padwa and L. Hamilton, *J. Heterocycl. Chem.*, **4**, 118 (1967); H. W. Heine, A. B. Smith, and J. B. Bower, *J. Org. Chem.*, **33**, 1097 (1968); K. T. Potts and U. P. Singh, *Chem. Commun.*, 66 (1969).
(22) M. Bergmann and L. Zervas, *Biochem. Z.*, **203**, 280 (1928).
(23) A. Neuberger, *Advan. Protein Chem.*, **4**, 297, 358 (1948).
(24) J. W. Cornforth in "Heterocyclic Compounds," Vol. 5, R. C. Elderfield, Ed., John Wiley & Sons, Inc., New York, N. Y., 1957, pp 352, 367.
(25) Th. Wieland and H. Determann, *Angew. Chem.*, **75**, 539 (1963), in particular p 550.
(26) C. Reichardt, *Angew. Chem. Intern. Ed. Engl.*, **4**, 29 (1965).
(27) G. Kille and J. P. Fleury, *Bull. Soc. Chim. Fr.*, 4636 (1968).

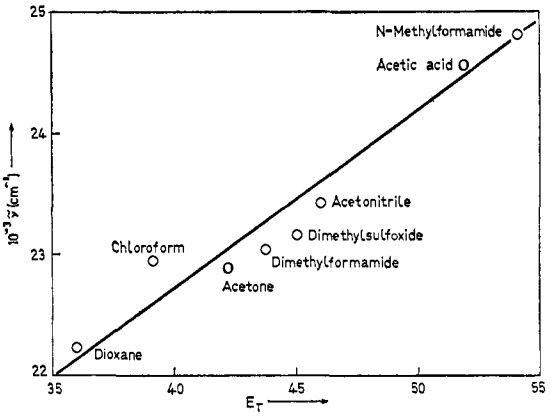
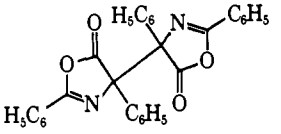
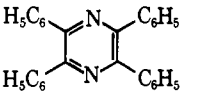


Figure 1. Relationship between the wave number of long-wave uv max of **25** and the solvent parameter E_T.

pounds prohibits the study of its tautomeric equilibrium in solution. Nevertheless, the long-wave absorption band of the mesoion is absent in dioxane solution (<0.1 mg/10 cc); the weak band with a λ_{max} at 272 mμ we ascribe to the tautomeric oxazolin-5-one **24**.



27



28

Incidentally, we observed that treatment of α-benzamidophenylacetic acid with acetic anhydride in the presence of air yielded minor amounts of a dehydro dimer along with **23**. The spectral similarity to **23**, the strong C=N valence vibration at 1648 cm^{-1}, indicative of a cyclic imido ester, together with the absence of a tertiary 4-H in the nmr spectrum suggest the structure **27**. Similar dehydro dimerizations of azlactones have been previously carried out with mercuric acetate.[28a]

Diphenyloxazolinone (**23**) underwent gradual decomposition in boiling xylene. Thus, on heating for 24 hr 8% 2,3,5,6-tetraphenylpyrazine (**28**) was isolated. A closer investigation of this azlactone thermolysis remains to be carried out.

Experimental Section

Melting points are uncorrected. The ir spectra were recorded with a Leitz III instrument, uv spectra with a Zeiss spectrometer RPQ 20A, and nmr spectra with a Varian-A-60 spectrometer with tetramethylsilane as an internal standard.

Azlactones and Ethoxyoxazoles. 4-Methyl-2-phenyl-Δ²-oxazolin-5-one (1), 19.4 g (74%), was obtained from 29.0 g of N-benzoylalanine by the procedure of Mohr:[29] mp 38.4–39.6° (lit.[29] 39–39.5°); ir (KBr) 1830 (C=O), 1662 (C=N), 694, 781 cm^{-1} (aromatic CH).

N-Acetyl-C-phenylglycine (4) was prepared in 62% yield by established procedures.[30]

4,4-Dimethyl-2-phenyl-Δ²-oxazolin-5-one (8) was obtained as described previously:[31] ir (KBr) 1821 (C=O), 1622 (C=N), 695, 755, 782 cm^{-1} (aromatic CH).

2,4-Diphenyl-Δ²-oxazolin-5-one (23). Benzoylation of C-phenylglycine[32] according to the Schotten–Baumann procedure resulted in a 91–96% crude yield. After recrystallization from ethanol and drying at 130° pure α-benzamidophenylacetic acid was obtained, mp 177–180° (lit.[33] 174°). The following procedure expands the very brief description of the cyclization (50% yield) given by Cornforth.[28b] Thus, 35.0 g (137 mmol) of finely powdered α-benzamidophenylacetic acid was stirred with 55 cc of pure acetic anhydride under nitrogen at 50–60°. A clear yellow solution was obtained in about 15 min. Acetic acid and excess acetic anhydride were rapidly removed *in vacuo* at 50° (bath temperature), the residue taken up in a minimum amount of warm, absolute benzene, the solution treated with a small amount of aluminum oxide and diluted with warm petroleum ether (bp 60–80°) until slightly turbid. After scratching or seeding, followed by storage of the solution under nitrogen, 18.4 g of **23** was obtained as nearly colorless needles, mp 103.5–105.5° (the reported value of mp 80–81°[28b] must be in error). From the mother liquor an additional 1.7 g of material, mp 103–104°, was collected for a combined yield of 62%. After recrystallization from petroleum ether colorless needles were obtained, melting point as above: ir (KBr) 1820 (C=O) with shoulders at 1790 and 1749 cm^{-1}, 1645 cm^{-1} (C=N), 694, 704, 767, 783 cm^{-1} (aromatic CH); uv max (dioxane) 244 mμ (log ε 4.26).

Anal. Calcd for $C_{15}H_{11}NO_2$: C, 75.93; H, 4.67; N, 5.90. Found: C, 75.92; H, 4.63; N, 5.73.

Bis-4,4-(2,4-diphenyl-Δ²-oxazolin-5-one) (27) was isolable when air was not excluded during the preparation of **23**. On treatment with acetone, the product fraction, only slightly soluble in petroleum ether, left colorless, insoluble crystals which after recrystallization from methylene chloride–acetone decomposed at 198°. The ir (KBr) spectrum is very similar to that of **23**, 1821 and 1733 cm^{-1} (C=O, the latter somewhat stronger), 1646 cm^{-1} (C=N); uv max (dioxane) 252 mμ (log ε = 4.47).

Anal. Calcd for $C_{30}H_{20}N_2O_4$: C, 76.26; H, 4.27; N, 5.93; mol wt, 472.5. Found: C, 75.87; H, 4.23; N, 5.95; mol wt, 471 (osmometr. C_6H_6).

Hydrolysis of 23. A 500-mg sample of **23** was heated on a steam bath in 10 cc of dioxane and 10 cc of water containing 3 drops of 2 *N* HCl. After cooling 455 mg of benzamidophenylacetic acid was separated by filtration. Recrystallization from ethanol provided a sample of mp 178–180° (lit.[33] 174°).

Thermolysis of 23. On heating 0.80 g (3.4 mmol) of **23** in 7 cc of xylene in a 140° bath, 0.3 equiv of CO_2 was evolved in 6 hr and 0.5 equiv in 24 hr. The dark solution was chromatographed (neutral aluminum oxide) and eluted with petroleum ether and then with benzene. From the benzene eluate 53 mg (8%) of 2,3,5,6-tetraphenylpyrazine (**28**) was isolated; colorless needles from petroleum ether, mp 247–249° (lit.[34] 247.5°). As described, **28** yielded a red solution in concentrated sulfuric acid.[34]

Anal. Calcd for $C_{28}H_{20}N_2$: C, 87.47; H, 5.24; N, 7.29. Found: C, 87.95; H, 5.47; N, 7.85.

4-Phenyl-2-(4-nitrophenyl)oxazolium 5-Oxide (26).[27] A slight variation in procedure increased the previous yield of 55% to 81%. Thus, 10.0 g of N-(4-nitrobenzoyl)phenylglycine[35] was stirred in 50 cc of acetic anhydride for 15 min at a bath temperature of 80°. After addition of 50 cc of benzene, 7.60 g of **26** separated on cooling, mp 174–175° dec (lit.[27] 174°). The benzene-soluble portion of the mother liquor, stripped to dryness at 60° *in vacuo*, provided 195 mg of the light yellow O-acetyl derivative, mp 158–161° dec, previously obtained by Kille and Fleury.[27]

5-Ethoxy-4-methyl-2-phenyloxazole (12). From ethyl α-benzamidopropionate and phosphorus pentachloride in dry chloroform,[28c] a 71% yield of a pale yellow oil was obtained after high vacuum distillation; picrate (from ethanol), mp 126–128° (lit.[28c] 127°).

5-Ethoxy-2,4-diphenyloxazole (13).[28c] In 65 cc of chloroform, 8.4 g of ethyl α-benzamidophenylacetate and 7.0 g of phosphorus pentachloride were refluxed for 1 hr. After washing with water, high vacuum distillation and recrystallization from petroleum ether gave 6.40 g (81%) of **13**, mp 44–46° (lit.[28c] 47–48°, 41%).

Cycloadditions. Dimethyl 2-Methyl-5-phenylpyrrole-3,4-dicarboxylate (3). (a) A 1.75-g (10.0 mmol) sample of **1** and 2.84 g (20 mmol) of dimethyl acetylenedicarboxylate were refluxed for 90 min in 10 cc of xylene; a total of 10 mmol of CO_2 evolved, 5.0 mmol after 12 min. The solvent and excess dipolarophile were removed *in vacuo;* two recrystallizations from methanol gave 1.95 g (71%) of colorless crystals: mp 126.5–127.5°; ir (KBr)

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3280 (NH), 1703 (C=O), 1288 and 1220 cm^{-1} (C—O) and 696, 763 and 784 cm^{-1} (aromatic CH).

Anal. Calcd for $C_{15}H_{15}NO_4$: C, 65.92; H, 5.53; N, 5.13 Found: C, 66.23; H, 5.59; N, 5.28.

(b) A 1.93-g (10.0 mmol) sample of **4** was heated with 5.0 cc (41 mmol) of dimethyl acetylenedicarboxylate in 10 cc of acetic anhydride for 15 min in a 130° bath; 10 mmol of CO_2 was evolved, half of which was generated during the first 30 sec. The light-brown solution was concentrated under vacuum at 11 mm and the residue recrystallized from methanol to give 2.14 g (78%) of colorless crystals, mp 129–130°; identity with the above product **3** was shown by mixture melting point and ir.

(c) A 1.51-g (10.0 mmol) sample of C-phenylglycine was heated as above with 5.0 cc of dimethyl acetylenedicarboxylate and 15 cc of acetic anhydride for 15 min at 130°. Carbon dioxide evolution was again quantitative. Workup as above yielded 2.04 g (75%) of **3**, mp 129–130°.

Conversion of 3 to 2-Methyl-5-phenylpyrrole (6). A 300-mg sample of **3** was saponified in 10 cc of boiling 30% ethanolic KOH solution. On exposure to light, the dicarboxylic acid **5** turned red. A mixture of this acid with calcium oxide was destructively distilled from a micro flask under 15 mm. The distillate, crystallized from 70% methanol, gave flakes of mp 98–99° (lit.[36] 101°). Ir and mixture melting point comparisons with an authentic sample[5] of **6** confirmed its identity.

Dimethyl 2-Ethoxy-5-phenylfuran-3,4-dicarboxylate (15). (a) A 0.51-g (2.5 mmol) sample of **12** did not react with 0.40 g (2.8 mmol) of dimethyl acetylenedicarboxylate at 20°. However, after 10 min at 100°, a yellow solution was formed from which excess dienophile was removed under vacuum at 0.01 mm. The residue, recrystallized from ether–petroleum ether, gave 543 mg (71%) of colorless prisms: mp 80–83°, pure mp 83–84° (ether); ir (KBr) 1735 (3-CO_2CH_3), 1691 (4-CO_2CH_3), strong bands at 1600, 1468, 1354, 1050 cm^{-1}; uv max (ethanol) 288 mμ (log ε = 4.27).

Anal. Calcd for $C_{16}H_{16}O_6$: C, 63.15; H, 5.30. Found: C, 63.32; H, 5.51.

(b) Similarly 2.0 g (7.5 mmol) of **13** was heated 3 hr with 2.0 g (14 mmol) of dimethyl acetylenedicarboxylate and 2 cc of xylene in a 100° bath. Workup as above gave 1.76 g (77%) of **15**, mp 82–83°, identical by ir comparison and mixture melting point with the product obtained from **12**. Benzonitrile was identified in the distillate by gas chromatography.

Alkaline Hydrolysis of 15. A 0.80-g (2.6 mmol) sample of **15** was treated with 5 g of potassium hydroxide in 10 cc of water and 15 cc of methanol for 15 hr at 20° and 2 hr at the boiling point. After diluting with water, removal of methanol *in vacuo*, and acidification with HCl, there was obtained by filtration 0.21 g (29%) of 2-ethoxy-5-phenylfuran-3,4-dicarboxylic acid (**16**), mp 158–159° dec.

Anal. Calcd for $C_{14}H_{12}O_6$: C, 60.87; H, 4.38. Found: C, 60.85; H, 4.32.

The aqueous filtrate was extracted with ether and the residue of the ether solution distilled at 175–180° (0.001 mm) (bath). The product, 192 mg (41%) of β-benzoylpropionic acid (**18**), gave colorless crystals from methylene chloride–petroleum ether, mp 113–115° (lit.[37] 116°) Identity was also confirmed by nmr.

Anal. Calcd for $C_{10}H_{10}O_3$: C, 67.40; H, 5.66. Found: C, 67.68; H, 5.59.

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Detection of Alkylcyclopropane Intermediates during Carbonium Ion Rearrangements in Antimony Pentafluoride Tritiated Fluorosulfonic Acid

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Abstract: During the rearrangement of many butyl, amyl, and hexyl cations in the SbF_5–HSO_3F system, a species forms which can exchange a single proton with the acid. The species may be regarded as either a protonated cyclopropane, or a proton and a cyclopropane moiety. It has been detected in both chain branching isomerizations and those leading to a methyl shift, but not in the isomerization of the neopentyl to the *t*-amyl cation.

It has been shown that butyl, amyl, and hexyl cations can be trapped by hydride transfer from methylcyclopentane in 2 *M* SbF_5–HSO_3F to give kinetically controlled products.[1] Various results suggested that protonated alkylcyclopropanes were intermediates in many of the rearrangements observed, It was hypothesized that such a species might contain a loosely bound proton that would be susceptible to exchange with the acid, and the current work was undertaken to examine this theory. Indeed, it may be demonstrated that a number of simple rearrangements do proceed through the formation of such a species which, in general, can be detected after adding a small amount of water to the acid, thus increasing the concentration of nucleophiles and catalyzing the exchange.

Cyclopropyl intermediates in these and similar rearrangements have been proposed before;[2–6] some of the earliest studies of the cleavage of representative ring

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