

Electron transfer reactions. Reaction of Δ^2 -oxazolin-5-ones and related substrates with potassium¹

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The reaction of several Δ^2 -oxazolin-5-ones (**1a-c**, **12**) and bioxazolinones (**17**, **26**) with potassium in THF has been investigated. Treatment of **1a** with potassium in THF gave a mixture of dibenzamide (**11a**), *N*-benzoyl-*C*-phenylglycine (**6a**), and *C*-phenylglycine (**10a**). A higher yield of **11a** was obtained, together with benzoic acid (**9**), when the reaction of **1a** was carried out in THF saturated with oxygen. The reaction of **1b** gave a mixture of β -phenylalanine (**10b**) and **9**, whereas **1c** gave a mixture of *N*-benzoyl-*C*,*C*-diphenylglycine (**6c**) and *N*-benzoyl-*C*,*C*-diphenylmethylamine (**5c**). Similarly, the reaction of **12** gave a mixture of α -benzamidocinnamic acid (**15**) and **9**. The reaction of the bioxazolinone **17** with potassium gave a mixture of **11a**, **6a**, and **10a**, along with an appreciable yield of 2,3,5,6-tetraphenylpyrazine (**25**), whereas **26** under analogous conditions gave a mixture of **15**, **6b**, and benzamide (**29**). Reasonable mechanisms, involving the initial formation of radical anion intermediates and their subsequent transformation to give the observed products, have been suggested. Potassium superoxide oxidation of some of these substrates gives similar product mixtures. Cyclic voltammetric studies have been carried out to measure the reduction potentials of **1a-c**, **12**, **17**, and **26** in the generation of their radical anions. The radical anions of these substrates were also generated pulse radiolytically in methanol and their spectra showed absorption maxima in the region 295–350 nm.

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On a étudié la réaction de plusieurs Δ^2 -oxazolinones-5 (**1a-c**, **12**) et bioxazolinones (**17**, **26**) avec le potassium dans le THF. La réaction de **1a** avec le potassium dans le THF conduit à un mélange de dibenzamide (**11a**), de *N*-benzoyl *C*-phénylgylicine (**6a**) et de *C*-phénylgylicine (**10a**). Lorsqu'on a effectué la réaction de **1a** dans du TFH saturé en oxygène, on a obtenu de l'acide benzoïque (**9**) et un meilleur rendement de **11a**. La réaction du produit **1b** conduit à un mélange de β -phénylalanine (**10b**) et de composé **9**; par ailleurs, le composé **1c** conduit à un mélange de *N*-benzoyl *C*,*C*-diphénylgylicine (**6c**) et de *N*-benzoyl *C*,*C*-diphénylméthylamine (**5c**). De la même manière, la réaction du composé **12** conduit à un mélange d'acide α -benzamidocinnamique (**15**) et de composé **9**. La réaction de la bioxazolinone **17** avec le potassium conduit à un mélange de composés **11a**, **6a** et **10a** aux côtés d'une quantité appréciable de tétraphényl-2,3,5,6 pyrazine (**25**); par ailleurs, le composé **26** soumis aux mêmes conditions conduit à un mélange des composés **15**, **6b** et de benzamide **29**. On suggère des mécanismes raisonnables impliquant la formation initiale d'intermédiaires anions radicalux et leurs transformations subséquentes pour donner les produits observés. L'oxydation de quelques-uns de ces substrats par le superoxyde de potassium conduit à des mélanges réactionnels semblables. On a effectué des études de voltamétrie cyclique pour mesurer les potentiels de réduction des composés **1a-c**, **12**, **17** et **26** lors de la génération de leurs radicalux anions. On a aussi généré les radicalux anions de ces substrats par radiolyse pulsée dans le méthanol; leurs spectres présentent des maxima d'absorption dans la région de 295–350 nm.

[Traduit par la revue]

Introduction

In a recent investigation (1), we examined the reactions of several 2(3*H*)-furanones and bifurandiones with potassium in THF and showed that several products, arising through the initial formation of radical anions and their subsequent reaction with oxygen, are formed in these cases. Thus the reaction of 3,3,5-triphenyl-2(3*H*)-furanone with potassium in THF, for example, gave a mixture of 4-oxo-2,2,4-triphenylbutanoic acid, 1,3,3-triphenyl-2-propen-1-one, and benzoic acid. The reaction of a bifurandione such as 2,2',3,3',4,4'-hexaphenyl-2,2'-bifuran-5,5'(2*H*,2'*H*)-dione with potassium, on the other hand, gave a mixture of a 2(5*H*)-furanone, 2,3-diphenylpro-

penoic acid, and benzoic acid. In this context, it was felt worthwhile to investigate the reaction of some representative Δ^2 -oxazolin-5-ones and bioxazolinones with potassium in THF, to study the type of products formed in these cases and also their reaction pathways.

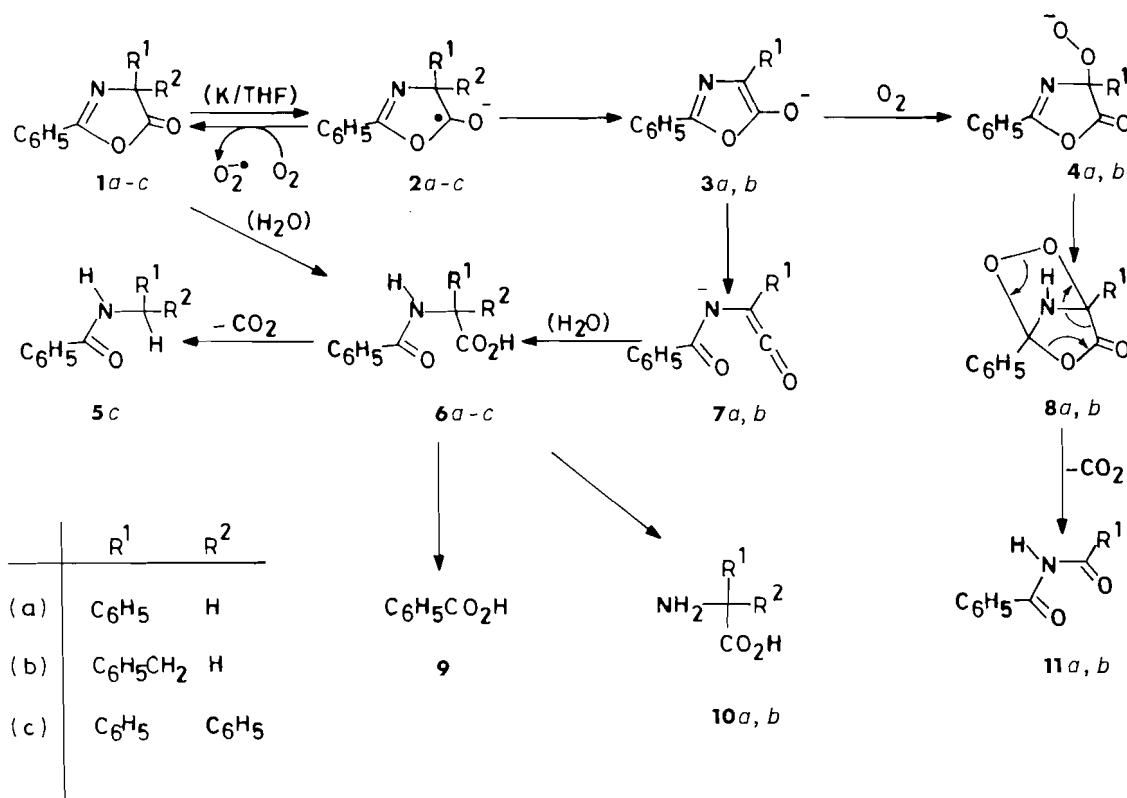
Results and discussion

We have examined, in the present studies, the reactions of 2,4-diphenyl- Δ^2 -oxazolin-5-one (**1a**), 4-benzyl-2-phenyl- Δ^2 -oxazolin-5-one (**1b**), 2,4,4-triphenyl- Δ^2 -oxazolin-5-one (**1c**), and 4-benzylidene-2-phenyl- Δ^2 -oxazolin-5-one (**12**). In addition, the reactions of two bioxazolinones such as bi-4,4'-(2,4-diphenyl- Δ^2 -oxazolin-5-one) (**17**) and bi-4,4'-(4-benzyl-2-phenyl- Δ^2 -oxazolin-5-one) (**26**) have been investigated.

The reaction of **1a** with potassium in THF, for example, gave

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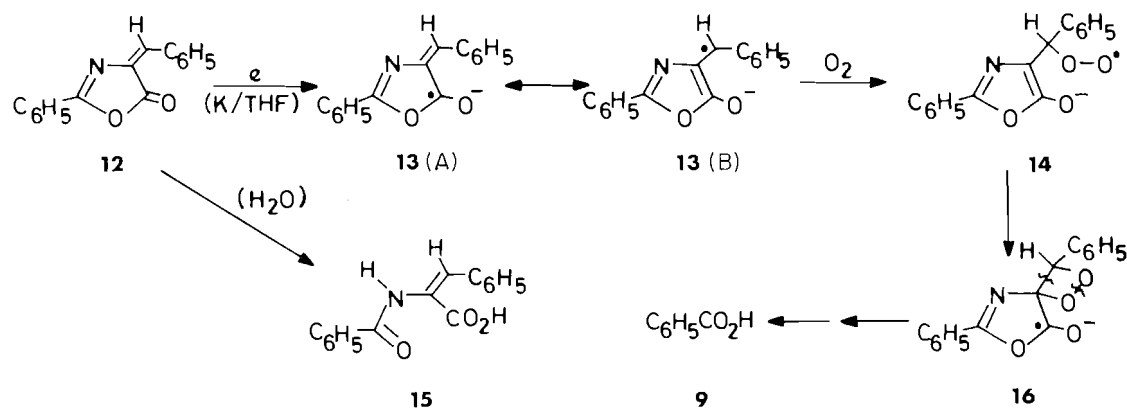


SCHEME 1.

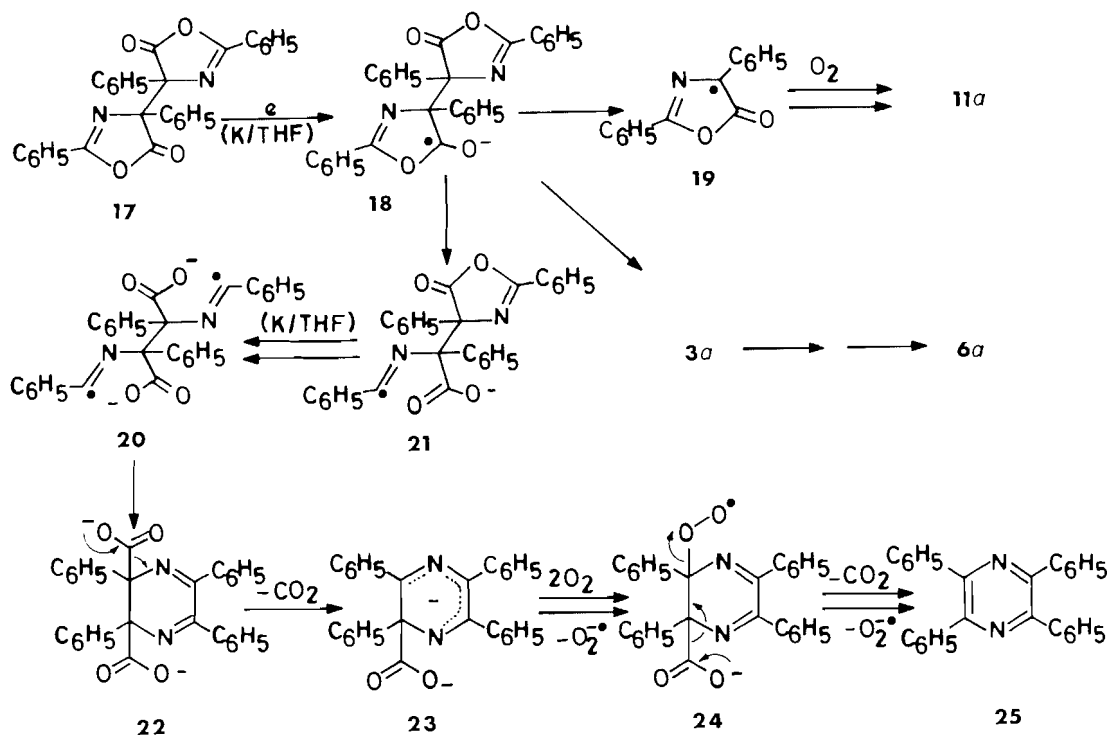
a mixture of dibenzimide (**11a**), *N*-benzoyl-*C*-phenylglycine (**6a**), and *C*-phenylglycine (**10a**). When the reaction of **1a** with potassium, however, was carried out in THF saturated with oxygen, a much higher yield of **11a** was obtained, along with appreciable amounts of benzoic acid (**9**). The reaction of **1b** with potassium in THF gave a mixture of β-phenylalanine (**10b**) and benzoic acid. Under analogous conditions, the reaction of **1c** with potassium in THF gave a mixture of *N*-benzoyl-*C*,*C*-diphenylglycine (**6c**) and *N*-benzoyl-*C*,*C*-diphenylmethylamine (**5c**). On the other hand, when the reaction of **1c** with potassium was carried out in THF saturated with oxygen, a mixture of **6c**, **5c**, and benzoic acid was formed.

The formation of the different products in the reaction of **1a-c** with potassium in THF could be understood in terms of the pathway shown in Scheme 1. It has been assumed that the initial step in the reaction involves an electron transfer process leading to the formation of the radical anions **2a-c**, which can, through the loss of a hydrogen atom, give the anionic intermediates **3a,b**. These intermediates **3a,b**, in turn, can lead to the carboxylic acids **6a,b**, through the corresponding ketene intermediates **7a,b**. The carboxylic acids **6a-c** can also be directly formed from **1a-c**, under hydrolytic conditions of work-up. Products such as **5c**, **9**, and **10a,b** in these reactions, however, could arise through the further transformations of **6a-c**. The formation of **11a,b**, on the other hand, could be understood in terms of the reaction of **3a,b** with oxygen, under work-up conditions, to give the hydroperoxy intermediates **4a,b**, which will then lead to the observed products through the endoperoxides **8a,b**. The fact that enhanced yields of **11a** were obtained in the reaction of **1a** with potassium in THF saturated with oxygen, and also when treated with potassium superoxide in benzene containing 18-crown-6, would support the involvement of oxygen and superoxide in the transformations of **1a-c**, as implicated in Scheme 1. It may be pointed out here that recent

studies by Bates *et al.* (2) have shown that 4-isopropyl-2-phenyl-Δ²-oxazolin-5-one and 4-benzyl-2-phenyl-Δ²-oxazolin-5-one are readily converted to the corresponding acyclic imides, *N*-isobutyrylbenzamide and *N*-(phenylacetyl)benzamide, respectively, on bubbling oxygen gas through their solutions in dimethyl sulfoxide. The formation of the cyclic imides corresponding to **11a,b** in these reactions has been explained in terms of hydroperoxy intermediates, analogous to **4a,b** (Scheme 1). Similarly, Warnhoff and co-workers (3) have shown that oxygen reacts with 4-alkylidene-2-phenyl-Δ²-oxazolin-5-ones in the presence of triethylamine to give the corresponding imides, again arising through hydroperoxy intermediates, analogous to **4a,b**, shown in Scheme 1. The reaction of **1b** with potassium superoxide and 18-crown-6 in benzene likewise gave a mixture of the oxygenated products *N*-benzoylphenylacetamide (**11b**), *N*-benzoyl-β-phenylalanine (**6b**), and benzoic acid (**9**), whereas the reaction of **1c** with potassium superoxide and 18-crown-6, under analogous conditions, gave an excellent yield of *N*-benzoyl-*C*,*C*-diphenylglycine (**6c**). It may be mentioned in this connection that recent studies by Chuaqui *et al.* (4) have shown that the reaction of potassium superoxide with Δ²-oxazolin-5-ones gives different products depending on the substituents present in the oxazolinone ring system. Thus, the reaction of 4,4-dimethyl-2-phenyl-Δ²-oxazolin-5-one with potassium superoxide gave the ring-opened product, *N*-benzoyl-α-aminoisobutyric acid, whereas the reaction of 4-ethyl-2-phenyl-Δ²-oxazolin-5-one gave a mixture of *N*-benzoyl-α-aminobutyric acid and *N*-benzoylpropionamide. The formation of the ring-opened α-amino acid derivatives in these reactions has been explained in terms of the initial nucleophilic attack of the superoxide on the starting Δ²-oxazolin-5-ones, followed by further transformation. The formation of *N*-benzoylpropionamide in the reaction of 4-ethyl-2-phenyl-Δ²-oxazolin-5-one, however, has been explained in



SCHEME 2.



SCHEME 3.

terms of a 1,3-dipolar cycloaddition of singlet oxygen to the N-protonated zwitterionic form of the oxazolinone, followed by the loss of CO_2 and further transformations. We feel that under our reaction conditions the pathway shown in Scheme 1, involving the radical anion intermediates 2a-c, may be operative (see later reports on cyclic voltammetric and pulse radiolysis studies).

The reaction of 4-benzylidene-2-phenyl- Δ^2 -oxazolin-5-one (12) with potassium in THF gave a mixture of α -benzamidocinnamic acid (15) and benzoic acid (9). The formation of these products, on the basis of analogy to the reactions of other Δ^2 -oxazolinones, can be rationalized in terms of the pathway shown in Scheme 2.

The reaction of a bioxazolinone such as 17 with potassium in THF gave a mixture of dibenzimide (11a), *N*-benzoyl-*C*-phenylglycine (6a), *C*-phenylglycine (10a), and 2,3,5,6-tetraphenylpyrazine (25) (Scheme 3), whereas the reaction of 26 with potassium in THF gave a mixture of α -benzamidocinnamic acid (15), *N*-benzoyl- β -phenylalanine (6b), and benzamide (29) (Scheme 4). The reaction of 26 with potassium superoxide

and 18-crown-6, however, gave a mixture of 15 and benzoic acid (9). The formation of the different products in the reaction of 17 and 26 with potassium in THF could be rationalized in terms of the pathways shown in Schemes 3 and 4. The initially formed radical anion 18 in the case of 17, for example, could undergo fragmentation to give both the radical 19 and the anionic species 3a, which in turn could lead to 11a and 6a, respectively, as shown in Scheme 3. The radical anion intermediate 18 could also undergo transformation to give 21, which could ultimately lead to 2,3,5,6-tetraphenylpyrazine (25), through the intermediates 20, 22, 23, and 24, as shown in Scheme 3. It may be pointed out here that 25 has also been reported to be formed from 17 in small amounts under thermal conditions (5). Similarly the radical anion 27, formed from 26, could lead to the different products as shown in Scheme 4.

Cyclic voltammetric studies

As highlighted in our earlier studies (20), electrochemical investigations would prove valuable in the characterization of radical anions, the primary intermediates involved in the

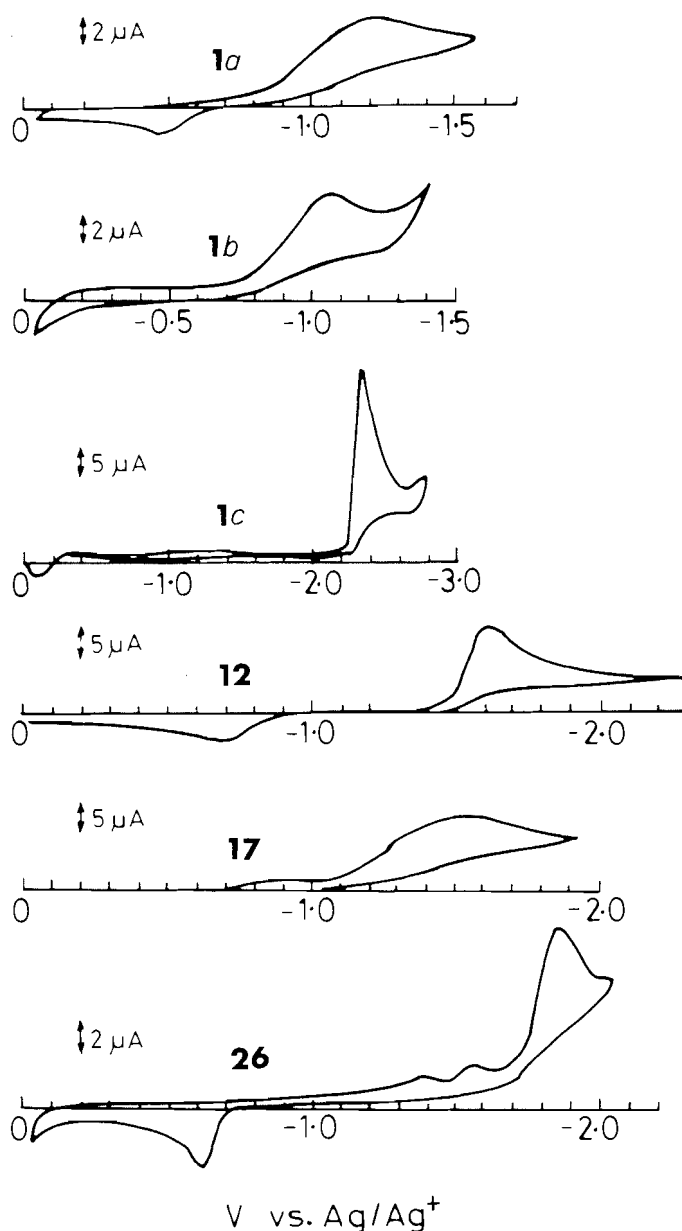
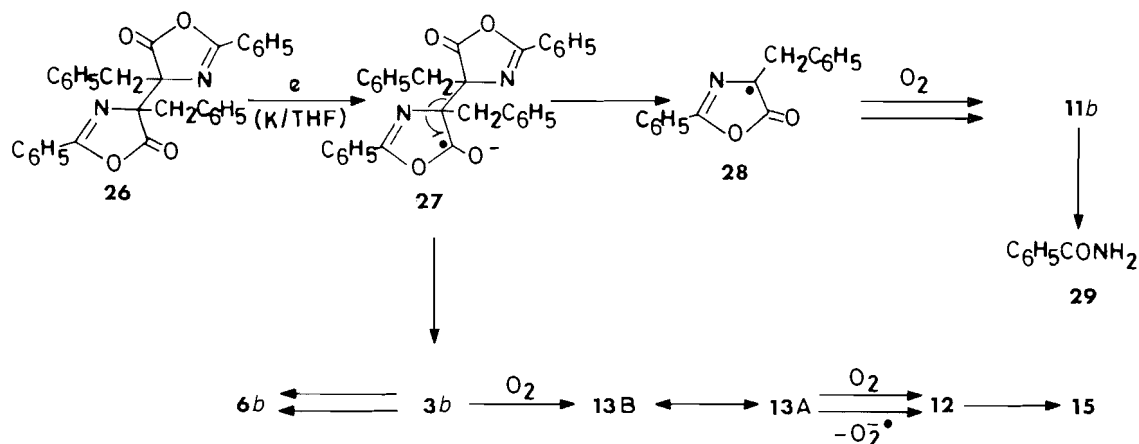


FIG. 1. Cyclic voltammograms of **1a-c**, **12**, **17**, and **26** in de-aerated acetonitrile containing 0.1 M tetrabutylammonium perchlorate (TBAP). Sweep rate was 200 mV/s.

reaction of different unsaturated organic substrates with potassium in THF. In the present study, we have generated electrochemically the radical anions of the Δ^2 -oxazolin-5-ones **1a-c**, **12**, and the bioxazolinones **17** and **26**, the substrates under investigation. The cyclic voltammograms of **1a-c**, **12**, **17**, and **26** are shown in Fig. 1 and the reduction peak potentials are summarized in Table 1. All the substrates exhibited irreversible reduction peaks with the reduction potentials in the range of -0.9 to -2.35 V versus Ag/Ag^+ reference.

Pulse radiolysis studies

It has been reported earlier that the radical anions of unsaturated organic compounds can be generated through their reaction with solvated electrons (e_s^-) under pulse radiolytic conditions (6–8). In the present study, the radical anions of the Δ^2 -oxazolin-5-ones **1a-c** and **12** and the bioxazolinones **17** and **26** were generated pulse radiolytically in methanol, and their absorption spectra are presented in Fig. 2. These radical anions exhibited strong absorption maxima in the region of 295–350 nm and were shortlived in methanol ($\tau_{1/2} = 2.3$ – 214 μs). As is evident from Table 1, these radical anions are formed from their appropriate precursors through reaction with solvated electrons under diffusion controlled rates.

Experimental

All melting points are uncorrected and were determined on a Mel-Temp apparatus. Petroleum ether was the fraction with bp 60–80°C. THF was dried over sodium and distilled immediately before use. Gold label (Aldrich) acetonitrile was used for cyclic voltammetric studies and spectral grade methanol (Fisher Scientific) was used for pulse radiolysis.

Starting materials

2,4-Diphenyl- Δ^2 -oxazolin-5-one (**1a**) (**5b**), mp 104–105°C; 4-benzyl-2-phenyl- Δ^2 -oxazolin-5-one (**1b**) (**9**), mp 69–70°C; 2,4,4-triphenyl- Δ^2 -oxazolin-5-one (**1c**) (**10**), mp 136–137°C; 4-benzylidene-2-phenyl- Δ^2 -oxazolin-5-one (**12**) (**11**), mp 165–166°C; bi-4,4'-(2,4-diphenyl- Δ^2 -oxazolin-5-one) (**17**) (**12**, **13**), mp 193–194°C; and bi-4,4'-(4-benzyl-2-phenyl- Δ^2 -oxazolin-5-one) (**26**) (**12**, **13**), mp 209–210°C, were prepared by reported procedures.

Reaction of Δ^2 -oxazolin-5-ones **1a-c** with potassium in THF

A general procedure was to shake 5.0 mmol of the appropriate Δ^2 -oxazolin-5-one with potassium (10 mmol) in dry THF (125 mL) for several hours in a stoppered flask. A few clean, broken glass pieces were added to the mixture to ensure a fresh surface of the metal throughout the reaction. The reaction mixture underwent pronounced color changes, indicative of the formation of radical anion inter-

TABLE 1. Electrochemical, spectral, and kinetic data of **1a-c**, **12**, **17**, and **26**

	Reduction peak potential, ^a E_p (V vs. Ag/Ag ⁺)	Absorption maxima (nm)		$k^{b,c}$ ($10^{10} M^{-1} s^{-1}$)	$\tau_{1/2}^{b,d}$ (μs)
		Starting material ^a	Radical anion ^b		
1a	-1.05	235	315	1.1	4.5
1b	-1.10	240, 340, 360, 380	295	1.6	2.6
1c	-2.35	247	295	1.6	2.3
12	-1.56	258, 344, 360, 380	390	2.0	2.3
17	-0.9, -1.33, -1.55	222	310	1.1	5.3
26	-1.4, -1.58, -1.87	244	350	1.5	214.0

^aIn acetonitrile containing 0.1 M tetrabutylammonium perchlorate.

^bIn methanol.

^cRate constant for the reaction of the substrate with solvated electron in methanol.

^dHalf-life of the radical anion in methanol.

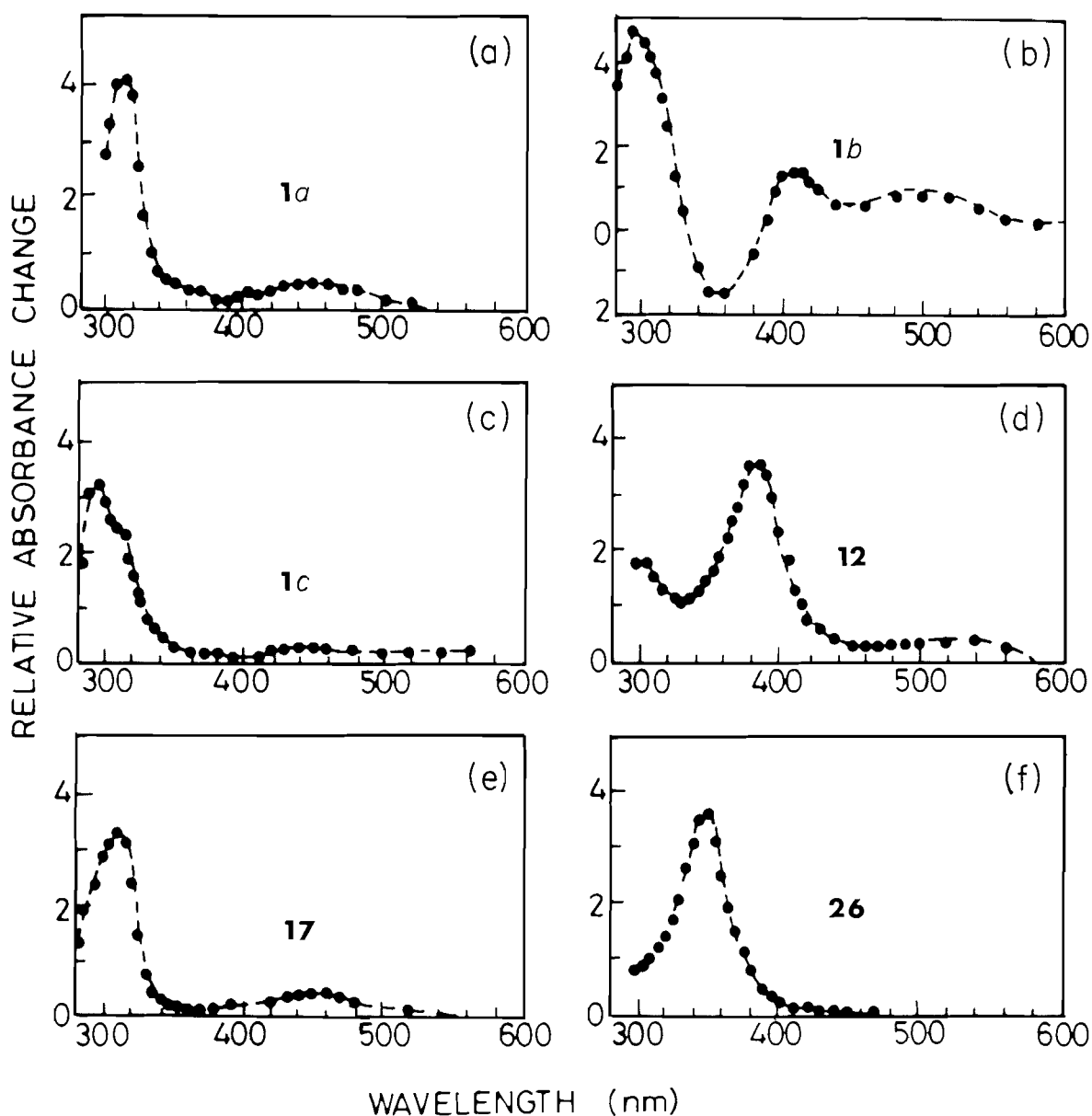


FIG. 2. Absorption spectra of the pulse radiolytically generated radical anions from **1a** (a), **1b** (b), **1c** (c), **12** (d), **17** (e), and **26** (f) in nitrogen saturated methanol, observed at 0.04 μs after the electron pulse.

mediates. On completion of the reaction, the mixture was poured into moist THF (100 mL) to destroy any unchanged potassium and the solvent was removed under vacuum. The residual solid was treated with water (10 mL) and extracted with ethyl acetate. Work-up of the organic layer by removal of the solvent under vacuum and fractional crystallization from suitable solvents gave some of the reaction products. Acidification of the aqueous layer with dilute hydrochloric acid, followed by work-up in the usual manner, gave some of the acidic products, which were purified by recrystallization from suitable solvents.

Reaction of 1a

Treatment of **1a** (1.2 g, 5.0 mmol) with potassium (0.39 g, 10 mmol) in THF for 4 h and work-up in the usual manner gave 140 mg (12%) of dibenzamide (**11a**) (solid from ethyl acetate extract was fractionally crystallized from benzene), mp 144–145°C (mixture mp) (14); 250 mg (33%) of *C*-phenylglycine (**10a**) (mother liquor after removal of **11a** was evaporated under vacuum and the residual solid was recrystallized from ethanol), mp 270–280°C (mixture mp) (15); and 350 mg (27%) of *N*-benzoyl-*C*-phenylglycine (**6a**) (acidification of the aqueous layer with dilute hydrochloric acid and recrystallization from ethanol), mp 117–178°C (mixture mp) (**5b**).

Treatment of **1a** (500 mg, 2.1 mmol) with potassium (160 mg, 4.1 mmol) in THF saturated with oxygen (100 mL) for 10 h and work-up in the usual manner gave 190 mg (40%) of **11a** (extraction of the reaction mixture with methylene chloride, chromatographing the residual solid over alumina, elution with ethyl acetate–benzene (4:6), and recrystallization from benzene), mp 144–145°C (mixture mp), and 80 mg (32%) benzoic acid (**9**) (acidification of the aqueous layer with dilute hydrochloric acid and recrystallization from hot water), mp 120–121°C (mixture mp).

Reaction of 1b

Treatment of **1b** (1.25 g, 5.0 mmol) with potassium (0.39 g, 10 mmol) in THF for 4 h and work-up in the usual manner gave 200 mg (33%) of benzoic acid (**9**) (acidification of the aqueous layer with dilute hydrochloric acid and recrystallization from hot water), mp 120–121°C (mixture mp); 300 mg (37%) of β -phenylalanine (**10b**) (removal of the solvent under vacuum from the ethyl acetate extract and fractional crystallization from ethanol), mp 284–288°C (mixture mp); and 70 mg (6%) of recovered starting material **1b** (mother liquor after removal of **10b** was evaporated under vacuum and recrystallized from petroleum ether).

Reaction of 1c

Treatment of **1c** (1.56 g, 5.0 mmol) with potassium (0.39 g, 10 mmol) in THF for 45 h and work-up in the usual manner gave 0.5 g (30%) of *N*-benzoyl-*C*,*C*-diphenylglycine (**6c**) (extraction of the reaction mixture with methylene chloride, removal of the solvent under vacuum, and recrystallization from benzene), mp 166–167°C (mixture mp) (10), and 0.81 g (57%) of *N*-benzoyl-*C*,*C*-diphenylmethylamine (**5c**) (acidification of the aqueous layer with dilute hydrochloric acid and recrystallization from ethanol), mp 191–192°C (mixture mp) (10).

Treatment of **1c** (0.4 g, 1.28 mmol) with potassium (80 mg, 2 mmol) in THF saturated with oxygen (100 mL) for 6 h and work-up in the usual manner gave 80 mg (19%) of **6c**, mp 166–167°C (mixture mp); 250 mg (68%) of **5c**, mp 191–192°C (mixture mp); and 50 mg (32%) of benzoic acid (**9**), mp 120–121°C (mixture mp).

Reaction of 4-benzylidene-2-phenyl- Δ^2 -oxazolin-5-one (**12**) with potassium in THF

A mixture of **12** (1.15 g, 4.6 mmol) and potassium (0.39 g, 10 mmol) was shaken in THF (125 mL) for 3 h and poured into moist THF (100 mL). Removal of the solvent under vacuum gave a solid, which was treated with water (10 mL) and extracted with methylene chloride. Acidification of the aqueous layer gave 0.48 g (39%) of α -benzamidocinnamic acid (**15**), mp 222–224°C (mixture mp) (16), after recrystallization from ethanol. The mother liquor on concentration gave 0.22 g (39%) of benzoic acid (**9**), mp 120–121°C, after recrystallization from hot water. Removal of the solvent from the methylene chloride extract

gave 0.1 g (9%) of the unchanged starting material (**12**), mp 165–166°C (mixture mp).

Reaction of bi-4,4'-(2,4-diphenyl- Δ^2 -oxazolin-5-one) (**17**) with potassium in THF

A mixture of **17** (0.94 g, 2.0 mmol) and potassium (0.25 g, 6.4 mmol) was shaken in THF for 5 h. Work-up as in the earlier cases by treatment with moist THF and removal of the solvent under vacuum gave a solid, which was treated with water (10 mL) and extracted first with benzene and later with ethyl acetate. Removal of the solvent from the benzene extract gave 0.15 g (17%) of dibenzimide **11a**, mp 144–145°C (mixture mp). Removal of the solvent from the ethyl acetate extract gave 80 mg (14%)³ of *C*-phenylglycine (**10a**), mp 270–280°C (mixture mp), after recrystallization from ethanol. The mother liquor on evaporation gave 0.31 g (41%) of 2,3,5,6-tetraphenylpyrazine (**25**), mp 248–249°C (mixture mp) (17), after recrystallization from ethanol. Acidification of the aqueous layer with dilute hydrochloric acid gave 80 mg (8%)³ of *N*-benzoyl-*C*-phenylglycine (**6a**), mp 177–178°C (mixture mp).

Reaction of bi-4,4'-(4-benzyl-2-phenyl- Δ^2 -oxazolin-5-one) (**26**) with potassium in THF

A mixture of **26** (0.95 g, 1.9 mmol) and potassium (0.25 g, 6.4 mmol) in THF (125 mL) was shaken for 5 h. Work-up in the usual manner by treatment of the reaction mixture with moist THF and removal of the solvent under vacuum gave a solid, which was treated with water (10 mL) and extracted with benzene and later with ethyl acetate. Removal of the solvent from the benzene extract gave 0.2 g (20%)³ of **15**, mp 222–224°C (mixture mp), after recrystallization from ethanol. Removal of the solvent from the ethyl acetate extract gave 0.15 g (15%) of **6b**, mp 186–187°C (mixture mp), after recrystallization from methanol. The mother liquor was concentrated to give a solid, which was recrystallized from methanol to give 50 mg (11%)³ of benzamide (**29**), mp 128–129°C (mixture mp).

Reaction of Δ^2 -oxazolin-5-ones **1a**–**c** with potassium superoxide

A general procedure was to stir a mixture of 2 mmol of the appropriate Δ^2 -oxazolin-5-one, 4 mmol of potassium superoxide, and 2 mmol of 18-crown-6 in benzene (100 mL) for 24 h at room temperature. On completion of the reaction, the excess of superoxide was destroyed by adding water (20 mL) and extracted with an aqueous solution of sodium chloride. The aqueous layer was acidified with dilute hydrochloric acid and extracted with suitable solvents to give some of the products. Work-up of the organic layer gave the remaining products.

Reaction of 1a

A mixture of **1a** (0.5 g, 2 mmol), potassium superoxide (0.29 g, 4.1 mmol), and 18-crown-6 (0.53 g, 2.1 mmol) was stirred for 24 h and worked up in the usual manner. The aqueous layer was acidified with dilute hydrochloric acid and extracted with ethyl acetate. Removal of the solvent under vacuum gave 40 mg (7%) of **6a**, mp 177–178°C (mixture mp), after recrystallization from ethanol. Removal of the solvent from the organic layer gave 260 mg (55%) of **11a**, mp 144–145°C (mixture mp), after recrystallization from benzene.

Reaction of 1b

Treatment of **1b** (0.4 g, 1.6 mmol) with potassium superoxide (0.22 g, 3.1 mmol) and 18-crown-6 (0.4 g, 1.6 mmol) in benzene (60 mL) for 24 h and work-up as in the earlier case gave 100 mg (23%) of **6b** (acidification of the aqueous layer with dilute hydrochloric acid, extraction with ethyl acetate, and recrystallization from methanol), mp 186–187°C (mixture mp); 90 mg (46%) of **9** (concentration of the mother liquor and fractional crystallization from hot water), mp 120–121°C (mixture mp); and 80 mg (21%) of **11b** (from organic layer), mp 129–130°C, after recrystallization from benzene (lit. (18) mp 129–130°C).

³Yield based on the assumption that one mole of the starting material gives two moles of the product.

Reaction of 1c

Treatment of a mixture of **1c** (0.67 g, 2.1 mmol), potassium superoxide (0.56 g, 7.9 mmol), and 18-crown-6 (1.0 g, 3.9 mmol) in benzene for 24 h and work-up in the usual manner gave 0.6 g (85%) of **6c** (acidification of the aqueous layer with dilute hydrochloric acid and recrystallization from ethanol), mp 166–167°C (mixture mp), and 70 mg (10%) of recovered starting material **1c** (removal of the solvent from the organic layer under vacuum and recrystallization from ethanol).

Reaction of bi-4,4'-(4-benzyl-2-phenyl- Δ^2 -oxazolin-5-one) (26) with potassium superoxide

A mixture of **26** (0.5 g, 1.0 mmol), potassium superoxide (0.14 g, 2.0 mmol), and 18-crown-6 (0.26 g, 1.0 mmol) in benzene (80 mL) was stirred at room temperature for 24 h. Work-up of the mixture as in the earlier cases gave 0.15 g (28%)³ of **15** (acidification of the aqueous layer with dilute hydrochloric acid and recrystallization from ethanol), mp 222–224°C (mixture mp); 50 mg (21%)³ of **9** (from mother liquor), mp 120–121°C (mixture mp); and 200 mg (40%) of recovered starting material **26** (removal of the solvent from the organic layer and recrystallization from benzene – petroleum ether (1:9)), mp 209–210°C (mixture mp).

Cyclic voltammetry

Measurements were made with a Princeton Applied Research (PAR) Model 173 potentiostat/galvanostat, a PAR Model 175 universal programmer, and a Kipp and Zonen X–Y recorder. Experiments were performed in a standard three-compartment cell equipped with a Pt-disc working electrode, a Pt-wire counter electrode, and a Ag/Ag⁺ reference electrode. The cyclic voltammograms were recorded in a deaerated acetonitrile containing 0.1 M tetrabutylammonium perchlorate (TBAP). The direction of the initial scan was cathodic and the scan rate was 200 mV/s.

Pulse radiolysis

The description of the pulse radiolysis apparatus, which allows the determination of the transient spectra at various time intervals after the pulse and the kinetic measurements of the spectral changes, has been reported earlier (19). The irradiation was carried out with 5-ns electron pulses from the Notre Dame 8-MeV ARCO LP-7 linear accelerator, using dose rates of $\sim 2 \times 10^{16}$ eV/g per pulse. The solutions of the appropriate substrates in methanol were deaerated before pulse radiolysis by bubbling nitrogen for at least 30 min and the deaeration was continued in the reservoir from which the solution was allowed to flow slowly and continuously through the cell. The rate constants for the reactions with solvated electrons (e_s^-) were determined from the kinetic analysis of the enhanced rate of decay of e_s^- in the presence of the appropriate substrate or from the growth rate of the radical anion.

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