Anal. Calcd for $C_{15}H_{19}NO_2$: C, 73.44; H, 7.81; N, 5.71. Found: C, 73.88; H, 7.70; N, 5.87.

Fraction 2 (R_f 0.35), 2.7 g crude, was crystallized as above: yield 1.2 g (9%); mp 133–134°; nmr ($CDCl_3$) δ 7.7–7.4 (m, 1), 7.3–6.8 (m, 3), 4.60 (d, J = 3 Hz, 2), 4.6–4.1 (m, 1), 3.80 (s, 2, exchange with D_2O), 3.55 (s, 3), 3.1–2.6 (m, 1), 2.3–1.3 (m, 6).

Anal. Calcd for $C_{15}H_{19}NO_2$: C, 73.44; H, 7.81; N, 5.71. Found: C, 74.05; H, 7.77; N, 5.79.

4a-Hydroxy-7-methyl-1,2,3,4,4a,11c-hexahydro[1]benzopyrano[3,4-*b*]indole (29).—A suspension of 8 g of the lactam **12** in 100 ml of tetrahydrofuran was added under stirring and cooling in an atmosphere of nitrogen to a mixture of $LiAlH_4$ (3.6 g) and 20 ml of tetrahydrofuran. After stirring for 2 hr at 0°, the reaction products were worked up as usual and separated on a silica column, using $CHCl_3$–MeOH (97:3) as eluent. The main fraction, corresponding to an R_f of 0.5 on tlc, was crystalline after evaporation (5 g). Recrystallization from ethanol–petroleum ether yielded 4 g (50%) of **29**: mp 135–139°; ir (KBr) 3440 cm^{-1}; nmr ($CDCl_3$) δ 7.7–7.0 (m, 4), 4.95 (s, 2), 3.55 (s, 3), 3.2–1.5 (m, 10); mass spectrum (70 eV) parent 257.

Anal. Calcd for $C_{16}H_{19}NO_2$: C, 74.68; H, 7.44; N, 5.44. Found: C, 75.01; H, 7.69; N, 5.65.

4a-Hydroxy-10-methoxy-7-methyl-1,2,3,4,4a,11c-hexahydro-[1]benzopyrano[3,4-*b*]indole (30).—The reduction of **13** was performed analogously to the one described for the preparation of **29**. In this case, the reaction was carried out at room temperature and the reaction product was crystallized without chromatography in 68% yield from chloroform: mp 165–168°; nmr (DMSO-d_6) δ 7.4–6.6 (m, 3), 5.70 (s, 1, exchange), 4.85 (s, 2), 4.55 (broad s, 1), 3.73 (s, 3), 3.48 (s, 3), 3.0–0.9 (m, 8).

Anal. Calcd for $C_{17}H_{21}NO_3$: C, 71.05; H, 7.37; N, 4.87. Found: C, 71.02; H, 7.35; N, 5.07.

2-(5-Methoxy-1,2-dimethyl-3-indolyl)cyclohex-2-enone (33).—A solution of the semiketal **30** (8 g) in dioxane (80 ml) containing 4 ml of 4 N HCl was allowed to stand for 30 min at room temperature. It was diluted with 100 ml of 2 N Na_2CO_3 and extracted with two 200-ml portions of ethyl acetate. The residue after washing, drying, and evaporation (8 g) was chromatographed on silica using $CHCl_3$–CH_3OH (99:1) as eluent. A main fraction was obtained crystalline in 50% yield (4 g). After recrystallization from ethanol, 1.9 g (25%) of the unsaturated ketone **33** was obtained analytically pure: mp 107–108°; ir (KBr) 1675 cm^{-1}; nmr ($CDCl_3$) δ 7.3–6.6 (m, 4), 3.78 (s, 3), 3.57 (s, 3), 2.8–2.0 (m, 6), 2.22 (s, 3).

Anal. Calcd for $C_{17}H_{19}NO_2$: C, 75.81; H 7.11; N, 5.20. Found: C, 75.65; H, 7.17; N, 5.20.

2-(5-Methoxy-1,2-dimethyl-3-indolyl)cyclohexanone (7m).—The unsaturated ketone **33** (0.5 g) was hydrogenated in ethanol (50 ml) with palladium (5%) on carbon at room temperature and atmospheric pressure in the usual way. The residue after filtration and evaporation yielded crystals from ethanol, which were identical (melting point, ir, nmr, tlc) with the material obtained according to eq 1 (see Table III).

Registry No.—**7a,** 32544-44-8; **7a** oxime, 32500-86-0; **7a** thiosemicarbazone, 32500-87-1; **7b,** 32500-88-2; **7b** thiosemicarbazone, 32500-89-3; **7c,** 32500-90-6; **7d,** 32500-91-7; **7d** oxime, 32500-92-8; **7d** thiosemicarbazone, 32500-93-9; **7e,** 32500-94-0; **7e** oxime, 32500-95-1; **7e** thiosemicarbazone, 32500-96-2; **7f,** 32500-97-3; **7f** oxime, 32500-98-4; **7f** thiosemicarbazone, 32500-99-5; **7g,** 32544-45-9; **7g** oxime, 32501-00-1; **7g** thiosemicarbazone, 32501-01-2; **7h,** 32500-28-0; **7h** oxime, 32500-29-1; **7h** thiosemicarbazone, 32500-30-4; **7i,** 32605-77-9; **7k,** 32544-46-0; **7k** oxime, 32500-31-5; **7k** thiosemicarbazone, 32500-32-6; **7l,** 32500-33-7; **7l** oxime, 32500-34-8; **7l** thiosemicarbazone, 32500-35-9; **7m,** 32500-36-0; **7m** thiosemicarbazone, 32500-37-1; **7n,** 32500-38-2; **7n** thiosemicarbazone, 32500-39-3; **7o,** 32500-40-6; **7o** oxime, 32500-41-7; **9,** 32500-42-8; **10,** 32500-43-9; **11,** 32500-44-0; **12,** 32500-45-1; **13,** 32500-46-2; **14,** 32544-47-1; **14** thiosemicarbazone, 32500-47-3; **15a,** 32500-48-4; **15b,** 32500-49-5; **17,** 32500-50-8; **18,** 32500-51-9; **19,** 32500-52-0; **20,** 32500-53-1; *cis*-**21, -22,** 32500-54-2; *trans*-**21, -22,** 32500-55-3; *cis*-**23, -24,** 32500-56-4; *trans*-**23, -24,** 32500-57-5; *cis*-**25,** 32500-58-6; *trans*-**26,** 32500-59-7; *cis*-**27, -28,** 32500-60-0; *trans*-**27, -28,** 32500-61-1; **29,** 32500-62-2; **30,** 32500-63-3; **33,** 32500-64-4.

Acknowledgment.—The author is indebted to Miss E. Dubois and Mrs. A. Thomas for skillful technical assistance and to Dr. F. K. Hess for helpful discussions.

Synthesis of Dinitroxides

URS R. JOSS[1] AND MELVIN CALVIN*[2]

Laboratory of Chemical Biodynamics, Lawrence Berkeley Laboratory, and Department of Chemistry, University of California, Berkeley, California 94720[3]

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The synthesis of seven stable nitroxide biradicals has been completed. Five of these compounds, namely, *N*-(1-oxyl-2,2,6,6-tetramethylpiperidyl)-*N'*-(1-oxyl-2,2,6,6-tetramethyl-4-methoxycarbonylpiperidyl)urea, 1-oxyl-2,2,5,5-tetramethylpyrrolyl-4-*N*-(1-oxyl-2,2,5,5-tetramethylpyrrolidyl-3-methylene)carboxamide, 1-oxyl-2,2,5,5-tetramethylpyrrolidine-3-*N*-(1-oxyl-2,2,6,6-tetramethylpiperidyl-4)carboxamide, 1,2-bis(1-oxyl-2,2,6,6-tetramethyl-4-methoxycarbonylpiperidyl-4)oxalic acid diamide, and 1,2-bis(1-oxyl-2,2,6,6-tetramethylpiperidyl-4)-succinic acid diamide, fulfill the two conditions which are postulated for their application as a flexible strain gauge in biological material: a distance of 7–11 Å between the two radical units in order to guarantee an interaction between the two unpaired electrons and a certain rigidity in the connecting chain in order to achieve a high resolution of the esr spectrum.

In this paper we describe the synthesis of new stable biradicals in the class of nitroxides of pyrrolines, pyrrolidines, and piperidines. Stable biradicals have been proposed as a flexible strain gauge, which would be attached to a biological sample (membrane or macromolecule) at two points, deform together with the support, and transduce the strain into the interaction-dependent features of the esr spectrum.[4,5]

***N,N'*-Bis(1-oxyl-2,2,6,6-tetramethyl-4-cyano-4-piperidyl)diaminoethane (I).**—This biradical in the class of the bis(α-imino acid nitriles) was obtained by a

(1) Fellow of the Stiftung für Stipendien auf dem Gebiete der Chemie Basle, Switzerland.

(2) To whom correspondence should be addressed.

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(4) M. Calvin, H. H. Wang, G. Entine, D. Gill, P. Ferruti, M. A. Harpold, and M. P. Klein, *Proc. Nat. Acad. Sci. U. S.*, **63**, 1 (1969).

(5) P. Ferruti, D. Gill, M. P. Klein, H. H. Wang, G. Entine, and M. Calvin, *J. Amer. Chem. Soc.*, **92**, 3704 (1970).

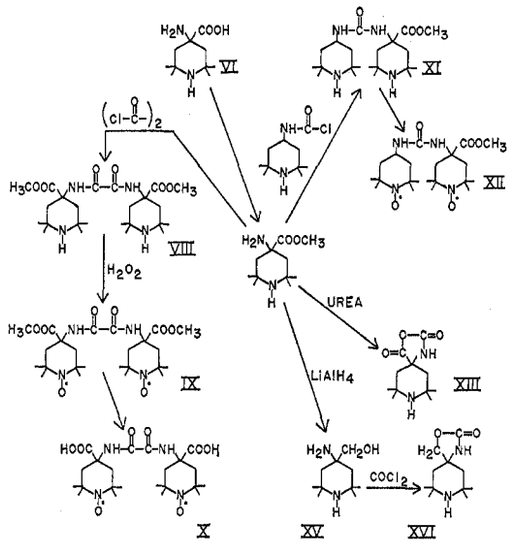
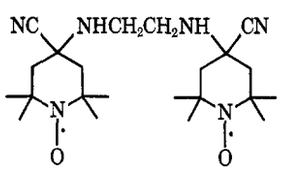


Figure 1.—Synthetic scheme for derivatives of 2,2,6,6-tetramethyl-4-carboxypiperidine (VI).

modified synthesis according to Strecker with 1-oxyl-2,2,6,6-tetramethyl-4-piperidone and ethylenediamine. Compound I is very easily hydrolyzed back to its starting materials, and is, therefore, not useful for biological applications.



I

1-Oxyl-2,2,5,5-tetramethylpyrrolyl-4-*N*-(1-oxyl-2,2,5,5-tetramethylpyrrolidyl-3-methylene)carboxamide (III).—This compound was prepared by acylation of 2,2,5,5-tetramethyl-3-aminomethylpyrrolidine (V) with 1-oxyl-2,2,5,5-tetramethyl-3-chloroformylpyrroline (IV), to 1-oxyl-2,2,5,5-tetramethylpyrrolyl-4-*N*-(1-oxyl-2,2,5,5-tetramethylpyrrolidyl-3-methylene)carboxamide (III), followed by oxidation. Compound V was prepared by reduction of 2,2,5,5-tetramethylpyrrolidine-3-carboxamide with lithium aluminum hydride.

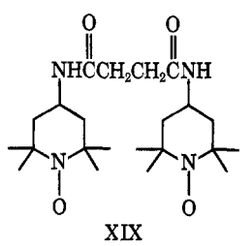
Derivatives of 2,2,6,6-Tetramethyl-4-amino-4-carboxypiperidine (VI).—Figure 1 gives a summary of the derivatives of VI. We prepared three biradicals from VI, which is described by Rassat,[6] namely, the amides IX, X, and XII, using the methyl ester of VI (VII) as a key intermediate.

***N*,*N*′-Bis(1-oxyl-2,2,6,6-tetramethyl-4-methoxycarbonylpiperidyl-4)oxalic acid diamide (IX)** was prepared by acylation of VII with oxalyl chloride, which yields the diamide VIII. It is converted to IX by oxidation with hydrogen peroxide. Mild alkaline hydrolysis yields 1,2-bis(1-oxyl-2,2,6,6-tetramethyl-4-carboxypiperidyl-4)oxalic acid diamide (X).

***N*-(1-oxyl-2,2,6,6-tetramethylpiperidyl-4)-*N*′-(1-oxyl-2,2,6,6-tetramethyl-4-methoxycarbonylpiperidyl-4)-urea (XII).**—We obtained XII by selective acylation of VII with the carbamic acid chloride of 2,2,6,6-tetramethyl-4-aminopiperidine and oxidation of the unsymmetrical *N*,*N*′-disubstituted urea XI with hydrogen peroxide in 60% yield. The inverse procedure, namely, the reaction of the carbamic acid chloride of VII with 2,2,6,6-tetramethyl-4-aminopiperidine, gave only 30% XI.

We obtained the hydantoin XIII exclusively in our attempts to prepare the *symmetrical urea* XIV by melting together 2 mol of VII and 1 mol of urea. Neither did we get the urea which could be expected from the reaction of 2 mol of 2,2,6,6-tetramethyl-4-amino-4-hydroxymethylpiperidine (XV) with 1 mol of phosgene or urea, but we did obtain the oxazolidone XVI in good yield.

Derivatives of 2,2,6,6-Tetramethyl-4-aminopiperdine (XVII). *N*,*N*-Bis(1-oxyl-2,2,6,6-tetramethylpiperidyl-4)succinic Acid Diamide (XIX).—We obtained XIX by condensation of 2 mol of XVII with 1 mol of succinyl chloride to XVIII and oxidation of XVIII with hydrogen peroxide. Rozantsev obtained



XIX

XIX by condensing succinyl chloride with 1-oxyl-2-2,6,6-tetramethyl-4-aminopiperidine.[7]

1-Oxyl-2,2,5,5-tetramethylpyrrolidine-3-*N*-(1-oxyl-2,2,6,6-tetramethylpiperidyl-4)carboxamide (XX).—We prepared XX by acylation of XVII with 1-oxyl-2,2,5,5-tetramethylpyrrolidine-3-carboxylic acid and 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide and oxidation with hydrogen peroxide.

Experimental Section

Biradical I.—Ethylenediamine (0.02 mol) was almost neutralized with HCl (pH 8) and 2.20 g (0.046 mol) of NaCN was added. After mixing, 5 ml of ethanol was added and the mixture was cooled at −10°. Within 2 hr a saturated solution of 6.84 g (0.04 mol) of 2,2,5,5-tetramethylpiperidine(1)oxyl in 90% ethanol was added, while the reaction mixture was kept at −10 to 0° and stirred. The resulting clear orange mixture was stirred for 0.5 hr with the same volume of ice, whereupon compound I precipitated. After the addition of 5 ml of water, I was separated by filtration and washed with water. The product was almost pure and has a melting point of 126° after drying over P_2O_5 *in vacuo* at room temperature. It can be recrystallized in benzene, ir 3300 ($-NH_2$) and 2219 cm^{-1} (CN).

Anal. Calcd: C, 63.15; H, 9.1; N, 20.1. Found: C, 63.14; H, 9.13; N, 20.24.

Biradical III.—Five grams of 2,2,5,5-tetramethyl-4-carbamidopyrrolidine and 2.5 g of $LiAlH_4$ were refluxed for 2 days in absolute ether. Water and solid KOH were added, and the solvent was evaporated from the filtered reaction mixture. The residue was fractionated *in vacuo*. The yield was 3 g of a colorless liquid at 90–92° (12 Torr), ir 3365, 3305, 3180, 1583 cm^{-1}.

A mixture of 2,2,5,5-tetramethyl-4-carboxypyrroline-1-oxyl and 0.1 ml of pyrridine in 3 ml of benzene was cooled to 0° and 0.09 ml of thionyl chloride was slowly added. After standing at room temperature for 1 hr, the solution of the acid chloride was separated from the pyridine–HCl with a filter pipette and concentrated in the argon stream, until the mixture did not smell of $SOCl_2$ anymore. The material was cooled at 0°, and 155 mg of 2,2,5,5-tetramethyl-4-aminomethylpyrrolidine was added. After

(6) A. Rassat and P. Rey, *Bull. Soc. Chim. Fr.*, 815 (1967).

(7) E. G. Rozantsev and V. I. Suskina, *Izv. Akad. Nauk SSSR., Ser. Khim.*, **9**, 2148 (1968).

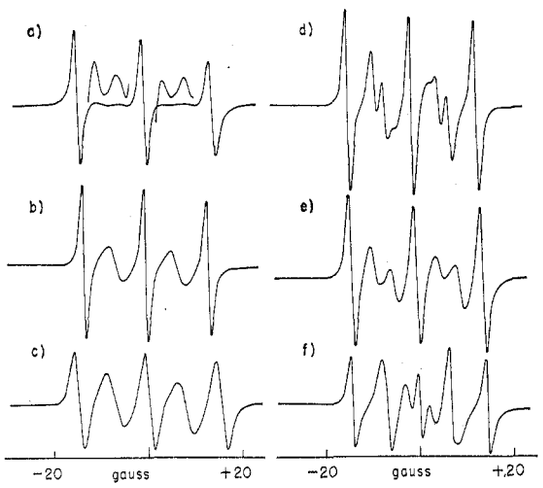


Figure 2.—First-derivative esr spectra of biradicals III, IX, XIX, and XX in different solvents: IX (a) in water and (b) in chloroform; XIX (c) in water and (d) in chloroform; III (e) and XX (f) in water. The spectra of oxygen-free solutions of III and XX in chloroform show the same resolution.

stirring for 2 hr at room temperature, the precipitated hydrochloride was brought into solution by adding 1 *M* NaOH. The organic layer was washed with water and the solvent was evaporated. The residue was oxidized with hydrogen peroxide without purification,[8] yield 250 mg of raw product, yellow needles, mp 182.5° (cyclohexane–benzene), ir 3448, 3360, 1664, 1615 cm^{-1} (double bond).

Anal. Calcd: C, 64.14; H, 9.20; N, 12.51. Found: C, 64.15; H, 9.22; N, 12.60.

Amino Acid Ester VIII.—Two grams of VI was dissolved in 20 ml of absolute methanol and the mixture was saturated with HCl gas. Methanol was removed *in vacuo* after 10 hr and the same procedure was repeated. The residue of the amino acid methyl ester hydrochloride was made alkaline with 15% KOH at 0°, and the free ester was extracted with chloroform. After washing with water, drying, and evaporating the chloroform, the residue crystallized as large, colorless crystals, mp 88–89°. After recrystallization in cyclohexane–petroleum ether (bp 30–60°) the melting point was 91.5°, yield 60% over-all, ir 3375 (–NH), 3300 ($-NH_2$), 1725 cm^{-1} (C=O).

Anal. Calcd: C, 62.0; H, 9.88; N, 13.13. Found: C, 62.08; H, 10.04; N, 13.02.

Biradical IX.—To a solution of 107 mg of amino acid ester VII in 2 ml of chloroform, 0.021 ml of oxalyl chloride was added under argon at −5°. After 2 hr at 0° and 24 hr at 20° the white precipitate was separated by filtration and recrystallized in petroleum ether and cyclohexane, yield 70–80%, mp 179.5°.

Anal. Calcd: C, 59.9; H, 8.9; N, 11.65. Found: C, 60.03; H, 8.96; N, 11.77.

IX was obtained by the usual oxidation procedure, according to Rozantsev,[10] mp 231°, ir 3390, 1741, 1685 cm^{-1}.

Biradical X.—A solution of 79 mg of diester IX in 2.5 ml of 0.5 *M* NaOH and 2 ml of methanol was kept at 40° for 3 hr and then at 20° for an additional 3 hr. The reaction mixture was acidified very carefully to pH 3–4 with HCl. The bright yellow diacid X precipitated and was collected by filtration and recrystallized in acetone under pressure at 100°, yield 70%, mp 230° dec, ir 3200, 2500, 1720, 1670 cm^{-1}.

Anal. Calcd: C, 54.55; H, 7.48; N, 11.58. Found: C, 54.50; H, 7.39; N, 11.37.

Biradical XI.—To a mixture of 155 mg of XVII in 2 ml of chloroform under argon, 0.8 ml of a 12.5% solution of phosgene in benzene was added at −20°. The mixture was warmed up to 0° and after 10 min 214 mg of amino acid ester VII in 1 ml of chloroform was slowly injected. The reaction mixture was stirred for 2 hr at 0° and for 30 min at 70°. Chloroform was evaporated *in vacuo*, and the residue was dissolved in 2 ml of 1 *M* HCl, kept at 60° for 30 min, cooled to 0°, and made alkaline to pH 12 with concentrated KOH. The white precipitate was filtered and washed with water, yield 200 mg, mp 260–270°.

(8) E. G. Rozantsev, "Free Nitroxyl Radicals," Plenum Press, New York, N. Y., 1970.

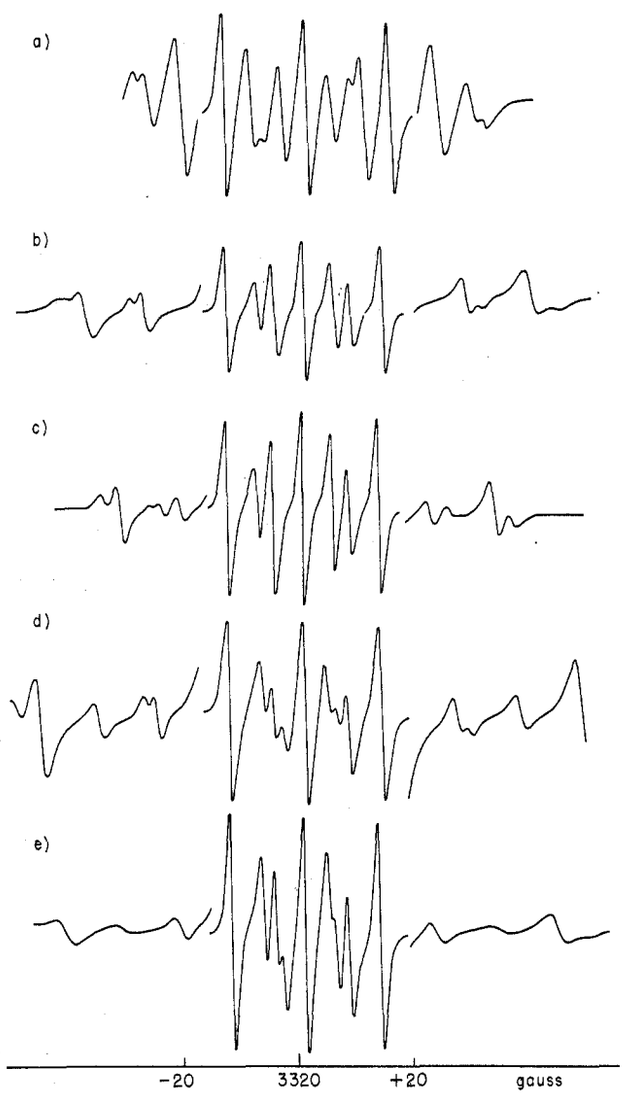


Figure 3.—First derivative esr spectra of biradical XII in (a) water, (b) chloroform, (c) benzene, (d) carbon tetrachloride, and (e) *n*-hexane. The *J* resonances ("side bands") are recorded at 10 times higher gain.

Oxidation with H_2O_2 and recrystallization of the crude biradical from methanol–cyclohexane and benzene yielded 120 mg of red needles, mp 241°, ir 3460, 3430, 3360, 1763, 1700 (s), 1507 cm^{-1}.

Anal. Calcd: C, 59.1; H, 8.95; N, 13.15. Found: C, 59.58; H, 8.73; N, 13.50.

Biradical XIX.—To 1.56 g of XVII in 20 ml of chloroform, 0.78 g of succinoyl chloride in 5 ml of chloroform was added slowly. After 1 hr, the white precipitate was filtered and 10% aqueous NaOH solution was added. The free base was extracted with chloroform, and the extract was washed with saturated sodium chloride solution and dried with sodium sulfate. After recrystallization in isopropyl alcohol, the white amide dihydrate melted at 204°. Oxidation with hydrogen peroxide yielded 90% XIX, mp 180° (lit. mp 178.5–180°).

Anal. Calcd: C, 62.7; H, 9.50; N, 13.25. Found: C, 62.75; H, 9.61; N, 13.37.

Biradical XX.—A mixture of 186 mg (1 mmol) of 2,2,5,5-tetramethyl-4-carboxypyrrolidine-1-oxyl, 200 mg (1.05 mmol) of 1-ethyl-3-(dimethylaminopropyl)carbodiimide HCl, and 155 mg (1 mmol) of XVII in 5 ml of chloroform was kept overnight at 40° under argon. After evaporation of the solvent the residue was oxidized by the usual method overnight with hydrogen peroxide without any purification. The crude red biradical was recrystallized once from benzene–cyclohexane, yield 30% over-all, mp 179.5°, ir 3425, 3332, 1667 cm^{-1}.

Anal. Calcd: C, 62.9; H, 9.54; N, 12.93. Found: C, 63.00; H, 9.60; N, 12.94.

Hydantoin XII by a Substitution with Urea.—Two moles of

VII and 1 mol of urea were mixed together and heated to 160–170° in 15 min. At 140° the mixture started evolving NH_3, and became turbid. After 30 min at 170° the mixture was a white solid. After cooling down, about 120 mg of starting material VII was extracted with toluene. The residue consisted of pure hydantoin XIII (identified by comparison of its ir spectrum with the ir spectrum of hydantoin obtained by a Strecker synthesis with 2,2,6,6-tetramethyl-4-oxopiperidine).

The oxazolidone XVI was made in an analogous procedure with amino alcohol XV.

Amino Alcohol XV.—Amino acid ester VII (214 mg) and 115 mg of $LiAlH_4$ were stirred in 5 ml of ether for 15 min. Water (0.8 ml) was added and then 30 ml of ether. Filtration and evaporation of the solvents yielded 200 mg of XV, mp 121.5° (petroleum ether–benzene), ir (Nujol) 3620, 3340, 3160, 1580 cm^{-1}.

Anal. Calcd: C, 64.5; H, 11.8; N, 15.05. Found: C, 64.85; H, 11.98; N, 15.04.

Esr Spectra.—The spectra described here have been taken at X band in a Varian E-3 spectrometer. Some preliminary studies were done with different solvents. The solutions were degassed and sealed off in a vacuum line. Radical concentrations were sufficiently low to eliminate intermolecular exchange broadening. The spectra were taken at 20°.

A selection of spectra of biradicals III, IX, XIX, and XX is shown in Figure 2. Figure 3 shows the spectra of biradical XI in five solvents of different polarities. Biradicals I and X showed three sharp lines and two broad lines inbetween. This type of spectrum has been discussed by Ferruti and coworkers.[5]

Registry No.—I, 34386-54-4; III, 34386-55-5; VII, 34386-56-6; IX, 34402-55-6; X, 34386-57-7; XI, 34402-56-7; XV, 32923-90-3; XIX, 21184-43-0; XX, 34386-59-9.

Sulfur Dioxide Extrusion from 2,5-Diaryl-4-hydroxy-3-ketotetrahydrothiophene 1,1-Dioxides. A Novel Synthesis of 1,4-Diarylbutane-2,3-diones[1]

MICHAEL CHAYKOVSKY,* MAY H. LIN, AND ANDRE ROSOWSKY

The Children's Cancer Research Foundation and the Department of Biological Chemistry, Harvard Medical School, Boston, Massachusetts 02115

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Five 2,5-diaryl-4-hydroxy-3-keto-2,3-dihydrothiophene 1,1-dioxides (**4a–e**) were prepared and reduced with zinc dust in acetic acid–ethanol–THF at 5–10° to 2,5-diaryl-4-hydroxy-3-ketotetrahydrothiophene 1,1-dioxides (**5a–e**). These products, in acetic acid–sodium acetate solution at 100–110°, underwent fragmentation to 1,4-diarylbutane-2,3-diones (**6a–e**) with loss of sulfur dioxide. Nmr analysis showed that the latter products consisted of mixtures of diketo and monoenol forms, with the monoenol predominating. It is proposed that the fragmentation reaction proceeds *via* a concerted elimination of sulfur dioxide from a 3-sulfolene intermediate.

α diketones have found a wide range of use in organic synthesis. However, one class of α diketones, the 1,4-diarylbutane-2,3-diones, appears infrequently in the chemical literature. The synthesis of only two compounds of this type has been reported: 1,4-diphenylbutane-2,3-dione and the 1,4-bis(4′-methoxyphenyl) analog. The former was prepared[2] by reaction of benzylmagnesium chloride with phenylacetaldehyde cyanohydrin, followed by hydrolysis and oxidation of the resulting acyloin with cupric acetate. The acyloin condensation has been reported to fail with ethyl phenylacetate.[3] According to a more recent report,[4] however, the reaction of ethyl 4′-methoxyphenylacetate proceeds in good yield to the corresponding acyloin, which upon oxidation gives 1,4-bis(4′-methoxyphenyl)-butane-2,3-dione.

For the general synthesis of substituted 1,4-diarylbutane-2,3-diones, the cyanohydrin method suffers from the lengthy preparation of intermediates. The acyloin method appears limited in its scope and is certainly unsuitable for the synthesis of analogs with halogen substituents since it involves the use of metallic sodium. We report here a new method for the synthesis of 1,4-diarylbutane-2,3-diones, which is fairly general in its scope and uses readily available starting materials. This method involves the intermediate synthesis of 2,5-diaryl-4-hydroxy-3-keto-2,3-dihydrothiophene 1,1-dioxides (*e.g.*, **4**), a class of compounds first prepared by Overberger and coworkers.[5]

Following the general route of Overberger[5a,c] (see Scheme I), treatment of 3,4-dimethylbenzyl chloride **1a** with sodium sulfide in aqueous ethanol yielded the sulfide **2a** (95%), which was oxidized with 30% hydrogen peroxide in acetic acid to sulfone **3a** (92%). Condensation of **3a** with excess diethyl oxalate in the presence of sodium ethoxide gave the cyclic diketo sulfone **4a** (80%), which exists in the tautomeric forms indicated.

We were interested in determining if compounds such as **4a** could be converted into 1,4-diarylbutane-2,3-diones by the action of reducing agents which are known to cause reductive cleavage of β-keto sulfones to ketones.[6] When **4a** was treated with zinc dust in acetic acid–ethanol–THF mixtures at 5–10° for 30 min, the major product isolated was the hydroxy-keto sulfone **5a** (73%) rather than the butanedione **6a**. Thin layer chromatography (silica gel, benzene) of samples of the reaction mixture indicated the formation of only a minor amount of **6a** as a fast-moving spot. At higher temperatures further reduction of these products becomes a significant side reaction. The structure of

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