Table I. Synthesis and Regioselective Hydrolysis of Seven Boc-Tripeptide Amides Containing an Internal Residue of Pyroglutamic Acid

	peptide 2, R = H		k' value[a]			hydrolysis[b]			yield, %	
code	structure	yield, %	1	2	5	k_α	k_γ	k_α/k_γ	5	1
a	Boc-Ala-Glp-Asn-$NHCH_3$	83	0.45	1.06	0.15	100	5.4	18.3	94.9	5.1
b	Boc-Met-Glp-Asn-$NHCH_3$	84	1.60	3.01	0.15	59	4.5	13.1	92.9	7.1
c	Boc-Glu-Glp-Val-NH_2	81	1.36	2.29	0.24	27	2.0	13.2	93.0	7.0
d	Boc-Glu-Glp-Asn-$NHCH_3$	78	0.38	0.93	0.15	36	3.5	10.2	91.1	8.9
e	Boc-Gly-Glp-Val-NH_2	79	0.99	1.72	0.24	51	8.4	6.0	85.8	14.2
f	Boc-Ala-Glp-Val-NH_2	86	1.44	2.52	0.24	56	9.5	5.9	85.5	14.5
g	Boc-Leu-Glp-Val-NH_2	82	2.54	4.73	0.18	14	3.5	4.1	80.4	19.6

[a] Relative retention time on octadecyl-silica, where $k' = (t_{peptide}/t_{solvent}) - 1$ and t is the retention time in 6% CH_3CN containing 0.05% CF_3CO_2H (except 12% CH_3CN for g). [b] Apparent first-order rate constants (10^{-6} s^{-1}) for hydrolysis of 2 in 150 mM NaCl/10 mM Na phosphate at 37 °C and pH 8.3 (except pH 8.0 for 2c and 2d).

fragment-induced mass spectrum[14] and gave a characteristic 300-MHz proton magnetic resonance spectrum. Formation of lactams **2a–g** was accompanied by <1% of imides **3a–g** as measured chromatographically. Reaction of Boc-Ile-Glu-Gly-NH_2 (**1h**) with CDI, however, provided only 2% of the five-membered lactam **2h** and 95% of the six-membered imide **3h**. The extent of this alternate mode of cyclization is evidently determined by the relative bulk of side chains R^1 and R^2 of the flanking residues.

Hydrolysis. Apparent first-order rate constants k_γ for ring opening at the Glp γ carbonyl and k_α for chain fragmentation at the α carbonyl of the preceding residue were measured for peptides **2**, R = H, in phosphate-buffered saline at pH 8.0 or 8.3 and 37 °C. Solutions were analyzed over 5–6 h by reverse-phase liquid chromatography monitored at 220 nm (Table I). Corrected peak areas of lactams **2** and their hydrolysis products **1** and **5**[15] were used to calculate their mole fractions at various times and rate constants k_α and k_γ. The latter varied with the bulk of side chains R^1 and R^2. Replacement of Ala-1 by the larger residue Glu decreased k_α by 2- or 3-fold and k_γ by 2- or 5-fold, and replacement by Leu decreased k_α by 7-fold. Only modest rate changes were seen on substitution of Ala-1 by the smaller residue Gly or of Asn-3 by the β-branched residue Val. The regioselectivity ratio k_α/k_γ varied from 4.1 to 18.3 and did not generally correlated with the magnitude of k_α (compare **2c** and **2f**). In all seven cases, hydrolysis proceeded with 80–95% regioselectivity through attack at the α carbonyl group.[17]

Model Studies. The hydrolytic rate constants for these model tripeptides are similar to those we have observed[7] at pH 7.3 and 37 °C for synthetic hexapeptide lactams of type A, R = CH_2C-H_2CO_2H ($k_\alpha = 32 \times 10^{-6}$ s^{-1}, $k_\gamma = 3.7 \times 10^{-6}$ s^{-1}) or CH_3 ($k_\alpha = 65 \times 10^{-6}$ s^{-1}, $k_\gamma = 7.0 \times 10^{-6}$ s^{-1}). In both cases, hydrolysis proceeded with 90% regioselectivity, which is typical of an internal Glp residue (Table I).

Many peptide hormones, such as thyroliberin[18] (TRH), luliberin[19] (LH-RH), serum thymic factor[20] (FTS), and neurotensin[21] bear an N-terminal Glp residue. The present model studies suggest that some of these residues might also arise by regioselective hydrolysis with chain fragmentation of a precursor polypeptide containing an internal Glp residue.

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(16) Z-Glp-Val-NH_2, prepared in 89% yield by mixed anhydride coupling of Z-Glp with Val-NH_2, was deprotected by catalytic transfer hydrogenolysis to furnish Glp-Val-NH_2 in 89% yield. Similarly prepared were Z-Glp-Asn-NH-CH_3 (77% yield) and Glp-Asn-NH-CH_3 (96% yield).

(17) Hydrolysis of a benzoyl dipeptide or tripeptide amide containing an internal Glp residue gave the fragment having an N-terminal Glp residue in 36–50% isolated yield.[8,9]

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"S_2": Generation and Synthetic Application

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Although reference to singlet oxygen ($^1O_2$) first appeared in the literature in 1924,[2,3a] it is primarily during the past two decades that most of its chemistry has been delineated.[3] The recognition that this form of molecular oxygen might play a central role in many of the important oxygen-related biological processes[3,4] has served to catalyze a current widespread interest in its chemical and biochemical reactivity. For several years now, in anticipation that singlet sulfur ($^1S_2$) might emulate singlet oxygen chemistry, we, among others, have been actively pursuing possible synthetic avenues for its preparation. We herein describe a procedure for the facile generation of "S_2"[5] and its application via the Diels–Alder reaction to the synthesis of cyclic disulfides.

Among the many procedures available for the generation of singlet oxygen ($^1O_2$),[3a,6] one of the most attractive is by means of the controlled, thermally induced decomposition of a phosphine or phosphite ozone adduct. These are conveniently prepared from

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(5) (a) While we have not been able to isolate or spectroscopically characterize this highly reactive form of sulfur, it is likely, by spin conservation arguments, that it is formed in the singlet state. It should be noted, however, that the ground state of S_2 is a triplet in direct analogy to O_2. Further, the singlet state of $^1S_2$ has been measured at ca. 13 kcal above the ground state (see: Strausz, O. P.; Donavan, R. J.; de Sorgo, M. *Ber. Bunsenges. Phys. Chem.* **1968**, *72*, 253). Also, it has been claimed that S_2 is formed in the photolysis of *O*-ethyl thioacetate to give ca. 2% of a trapped Diels–Alder adduct among a mixture of other sulfurated products. See: Jahn, R.; Schmidt, U. *Chem. Ber.* **1975**, *108*, 630. (b) Salahub, D. R.; Foti, A. E.; Smith, V. H., Jr. *J. Am. Chem. Soc.* **1978**, *100*, 7847 and references cited therein. For some literature reviews on elemental sulfur (S_n), see: Steudel, R. *Top. Curr. Chem.* **1982**, *102*, 149. Maxwell, L. R.; Mosley, V. M.; Hendricks, S. B. Phys. *Rev.* **1936**, *50*, 41. Kutney, G. W.; Turnbull, K. *Chem. Rev.* **1982**, *82*, 334. Meyer B. *Ibid.* **1976**, *76*, 367. See also: Tebbe, F. N.; Wasserman, E.; Peet, W. G.; Vatvars, A.; Hayman, A. C. *J. Am. Chem. Soc.* **1982**, *104*, 4971.

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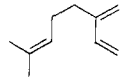
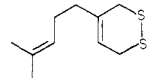
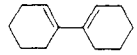
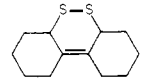
Table I.

$$R_3MSSSMR_3 + 4 + Ph_3PBr_2 \xrightarrow[25\ ^\circ C]{CH_2Cl_2} 2R_3MBr + 5 + Ph_3P{=}S$$
2 3

entry	4	5[10a]	isolated yield,[10b] % (by ^{1}H NMR)
1			35
2			20 (42)[10c]
3			35 (65)[10d]
4			50 (70)

the direct ozonolysis of triaryl- or trialkoxy-substituted phosphorus-containing substrates (eq 1).[6a] The utility of this process

$$R_3P + O_3 \rightarrow \underset{\mathbf{1}}{R_3PO_3} \xrightarrow{\Delta} R_3P{=}O + {}^1O_2 \qquad (1)$$

lies with the ready availability of the reagents and the ease by which the ozone adduct **1** collapses into its corresponding oxide to liberate singlet oxygen. Since formation of phosphine sulfides is also known to be energetically favorable,[7] an analogous approach to the generation of singlet sulfur ($^1S_2$) merited special consideration. However, unlike O_3, S_3[5b] is not easily available, and its equivalent source first had to be secured. Our previous work with group 4 organometallic reagents in organic synthesis[8] led us to prepare a series of silyl- and germanium-protected trisulfides[9] which could serve as latent stable masked sources for the S_3 unit.

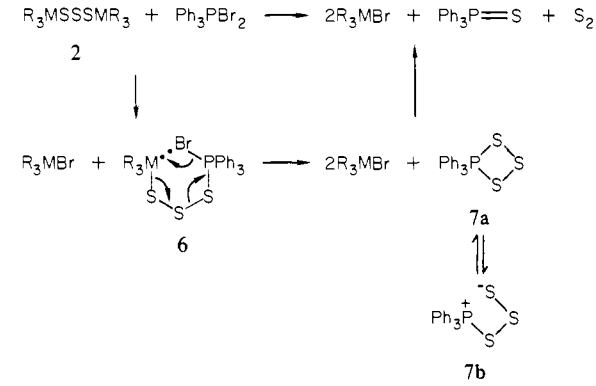
Thus, treatment of trisulfides **2** with triphenylphosphine dibromide (eq 2) quantitatively gave after workup the corresponding

$$\underset{\mathbf{2}}{R_3MSSSMR_3} + Ph_3PBr_2 \xrightarrow[25\ ^\circ C]{CH_2Cl_2} \underset{\mathbf{3}}{2R_3MBr} + Ph_3P{=}S + {}^1/_4S_8 \qquad (2)$$

a, M = Si; R = C_6H_5. **b**, M = Ge; R = C_6H_5. **c**, M = Ge; R = C_6H_{11}. **d**, M = Ge; R = *p*-$CH_3C_6H_4$

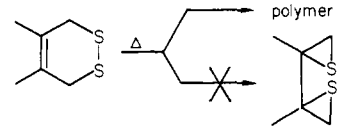
amounts of bromides **3**, triphenylphosphine sulfide, and elemental sulfur. *However, when the same reaction is carried out in the presence of a conjugated diene, formation of elemental sulfur is efficiently suppressed with concomitant formation of the corresponding Diels–Alder adduct* **5**[10a] *from the addition of an* S_2 *unit to the diene (see Table I)*! Further, the adducts obtained by this method, unlike those from the addition of "activated" elemental sulfur to olefinic compounds,[10d,11] appear to be free from polysulfide contamination and indiscriminate sulfuration.

Scheme I



Although we assume by analogy to the singlet oxygen case (eq 1) that phosphine sulfide **7** (Scheme I), or its probable immediate precursor **6**, is the responsible agent from which S_2 is liberated, our initial attempts to isolate or spectroscopically characterize these intermediates have not been fruitful.

The disulfide Diels–Alder adducts **5** (Table I) prepared by this type of S_2 addition are particularly thermally sensitive to polymerization[10d,12] and are not prone to rearrange into their corresponding bis(episulfides) (eq 3). This is in sharp contrast to the



(3)

analogous singlet oxygen derived cyclic peroxides.[3] Also, our experimental results with simple olefins such as tetramethylethylene, 9,10-octalin, and norbornylene as well as with diphenylacetylene indicate that S_2 unlike $^1O_2$ does not undergo [2 + 2] addition or the "ene" reaction which is quite common to singlet oxygen chemistry.[3,6,14] Thus, the reactivity of S_2 toward olefinic compounds appears to be limited to Diels–Alder additions and is quite distinct from that of singlet or triplet atomic sulfur, which respectively afford mercaptans (from carbon–hydrogen insertion of a sulfur atom) and episulfides.[15]

Finally, our synthetic strategy in using organometallic reagents **2** for the generation of S_2 was conceived to permit synthetic versatility by which a simple permutation of the heteroatom moiety (eq 4) could allow access to other transient reactive heteroatomic

$$R_3MXYXMR_3 + Ph_3PBr_2 \rightarrow 2R_3MBr + Ph_3P{=}X + \text{"XY"} \qquad (4)$$

X = O, S, Se; Y = O, S, S_2, S(O), Se, Se_2, Se(O)

species. We are presently investigating the application of this new methodology to the synthesis of analogous heterocycles, as well as bridged bicyclic heteroatom derivatives, and will report on our results in due course.

Acknowledgment. We thank Research Corporation, the Natural Sciences and Engineering Research Council of Canada, and le Ministère de l'Education du Québec for financial assistance. We especially thank Professors A. G. Shaver, J. P. Snyder, and D.

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Gravel for their very helpful discussions.

Registry No. 2a, 17698-48-5; **2b**, 85185-50-8; **2c**, 85185-49-5; **2d**, 88179-92-4; **3a**, 6990-64-3; **3b**, 3005-32-1; **3c**, 3005-32-1; **3d**, 72454-26-3; $CH_2{=}C(CH_3)C(CH_3){=}CH_2$, 513-81-5; $CH_2{=}C(Ph)C(Ph){=}CH_2$, 2548-47-2; $CH_3C(CH_3){=}CHCH_2CH_2C(=CH_2)CH{=}CH_2$, 123-35-3; Ph_3PBr_2, 1034-39-5; $Ph_3P{=}S$, 3878-45-3; S_2, 23550-45-0; 1,1'-dicyclohexenyl, 1128-65-0; 3,6-dihydro-4,5-dimethyl-1,2-dithiin, 18655-88-4; 3,6-dihydro-4,5-dimethyl-1,2-dithiin, 34804-73-4; 3,6-dihydro-4-(4-methylpenta-3-enyl)-1,2-dithiin, 73188-23-5; 1,2,3,4,4a,6a,7,8,9,10-decahydrodibenzo[*c,e*][1,2]dithiin, 88157-92-0.

Isomeric Species of $[AuCH_2P(S)(C_6H_5)_2I]_2$. Mixed-Valent Au(I)/Au(III) and Isovalent Au(II)-Au(II) Complexes with the Same Methylenethiophosphinate Ligand

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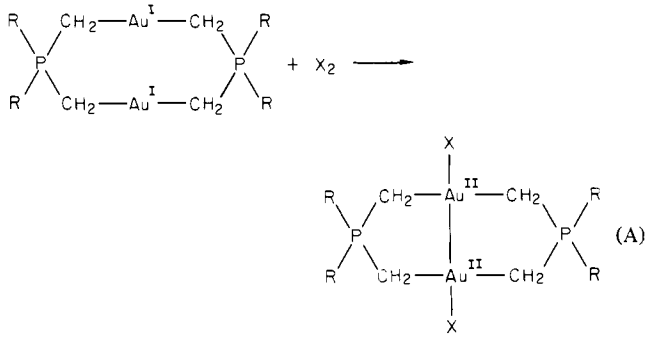
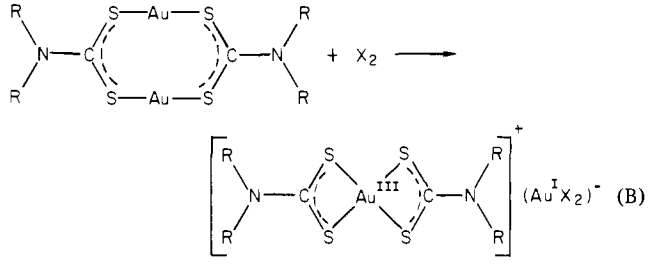
While continuing our studies with methylenethiophosphinate complexes[1] and organogold ylide complexes,[2,3] we have synthesized a new dinuclear gold ylide species $[AuCH_2P(S)(C_6H_5)_2]_2$, [Au(mtp)]$_2$ (I). The oxidative-addition properties of this species have proved to be especially interesting since both two-center and single-center, two-electron oxidative-addition products have been obtained incorporating I_2. The oxidative addition of halogens and pseudohalogens to dimeric Au(I) phosphorus ylide complexes to yield Au(II)-Au(II) species is now well established[3-5] (reaction A). Analogous dinuclear dithiocarbamate gold(I) compounds



(A)

X = Cl, Br, I, S_2CNR_2

are oxidized at room temperature to monomeric Au(I)/Au(III) complexes under similar conditions[6-9] (reaction B).



(B)

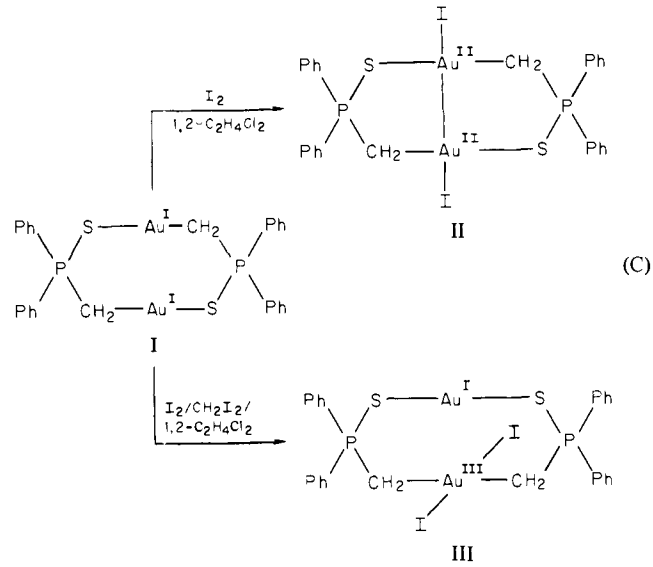
X = Cl, Br, I, CN

Table I. Selected Bond Distances (Å)

	I	II	III[a]
Au···Au	3.040 (1)	2.607 (1)	3.050 (3)
		2.611 (1)	
Au-C	2.115 (9)	2.092 (15)	2.12 (4)
		2.101 (15)	2.13 (5)
Au-S	2.323 (3)	2.370 (5)	2.308 (13)
		2.369 (4)	2.316 (12)
Au-I		2.693 (2)	2.615 (4)
		2.681 (1)	2.611 (4)
P-C	1.750 (8)	1.798 (15)	1.77 (5)
		1.762 (15)	1.87 (5)
P-S	2.018 (3)	2.014 (6)	2.02 (2)
		2.030 (5)	2.01 (2)

[a] Preliminary refinement to 10%.

Methylenethiophosphinate complexes are expected to exhibit properties characteristic of both phosphorus ylide and dithioate complexes. This is indeed the case with the chemistry of [Au(mtp)]$_2$. In separate reactions, the oxidative addition of iodine to I has yielded both an isovalent Au(II)-Au(II) complex, II, as observed with gold(I) phosphorus ylide dimers, and a unique mixed-valent Au(I)/Au(III) isomer, III, (C).



(C)

All three compounds, I-III, have been characterized structurally by X-ray diffraction methods.[23] The Au(I)-Au(I) dimer, I, has

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