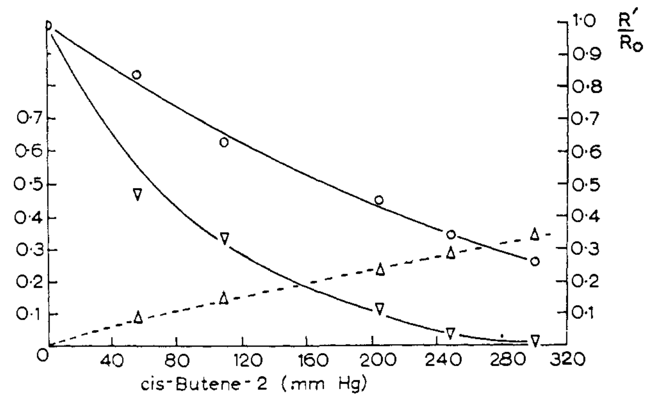


Figure 1. Dependency of rates of product formation on *cis*-butene-2 pressure at 46°. The left-hand ordinate presents the quantum yield of *trans*-butene-2 production (△). The right-hand ordinate shows the ratio of rate of production of ethylene (▽) and of carbon monoxide (○) in the presence (R') and absence (R_0) of *cis*-butene-2.

in a cylindrical quartz cell (100 ml) with filtered light from a high-pressure mercury arc providing a beam having a spectral half-band width of 100 A centered upon the 3130-A line. Light intensities were monitored photoelectrically, and absorbed intensities of 10^{-12} einstein ml^{-1} sec^{-1} were employed. The temperature was constant at 46° and the duration of each experiment was 4 hr. The effect of varying pressure of *cis*-butene-2, in the presence of 30 mm of ketene, upon the rates of production of carbon monoxide and ethylene and quantum yield of *trans*-butene-2 is shown in Figure 1.

The reduction in the rate of formation of carbon monoxide is compatible with a direct quenching of an excited state of ketene which would dissociate in the absence of butene-2. Ethylene production diminishes more rapidly and is approaching zero while the yield of carbon monoxide is still finite though decreasing. This behavior is ascribed to the dual effect of the *cis*-butene-2 in quenching the excited ketene molecule and in removing CH_2, yielding products which have been characterized elsewhere.[9] Examination of the yields of addition products at varying *cis*-butene-2 pressures has shown that they pass through a maximum at intermediate butene-2 concentrations. This observation may be interpreted here in terms of the dual mechanism mentioned above.

A consequence of the quenching of excited ketene molecules by olefins will be a temporal effect in the photolysis of ketene alone; *i.e.*, as ethylene concentration increases during irradiation, the rate of decomposition should fall. Of greater importance, in the light of recent work in this field, is the effect of added olefin in quenching excited triplet-state ketene. This alters the distribution of methylene between its singlet and triplet states, which arise out of necessity from the appropriate ketene states by the spin conservation rule, from that which would obtain in the absence of the olefin. Conclusions concerning the behavior of the excited states of the parent ketene molecule, drawn from a study of the distribution of $^3CH_2$ and $^1CH_2$ addition products with added olefin, must be regarded as tentative unless account has been taken of the triplet-quenching properties of the added gas.

The isomerization of *cis*-butene-2 measured in this investigation may arise from an energy-transfer reaction involving triplet-state ketene molecules or from attack by singlet or triplet methylene upon the olefin. Data, at present available, favor the former mechanism as the major reaction path to isomerization. Thus, the decline in production of ethylene is accompanied by a steady increase in isomerization, while yields of addition products of methylene with *cis*-butene-2 pass through a maximum and are decreasing at higher pressures of added olefin. A further examination of the pressure dependencies of each of these processes will enable the course of isomerization to be characterized, while detailed study of the relative yields of addition produces will elucidate the rate of singlet and triplet methylene in a manner analogous to that described by Rabinovitch, *et al.* In view of the observation that the long wave limit of the ketene absorption spectrum lies at about 4100 A, it may be concluded that the energy possessed by the first excited triplet state will be less than 70 kcal mole^{-1}, in which event the efficiency of energy transfer to yield butene-2 triplet (70–72 kcal mole^{-1}) will be dependent upon vibrational energy possessed by the ketene triplet (*e.g.*, see ref 8).

Acknowledgment. The authors are grateful to Dr. A. N. Strachan for providing ketene and for helpful discussion, and to the Petroleum Research Fund for a grant.

R. B. Cundall, A. S. Davies
Department of Chemistry, The University
Nottingham, England

Received January 3, 1966

---

[9] *E.g.*, see ref 2; also H. M. Frey, *J. Am. Chem. Soc.*, **82**, 5947 (1960); J. W. Simons and B. S. Rabinovitch, *J. Phys. Chem.*, **68**, 1322 (1964).

Photoreduction of a β,γ-Unsaturated Ketone[1]

Sir:

Although the excited state corresponding to the ~300-mμ transition of certain β,γ-unsaturated ketones probably involves, in addition to the normal $\pi^* \leftarrow n$ transition, a contribution from a $\pi^* \leftarrow \pi$ type transition of the extended chromophore,[2] the only chemical effect attributed to this interaction of ethylenic and carbonyl linkages in the excited state is the light-induced geometrical isomerization of *trans*-4-hexen-2-one.[3] We now present the second example of such an interaction.

Irradiation of ketone **2** (λ_{max}^{EtOH} 307 mμ (ε 101)) in methylene chloride solution with a mercury arc (Corex filter) provides the saturated ketone **3** (λ_{max}^{EtOH} 300 mμ (ε 22)) in 30–35% yield[4] along with 1,1,2,2-tetrachloroethane, τ 4.08 ppm. When 0.028 *M* **2** in methylene chloride containing 0.25 *M* norbornene was irradiated, the rate of formation of **3** over 70% reaction was the same as when no added olefin was present. This result

---

[1] We are grateful to the Petroleum Research Fund administered by the American Chemical Society for support of this research.

[2] A. Moscowitz, K. Mislow, M. A. W. Glass, and C. Djerassi, *J. Am. Chem. Soc.*, **84**, 1945 (1962); R. C. Cookson and S. MacKenzie, *Proc. Chem. Soc.*, 423 (1961), and references cited there.

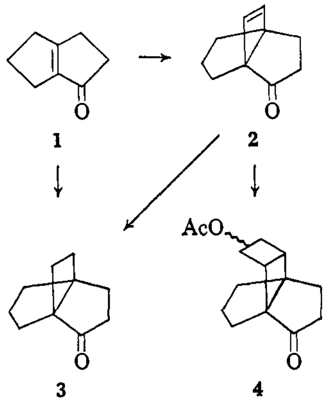
[3] H. Morrison, *Tetrahedron Letters*, 3653 (1964); *J. Am. Chem. Soc.*, **87**, 932 (1965).

[4] The concentration of **3** reaches this maximum value at ~70% reaction. The photochemistry of **3** will be discussed separately.

indicates the absence of intermolecular sensitization in the photoreduction.[5]

Photochemical cycloaddition of 1,2-dichloroethylene to bicyclo[3.3.0]oct-1(5)-en-2-one (**1**),[6] formation of the ethylene ketals, dechlorination with sodium in liquid ammonia, and hydrolysis of the ketal gave ketone **2**, semicarbazone mp 185°, in 67% yield from **1**.[7] The photoreduction product is identical with samples of ketone **3** obtained from hydrogenation of **2** and from photoaddition of ethylene to **1**; semicarbazones mp 200–202° dec and mmp 200–202° dec.

This photoreduction of a β,γ-unsaturated ketone[8] suggests that light-induced cycloaddition at the β,γ-double bond might be possible. Irradiation of ketone **2** in benzene solution containing vinyl acetate gave, after chromatography on alumina, a keto acetate in 30% yield, mol wt 234,[11] $\tilde{\nu}_{\max}^{\mathrm{CCl_4}}$ 1740 (very intense), 1415, 1380, and 1235 cm^{-1}; τ 4.88 ppm, broad (1 H), and two overlapping, unresolved multiplets centered at τ 7.54 and 8.18 ppm with a sharp singlet prominent at τ 8.00 ppm (17 H). The spectral evidence is compatible, but not exclusively so, with gross structure **4** for the 1 : 1 adduct. It is clear, however, that cycloaddition has occurred at a β,γ double bond.



---

(5) D. Scharf and F. Korte, *Tetrahedron Letters*, 821 (1963), found that norbornene underwent dimerization when irradiated in the presence of acetone or dicyclopropyl ketone.

(6) We are grateful to the Badische Anilin- und Soda-Fabrik for a generous gift of 1.

(7) H. O. House and T. H. Cronin, *J. Org. Chem.*, 30, 1061 (1965).

(8) The Büchi rearrangement[9] is the preferred path even in methylene chloride or ethanol for those β,γ-unsaturated ketones in which this path is not prevented for geometrical reasons.[10]

(9) G. Büchi and E. M. Burgess, *J. Am. Chem. Soc.*, **82**, 4333 (1960).

(10) R. L. Cargill, M. E. Beckham, A. E. Siebert, and J. Dorn, *J. Org. Chem.*, 30, 3647 (1965), and references cited there.

(11) We are grateful to Professor A. L. Burlingame and Dr. H. K. Schnoes, University of California, Berkeley, for mass spectra of this adduct and of ketones 2 and 3.

Robert L. Cargill, John R. Damewood, Mary M. Cooper
Department of Chemistry, University of South Carolina
Columbia, South Carolina 29208

Received December 4, 1965

1-Deamino-1,6-L-selenocystine-oxytocin, a Highly Potent Isolog of 1-Deamino-oxytocin[1]

Sir:

Recently we reported the synthesis and pharmacological properties of 6-hemi-L-selenocystine-oxytocin (6-seleno-oxytocin) and its deamino analog.[2] The present communication concerns the synthesis of 1-deamino-1,6-L-selenocystine-oxytocin (deamino-diseleno-oxytocin), the structure of which is shown in Figure 1. This molecule is identical with deamino-oxytocin[3] except that both sulfur atoms have been replaced by selenium atoms.

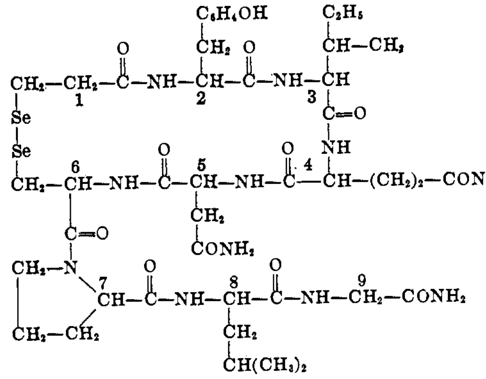


Figure 1. Structure of 1-deamino-1,6-selenocystine-oxytocin, with numbers indicating the positions of the component amino acid residues.

The protected tetrapeptide, N-carbobenzoxy-Se-benzyl-L-selenocysteinyl-L-prolyl-L-leucylglycinamide,[2] served as starting material for the synthesis of the deamino-diseleno-oxytocin. After removal of the carbobenzoxy group by hydrogen bromide–acetic acid the tetrapeptide was lengthened by the stepwise *p*-nitrophenyl ester procedure earlier employed in this laboratory for the synthesis of oxytocin[4] and deamino-oxytocin[3] to give the protected intermediate, Se-benzyl-β-selenopropionyl-L-tyrosyl-L-isoleucyl-L-glutaminyl-L-asparaginyl-Se-benzyl-L-selenocysteinyl-L-prolyl-L-leucylglycinamide.[5,6] The isolog was obtained after the cleavage of the protecting groups from this intermediate by sodium in liquid ammonia, followed by ring closure through treatment with ferricyanide. Subsequently, the ferrocyanide and ferricyanide ions were removed with the ion-exchange resin AG3X4 in the chloride form. The deamino-diseleno-oxytocin was isolated by countercurrent distribution in a 1-butanol–benzene–0.05% acetic acid system (3:2:5) in which it possessed a *K* value of approximately 1.5; $[\alpha]^{22}\mathrm{D}$ $-51.0°$ (c 0.25, 1 *N* acetic acid). *Anal.* Calcd for $C_{43}H_{65}N_{11}O_{12}Se_2$: N, 14.2. Found: N, 14.0. Upon thin layer chromatography in 1-butanol–acetic acid–water (4:1:5, upper phase) deamino-diseleno-oxytocin traveled as a single spot, although a trace of chromogenic material remained at the origin, as indicated by the platinic iodide reagent of Toennies and Kolb.[7]

Upon bioassay deamino-diseleno-oxytocin exhibited

---

(1) This work was supported in part by Grant HE-01675 from the National Heart Institute, U. S. Public Health Service.

(2) R. Walter and V. du Vigneaud, *J. Am. Chem. Soc.*, **87**, 4192 (1965).

(3) V. du Vigneaud, G. Winestock, V. V. S. Murti, D. B. Hope, and R. D. Kimbrough, Jr., *J. Biol. Chem.*, **235**, PC64 (1960); D. B. Hope, V. V. S. Murti, and V. du Vigneaud, *ibid.*, 237, 1563 ((1962); B. M. Ferrier, D. Jarvis, and V. du Vigneaud, *ibid.*. 240, 4264 (1965).

(4) M. Bodanszky and V. du Vigneaud, *J. Am. Chem. Soc.*, **81**, 5688 (1959).

(5) The *p*-nitrophenyl Se-benzyl-β-selenopropionate (mp 38–39°) was prepared by condensation of *p*-nitrophenol with Se-benzyl-β-selenopropionic acid in the presence of dicyclohexylcarbodiimide. *Anal.* Calcd for $C_{16}H_{15}NO_4Se$: C, 52.8; H, 4.15; N, 3.85. Found: C, 52.7; H, 4.31; N, 3.76. The Se-benzyl-β-selenopropropionic acid (mp 74–76°) was synthesized by the base-catalyzed β-addition of benzylselenol to acrylic acid. *Anal.* Calcd for $C_{10}H_{12}O_2Se$: C, 49.4; H, 4.98. Found: C, 49.4; H, 4.98.

(6) All intermediate peptides showed correct C, H, and N analyses, which were carried out by Galbraith Laboratories, Knoxville, Tenn.

(7) G. Toennies and J. J. Kolb, *Anal. Chem.*, **23**, 823 (1951).