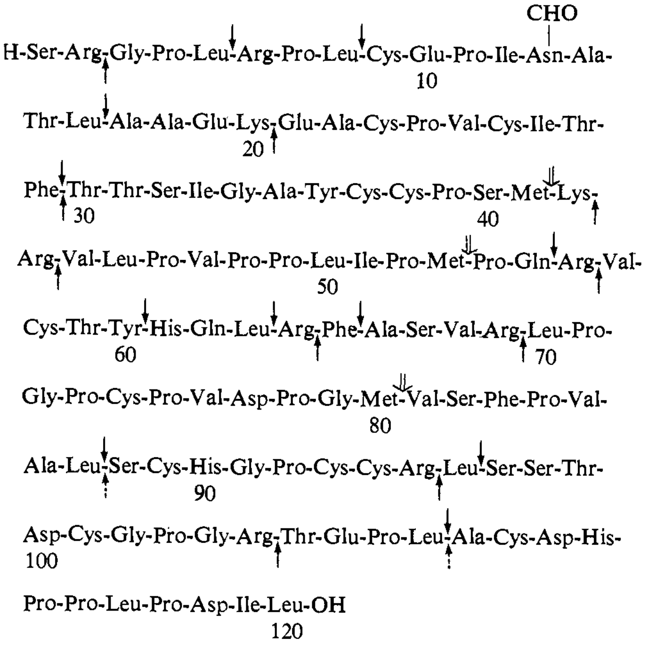
**Chart II.** Amino Acid Sequence of Ovine ICSH-β (CII)[a]



[a] See footnote *a*, Chart I.

of 96 amino acid residues. There are two carbohydrate moieties which are linked to asparagine residues in positions 56 and 82. Liao and Pierce[20] have recently shown that thyrotropin (TSH) consists of chemically dissimilar subunits as does ICSH, and one of the subunits, TSH-α, is very similar to ICSH-α. Pierce, *et al.*,[21] have also determined the amino acid sequences of the TSH subunits. Comparison of the structure of ICSH-α (Chart I) with that of TSH-α reveals that the two are nearly identical. This is all the more remarkable when one considers that the TSH was of bovine origin while the ICSH in this study is of the ovine species.

ICSH-β (Chart II) consists of 120 residues in contrast to the 96 of ICSH-α, contains but one carbohydrate moiety (residue 13), and possesses 12 half-cystine residues compared to the 10 in ICSH-α. The sequence of the peptides previously described[11] is located in the region of 42–80. Liu, *et al.*,[22] in a preliminary communication have also postulated a structure for the ICSH-β subunit. There are certain differences worthy of note. Their structure lacks the carboxyl terminal sequence · · · Ile-Leu present in our formulation. Also, their structure lacks two half-cystine residues (no. 38 and 93) as well as a threonine residue (no. 28) found in the structure presented in Chart II. Additionally, Liu, *et al.*,[22] postulated the amino terminal serine residue to be acylated.

**Acknowledgment.** The authors wish to thank the collaboration of Dr. T. S. A. Samy in the early studies on the structure of ICSH-β and the assistance of Daniel Gordon with amino acid analysis. H. P. is a Career Development Awardee, National Institutes of Health. This work was supported in part by Grant No. A-6097 from the National Institute of Arthritis and Metabolic Diseases, United States Public Health Service and the Geffen Foundation.

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*Received December 21, 1970*

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(20) T-H. Liao and J. G. Pierce, *J. Biol. Chem.* **245**, 3275 (1970).

(21) J. G. Pierce, T-H. Liao, S. M. Howard, and B. Shome, paper presented at the Laurentian Hormone Conference, Mont Tremblant, Canada, Sept, 1970.

(22) W-K. Liu, C. M. Sweeney, H. S. Nahm, G. N. Holcomb, and D. N. Ward, *Res. Commun. Chem. Pathol. Pharmacol.*, 1, 463 (1970).

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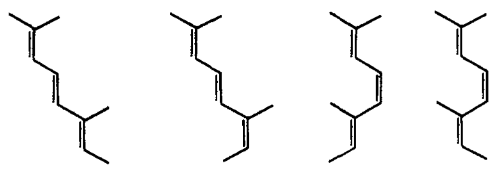
## Photochemistry of Polyenes. I. A Comparative Study of Cis–Trans Isomerization from the $S_1$ and $T_1$ States of a Conjugated Triene (Alloocimene)

*Sir:*

Studies of the photochemical reaction of conjugated trienes have been largely limited to direct irradiation leading to electrocyclic or sigmatropic rearrangements.[1] The cis–trans isomerization reaction has been studied only in a cursory manner.[1d–f] In this communication, we wish to report some of our findings from the isomerization studies.

The triplet state energies of the trans and cis isomers of 1,3,5-hexatriene are 47 and 48 kcal/mol, respectively.[1e,2] Therefore, triene triplet states can be readily populated with most of the conventional photosensitizers. On the other hand, isomerization by direct irradiation can be effected by employing light of 2537 Å.[1]

The presence of several possible isomers in a substituted triene complicates cis–trans isomerization studies. The most complex case would be a triene with different substituents at the terminal positions giving a maximum of eight isomers. To reduce complexity while not sacrificing interesting information we studied the alloocimene, 2,6-dimethyl-2,4,6-octatriene, system where only four geometric isomers are possible. All four isomers are readily isolable and their structures known.[3]



TT TC CT CC

Isomers TT and TC are present in commercial alloocimene, thus most readily available. Isomers CT and CC can be obtained from an irradiated[4] mixture of the triene. By preparative glc all four isomers have been isolated in at least 90% purity. Direct and sensitized (by benzophenone) irradiation of dilute solutions of pure isomers were performed. Progress of the reactions was followed by glc analyses of aliquots

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(1) (a) G. J. Fonken, *Tetrahedron Lett.*, 549 (1962); (b) J. Meinwald and P. H. Mazzocchi, *J. Amer. Chem. Soc.*, **88**, 2850 (1966); **89**, 1755 (1967); (c) O. L. Chapman, G. W. Borden, R. W. King, and B. Winker, *ibid.*, **86**, 2660 (1964); (d) K. J. Crowley, *J. Org. Chem.*, **33**, 3679 (1968); (e) N. G. Minnaard, Ph.D. Dissertation, University of Leiden, 1970; (f) G. M. Sanders, J. Pot, and E. Havinga, *Fortschr. Chem. Org. Naturst.*, 27, 131 (1969).

(2) D. F. Evans, *J. Chem. Soc.*, 1736 (1960).

(3) See discussions in ref 1d and references cited therein.

(4) The photostationary state composition varies with triene concentration. At 0.05 *M*, the stationary mixture (sensitizer–benzophenone) contains 18 and 15% of CC and CT, respectively.

**Table I.** Direct Irradiation[a] of Dilute Solutions of Alloocimene Isomers[b]

| Set | Time of $h\nu$, min | Isomer composition, %[c] | | | |
|---|---|---|---|---|---|
| | | TT | TC | CT | CC |
| I | 0 | 99.8 | 0.2 | 0 | 0 |
| | 4 | 99.5 | 0.5 | 0 | 0 |
| | 8 | 98.3 | 1.6 | 0.1 | 0 |
| | 12 | 95.3 | 4.1 | 0.6 | 0.1 |
| | 18 | 86.1 | 11.9 | 1.9 | 0.1 |
| II | 0 | 0.2 | 99.8 | 0 | 0 |
| | 4 | 0.7 | 98.5 | 0.1 | 0.6 |
| | 8 | 1.3 | 96.6 | 0.1 | 1.9 |
| | 12 | 2.2 | 95.0 | 0.2 | 2.4 |
| | 25 | 3.5 | 90.6 | 0.4 | 5.1 |
| III | 0 | 0 | 0 | 90.8 | 9.2 |
| | 2 | 1.5 | 0 | 89.8 | 8.7 |
| | 4 | 3.1 | 0.2 | 87.3 | 9.4 |
| | 6 | 6.1 | 0.6 | 82.6 | 10.7 |
| | 9 | 8.5 | 1.0 | 79.5 | 10.9 |
| IV | 0 | 0 | 0 | 1.7 | 98.3 |
| | 2 | 0 | 1.8 | 2.3 | 95.9 |
| | 4 | 0.6 | 4.1 | 2.7 | 92.6 |
| | 9 | 0.6 | 8.0 | 3.5 | 87.9 |
| | 15 | 0.9 | 14.3 | 4.8 | 80.0 |

[a] *n*-Hexane solution. Unfiltered light from a low-pressure Hg lamp (UV Products Inc., Tube 50053). [b] Approximate triene concentrations, 0.05 *M*. [c] Other stable isomers never accumulated to a total amount of 1%.

**Table II.** Photosensitized[a] Irradiation of Dilute Solution of Alloocimene Isomers[b]

| Set | Time of $h\nu$, min | Isomer composition, %[d] | | | |
|---|---|---|---|---|---|
| | | TT | TC | CT | CC |
| I[c] | 0 | 98.8 | 1.7 | 0.5 | 0 |
| | 2 | 93.3 | 5.2 | 0.6 | 0.9 |
| | 40 | 57.7 | 22.4 | 9.4 | 10.4 |
| | 70 | 44.7 | 25.4 | 13.9 | 16.0 |
| II | 0 | 8.8 | 90.2 | 0.4 | 0.6 |
| | 1 | 9.8 | 88.0 | 0.9 | 1.4 |
| | 5 | 13.3 | 78.7 | 2.7 | 5.2 |
| | 30 | 30.2 | 41.0 | 12.9 | 15.8 |
| III | 0 | 0 | 0 | 90.7 | 9.3 |
| | 2 | 2.2 | 0.7 | 88.7 | 8.5 |
| | 4 | 4.6 | 1.5 | 84.6 | 9.4 |
| | 7 | 9.5 | 4.6 | 75.2 | 10.7 |
| | 10 | 15.0 | 6.1 | 67.0 | 11.9 |
| IV | 0 | 0 | 0 | 3.0 | 97.0 |
| | 2 | 0.2 | 0 | 4.1 | 95.7 |
| | 4 | 1.2 | 0.8 | 3.7 | 94.4 |
| | 9 | 4.5 | 2.9 | 6.2 | 86.4 |
| | 12 | 7.6 | 5.0 | 5.9 | 81.5 |

[a] Benzophenone (0.1 *M*) in *n*-hexane. [b] Irradiated at room temperature with 3660-Å light in the merry-go-round apparatus [F. G. Moses, R. S. H. Liu, and B. M. Monroe, *Mol. Photochem.*, **1**, 245 (1969)]. [c] Approximate triene concentrations, 0.05 *M*. [d] Other photoproducts were not detected under these conditions.

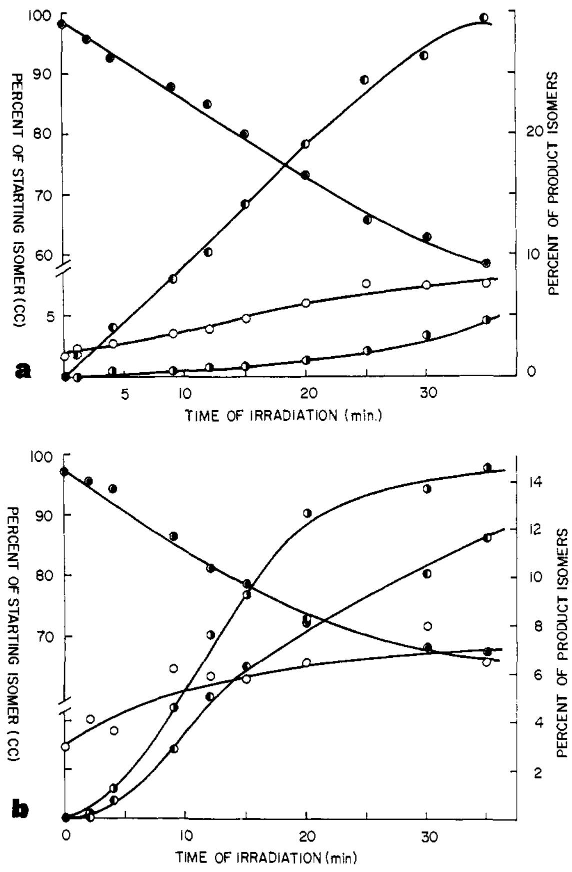

Figure 1. (a) Direct irradiation of dilute solutions of *cis,cis*-2,6-dimethyl-2,4,6-octatriene (CC). (b) Photosensitized irradiation of dilute solutions of *cis,cis*-2,6-dimethyl-2,4,6-octatriene (CC) (⊙, CC; ○, CT; ◐, TC; ◑, TT).

taken at various intervals. The results are shown in Tables I and II. Figure 1 also graphically displays the results of the CC isomer for better comparison; results for other isomers, when plotted, show similar behavior.

Examination of the data reveals one consistent trend for all four isomers, which is most clearly shown in plots such as in Figure 1. Conversion involving simultaneous isomerization around two double bonds, *e.g.*, CC–TT, CT–TC, etc., takes place only in the sensitized reaction and not from direct irradiation. Therefore, the TT curve in Figure 1b rises together with those of CT and TC clearly indicating the formation of TT being concurrent with the other two isomers, while Figure 1a shows the absence of TT at early stages of irradiation and it becomes detectable only after significant accumulation of the CT and TC isomers suggesting formation of TT involving two consecutive steps of reaction.

The observed difference in the triplet and singlet state reactions indicates that intersystem crossing is not an important process in trienes and the trend is reminiscent of the results of 2,4-hexadiene.[5,6] In our case the results are consistent with the explanation[7] that involves the presence of diallyl (I) and methylenepentadienyl (II) intermediates which equilibrate rapidly in the $T_1$ state[8] but deactivate without significant interconversion in the $S_1$ state. That equilibrium is possible only in the triplet state could merely be the consequence of the expected longer lifetime of the triplet state of a molecule as compared to its corresponding singlet state.

Consistent with the expected long lifetime of triene triplets, we have observed efficient dimer formation in sensitized irradiation of hexatriene even at low con-

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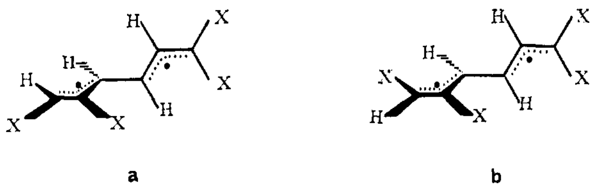
(5) Sensitized reaction: J. Saltiel, L. Metts, and M. Wrighton, *J. Amer. Chem. Soc.*, **91**, 5684 (1969).

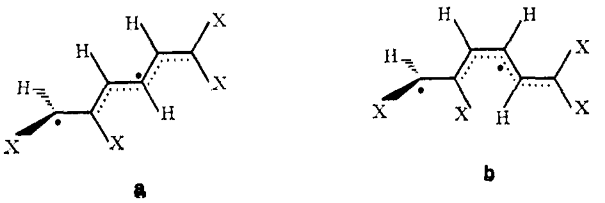
(6) Direct irradiation: J. Saltiel, L. Metts, and M. Wrighton, *ibid.*, **92**, 3227 (1970).

(7) A single 1,6-diradical intermediate could also account for the triplet state results. For VB calculation on such a moiety, see: M. Barfield, *J. Chem. Phys.*, 47, 3831 (1967).

(8) A more detailed description would involve superposition of two potential surfaces, one for equilibrating diallyl intermediates Ia, b, etc., and the other methylenepentadienyl intermediates IIa, b, etc. An analysis of the shape of these potential surfaces would have to await results from detailed quenching studies.



I



II
X = $CH_3$

centrations.[9] Also, quenching processes involving triene triplets have been observed.[10] Quantitative studies on these bimolecular processes will be the subject of a future communication.

Data in Tables I and II also show that excited state bond orders cannot be used reliably in predicting the direction of isomerization, *i.e.*, whether preferentially around the central or the terminal double bond. Calculations on 1,3,5-hexatriene give significantly lower central bond orders as compared with that of the terminal bond in both the $S_1$ and $T_1$ states,[11] thus suggesting that isomerization was favored around the central double bonds. Experimentally, such a trend is not evident and, in fact, if anything the results are more consistent with isomerization favored around the terminal double bond. Surely the observed differences are partly due to the methyl groups which not only perturb the $\pi$ system but also, more significantly, add considerable nonbonded interactions (methyl–methyl and methyl–vinyl H). Furthermore, considering that the excited bond order can only be a kinetic factor in determining the initial distribution of the relaxed intermediates, and that the final product composition should further be affected by the thermal stability of these intermediates and the magnitude of individual decay rate constants from these intermediates, the inadequacy in predicting the direction of isomerization is perhaps not surprising.

**Acknowledgment.** This work was partially supported by a University of Hawaii Biomedical Grant and by the Sloan Foundation. Discussions with Dr. H. E. Simmons on properties of polyenes have been most helpful.

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[9] Unpublished results of S. Arslanian and R. S. H. Liu; also ref 1e.

[10] Unpublished results of Y. Butt and R. S. H. Liu.

[11] See, *e.g.*, calculations based on SCF–CI methods by H. E. Simmons, *Progr. Phys. Org. Chem.*, 7, 1 (1970). We wish to thank Dr. Simmons for a copy of the manuscript prior to its publication.

[12] Alfred P. Sloan Fellow, 1970–1972.

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*Received December 28, 1970*

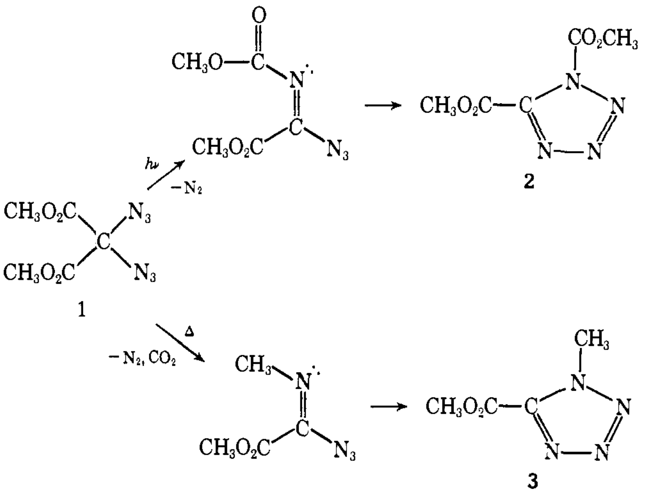
## Thermal Decomposition of Geminal Diazides

*Sir:*

Earlier we reported that photolysis of dimethyl diazidomalonate (**1**) proceeds with loss of one molecule of nitrogen, followed by migration of the carbomethoxy group from carbon to nitrogen to yield an azomethine azide which cyclizes to the tetrazole (**2**). Separate irradiation of the tetrazole (**2**) caused loss of nitrogen and intramolecular cyclization to the oxadiazole (**4**).[1]

We now report that the thermal pathway is strikingly different.[2–4] The analogous loss of nitrogen is observed but the resulting intermediates follow different product-forming pathways. Thermolysis causes loss of both nitrogen and carbon dioxide to yield the *N*-methyl azomethine azide which cyclizes to **3**. Photolysis and thermolysis are compared in Scheme I.

**Scheme I**



Each pathway is completely specific; there is no crossover in products. Importantly, thermolysis of **2** does not yield **3**. While photolysis of **2** yielded only oxadiazole (**4**), thermolysis yields oxadiazolone (**5**) (Scheme II).[4]

The dichotomy in behavior of geminal diazides upon photolysis relative to thermolysis was found to hold generally for other derivatives.[5]

Photolysis of **6a** or **6b** proceeded with loss of one molecule of nitrogen and migration of the carboxamido and *N*-methylcarboxamide groups, respectively. Pyrolysis followed the fragmentative pathways trans-

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[1] R. M. Moriarty, J. M. Kliegman, and C. Shovlin, *J. Amer. Chem. Soc.*, **89**, 5958 (1967).

[2] A strong precautionary note concerning the explosive nature of the geminal diazides is in order. We have already referred to this property[3] but more recent experiences reveal that they are more hazardous than formerly believed. Under no circumstances should pure neat samples be heated above 100°. A pure neat 0.500-g sample heated to 130° evolved nitrogen briskly prior to a brisant explosion which shattered a heavy safety shield, badly damaged a fume hood, and startled the experimentalist. No explosive decompositions were observed in the course of thermolyses carried out in dilute tetralin.

[3] R. M. Moriarty, J. M. Kliegman, and C. Shovlin, *J. Amer. Chem. Soc.*, **90**, 5947 (1968).

[4] Thermolyses were carried out in tetralin solution at 185°. All new compounds gave correct microanalyses. Tetrazole **3** had: mp 108–109°; $\nu_{CO}$ 1745 cm$^{-1}$; nmr ($CDCl_3$, TMS) $\delta$ 4.50, 4.10 ppm (singlets); *m/e* 114 (P − 28). 2-Methyl-3-carbomethoxy-1,2,4-oxadiazolin-5-one (**5**) obtained in 50% yield had: mp 77–78°; $\nu_{CO}$ 1790 cm$^{-1}$; nmr ($CDCl_3$, TMS) $\delta$ 5.70, 5.97 ppm (singlets); *m/e* 158, 114 (P − $CO_2$).

[5] Diazidomalonamide (**6a**) has mp 157–158°, lit.[6] mp 162°. 5-Carboxamidotetrazole (**8a**) obtained in 94% yield has mp 231–232°. Base hydrolysis yielded tetrazole in 80%. Photolysis of **6a** in acetonitrile using a water-cooled Hanau Q81 high-pressure mercury vapor lamp yielded 1,5-dicarboxamidotetrazole (**7a**), 53%, mp 200° dec. Treatment with 30% ammonium hydroxide yielded 5-carboxamidotetrazole as its ammonium salt. *N,N*-Dimethyldiazidomalonamide (**6b**) had mp 104–105°; pyrolysis yielded **8b** in 90% yield, mp 235–236°, $\nu_{CO}$ 1665 cm$^{-1}$.

[6] M. O. Forster and R. Muller, *J. Chem. Soc.*, 126 (1910).