ceeds in a nonconcerted fashion. Stepwise mechanisms for photochemical 1,3-allylic shifts have been established previously for cases which involve either the migration of saturated ring carbons in cyclopentenone[3a,b,d,f] and bicyclo[4.1.0]hept-2-ene systems[3c] or the migration of benzoyl through radical recombination.[13] In all these cases excitation to the first singlet state sufficed, and evidence for a reactive triplet is available in most. Other interesting examples, which stand in juxtaposition to our results, are the concerted 1,3-allylic photorearrangements of cyclic and aliphatic 1,1-dicyano-4-phenyl-1-butene systems which occur with retention of configuration at the migrating benzylic carbon.[2,3e,g] They have been attributed to the π,π^* singlet state of the $C{=}C(C{\equiv}N)_2$ system. As shown previously,[4a] the reactive state responsible for a → c + d is not populated by way of the lowest lying singlet state, S_1 (n, π^*), which crosses over to triplet.[14] It is possibly identical with the thermally equilibrated S_2 state which in conjugated ketones has the lowest energy π,π^* configuration. Our present findings together with the literature examples therefore show that spin multiplicity of the reactive state is not the controlling factor for concerted vs. stepwise mechanisms in photochemical 1,3-allylic shifts. Other properties of the chromophore or the migrating group must be involved.

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References and Notes

(1) J. A. Berson and G. L. Nelson, *J. Am. Chem. Soc.*, **89**, 5503 (1967).

(2) R. C. Cookson and J. E. Kemp, *Chem. Commun.*, 385 (1971).

(3) (a) L. S. Besford, R. C. Cookson, and J. Cooper, *J. Chem. Soc. C*, 1385 (1967); (b) R. C. Cookson and D. C. Warrell, *ibid.*, 1391 (1967); (c) P. J. Kropp, *J. Am. Chem. Soc.*, **89**, 1126 (1967); (d) R. L. Cargill, B. M. Gimarc, D. M. Pond, T. Y. King, A. B. Sears, and M. R. Willcott, *ibid.*, **92**, 3809 (1970); (e) R. C. Cookson, J. Hudec, and M. Sharma, *Chem. Commun.*, 107 (1971); (f) R. L. Cargill, A. B. Sears, J. Boehm, and M. R. Willcott, *J. Am. Chem. Soc.*, **95**, 4346 (1973); (g) M. Sharma, *ibid.*, **97**, 1153 (1975).

(4) (a) J. Gloor and K. Schaffner, *Helv. Chem. Acta*, **57**, 1815 (1974); (b) K. Schaffner, *Pure Appl. Chem.*, **33**, 329 (1973).

(5) The radical nature of intermediate b is not established experimentally.[4a,6] In fact both ion and radical pair forms may be intermediate stages leading from excited to ground state.

(6) A photo-CIDNP study of the reaction, the a priori imperative method to detect the *radical* bond cleavage-pair recombination mechanism a ⇄ b → c (+ d), failed to give conclusive results owing to low quantum yield and insufficient intensity at <260 nm. We thank Professor H. Fischer and A. Henne, University of Zurich, for exploratory experiments.

(7) (a) The possibility of competition by a concerted antarafacial shift with inversion of configuration is discarded in view of the sterically highly unfavorable transition state required; (b) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

(8) Compounds (R^*)- and (S^*)-1 were prepared by HCl-catalyzed treatment of *rac*-1-ethylenedioxy-3,4-dimethyl-4-formylcyclohex-2-ene[9] with methanol and isopropyl alcohol and chromatographic separation into enriched mixtures (~9:1 ratios) of either diastereoisomer.

(9) E. Baggiolini, H. P. Hamlow, and K. Schaffner, *J. Am. Chem. Soc.*, **92**, 4906 (1970).

(10) Satisfactory uv, ir, ^{1}H NMR, and mass spectral data were obtained for all compounds 1 and 2.

(11) The relative configurations of 1 and 2 have been chosen arbitrarily and are irrelevant for the evaluation of our results.

(12) For NMR analysis the samples were taken to dryness and redissolved in hexadeuteriobenzene.

(13) H.-U. Gonzenbach, K. Schaffner, B. Blank, and H. Fischer, *Helv. Chim. Acta*, **56**, 1741 (1973).

(14) On n → π^* excitation 1 and 10-dimethoxymethyl-$\Delta^{1(9)}$-octal-2-one, which undergoes rearrangement analogous to a → c,[4] exhibit triplet reactivity, and the bicyclic enone shows the same phosphorescence characteristics as the parent methyloctalone (G. Marsh, D. R. Kearns, and K. Schaffner, *J. Am. Chem. Soc.*, **93**, 3129 (1971)).

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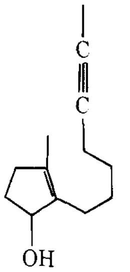
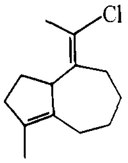
A Novel Synthesis of Longifolene[1]

Sir:

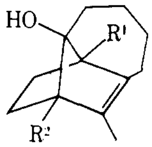
In some exploratory work aimed at developing a new hydroazulene synthesis, we examined the stannic chloride-catalyzed cyclization of the heptynylmethylcyclopentenol (**1**). While the reaction did indeed afford the hydroazulene system (formula **2**) in analogy to the established mode of polyene cyclizations involving the methylacetylenic terminating group,[2] an additional crystalline alcohol was produced, the spectral properties of which were consonant with a tricyclic structure, either **3** or **4**.[3] Recognizing that this presumed bridged-ring structure possessed the basic ring system of longifolene (**14**), our attention was turned to the preparation of the appropriately substituted substrate, namely, the enynol **8** (Chart I), cyclization of which would be expected to give, along with a hydroazulenic substance, the product **9** which is a potential synthon for producing longifolene. The preparation of the tricyclic alcohol **8** and its conversion into longifolene is the subject of the present communication.



1

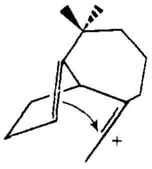


2

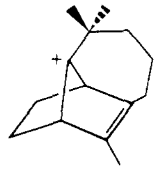


3. $R^2 = H; R^1 = CH_3$
4. $R^2 = CH_3; R^1 = H$

Although the mechanism of the cyclization of the enynol **1** is open to question,[4] the anticipated cyclization of **8** can be rationalized as follows. It is reasonable to hypothesize that the allylic alcohol **8** would first cyclize to give the vinyl cation A.[5] Reaction of A with an external nucleophile would then yield a hydroazulenic substance. On the other hand, intramolecular nucleophilic attack of the vinyl cation by the olefinic bond in the five-membered ring,[6] as suggested in formula A, would result in further cyclization to yield the interesting cation B which embodies the unusual feature of destabilization due to an apparent violation of Bredt's rule but, on the other hand, the potential stabilizing characteristic of the 7-*anti*-norbornenyl cation.[7] Nucleophilic attack of the cation B by water would yield the 7-*anti*-norbornenyl system **9**. These theoretical considerations, in addition to increasing our optimism about the success of the envisaged synthetic scheme, suggest that the formation of **9** might be favored over the bicyclic product by minimizing the availability of nucleophiles in the cyclization medium. This objective has been realized and the refined version of the total synthesis is set forth below.



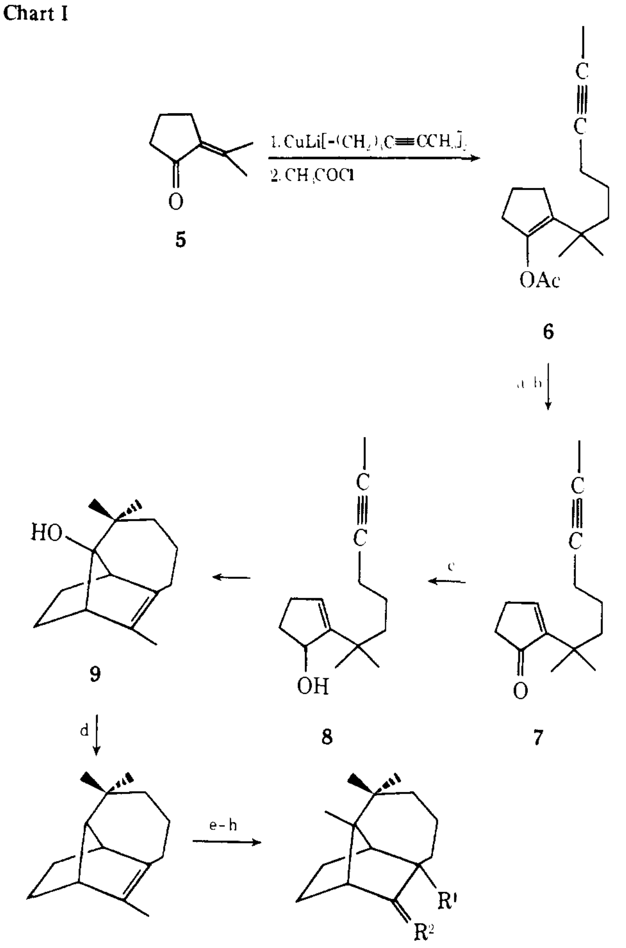
A



B

Metalation[8] of 1-iodo-4-hexyne[9] at −78° with 2 mol equiv of *tert*-butyllithium in ether gave 4-hexynyllithium which was treated with 0.5 mol equiv of tetrakis[iodo(tri-*n*-butylphosphine)copper(I)][10] followed by 0.5 mol equiv of 2-isopropylidenecyclopentanone (**5**).[11] This solution, con-

Chart I



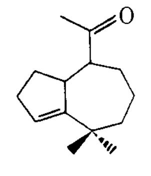
11, $R^1 = H; R^2 = CH_2$
12, $R^1 = H; R^2 = O$
13, $R^1 = CH_3; R^2 = O$
14, $R^1 = CH_3; R^2 = CH_2$

[a] In 2.1 mol equiv of CH_3Li in ether at 0°; 1 mol equiv of Br_2 in CH_2Cl_2, −78°. [b] In 4 mol equiv of 2,4,6-$(CH_3)C_6H_2CO_2N(CH_3)_4$ in acetone, 1 hr, 25°. [c] In 1 mol equiv of $LiAlH_4$ in ether, 0°, 1 hr. [d] 2 mol equiv of $ZnBr_2$, 3 mol equiv of $NaBH_3CN$, ether, 2 hr, 25°. [e] To give 11, a small excess of p-$CH_3C_6H_4SO_3H$ was added to the previous mixture, 30 min, 25°. [f] To give 12, 0.01 mol equiv of RuO_2, 50% H_2O in t-BuOH, large excess of H_5IO_6–$NaIO_4$, 18 hr, 25° (ref 15). [g] To give 13, 10 mol equiv of LiN(iPr)$_2$, THF, 10 mol equiv MeI, −78°; then 2 hr at 25°. [h] To give 14, CH_3Li; $SOCl_2$–pyridine (ref 16).

taining the enolate anion of the 1,4-adduct, was allowed to warm to 0°, then 2 mol equiv of acetyl chloride was added. Florisil chromatography followed by distillation[12] at 110° (0.02 mm) afforded the enol acetate **6**[13] in 84% yield. Conversion of **6** to the lithium enolate followed by bromination afforded the crude α-bromo ketone which was dehydrobrominated by treatment with tetramethylammonium mesitoate in acetone[14] at room temperature, giving, after silica gel chromatography and distillation[12] at 110° (0.22 mm), enone **7**[13] in 76% yield. Hydride reduction afforded enynol **8**[13] in 92% yield after chromatography on alkaline alumina followed by distillation[12] at 110° (0.02 mm).

The best conditions that were found for producing **9** involved adding a solution of 375 mg of the enynol **8** in 2 ml of ether to 50 ml of trifluoroacetic acid at 0° with stirring. After about 3 min, the mixture was neutralized with excess cold potassium carbonate solution. Chromatography on basic alumina (activity III) gave ketonic and alcoholic fractions. Distillation[12] of the alcoholic fraction at 100° (0.03 mm) gave 291 mg (75% yield) of crystalline carbinol **9**[13] (mp 63–64° after recrystallization): NMR ($CDCl_3$, TMS) δ 0.91 (s, 3 H), 0.93 (s, 3 H), 1.62 (s, 3 H), 0.90–2.35 (m, 13 H) ppm. The ketonic fraction (probably the hydroazulene **15**) amounted to 42 mg (11% yield). Distillation[12] at 80° (0.01 mm) gave material[13] with the following properties: NMR ($CDCl_3$, TMS) δ 1.01 (s, 3 H), 1.12 (s, 3 H), 2.13 (s, 3 H), 1.00–3.10 (m, 12 H), 5.45–5.75 (m, 1 H) ppm; ir $\lambda_{max}^{CHCl_3}$ 5.85 μ.

For the hydrogenolysis of the hydroxyl group of carbinol **9** we hoped that advantage could be taken of the known susceptibility of certain 7-*anti*-norbornenyl substituents to displacement by hydride, probably via the norbornenyl cation.[7c,d] Indeed the alcohol **9**, on treatment with sodium cyanoborohydride in the presence of zinc bromide (probably serving to assist ionization of the hydroxyl group) afforded hydrocarbon **10**[13] in 94% yield after distillation[12] at 120° (0.01 mm). The NMR spectrum showed absorption at δ 1.62 (s, 3 H) ppm for the vinyl methyl group, and no absorption in the vinyl proton region. Epoxidation of olefin **10** occurred readily, but rearrangement of the resulting epoxide has, as yet, given only poor yields of longicamphenylone **13**. Therefore the following, less direct route, was developed.



15

In the presence of acid, the olefinic bond of substance **10** readily isomerized to the exocyclic position (formula **11**), the driving force presumably being relief of strain in **10** due to the location of the olefinic bond at the bridgehead. This isomerization was performed by the addition of excess p-toluenesulfonic acid to the reduction reaction mixture at room temperature. Thus hydrocarbon **11**[13] was produced, after distillation[12] at 100° (0.03 mm), in 91% overall yield from **9**. The NMR spectrum showed absorption for the vinyl proton at δ 4.63 (s, 1 H) and 4.87 (s, 1 H) ppm. Ruthenium tetroxide-catalyzed periodate oxidation[15] converted **11** into the ketone **12** which was obtained in 72% yield after chromatography on basic alumina. The analytical specimen[13] was obtained after distillation[12] at 80° (0.1 mm). Methylation of the enolate anion of undistilled ketone **12** gave, after chromatography on basic alumina followed by distillation[12] at 100° (0.1 mm), the known racemic longicamphenylone **13**[13] in 84% yield (7% of ketone **12** being recovered). The NMR and solution ir spectra of the methylation product were identical with the corresponding spectra of naturally derived (+)-longicamphenylone. In addition the GC (coinjection) behavior of the two specimens was identical. The conversion of ketone **13** into racemic longifolene **14** was performed by the known procedure[16] involving addition of methyllithium followed by dehydration (80% yield[16]). The identity of the synthetic hydrocarbon was established by the usual comparison with the natural product.

Thus a total synthesis of racemic longifolene has been realized in 21% overall yield from 2-isopropylidenecyclopentanone (**5**). Previous total syntheses[16,17], are somewhat longer (overall yields <8%) mainly because they depend on step-by-step annelations.

Acknowledgment. We are indebted to the National Institutes of Health and the National Science Foundation for support of this research. We also wish to thank Professor McMurry for his generous gift of longifolene.

References and Notes

(1) A preliminary account of this work was first presented at the Van't Hoff Centenary Commemoration, May 3, 1974, University of Leiden.
(2) (a) W. S. Johnson, M. B. Gravestock, R. J. Parry, R. F. Myers, T. A. Bryson, and D. H. Miles, *J. Am. Chem. Soc.*, **93**, 4330 (1971); (b) W. S. Johnson, M. B. Gravestock, and B. E. McCarry, *ibid.*, **93**, 4332 (1971).
(3) Unpublished work of H. T. Hall, R. A. Volkmann, and W. S. Johnson. See the Ph.D. dissertation of H. T. Hall, Stanford University, 1973.
(4) A number of variants can be envisaged, including the "forbidden" concerted intramolecular cycloaddition of the acetylene residue to the cyclopentenyl cation to produce **3** or **4**.
(5) Cf. W. S. Johnson, M. B. Gravestock, R. J. Parry, and D. A. Okorie, *J. Am. Chem. Soc.*, **94**, 8604 (1972).
(6) Other examples of intramolecular reaction of olefinic bonds with vinyl cations may be found in ref 2a.
(7) (a) S. Winstein, M. Shatavsky, C. Norton, and R. B. Woodward, *J. Am. Chem. Soc.*, **77**, 4183 (1955); (b) S. Winstein and C. Ordronneau, *ibid.*, **82**, 2084 (1960); (c) H. C. Brown and H. M. Bell, *ibid.*, **85**, 2324 (1963); (d) S. Winstein, A. H. Lewin, and K. C. Pande, *ibid.*, **85**, 2324 (1963).
(8) Cf. P. T. Lansbury, V. R. Haddon and R. C. Stewart, *J. Am. Chem. Soc.*, **96**, 896 (1974).
(9) P. E. Peterson, R. J. Bopp, and M. M. Ajo, *J. Am. Chem. Soc.*, **92**, 2834 (1970), and references cited therein.
(10) G. B. Kaufman and L. A. Teter, *Inorg. Synth.*, **7**, 9 (1963).
(11) G. Vanon and A. Apchie, *Bull. Soc. Chim. Fr.*, 667 (1928).
(12) Bulb-to-bulb evaporative distillation using a Buchi Kugelrohrofen.
(13) The NMR and ir spectra were entirely consistent with the assigned structure, and satisfactory C, H analyses were obtained.
(14) The method of W. S. Johnson, P. J. Kropp, and K. O. Gelotte, see footnote 4 of W. S. Johnson, J. F. W. Keana, and J. A. Marshall, *Tetrahedron Lett.*, 193 (1963).
(15) Unpublished procedure of David A. Schooley, Zoecon Corp. We wish to thank Dr. Schooley for making this information available to us.
(16) J. E. McMurry and S. J. Isser, *J. Am. Chem. Soc.*, **94**, 7132 (1972).
(17) E. J. Corey, M. Ohno, R. B. Mitra, and P. A. Vatakencherry, *J. Am. Chem. Soc.*, **86**, 478 (1964).

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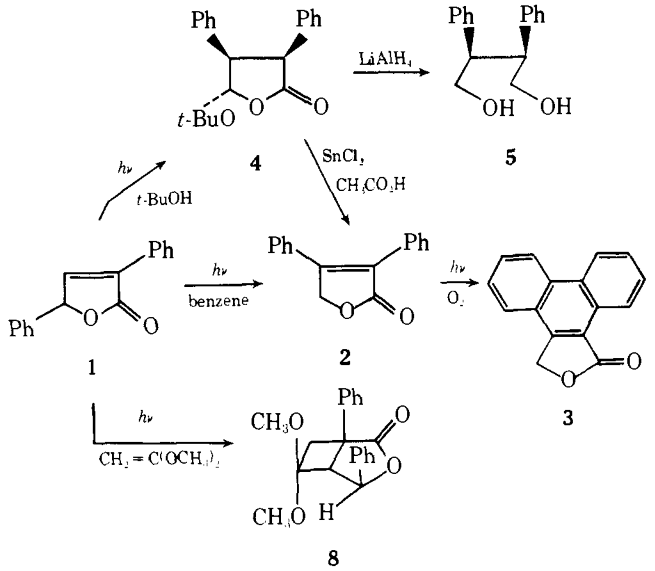
Photochemical Rearrangement in the 2(5*H*)-Furanone System[1]

Sir:

Light-induced transformations of five-membered enol lactones have been the subject of recent intensive study.[2-6] These compounds undergo a facile decarbonylation when subjected to ultraviolet excitation and produce α,β-unsaturated ketones as primary photoproducts. Chapman and McIntosh have previously noted that a critical requirement for clean photochemical cleavage of the acyl-oxygen bond is the presence of a double bond adjacent to the ether oxygen.[3] Stabilization of the incipient oxy radical was considered to be a determining factor in the photocleavage of this bond. In sharp contrast to the extensive studies concerned with the photochemistry of enol lactones, only scattered reports have appeared concerning the photochemical behavior of the related α,β-unsaturated-γ-lactone system.[7-9] We now wish to report a novel rearrangement which occurs on irradiation of an α,β-unsaturated-γ-lactone and to describe some of the salient features of this reaction.

Irradiation of 3,5-diphenyl-2(5*H*)-furanone[10] (**1**) in benzene under an argon atmosphere with Corex-filtered light for 1.5 hr gave 3,4-diphenyl-2(5*H*)-furanone[11] (**2**) in quantitative yield. If molecular oxygen is present, **2** reacts further by the well-known stilbene-phenanthrene cyclization route to produce phenanthro[9,10-*c*]furanone (**3**), mp 253-254°.[12] Studies on the photochemical behavior of **1** were also carried out using *tert*-butyl alcohol as the solvent (Scheme I). In this case, the only product isolated (87%) was *cis*-3,4-diphenyl-*trans*-5-*tert*-butoxy-γ-lactone (**4**), mp 113-114°. Elemental analysis, the infrared spectrum ($CHCl_3$, 1776 cm^{-1}), the mass spectrum (*m/e*, 286 ($M^+ - CO_2$)), and the NMR spectrum (100 MHz, δ 1.30 (s, 9 H), 3.68 (dd, 1 H, J = 9.0 and 2.0 Hz), 4.48 (d, 1 H, J = 9.0 Hz), 5.85 (d, 1 H, J = 2.0 Hz), 6.70-7.10 (m, 10 H)) suggest **4** as the structure of the photoadduct.[13] An alternative structure in which *tert*-butyl alcohol had added across the C-C double bond in a Michael fashion was ruled out on the basis of chemical degradation studies. Treatment of **4** with stannous chloride in refluxing acetic acid gave **2**, while reduction of **4** with lithium aluminum hydride gave the known *meso*-2,3-diphenyl-1,4-butanediol (**5**).[14] Further evidence which supports the stereochemical assignment was obtained by the observation that **4** was cleanly epimerized to *trans*-3,4-diphenyl-*trans*-5-*tert*-butoxy-γ-lactone (**6**), mp 86-87°, on treatment with lithium diisopropylamide in tetrahydrofuran. Subsequent reduction of **6** with lithium aluminum hydride produced *d,l*-2,3-diphenyl-1,4-butanediol (**7**) which was identical with an authentic sample prepared by the lithium aluminum hydride reduction of *trans*-2,3-diphenylsuccinic anhydride.

Scheme I



The photochemical reaction of **1** with an excess of 1,1-dimethoxyethylene in benzene was also studied. Irradiation of the mixture for 1 hr gave a single photoadduct (**8**), mp 181-182°, in nearly quantitative yield whose structure was assigned on the basis of the following spectral properties: ir (KBr) 1760 cm^{-1}; NMR (100 MHz, $CDCl_3$) δ 2.30 (dd, 1 H, J = 12.0 and 1.5 Hz), 2.50 (d, 1 H, J = 12.0 Hz), 2.78 (s, 3 H), 3.30 (s, 3 H), 4.20 (s, 1 H), 4.80 benzylic proton (d, 1 H, J = 1.5 Hz long range W-coupling), and 7.0-7.8 (m 10 H). Under these conditions the photochemical rearrangement of **1** ⟶ **2** was completely suppressed.

Similar irradiation of 3,5,5-triphenyl-2(5*H*)-furanone (**9**) gave 3,4,5-triphenyl-2(5*H*)-furanone[12] (**10**) as the initial photoproduct (78%); longer irradiation led to the formation of phenylphenanthro[9,10-*c*]furanone[12] (**11**) in high