forded **1**, **2**, and, **5**, in ~1:5:2 molar ratios, in ~87% combined yield.

Reinvestigations of the work of Favorski and Nazarov[4] by Eberson[16] and by Bartlett et al.[17] suggest that saturated ketyls must have extraordinary reactivity towards ethylene. $\mathbf{1}\cdot^{-}\mathrm{Li}^{+}$ in solution indeed reacts cleanly with ethylene at −30° or above, to give the dialkoxide of the 1,4-diol **8** (Scheme IV). In addition, **1** and the alcoholate of **2** are formed; the formation of the solvent-"adduct" **5** (alcoholate) is suppressed. Thus reaction of $\mathbf{1}\cdot^{-}\mathrm{Li}^{+}$ prepared as before in THF at −75°, with a large excess (~15 equiv) of ethylene at −22° for 24 h, followed by hydrolysis and purification gave **1**, **2**, and **8** in ~3:2:3 molar ratios, in ~68% combined yield.

These experiments prepare the ground for the study of the reactions of transient ketyls in nonacidic media.[7]

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(6) Lithium rods (Metallgesellschaft, purity 99.4–99.8%) were hammered flat, etched to brilliance in methanol, and rinsed and cut into pieces in THF or DME.

(7) To our knowledge, a disproportionation of saturated ketyls has never been observed or considered. We have since discovered that lithium ketyls do undergo disproportionation. V. Rautenstrauch, manuscript in preparation.

(8) The color of the solution changed from colorless to light red-brown (~10 min), to dark brown (1–10 h).

(9) A large excess of deuterium oxide (ca. 23°) was added to the stirred, cold solutions. Alternatively, the cold solutions were poured into ice-cold water or aqueous acid. Clean disproportionation occurred under all conditions tried.

(10) Similar results were obtained when the reaction was carried out in DME at −48°, but $\mathbf{1}\cdot^{-}\mathrm{Li}^{+}$ appears to be somewhat less stable under these conditions. We have mainly worked with THF solutions which remain mobile at ca. −75°.

(11) Small amounts of the alcoholate of **2** are apparently formed by reaction of $\mathbf{1}\cdot^{-}\mathrm{Li}^{+}$ with (unlabeled) impurities in the medium. Trimethylsilylation of this alcoholate gives **4**.

(12) We exclude the presence of ternary mixtures of **1**, $\mathbf{1}\cdot^{-}\mathrm{Li}^{+}$, and the dianion $\mathbf{1}^{2-}2\mathrm{Li}^{+}$, of an equimolar mixture of **1** and $\mathbf{1}^{2-}2\mathrm{Li}^{+}$, and of the pinacolate corresponding to $\mathbf{1}\cdot^{-}\mathrm{Li}^{+}$. We have never found any pinacol.[9] In classical experiments, "lithium benzophenone ketyl" has been shown to behave analogously; hydrolysis with aqueous base yields 1:1 mixtures of benzophenone and benzhydrol. However, the ketyl and the ketyl radical dimerize, and the pinacol is cleaved. Hydrolysis of dilithium benzophenone dianion gives benzhydrol only. For a recent discussion see L. S. Trzupek, T. L. Newirth, E. G. Kelly, N. E. Sbarbati, and G. M. Whitesides, *J. Am. Chem. Soc.*, **95**, 8118 (1973).

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(14) Hirota's zero-field parameters for the rigid medium spectrum (77 K, methyltetrahydrofuran) of the structurally similar contact ion quadruplet derived from hexamethylacetone (lithium mirror) are $E/hc \approx 0, D/hc = 0.0210\ \mathrm{cm}^{-1}$ ($r = 5.0$ Å).[5e] The half-field transition was not observed.

(15) For clarity this is not explicitly formulated in the schemes; lithium cations are omitted.

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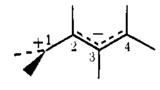
Coexistence of Two Oppositely Polarized Zwitterionic Forms on the Lowest Excited Singlet Surface of Terminally Twisted Butadiene. Two-Funnel Photochemistry with Dual Stereochemistry

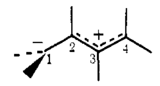
Sir:

The suggestion that certain photochemical rearrangements of hydrocarbons proceed through excited ionic intermediates was first made by Dauben.[1] For the photocyclization of butadiene to bicyclobutane[2] the orthogonal zwitterion I was proposed[1] as a primary intermediate. It has recently been shown[3] that the lowest excited zwitterionic states Z_1 and Z_2 of diradical species can indeed be strongly polarized. This *sudden polarization effect* occurs (a) if the overlap between the two radical sites is sufficiently weak and (b) if a dissymmetry exists between these two sites.[4] The high polarizability of the two zwitterionic states of ethylene had been predicted theoretically by Wulfman and Kumei.[5]



I

The sudden polarization effect was originally described in the following manner. For a given geometry, the lowest Z_1 state is polarized in one direction, and the upper neighboring Z_2 state is polarized in the opposite direction. In 90° twisted methylene–allyl with an arbitrary geometry (C_1C_2 = 1.50 Å, C_2C_3 = C_3C_4 = 1.40 Å), a minimal basis set calculation[6] gives the polarization shown in I for Z_1, while Z_2 adopts the polarization shown in II. Actually the favored polarization depends on the choice of basis set.



II

For the same geometry the polarization of the Z_1 and Z_2 states is reversed if an extended basis set[6] or polarization functions are used. Physically, however, such calculations are not too meaningful since the excited molecule, in either of the polarized forms I and II, will seek to optimize its energy by adopting the geometry most appropriate to that form. If the optimized geometries corresponding to I and II are sufficiently different, the form whose energy has been optimized should always lie, at its optimum geometry, *below* the form with the opposite polarization. The two optimized geometries should lie on the *same*, lowest singlet excited surface.

We have now carried out this dual geometry optimization for methylene–allyl in order to verify our assumption. The potential energy surface (Figure 1) for the lowest excited singlet state has indeed *two* minima[7] corresponding respectively to forms I and II in their optimized geometries. Form II lies lower in energy. The energies of the two wells differ by 9.2 kcal/mol, with an intermediate barrier of 6.6 kcal/mol between higher well I and lower well II. The energetic ordering of the wells is *independent of basis set.*[9] The figure also shows the optimized geometries of I and II and their charge distribution.

The photochemical implications of such a double-well potential are noteworthy. The presence of two wells allows the possibility of two distinct photochemical pathways for which the wells act as funnels.[10] If one well is much lower (10 kcal/mol, say) than the other, one pathway will predominate. If the two wells are relatively close in energy, the two paths should be competitive. Consider for instance the introduction of a terminal methyl group on the butadiene molecule (there are now four possible intermediate orthogonal methylene–allyl zwitterionic forms). We arbitrarily place II, 4-methyl at 0

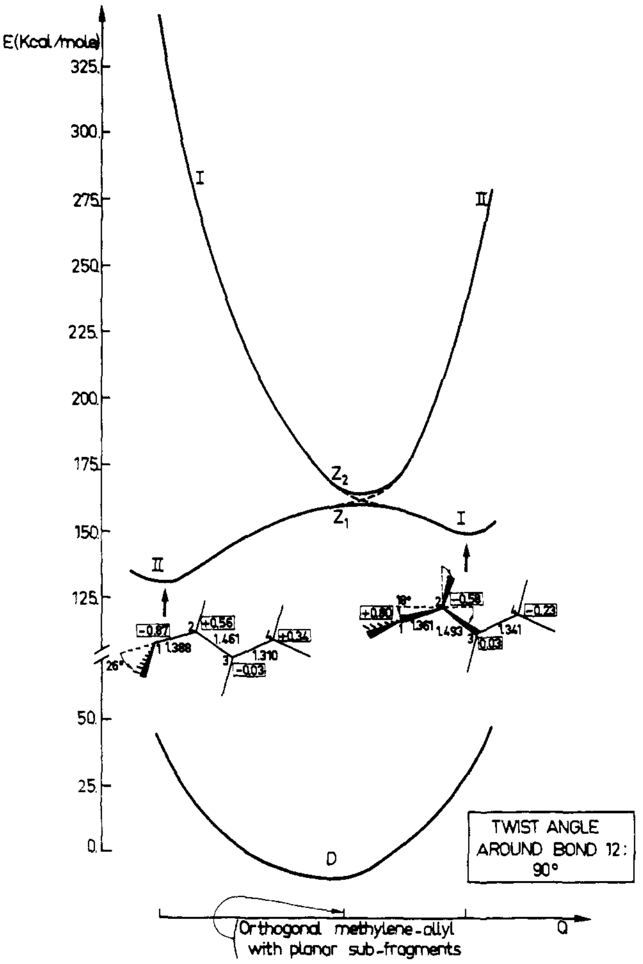


Figure 1. Potential surfaces for the lowest singlet states of 90° twisted methylene-allyl (minimal basis set). The coordinate Q is obtained by linear interpolation from the geometry of II to an intermediate geometry with planar subfragments, and from this intermediate geometry to the geometry of I. Bond lengths in this "half-way" skeleton are C_1C_2 = 1.375 Å, C_2C_3 = 1.475 Å, C_3C_4 = 1.325 Å (for this geometry II lies below I). Dotted lines show the avoided crossing between the configurations corresponding respectively to I and II.[7] Note that the diradical D is a *maximum*, or a near-maximum, along the coordinate for twisting around bond 12 (i.e., vertical excitation does not occur from D, but from the untwisted butadiene).

kcal/mol. Substitution by methyl at C-1 makes I, 1-methyl have a value of 0.1 kcal/mol. The energy difference between I and II has now decreased from 9.2 to 0.1 kcal/mol.[11] The terminal methyl group stabilizes the methylene positive center more than the allylic positive center, a reasonable result in view of the larger (0.80 at 1 in I vs. 0.34 at 4 in II) positive charge at the former center. If we *assume* that the methylene-allyl can in principle cyclize at 24 in *either* form I or form II, our results would indicate that: (a) unsubstituted butadiene cyclizes via II (allyl cation; disrotatory),[12] (b) 1-methylbutadiene cyclizes via both I and II (no stereospecificity), (c) 1,1-dimethylbutadiene cyclizes via I (allyl anion; conrotatory).[12] However, since minimal basis sets are notoriously inadequate for the energies of anions or anionic fragments (already the few extended basis set points appear to decrease the relative stability of II), and since also we have not reoptimized the geometries of I and II in the presence of the substituents, only the *qualitative trend* indicated by our results should be considered seriously.

This qualitative trend is *a smooth passage from disrotatory ring closure to conrotatory ring closure with increasing unsymmetrical terminal methyl (donor) substitution.* It would be interesting to test this prediction by investigating whether the observed conrotatory preference[13] in Dauben's pioneering experiment disappears in unsubstituted butadienes, using conveniently deuterium-labeled butadienes—or even better in a butadiene terminally substituted by an appropriate acceptor. Experimental confirmation would provide strong support for the zwitterionic nature of the primary intermediate and would reveal an extraordinary sensitivity of stereochemistry to substituents in photochemical reactions which proceed through zwitterionic intermediates.[14]

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(7) The double-well potential shown in the figure for the lowest excited *zwitterionic* state $^1Z_1$ should not be confused with the double-well potential obtained previously for an excited *diradical* state ^1D in highly polar solvents (L. Salem and W. D. Stohrer, *J. Chem. Soc., Chem. Commun.*, 140 (1975)). Here the origin of the double well is an avoided crossing between the two excited singlets,[8] whereas in the previous case the avoided crossing occurred between ground and excited singlet.

(8) J. Langlet and J. P. Malrieu, *Theor. Chim. Acta*, **33,** 307 (1974), point out that mixing of degenerate configurations in twisted butadiene may lead to local deformations of the nuclear geometry.

(9) The corresponding extended basis set values are 8.7 and 7.8 kcal/mol for the previously optimized geometries.

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(11) On the same energy scale, I, 4-methyl lies at 13.2 kcal/mol and II, 1-methyl at 12.1 kcal/mol.

(12) It might be argued that in the Z state the allylic anion (or cation) is an *excited* anion (or cation) and should therefore undergo disrotatory, rather than conrotatory, closure. Consideration of the orbital occupancies in the allyl fragment shows that this is not the case. The excitation energy of the molecule is used exclusively for 1–2 twisting and for separating the two charges, thus lifting the diradical to an excited zwitterionic state ($CH_2\cdot$, allyl· → CH_2^+, allyl$^-$).

(13) Conrotatory closure occurs in ethylidene–cyclooctene,[1a] which is equivalent to a 1,3,4-trialkyl derivative of butadiene. If we label the twisted double bond 12 (as in Figure 1), the substituted centers are 1, 3, and 4 for endocyclic twist and 1, 2, and 4 for exocyclic twist. We now *estimate* the relative stabilization of I and II by considering the net charges, in the *unsubstituted* system (Figure 1), at those positions which become alkyl-substituted. The stabilization of positive charges by the alkyl substituents is *optimized* in I by rotation about the endocyclic bond (the substituted centers bear charges +0.80, +0.03, −0.23), in II by rotation about the exocyclic bond (the substituted centers bear charges +0.56, +0.34, and −0.87). The larger net overall positive charge stabilized in I, and the poor interaction of a methyl group with a near-unit negative charge at a terminal carbon in II, can possibly make I the reactive species. We thank W. G. Dauben for a discussion of this case.

(14) Stereochemistry should also be temperature dependent (P. de Mayo, private communication, 1976).

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Conjugated Allenic 3-Oxo-5,10-secosteroids. Irreversible Inhibitors of Δ^5-3-Ketosteroid Isomerase

Sir:

The enzyme Δ^5-3-ketosteroid isomerase[1] (EC 5.3.3.1) from *Pseudomonas testosteroni* converts C_{19} and C_{21} Δ^5-3-ketosteroids to the corresponding Δ^4-3-ketosteroids. The proposed mechanism[1,2] involves enolization with removal of the axial 4β-hydrogen followed by ketonization of the $\Delta^{3,5}$-dienol with axial reprotonation at C-6. The hydrogen transfer from C-4