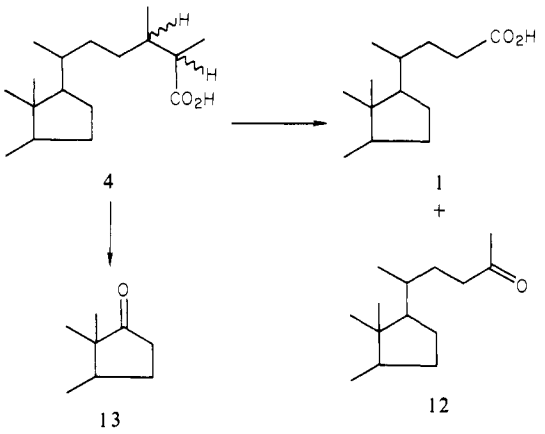
Chart II



This degradative mechanism of the branched side chain carbons (C-28 and C-29) of phytosterol differs from that of the insect system, which cleaves the C-24–C-28 bond via dehydrogenation, epoxidation, and fragmentation to yield desmosterol and acetaldehyde.[10]

Acknowledgment. This research was supported in part by a grant from the National Institutes of Health (GM-26838).

Registry No. 1, 1452-29-5; **2**, isomer 1, 82537-06-2; **2**, isomer 2, 82570-86-3; **2**, isomer 3, 82537-07-3; **2**, isomer 4, 82570-87-4; **4**, isomer 1, 82537-00-6; **4**, isomer 2, 82570-88-5; **4**, isomer 3, 82570-89-6; **4**, isomer 4, 82537-08-4; **5**, 66414-44-6; **6**, 66414-45-7; **7**, 82537-01-7; **8**, 82537-02-8; **9**, 82537-03-9; **10**, 82537-04-0; **11**, 74730-06-6; **12**, 82537-05-1; **13**, 63-05-8; sitosterol, 83-46-5; campesterol, 474-62-4; propionic acid, 79-09-4; bicarbonate, 71-52-3; acetic acid, 64-19-7.

(10) Ikekawa, N.; Fujimoto, Y.; Takasu, A.; Morisaki, M. *J. Chem. Soc., Chem. Commun.* **1980**, 709 and references cited therein.

Symmetrical Intermediates in C_9H_{12} Biradical Rearrangements. Possible Intervention of an Organic Tetraradical

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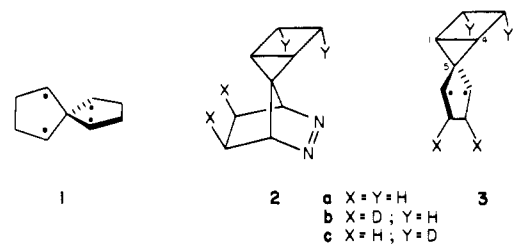
The present work addresses the possibility of generating and characterizing 1,4,6,9-spiro[4.4]nonatetrayl (**1**), an organic tetraradical. The singly occupied p orbitals of **1** interact extensively via spiroconjugation,[2] as shown by the orbital mixing diagram in



1 **2** a X=Y=H b X=D; Y=H c X=H; Y=D **3**

(1) NSF Predoctoral Fellow, 1980–1983.

(2) Simmons, H. E.; Fukunaga, T. *J. Am. Chem. Soc.* **1967**, *89*, 5208–15. Hoffmann, R.; Imamura, A.; Zeiss, G. D. *Ibid.* **1967**, *89*, 5215–20. Duerr, H.; Gleiter, R. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 559–69.

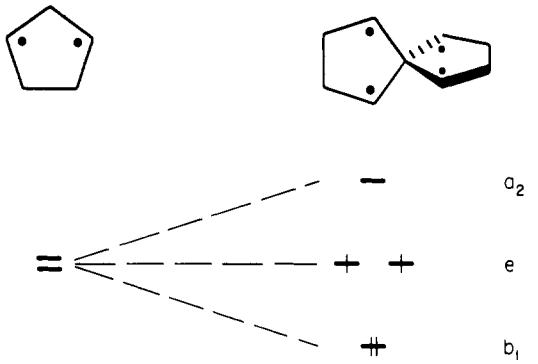


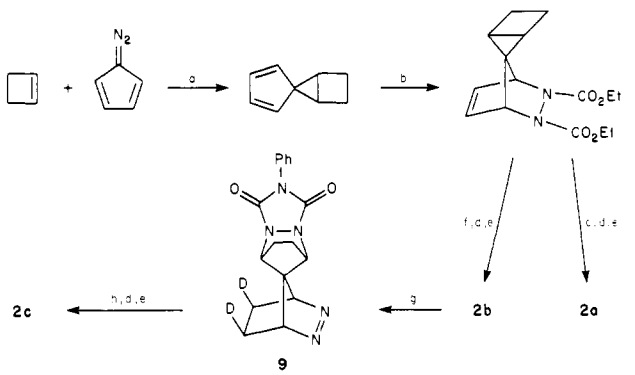
Figure 1. MO interaction diagram showing the effects of spiroconjugation in **1**.

Table I. Product Yields from 2

conditions	4	5	other
140 °C, 4 h	70.6[a]	29.4[a]	
$h\nu$, direct	86.7	9.6	3.6
$h\nu$, Ph_2CO sensitized	2.3	84.6[b]	13.0[b]

[a] Control experiments indicate that 4 → 5 under these conditions. Values are for 90% conversion of 2. [b] These products decompose slowly under the reaction conditions. Values are for 90% conversion of 2.

Scheme I



[a] $h\nu$, $\lambda > 425$ nm. [b] $EtO_2CN{=}NCO_2Et$. [c] $N_2H_4{\cdot}H_2O$, O_2. [d] KOH, *i*-PrOH. [e] O_2. [f] $N_2D_4{\cdot}D_2O$, O_2. [g] PTAD. [h] $h\nu$, $\lambda > 300$ nm, solid state.

Figure 1. Schweig's empirical formula for estimation of the spiroconjugative split in spiro[4.4]nonane derivatives predicts a 1.96-eV gap between the b_1 and a_2 molecular orbitals of **1** (D_{2d} symmetry).[3] Ab initio calculations[4] are fully consistent with this result. Thus, in a structural sense **1** is a tetraradical (two broken bonds),[5] but the electronic structure is that of a biradical (two electrons in a degenerate pair of nonbonding MO's).[6] The substantial energy lowering of the b_1 orbital could significantly stabilize **1** relative to a system containing four noninteracting radical centers.

These and other qualitative considerations led us to speculate that azoalkane **2** could give rise to novel chemistry indicative of **1**. Homolysis of the C1–C4 bond in the biradical **3** obtained upon N_2 loss from **2** relieves ca. 50 kcal/mol of strain energy and allows the full spiroconjugative stabilization of **1** to develop. Thus, the novel biradical → tetraradical sequence **3** → **1** seems feasible.

The synthesis of diazene **2** is outlined in Scheme I.[7] As shown

(3) Schweig, A.; Weidner, U.; Hill, R. K.; Cullison, D. A. *J. Am. Chem. Soc.* **1973**, *95*, 5426–7. This analysis assumes coefficients of $1/2^{1/2}$ for the radical p orbitals in the cyclopentanediyl fragments.

(4) McElwee-White, L.; Goddard, W. A., III; Dougherty, D. A., to be submitted for publication.

(5) Berson, J. A. *Acc. Chem. Res.* **1978**, *11*, 446–53.

(6) Salem, L.; Rowland, C. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 92–111.

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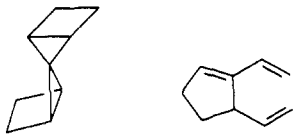
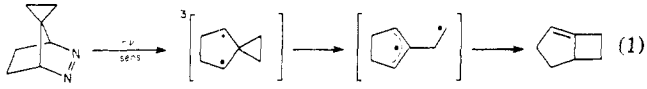
in Table I, decomposition by thermolysis, direct photolysis, or triplet-sensitized photolysis yields 5,5′-spirobis(bicyclo[2.1.0]-pentane) **4**, 2,3-divinylcyclopentene **5**, and a third minor product



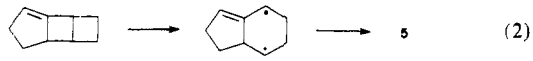
4 **5**

that we have not been able to isolate and which appears to be thermally labile. We shall concentrate on the triplet photochemistry of **2**.

The results for **2** parallel Roth's studies of 2,3-diazabicyclo-[2.2.1]hept-2-ene-7-spirocyclopropane **6**.[8] By direct analogy, one would expect sensitized photolysis of **2** to give **3**, which would subsequently cleave the C1–C5 bond and ultimately give **7**. This compound could be thermally labile and might be expected to rearrange to **5** at room temperature, via biradical **8** (eq 1 and 2).



6 (1)



7 **8** **5** (2)

As a test for this precedented route to **5**, we prepared **2b** with completely stereospecific exo-deuterium labeling (Scheme I).[9] Cleavage of the C1–C5 bond requires that the deuteriums of **2b** end up in the aliphatic CH_2's of **5**. However, any intervention by **1** would make all CH_2 groups equivalent and would thus produce aliphatic (A) and vinylic (V) deuteriums in **5**. As shown in Table II, sensitized photolysis of **2b** gives both **5**-A and **5**-V. The four aliphatic deuteriums of **5**-A are in a 1:1:1:1 ratio[9] as necessitated by the fact that the first-formed biradical **3** has a mirror plane of symmetry.

The **5**-A/**5**-V ratio from **2b** indicates that C1–C5 cleavage is occurring in **3**, along with some other path that makes the two five-membered rings of **3** equivalent.[10] If tetrayl **1** is involved in the scrambling mechanism, both five-rings become equivalent, and both *faces* of both rings become equivalent. A test for facial scrambling required azoalkane **2c**, since now the face differentiation provided by the deuteriums would not be lost in biradical **3c**. Synthesis of **2c** was accomplished by using an "azo transposition" sequence (Scheme I). *N*-Phenyltriazolinedione (PTAD) addition across the bicyclo[2.1.0]pentane moiety of **2b**,[11] followed by solid-state photolysis[12] of adduct **9**, ultimately leads to **2c** with a 4.0:1 mixture of endo/exo deuteriums.

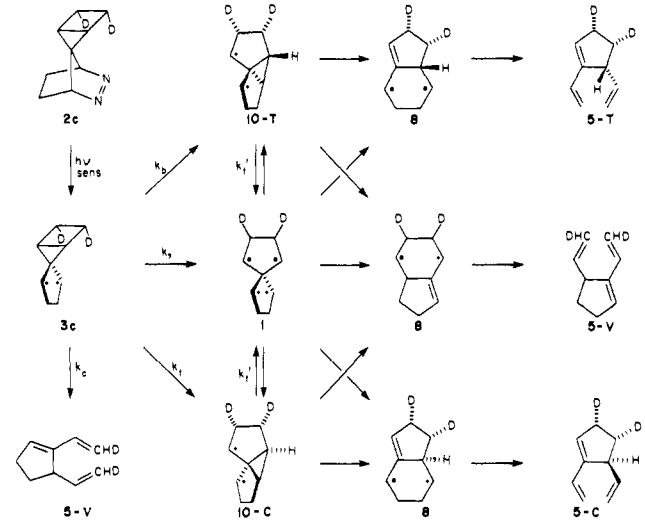
Sensitized photolysis of **2c** produced an excess of **5**-V, and more importantly, the aliphatic deuteriums in **5**-A are only *partially scrambled* (Table II). Thus, a path that interconverts the two five-rings of **3** but does not lead to complete equivalence of the ring faces is indicated. This result implicates an alternative symmetrical intermediate **10**, which has only C_2 symmetry. It

Table II. Distribution of ^2H in **5**

precursor	5-A/5-V	5-T/5-C[a]
2b	4.0:1.0	1.0:1.0
2c[b]	1.0:3.3	2.3:1.0

[a] Deuteriums cis or trans with respect to the proton on C3. [b] 4.0:1.0 endo/exo.

Scheme II



can be formed from **3** by an intramolecular S_H reaction with either backside (k_b) or frontside (k_f) attack (eq 3).

3 **10** (3)

Our current model for the sensitized photolysis of **2** is given in Scheme II.[13,14] The C1–C5 cleavage mechanism (k_c) must be operative, given the excess of **5**-V from **2c** and **5**-A from **2b**. This is the biradical analogue to a cyclopropylcarbinyl-to-allylcarbinyl rearrangement—a process that is quite facile in the parent free radical.[15a] However, our labeling studies require that some other process be competitive with this reaction. The alternative mechanism is best characterized by the ratio **5**-T/**5**-C from **2c**, which can be rationalized in two ways. One involves a competition between k_b and k_f, with k_b preferred by a factor of 4. The alignment for the backside attack is far removed from the 180° angle which is preferred in related reactions.[16] On the other hand, frontside free radical attack on a C–C bond is an unprecedented process, and a variety of studies has found a strong preference for backside attack.[16] However, it seems possible that the high strain of the C1–C4 bond and the unusual steric constraints in **3** could conspire to make k_b, k_f, and k_c all roughly competitive.

The alternative analysis involves a competition between k_b and tetraradical formation (k_t or $k_{t'}$). One way to envision this competition is as follows. In the conversion of **3** to **1**, the C1–C4 bond

(7) Spectral and analytical data will be presented in the full account of this work. Compound **5** has been prepared previously: Untch. K. G.; Martin, D. J. *J. Am. Chem. Soc.* **1965**, *87*, 4501–5. Skattebol, L.; Solomon, S. *Ibid.* **1965**, *87*, 4506–13.

(8) Roth, W. R.; Enderer, K. *Justus Liebigs Ann. Chem.* **1970**, *733*, 44–58.

(9) All stereochemical analyses are based on ^2H NMR on a Bruker WM 500 instrument (77.8 MHz for ^2H). All relevant signals were well resolved. In particular, the endo/exo ratios in **2b** and **2c** could be determined easily, and the four aliphatic signals from **5** were baseline resolved. Relaxation studies ensured that the integrals were reliable. Signal assignments for **5** were based on extensive decoupling and NOE experiments using 500-MHz ^1H NMR. Control experiments reveal that **4** is stable to the sensitized photolysis conditions and that **2c** does not rearrange to **2b** or scramble stereochemistry during the reaction.

(10) We have been unable to devise a path that specifically converts **2b** to **5**-V.

(11) Roth, W. R.; Martin, M. *Tetrahedron Lett.* **1967**, 4695–8. Chang, M. H.; Dougherty, D. A. *J. Org. Chem.* **1981**, *46*, 4092–3.

(12) Roth, W. R.; Martin, M. *Justus Liebigs Ann. Chem.* **1967**, *702*, 1–7.

(13) The fact that **5**-A/**5**-V from **2b** does not exactly equal **5**-V/**5**-A from **2c** suggests a kinetic isotope effect. However, we cannot at present assign the effect to any particular microscopic event(s).

(14) We have no data concerning the spin multiplicities of the various species of Scheme II. However, it seems certain that **3** is initially formed as a triplet, and it seems probable that any biradical in Scheme II that is long-lived enough to undergo rearrangement to another biradical is also a triplet.

(15) Ingold, K. U. In "Rearrangements in Ground and Excited States"; deMayo, P. D., Ed.; Academic Press: New York, 1980, Vol. 1, (a) pp 227–235, (b) p 180.

(16) Porter, N. A.; Nixon, J. R. *J. Am. Chem. Soc.* **1978**, *100*, 7116–7. Porter, N. A.; Cudd, M. A.; Miller, R. W.; McPhail, A. T. *Ibid.* **1980**, *102*, 414–6.

must open in a disrotatory manner. As this happens, the back lobes of the σ-bonding orbital swing into a much more favorable orientation for bonding with a radical center of the other ring. The distinguishing factor then becomes whether the C1–C4 bond cleaves all the way to **1** or whether an intramolecular backside trapping occurs.[17] Alternatively, the sequence **3c** → **10**-T could be quite stereospecific, but interconversion of **10**-T and **10**-C via **1** (k_t) is competitive with conversion of **10**-T to products.[19]

In summary, our anticipation that the unusual structural features of azoalkane **2** would give rise to new chemistry was confirmed. The conventional C1–C5 cleavage process (k_c) is operative in **3**, but it alone cannot explain the deuterium scrambling results. Our current model requires one of two unprecedented processes: frontside radical attack on a C–C bond or formation of an organic tetraradical (**1**). Studies to differentiate these alternatives and to further characterize the interesting C_9H_{12} potential energy surface are underway.

Acknowledgment. We gratefully acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society, the Research Corp., the Camille and Henry Dreyfus Foundation, and the National Science Foundation (Grant No. CHE-8024664) for support of this work and the use of the Southern California Regional NMR Facility (NSF Grant 7916324A1). We also thank Dr. William R. Croasmun for assistance in obtaining high-field NMR data.

Registry No. 1, 82482-44-8; **2a**, 82482-45-9; **2b**, 82482-46-0; **2c**, 82482-47-1; **4**, 82482-48-2; **5**, 3641-77-8; **5**-C, 82482-49-3; **5**-T, 82534-92-7; **5**-V, 82482-50-6; **9**, 82494-76-6; 5-diazo-1,3-cyclopentadiene, 1192-27-4; spiro[bicyclo[2.1.0]pentane]-5,1′-cyclopenta-2′,4′-diene, 82494-77-7; 2,3-bis[ethoxycarbonyl]-2,3-diazabicyclo[2.2.1]hept-5-ene-7,5′-spirobicyclo[2.1.0]pentane, 82482-51-7; cyclobutene, 822-35-5; PTAD, 4233-33-4; $EtO_2CN{=}NCO_2Et$, 1972-28-7.

(17) The conversion of **1** to **5** could occur by a sequence such as **1** → **10** → **8** → **5** or by a more direct **1** → **8** → **5** path. The latter sequence involves a reaction of **1** that is directly analogous to the unusually facile 1,5-vinyl migration of 1,3,6,8-spiro[4.4]nonatetraene.[18]

(18) Semmelhack, M. F.; Weller, H. N.; Foos, J. S. *J. Am. Chem. Soc.* **1977**, *99*, 292–4.

(19) Our model assumes that the conversion of **3** to **10** is irreversible. Given the high strain of a bicyclo[2.1.0]pentane moiety, **3** → **10** appears highly exothermic. In the free radical analogue,[15b] bicyclo[3.1.0]hex-2-yl rearranges very rapidly to 3-cyclopentenylmethyl and 3-cyclohexenyl (both reactions are analogues to **10** → **8**), but it has never been observed to rearrange to 5-bicyclo[2.1.0]pentylmethyl (the analogue to **10** → **3**). Note also that sequences such as **3c** → **10** → **3b** → **5** would have to produce a 1:1 mixture of **5**-C and **5**-T and thus cannot explain the scrambling result from **2c**.

α-Lithiomethylenetriphenylphosphorane, a Highly Reactive Ylide Equivalent

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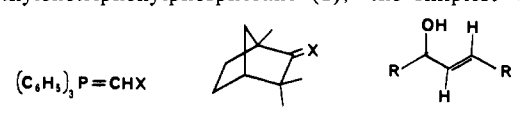
Received May 11, 1982

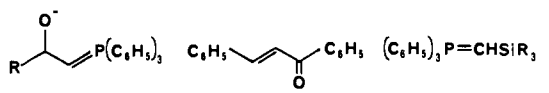
Methylenetriphenylphosphorane (**1**),[1] the simplest Wittig reagent, has been used in countless syntheses of terminal olefins since its introduction almost 2 decades ago. Despite its widespread utility, this reagent is known to be inapplicable with unreactive substrates such as epoxides or hindered ketones.[2] We describe herein a simple method for ylide activation that enlarges the range of application of **1** and suggests a variety of new synthetic possibilities.



(1) Wittig, G.; Schoellkopf, U. *Chem. Ber.* **1954**, *87*, 1318.

Although **1** is commonly prepared by deprotonation of methyltriphenylphosphonium ion with alkyllithium reagents, the literature contains no indication of the possibility of further deprotonation. However, it has been discovered that the reaction of **1** with *tert*-butyllithium in tetrahydrofuran (THF) solution[3] (−78 to −40 °C over 1 h and −40 °C for 1 h) produces a red to red-orange solution of the lithiated ylide **2** at concentrations up to 0.2 M. The lithiated ylide **2** can also be produced as an orange suspension in ether by the reaction of methyltriphenylphosphonium bromide with 2 equiv of *sec*-butyllithium (−78 to −40 °C for 1 h and 20 °C for 3 h) or from **1** with 1 equiv of *tert*-butyllithium (−78 to 20 °C over 2 h and 20 °C for 3 h) in ether. Although fenchone (**3**) is unaffected by treatment with **1** at temperatures up to 50 °C in a variety of solvents (e.g., THF, THF–hexamethylphosphoric triamide (HMPA), or dimethyl sulfoxide), it reacts with the lithiated ylide **2** in the presence of 20 equiv of HMPA (−50 to 20 °C for 1 h) to form an adduct that decomposes to the exo-methylene derivative **4** (87% yield) in the presence of excess *tert*-butyl alcohol at 20 °C for 12 h.[4]

Reaction of **2** in ether with 2 equiv of benzaldehyde or 2 equiv of hexanal (−78 to 20 °C for 2 h and 20 °C for 14 h) results in formation of the trans-allylic alcohol **5** (60%) or **6** (54%), respectively. Nucleophilic addition of **2** to the formyl group of an aldehyde is expected to give a 1:1 adduct, the β-oxido ylide **7**,[5]



7 **8** **9**

which has been shown previously[5] to react with a second equivalent of aldehyde to yield a trans-allylic alcohol (**5** or **6**). In these reactions of aldehydes and the above described reaction with fenchone, the crude reaction product was found by thin-layer chromatographic analysis not to contain significant quantities of the alcohol that would result from addition of the alkyllithium reagent used to generate **2** (*t*-BuLi or *sec*-BuLi) and the carbonyl compound. This fact shows that a full equivalent of the alkyllithium reagent is consumed in the reaction with **1** and adds further evidence for formulating the reagent as **2**. Still more evidence comes from the formation of **8** from the reaction of **2** (−78 °C, THF) with 1 equiv of benzoyl chloride followed by 1 equiv of benzaldehyde and from the formation of silylated ylides **9**[6] by reaction of **2** with 1 equiv of various trialkylchlorosilanes at −78 °C in THF.

The utility of **2** as a synthetic reagent is also demonstrated by the reaction with epoxides. Treatment of **2** in ether with cyclopentene oxide (0 °C for 2 h and 20 °C for 20 h) generates the γ-oxido ylide **10**, which reacts with benzaldehyde (−78 °C for 1.5 h and 20 °C for 8 h) to form the trans,trans-homoallylic alcohol

(2) See, for example: (a) McMurry, J. E.; Choy, W. *Tetrahedron Lett.* **1980**, *21*, 2477. (b) Sowerby, R. L.; Coates, R. M. *J. Am. Chem. Soc.* **1972**, *94*, 4758. (c) McMurry, J. E. *Ibid.* **1968**, *90*, 6821. (d) Boeckman, R. K., Jr.; Silver, S. M. *Tetrahedron Lett.* **1973**, 3497.

(3) All organometallic reactions were conducted under an atmosphere of dry argon. Solutions of **1** were prepared from methyltriphenylphosphonium bromide and *n*-butyllithium (1 equiv) in THF at 0 °C for 10 min and 20–25 °C for 20 min.

(4) All products were purified chromatographically and characterized by infrared, proton magnetic resonance, and mass spectroscopy.

(5) (a) Corey, E. J.; Yamamoto, H. *J. Am. Chem. Soc.* **1970**, *92*, 226, 3523. (b) Corey, E. J.; Yamamoto, H. *Ibid.* **1970**, *92*, 6636, 6637. (c) Corey, E. J.; Ulrich, P.; Venkateswarlu, A. *Tetrahedron Lett.* **1977**, 3231.

(6) See: (a) Schmidbaur, H.; Stühler, H. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 231. (b) Plenat, F. *Tetrahedron Lett.* **1981**, *22*, 4705.

0002-7863/82/1504-4724$01.25/0