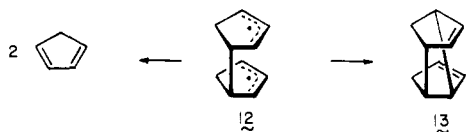


135 °C for 3 days. Although 10–15% unreacted **9b** is routinely recovered, even when the reaction time is extended, the ¹H NMR spectrum of the purified iodides (in CDCl₃) clearly reveals the presence of three epimers on the basis of the distinct methine signals at δ 3.73, 3.83, and 3.95. The isomer of **10** which has the 3.83 peak always predominates (50–70%).

Dehalogenation of **10** (as the epimeric mixture) with excess Na/K alloy (1:1 wt/wt) in ether overnight gave the desired pungent smelling, highly volatile, crystalline diene **1** which, however, could not be purified by preparative VPC. Although **1** can be readily sublimed, this procedure did not adequately remove small amounts of equally volatile byproducts. The preferred method of purification consists in conversion to its stable, colorless, crystalline silver nitrate complex **11** and subsequent liberation by conventional treatment with concentrated ammonium hydroxide solution. The ease with which **1** can be reversibly transformed to **11** contrasts markedly with the stability of its Rh(I) complexes.³ The ¹H NMR spectrum of the title hydrocarbon (C₆D₆, 90 MHz) features an upfield doublet at δ 1.83 (*J* = 9.98 Hz broadened by further small coupling, 2 H), a four-proton singlet at 2.33, a doublet of area 2 centered at 2.71 (*J* = 9.98 Hz), and a downfield singlet at 6.08 (4 H). Again as in its saturated counterpart,⁷ the trans-annular steric strain in **1** is easily detected spectroscopically. Its ¹³C NMR spectrum shows signals at 40.88 (d, ¹*J*_{CH} = 141), 45.59 (t, 133), and 141.71 (d, 165).

The photoelectron spectrum¹² of **1** is characterized by broad bands at low energies having a first IP at 8.65 ± 0.1 eV and the second at 8.90 ± 0.07 eV. The structural features of this diene are therefore conducive to very intimate coupling of its σ and π orbitals as judged, in particular, by the extreme broadness of the bands. Effective through-bond coupling of exceptionally high lying σ levels is unprecedented,¹³ although examples of preferred through-space overlap also do exist.¹⁴

Warming a solution of **1** in C₆D₆ brings about exceptionally clean Cope rearrangement to **3**. The progress of reaction was monitored by integration of magnetic resonance signals of key protons in both **1** (disappearance) and **3** (appearance) against the singlet absorption peak of internal dioxane standard. The skeletal isomerization conforms nicely to first-order kinetics with rate constants *k*_{58.5°} = 1.64 × 10⁻⁵ s⁻¹, *k*_{68.5°} = 5.68 × 10⁻⁵, and *k*_{79.5°} = 18.41 × 10⁻⁵. The corresponding activation parameters are Δ*H*[‡] = 26.1 kcal/mol and Δ*S*[‡] = -1.98 eu. After numerous half-lives, no spectroscopically detectable quantities of cyclopentadiene, *endo*-dicyclopentadiene, or *exo*-dicyclopentadiene (**13**) were seen. It would appear therefore that the prescribed conditions are not conducive to the generation of biradical **12** which might be expected either to fragment or reclose with formation of **13**.



Structural assignment to **3** as the syn,*cis* [2 + 2] cyclopentadiene dimer follows from its spectral properties: ¹H NMR (C₆D₆) δ 2.25 (m, 4 H), 2.89 (m, 2 H), 3.42 (m, 2 H), 5.44 (m, 2 H), and 5.77–5.83 (br m, 2 H). Double resonance studies revealed that independent saturation of the δ 2.89 and 5.44 signals causes the downfield olefinic peak to become a doublet (*J* = 5.1 Hz) and triplet (*J* = 4.0 Hz), respectively.

Mechanistically instructive is the overwhelming adherence by **1** to the synchronous six-electron rearrangement rather than to a stepwise homolytic pathway with initial generation of a pair of allyl radicals (cf. **12**). The observed reaction course delivers **3** whose strain, although less than that of its precursor (the **1** → **3** conversion is thermally irreversible), remains significant. The exclusion of more thermodynamically favored

products (e.g., **13**) can be regarded as an exploitable benefit of orbital symmetry. In the present instance, the synthetic implications are that **3**, as well as **1**, now becomes directly available for further experimental scrutiny.¹⁵

References and Notes

- (1) E. E. van Tamelen, J. I. Brauman, and L. E. Ellis, *J. Am. Chem. Soc.*, **93**, 6145 (1971).
- (2) Dicarbonyl derivatives of **2** and **3** have been reported previously: (a) E. Baggolini, E. G. Herzog, S. Iwasaki, R. Schorta, and K. Schaffner, *Helv. Chim. Acta*, **50**, 297 (1967); (b) P. E. Eaton and S. A. Cereface, *Chem. Commun.*, 1494 (1970).
- (3) A Rh(I) complex of **1** has been prepared independently by Professor P. E. Eaton, private communication.
- (4) Subsequent to the completion of this study, the authors were informed by Professor N. J. Turro that a Columbia University group had isolated **3** by an azo photolysis procedure.
- (5) (a) J. S. McKennis, L. Brener, J. S. Ward, and R. Pettit, *J. Am. Chem. Soc.*, **93**, 4957 (1971); (b) L. A. Paquette, R. F. Davis, and D. R. James, *Tetrahedron Lett.*, 1615 (1974); (c) L. A. Paquette, D. R. James, and G. Klein, unpublished work.
- (6) All compounds described herein have been characterized spectrally (IR and NMR) and as to composition (mass spectral, elemental analyses).
- (7) L. A. Paquette, G. Klein, and C. W. Doecke, *J. Am. Chem. Soc.*, preceding paper in this issue.
- (8) L. R. Smith, G. E. Gream and J. Meinwald, *J. Org. Chem.*, **42**, 927 (1977).
- (9) N. B. Chapman, J. M. Key, and K. J. Toyne, *J. Org. Chem.*, **35**, 3860 (1970).
- (10) (a) S. Masamune, H. Cuts, and M. G. Hogben, *Tetrahedron Lett.*, 1017 (1966); (b) N. A. Sasaki, R. Zunker, and H. Musso, *Chem. Ber.*, **106**, 2992 (1973); (c) H. Musso, *ibid.*, **108**, 337 (1975); (d) D. Bosse and A. de Meijere, *Tetrahedron Lett.*, 1155 (1977).
- (11) R. K. Crossland and K. L. Servis, *J. Org. Chem.*, **35**, 3195 (1970).
- (12) The authors are indebted to Professor K. N. Houk for kindly making this spectral determination.
- (13) (a) W. Schmidt and B. T. Wilkins, *Tetrahedron*, **28**, 5649 (1972); (b) E. Heilbronner as quoted in footnote 18 of H.-D. Martin, S. Kagabu, and R. Schwesinger, *Chem. Ber.*, **107**, 3130 (1974).
- (14) (a) H.-D. Martin and R. Schwesinger, *Chem. Ber.*, **107**, 3143 (1974); (b) H. Prinzbach, G. Sedelmeier, and H.-D. Martin, *Angew. Chem., Int. Ed. Engl.*, **16**, 103 (1977).
- (15) This work was generously supported by the National Science Foundation.

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Use of Phenyl Vinyl Sulfoxide as an Acetylene Equivalent in Diels–Alder Cycloadditions

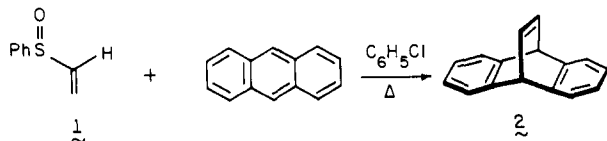
Sir:

As a consequence of the unreactive nature of acetylene in [4 + 2] cycloadditions¹ and the safety hazards associated with its handling at elevated temperatures and pressures, there has been sustained interest in the development of a reliable acetylene Diels–Alder synthon. A number of specialized and limited procedures have been developed, but all are multistep processes requiring the isolation of intermediates followed by functional group manipulation, and suffer from modest overall yields and/or undesirable side reactions. Some of the more frequently reported methods include (a) dehydrobromination of vinyl bromide adducts;² (b) zinc-induced dechlorination of *cis*-dichloroethylene-derived substrates;³ (c) thermal extrusion of cyclopentadiene from norbornadiene adducts;⁴ (d) cycloaddition of 2-thiono-1,3-dioxol-4-ene with reactive dienes^{5,6} followed by treatment with trimethyl phosphite,⁷ [Ni(COD)₂],⁸ or Fe(CO)₅;⁶ (e) comparable use of 2-phenyl-1,3-dioxol-4-ene;^{5,9} (f) diene addition to dimethyl acetylenedicarboxylate, hydrolysis, and decarboxylation, either by direct methods^{3c} or involving prior chromous ion reduction;¹⁰ and (g) formation of maleic anhydride adducts, hydrolysis, and oxidative decarboxylation by one of several techniques.¹¹ We now report the development of a high-yield, single-step alternative which exploits the dienophilicity of phenyl vinyl sulfoxide (**1**)

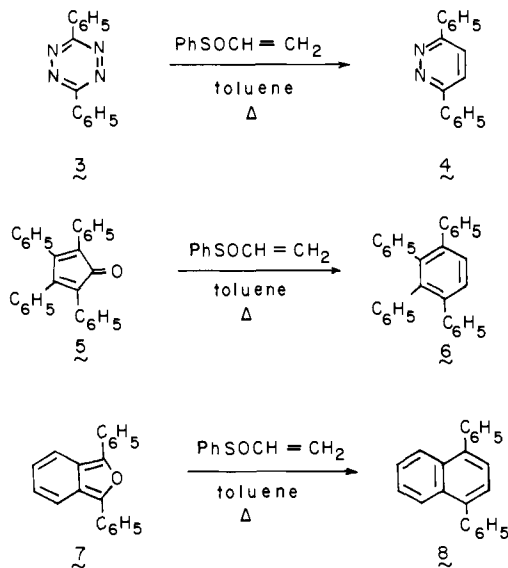
and the in situ thermal extrusion of phenylsulfenic acid (C_6H_5SOH) under the reaction conditions.

Although Diels–Alder cycloadditions of α,β -unsaturated sulfoxides containing a second activating substituent ($-SO_2R$, $-SOR$, $-COR$, etc) have been previously reported,^{12,13} the simpler vinyl sulfoxides $RSOCH=CH_2$ appear not to have received prior attention, perhaps because of disparaging claims of low reactivity (no data provided).¹⁴ The possibility seems not to have been considered that the rate of retrograde fragmentation might be equal to, or faster than, that of the forward reaction in certain cases. Notwithstanding, the now well-established lability of sulfoxides to thermal decomposition with olefin formation under relatively mild conditions¹⁵ suggested that reversibility (if indeed a factor) could be arrested and the cycloaddition effectively driven to completion.

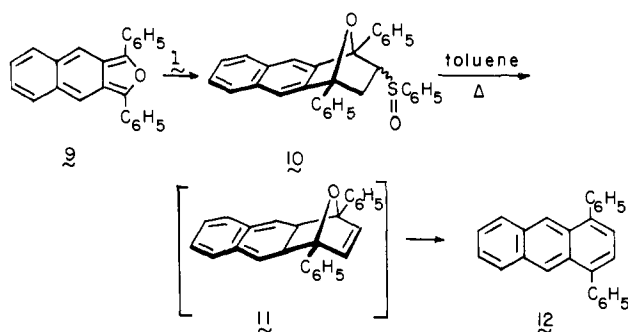
Access to phenyl vinyl sulfoxide (**1**) can be gained readily through reaction of ethyl phenyl sulfinate with vinylmagnesium bromide. In a typical application of the above logic, heating of anthracene and **1** (1.5 equiv) in chlorobenzene (130 °C) under nitrogen for 120 h followed by silica gel chromatography afforded dibenzobarrelene (**2**) in 83% isolated yield. Since comparable yields of **2** have heretofore not been approached,³ this one-step procedure constitutes a much improved route to the hydrocarbon.



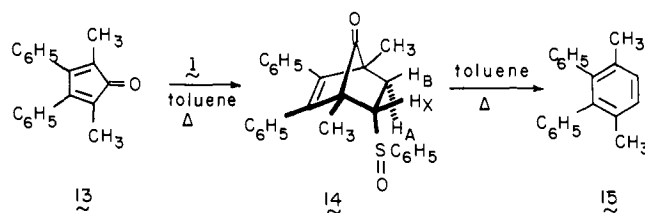
With more reactive dienes such as diphenyl-*s*-tetrazine (**3**), tetracyclone (**5**), and diphenylisobenzofuran (**7**), cycloaddition–elimination took place efficiently in toluene to deliver 1,4-diphenylpyridazine (**4**, 97%),¹⁶ 1,2,3,4-tetraphenylbenzene (**6**, 91%),¹⁷ and 1,4-diphenylnaphthalene (**8**, 93%).¹⁸ The latter



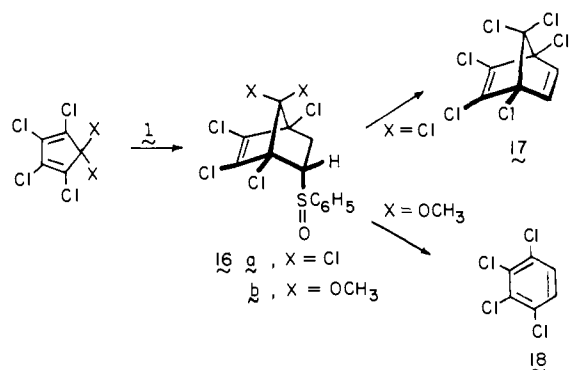
transformation is particularly worthy of note since in situ reductive extrusion of an oxygen atom from isobenzofuran adducts is unprecedented. Their aromatization usually requires catalytic reduction of the double bond and subsequent treatment with HBr in acetic acid.¹⁹ To gain insight into the origin of **8**, 1,3-diphenylnaphtho[2,3-*c*]furan (**9**)²⁰ was allowed to react with **1** in toluene at 40 °C for 6 h. Under these conditions, adduct **10** (exo-endo mixture; ¹H NMR analysis) was produced. When heated to the reflux temperature in toluene, **10** was converted directly to **12**²¹ in good yield. While, in general, the fate of the liberated C_6H_5SOH has not been investigated, it appears capable of deoxygenating **11** and related molecules.



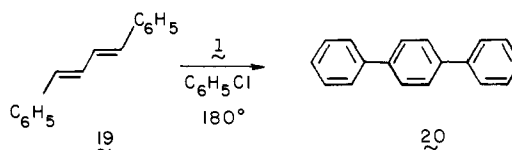
Intermediate cycloadducts have also been isolated with other dienophiles. For example, heating 2,5-dimethyl-3,4-diphenylcyclopentadienone (**13**) with **1** in toluene for 24 h afforded endo isomer **14** in 73% yield. Stereochemical assignment to **14** follows from the observed coupling constants $J_{BX} = 9.0$ Hz and $J_{AX} = 6.0$ Hz which are in excellent agreement with reported values in other norbornenyl systems.²² High-yield conversion of **13** to **15**²³ was accomplished upon more extended heating (60 h).



Both hexachlorocyclopentadiene and 5,5-dimethoxytetrachlorocyclopentadiene react readily with **1** as neat mixtures (100 and 60 °C, respectively) via the spectroscopically (¹H NMR) identifiable endo cycloadducts **16a** and **16b**. Expectedly, **16b** is ultimately converted principally to 1,2,3,4-tetrachlorobenzene (**18**) through extrusion of dimethoxycarbene from the intermediate 7-norbornadienone ketal,²⁴ while hexachloronorbornadiene **17**²⁵ results (83%) from continued heating of **16a**. The formation of **17** was seen to occur more efficiently in refluxing toluene solution (97%) when 1.5 equiv of pyridine was present. The possibly adventitious role of this base remains to be more fully explored.



In a representative acyclic example, 1,4-diphenyl-1,3-butadiene (**19**) was conveniently converted to *p*-terphenyl (**20**, 57%) upon cycloaddition with **1** in chlorobenzene at 180 °C (sealed tube). The utility of our method again becomes apparent when comparison is made with the best laboratory procedure previously available for preparing **20**.²⁶



Clearly, the ready availability and good thermal stability of **1** (recoverable after heating in dichlorobenzene at 180 °C for several days) are key factors in the broad application of this vinyl sulfoxide as an acetylene synthon. A significant feature of this scheme is the in situ thermal elimination of phenylsulfenic acid. While this by-product is not always innocuous (see above), it is frequently so. Consequently, its formation and likely subsequent disproportionation present little problem. Optimistically, the addition of tertiary amine bases will reduce any future potential complications to nil (work in progress).²⁷

References and Notes

- J. Hyman, E. Freireich, and R. E. Lidov, U.S. Patent 2 875 256; *Chem. Abstr.*, **53**, 13082 (1959).
- J. Sauer, *Angew. Chem., Int. Ed. Engl.*, **5**, 211 (1966); R. Huisgen, R. Grashey, and J. Sauer, "The Chemistry of Alkenes", S. Patai, Ed., Interscience Publishers, New York, N.Y., 1964, p 899.
- (a) S. J. Cristol and N. L. Hause, *J. Am. Chem. Soc.*, **74**, 2193 (1952); (b) S. J. Cristol and R. K. Bly, *ibid.*, **82**, 6155 (1960); (c) H. P. Figeys and A. Dralants, *Tetrahedron*, **28**, 3031 (1972).
- K. MacKenzie, *J. Chem. Soc.*, 473 (1960).
- W. K. Anderson and R. H. Dewey, *J. Am. Chem. Soc.*, **95**, 7161 (1973).
- J. Daub, U. Erhardt, J. Kappler, and V. Trautz, *J. Organomet. Chem.*, **69**, 423 (1974).
- E. J. Corey and R. A. E. Winter, *J. Am. Chem. Soc.*, **85**, 2677 (1963).
- M. Semmelhack and R. Stauffer, *Tetrahedron Lett.*, 2667 (1973).
- E. J. Corey and J. I. Shulman, *Tetrahedron Lett.*, 3655 (1968); G. H. Whitham and M. Wright, *J. Chem. Soc. C*, 883, 886, 891 (1971).
- L. A. Paquette and M. J. Wyvratt, *J. Am. Chem. Soc.*, **96**, 4671 (1974).
- R. A. Snow, C. R. Deegenhardt, and L. A. Paquette, *Tetrahedron Lett.*, 4447 (1976), and references cited therein.
- M. Bonincontro, G. Maccagnani, and F. Montanari, *Gazz. Chim. Ital.*, **92**, 1182 (1962), and earlier papers in this series; H. Hogeveen, G. Maccagnani, and F. Montanari, *J. Chem. Soc. C*, 1585 (1966); M. Cinquini, S. Colonna, and F. Montanari, *ibid.*, 1213 (1967).
- S. Danishefsky, R. K. Singh, and T. Harayama, *J. Am. Chem. Soc.*, **99**, 5810 (1977).
- S. Ghersetii, H. Hogeveen, G. Maccagnani, F. Montanari, and F. Taddei, *J. Chem. Soc.*, 3718 (1963). However, see E. G. Kataev and F. P. Tantsheva, *Dokl. Akad. Nauk SSSR*, **141**, 1101 (1961). For an application of phenyl vinyl sulfoxide to Michael reaction chemistry, consult G. A. Koppel and M. D. Kinnick, *J. Chem. Soc., Chem. Commun.*, 473 (1975).
- J. L. Kice and J. Campbell, *J. Org. Chem.*, **32**, 1631 (1967); B. M. Trost, T. N. Salzmann, and K. Hiroi, *J. Am. Chem. Soc.*, **98**, 4887 (1976); R. Tanikaga, H. Sugihara, K. Tanaka, and A. Kaji, *Synthesis*, 299 (1977).
- J. Sauer, A. Mielert, D. Lang, and D. Peter, *Chem. Ber.*, **98**, 1435 (1965).
- R. Breslow, P. Gal, H. W. Chang, and L. J. Altman, *J. Am. Chem. Soc.*, **87**, 5139 (1965).
- R. Weiss and A. Abeles, *Monatsh. Chem.*, **61**, 162 (1932).
- For a recent example, see F. A. Kaplan and B. W. Roberts, *J. Am. Chem. Soc.*, **99**, 518 (1977).
- M. P. Cava and J. P. Van Meter, *J. Am. Chem. Soc.*, **84**, 2008 (1962).
- Ch. Weizmann, E. Bergmann, and L. Haskelberg, *J. Chem. Soc.*, 391 (1939).
- K. L. Williamson, *J. Am. Chem. Soc.*, **85**, 516 (1963); M. Cinquini, S. Colonna, and F. Montanari, *J. Chem. Soc. C*, 572 (1970); J. L. Marshall, S. R. Walter, M. Barfield, A. P. Marchand, N. W. Marchand, and A. L. Segré, *Tetrahedron*, **32**, 537 (1976).
- L. Chardonens and H. Chardonens, *Helv. Chim. Acta*, **49**, 1931 (1966).
- R. W. Hoffmann and H. Häuser, *Tetrahedron*, **21**, 891 (1965), and references contained therein.
- D. I. Davies, P. Mason, and M. J. Parrott, *J. Chem. Soc. C*, 3428 (1971).
- L. F. Fieser and K. L. Williamson, "Organic Experiments", D. C. Heath, Lexington, Mass., 1975, p 169.
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Reversible Charge Control of Nortriquinacenyl-Tetracyclo[4.2.1.0^{3,5}.0^{4,9}]nonenyl Isomerizations

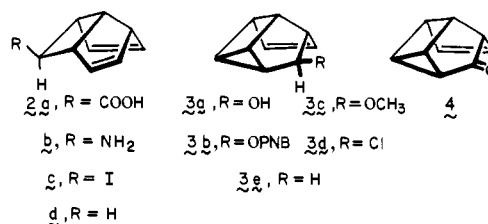
Sir:

As part of a study of "anchored" trishomoaromatic ions,¹ we previously established by classical methods that the nor-



triquinacenyl anion (**1**⁻) lacks the ability to stabilize its negative charge.^{1b} This result was subsequently corroborated by MINDO/3 calculations^{1b} and photoelectron spectral analysis of selected derivatives.² However, no experimental information was available concerning the thermodynamic stability of **1**⁻ relative to other (CH)₉⁻ isomers. Here we report on this question and describe in addition the full complement of reversible charge control criteria³ for this ring system which necessarily include pericyclic transforms of the related cation **1**⁺.

For systematic reasons, the present investigation began with the deamination of **2b** which can be readily prepared by Curtius rearrangement of acid **2a**^{1b} with diphenylphosphoryl azide.⁴ Upon treatment with sodium nitrite in 2 N perchloric acid,⁵ **2b** was cleanly transformed into **3a**, the structural as-



signment to which was substantiated by Eu(fod)₃ shifting of the ¹H NMR spectrum,⁶ oxidation with Collins' reagent to ketone **4** (ν 1705 cm⁻¹), and hydride reduction of **4** to produce the endo alcohol. With the availability of the endo epimer, it was possible to establish that this substance was not present within detectable limits (>2%) in the original reaction mixture. Quantitatively similar results were realized when iodide **2c**^{1b} was exposed to a threefold excess of silver perchlorate in 25% aqueous acetone at room temperature for 2.5 h in the dark.

To establish that the tetracyclic cation is capable of retaining its structural integrity under more diverse conditions, *p*-nitrobenzoate **3b** (mp 94.5–96.0 °C)⁷ was prepared and subjected to methanolysis (100 °C, 48 h). There was uniquely produced a 7:1 mixture of **3c** and the unrearranged endo-methyl ether. Quite clearly, a proclivity for skeletal rearrangement to **1**⁺ or other topologically isomeric cations is not operational.

Experiments intended to permit recognition of the relative thermodynamic stabilities of the related anions began with the reduction of iodide **2c** using sodium in liquid ammonia. This reaction provides nortriquinacene (**2d**) as the exclusive hydrocarbon product. When chloride **3d**, obtained from the corresponding alcohol with thionyl chloride in pyridine, was comparably reduced, nortriquinacene was again produced although contamination with significant amounts of hydrocarbon **3e** was easily diagnosed (VPC analysis). Despite the fact that serious limitations on the quantity of **3d** precluded execution of a wide range of experiments, we were able to establish that reactions conducted at -78 and -33 °C exhibited only a small temperature effect on the ratio of **2d** to **3e** (1.3–1.4:1).

The predescribed evidence demonstrates that carbon skeletons **1**^{*} and **5**^{*} are interconvertible by merely controlling the formal charge (*) on the system. As such, this example constitutes only the second complete set of experimental trans-

