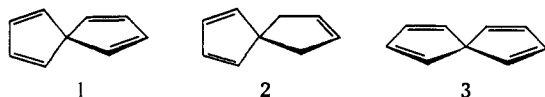# Spiro[4.4]nonatetraene and Spiro[4.4]nona-1,3,7-triene. Synthesis and Properties. Effects of Spiroconjugation

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Abstract: Spiro[4.4]nonatetraene (1) was prepared for the first time by a relatively direct synthesis starting from allyl bromide and diethyl malonate. Spiro[4.4]nona-1,3,7-triene (2) was obtained by a new route, starting from cyclopentadienide anion and 4,5-di(bromomethyl)-2,2-dimethyl-1,3-dioxolane (16). Comparison of the spectral and chemical properties of 1, 2, and spiro[4.4]nona-1,3-diene (10) revealed significant effects of spiroconjugation. The uv spectrum of 1 showed a red shift of 22 nm and lowered extinction coefficient compared to 2 and 10, completely consistent with earlier theoretical predictions.
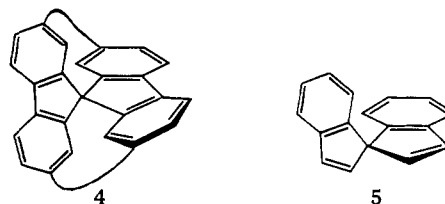
Spiro[4.4]nonatetraene (1) has appeared in the chemical literature frequently in recent years as a result of attempts at synthesis,[1,2] in discussions of the theories of spiroconjugation,[3-6] and as a potential example of stabilized planar tetracoordinate carbon (planar methane).[7] In this article we report the first synthesis of spiro[4.4]nonatetraene (1), an efficient synthesis of spiro[4.4]nona-1,3,7-triene (2), and the comparative properties of 1 and 2 which reflect the effects of spiroconjugation in 1.


At the outset of this work, a variety of derivatives of spiro[4.4]nonatetraene were known, but neither the parent system nor partially substituted derivatives had been obtained. Substituents make it difficult to separate the effects of spiroconjugation from perturbations due to substituents, and provide strong steric barriers which disfavor a square-planar configuration at the spiro carbon (*e.g.*, in 3).

Derivatives of 1 with fused aromatic rings have been prepared and studied primarily for their unique optical activity due to a screw axis of symmetry. For example, the vespirenes (*e.g.*, 4) are dissymmetric but not asymmetric and the assignment of absolute configuration is an interesting challenge.[8] The preparation and optical properties of the closely related spirobiindenes (*e.g.*, 5) were recently reported simultaneously by two groups.[9,10] Careful analysis of the electronic spectrum of 5 compared to indene did reveal a bathochromic shift of several bands in 5, consistent with spiroconjugation.[10]

The unique reaction of 1,2,3,4-tetrachlorodiazocyclopentadiene with dialkylacetylenes at 10–20° in the pres-

ence of π-allylpalladium chloride gives low yields of 1,2,3,4-tetraalkyl-6,7,8,9-tetrachlorospiro[4.4]nonatetraenes, such as 6.[11] Compound 6 shows uv max 272
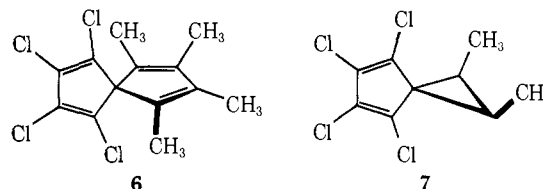
nm (ϵ 8600) and 320 (ϵ 560),[11] a distinct red shift for the intense absorption compared to the spectra of reasonable comparison compounds, such as 7 (uv max 287 nm (ϵ 5000)).[12] As reviewed briefly below, such a shift is consistent with spiroconjugation,[3,4] although the effects of the substituents lend some ambiguity. Parallel with other spirocycles,[13,14] 6 rearranges at 205–210° in the vapor phase chromatograph *via* apparent cleavage of a radial bond to give isoindene 8 and, finally, a 1,5-methyl shift to indene 9 (eq 1) in 65% yield. The
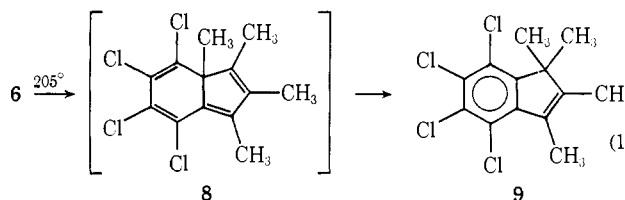
mechanism of the rearrangement is inferred from the product using well-known pathways; concertedness has not been established or ruled out, although both steps in eq 1 can be written as symmetry allowed 1,5-sigmatropic shifts.[15]

(1) (a) D. J. Cram and B. L. van Duuren, *J. Amer. Chem. Soc.*, 77, 3576 (1955); (b) D. Christiansen, Ph.D. Thesis, UCLA, 1971.

(2) D. Schönleber, *Chem. Ber.*, 102, 1789 (1969).

(3) H. E. Simmons and T. Fukunaga, *J. Amer. Chem. Soc.*, 89, 5208 (1967).

(4) R. Hoffmann, A. Imamura, and G. D. Zeiss, *ibid.*, 89, 5219 (1967).

(5) A. Tajiri and T. Nakajima, *Tetrahedron*, 27, 6089 (1971).

(6) R. Boschi, A. Dreiding, and E. Heilbronner, *J. Amer. Chem. Soc.*, 92, 123 (1970).

(7) R. Hoffmann, R. W. Alder, and C. F. Wilcox, Jr., *ibid.*, 92, 4992 (1970).

(8) (a) G. Haas and V. Prelog, *Helv. Chim. Acta*, 52, 1202 (1969); (b) G. Haas, P. B. Hulbert, W. Klyne, V. Prelog, and G. Snatzke, *ibid.*, 54, 491 (1971).

(9) J. H. Brewster and R. T. Prudence, *J. Amer. Chem. Soc.*, 95, 1217 (1973).

(10) R. K. Hill and D. A. Cullison, *ibid.*, 95, 1229 (1973).

(11) E. T. McBee, G. W. Calundann, and T. Hodgins, *J. Org. Chem.*, 31, 4260 (1966).

(12) E. T. McBee, J. T. Bosoms, and C. J. Morton, *ibid.*, 31, 768 (1966).

(13) For leading references, see (a) M. F. Semmelhack and R. J. DeFranco, *J. Amer. Chem. Soc.*, 94, 8838 (1972).

(14) J. J. Gajewski, *ibid.*, 92, 3688 (1970).

(15) R. B. Woodward and R. Hoffmann, "Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1969.

The synthesis of spiro[4.4]nonatetraene (1) was one object of the studies of Cram and coworkers;[1] well-precedented elimination pathways were shown to work well in the preparation of spiro[4.4]nona-1,3-diene (10, eq 2) but failed with exactly analogous experiments starting from spiro[4.4]nona-1,6-diene (11, eq 3).[1a]

(2)

(3)
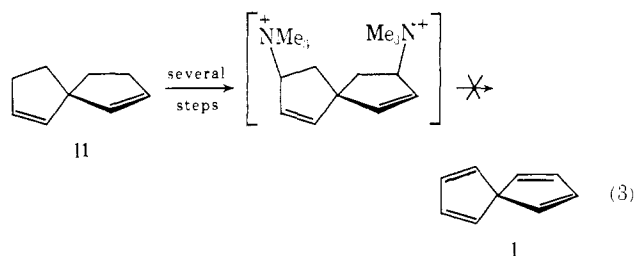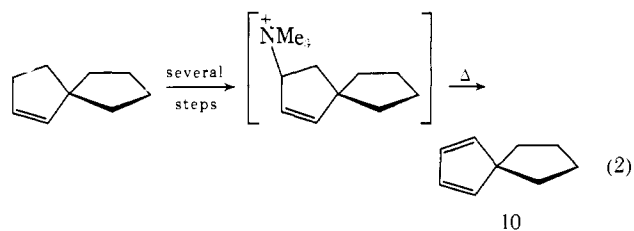
As part of a larger study, Schonleber reports that pyrolysis of the remarkable molecule, 12, leads to an amor-

12
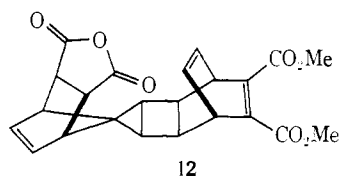
phous, insoluble solid.[2] An elaborate series of cyclo-reversions could have given spiro[4.4]nonatetraene, but none was detected. The failure of these experiments is 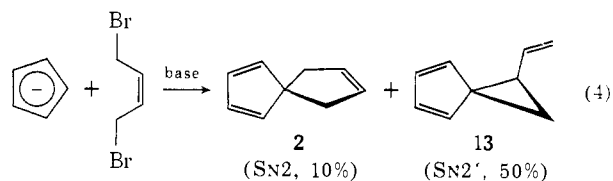not surprising in retrospect: they hinted at an unexpected thermal lability for 1 which has now become clear, as discussed below.

Spiro[4.4]nona-1,3,7-triene (2) was reported for the first time in the same work by Schonleber,[2] as a minor product from the reaction of sodium cyclopentadienide with 1,4-dibromo-cis-2-butene (eq 4). The


(4)

yield is low and the products (2 and 13) are difficult to separate on a preparative scale. Compound 2 shows no unusual spectral properties, and has not been studied at elevated temperatures.

**Synthesis of Spiro[4.4]nona-1,3,7-triene (2).** The spirotriene 2 was desired both as a comparison compound for 1 (similar geometry, but no spiroconjugation) and as a potential synthetic precursor of 1. The direct reaction (eq 4) was considered carefully with two objects: modification of the reaction conditions to improve the ratio of 2:13, and conversion of 13 into 2 by thermal rearrangement. Preliminary experiments suggested that the ratio of 13:2 generated according to eq 4 was relatively insensitive to changes in the cation (sodium, lithium) associated with the cyclopentadi-

enide anion, the leaving group (chloride, bromide), or the medium (benzene, tetrahydrofuran, tetraglyme, dimethylformamide).

Compounds 13 and 2 are related by a vinylcyclopropane–cylopentene rearrangement (eq 5), an efficient

(5)
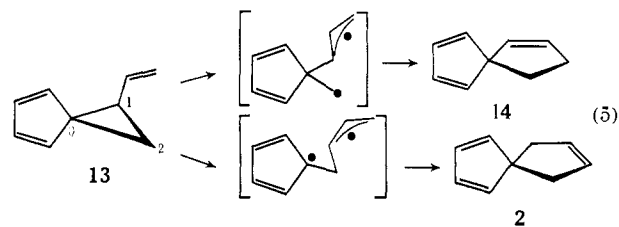
thermal process for simple vinylcyclopropane derivatives.[16] Radial cleavage (C_1–C_3) would give 2, while peripheral bond cleavage (C_1–C_2) would give 14, an unknown compound and as interesting as 2, for the same reasons. During the course of this work, two reports appeared concerning pyrolytic reactions of 13; in one case, indan was the only product,[2] while the other workers observed the precursor of indan, the isoindan 15.[17] The spirotrienes 2 and 14 were discussed as possible intermediates, but were not detected. It has been observed that spirotriene 2 (but not 14) is, in fact, a minor product (8%) in the pyrolysis of 13 (eq 6) and

(6)
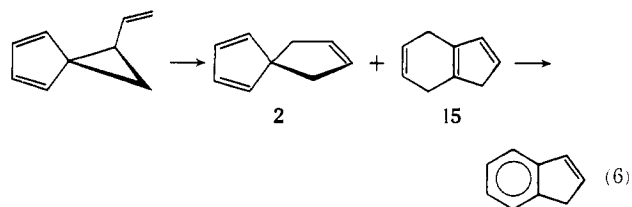
that 2 is *not* the precursor of 15 (the major product, 90%).[18] Neither solution phase (140–150°) nor gas phase flow pyrolysis (367°) provided a reasonable preparative method for 2.

An effective solution to the problem of predominant S_N2' reaction (eq 4) was found through the use of a 1,3-dioxolane unit as a masked π bond. Sodium cyclopentadienide was allowed to react with cis-4,5-di-(bromomethyl)-2,2-dimethyl-1,3-dioxolane (16)[19] in tetrahydrofuran at reflux in the presence of excess sodium hydride (eq 7). Isolation by fractional distillation

(7)
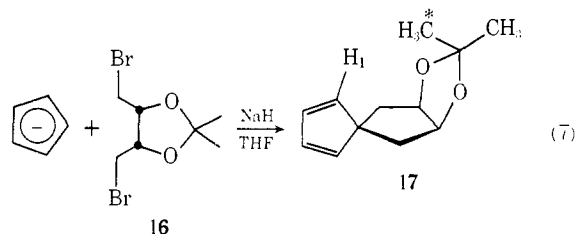
gave the spirodioxolane 17 in 61% yield. The chemical and spectral properties of 17 are in complete agreement with the proposed structure, including a unique low field absorption in the pmr spectrum, a broad multiplet at δ 6.75 integrating for one proton. This ab-

(16) R. Breslow in "Molecular Rearrangements," Vol. 1, P. de Mayo, Ed., Interscience, New York, N. Y., 1963, p 236 ff.
(17) M. Jones, Jr., R. Hochman, and J. Walton, *Tetrahedron Lett.*, 2617 (1970).
(18) M. F. Semmelhack and J. S. Foos, manuscript in preparation.
(19) M. S. Malinovskii, V. G. Dryuk, A. G. Yudasina, and N. N. Maksimenko, *Zh. Org. Khim.*, 2, 2086 (1966).

sorption is assigned to H_1 in structure **17**, based on the nuclear Overhauser effect from a double resonance experiment.[20] Irradiation of one of the signals due to the *gem*-dimethyl unit (δ 1.54) produced an enhancement of 22% in the area of the upfield vinyl resonance and no other change in the spectrum. The enhancement suggests a strong interaction between one of the methyl units (C* in **17**) and H_1; the unusual chemical shift is then an example of steric compression effects.[21]

The dioxolane **16** was obtained in high stereochemical purity by stereospecific epoxidation[19] of 1,4-dibromo-*trans*-2-butene (*m*-chloroperbenzoic acid) and condensation of the epoxide with acetone in the presence of stannic chloride (eq 8).[19] The product was a mixture
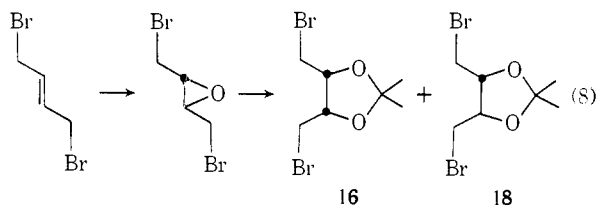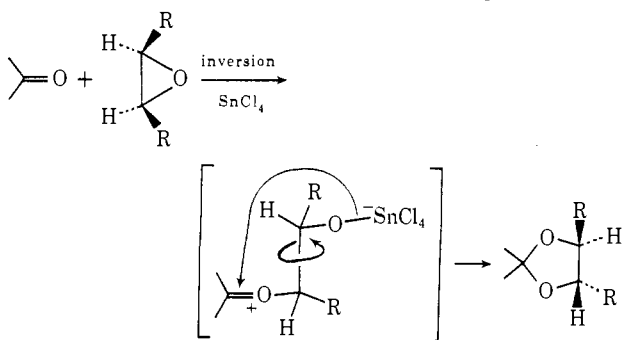

of cis (**16**, 81%) and trans (**18**, 19%) isomers in 95% overall yield; the isomers are partially separable by careful fractional distillation. The stereochemical assignments are based on pmr spectra; **16** produces two methyl group resonances (δ 1.47 and 1.35), while **18** shows a single peak at δ 1.42 as expected for two methyl groups in mirror-image environments. An earlier report on the preparation of **16** fails to discuss the stereochemical aspects of the reaction;[19] a closely related study showed that *trans*-epoxides generally give 1,3-dioxolanes with cis-4,5 substituents.[22] However, that result could be due to thermodynamic *or* kinetic control in the reaction with the ketone. We have shown that *cis*-2,3-di(chloromethyl)oxirane (**19**) produces *trans*-2,3-di(chloromethyl)-1,3-dioxolane (**20**) in 86% yield and >99% stereochemical purity, while *trans*-2,3-bis(chloromethyl)oxirane (**21**) gives *cis*-2,3-di(chloromethyl)-1,3-oxolane (**22**) (>95% pure, 60% yield); kinetic control obtains to provide high stereospecificity. This method of ketal formation, which has been known for many years but little used, is a valuable technique for control of stereochemistry in 1,3-dioxolane synthesis.[23]

(20) W. Phillipsborn, *Angew. Chem., Int. Ed. Engl.*, 10, 472 (1971).
(21) F. A. Bovey, "Nuclear Magnetic Resonance Spectroscopy," Academic Press, New York, N. Y., 1969, p 56.
(22) J. B. Miller, *J. Org. Chem.*, 25, 1279 (1960).
(23) A reasonable pathway for the reaction would involve nucleophilic attack by the acetone carbonyl oxygen on the oxirane–stannic chloride complex, followed by bond rotation and ring closure. A re-

lated study concerning the acid-catalyzed reaction of nitriles with oxiranes to give 1,3-oxazolones presents exactly parallel stereochemical results and similar rationale.[24]
(24) R. A. Wohl and J. Cannie, *J. Org. Chem.*, 38, 1787 (1973).
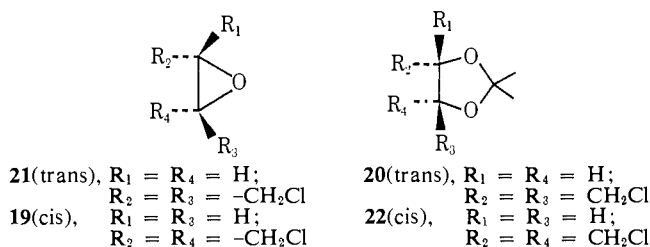
21(trans), $R_1 = R_4 = H$; $R_2 = R_3 = -CH_2Cl$
19(cis), $R_1 = R_3 = H$; $R_2 = R_4 = -CH_2Cl$

20(trans), $R_1 = R_4 = H$; $R_2 = R_3 = CH_2Cl$
22(cis), $R_1 = R_3 = H$; $R_2 = R_4 = CH_2Cl$

Spiro[4.4]nona-1,3-diene-7,8-diol (**23**) was obtained in 60–70% yield by hydrolysis of **17** under carefully controlled conditions; the product is sensitive to the acidic conditions and is not easily purified. Optimum conditions involve heating a solution of dioxolane **17** in aqueous methyl alcohol containing a few drops of 0.1 M hydrochloric acid. With the mixture at 90°, slow distillation was allowed while maintaining the original volume through addition of anhydrous methyl alcohol. After 3 hr, the viscous liquid spirodiol **23** was isolated in 70–80% yield by ether extraction. The purity appeared to be ca. 90% by pmr analysis, but neither distillation nor column chromatography served to provide a sample of high purity. In general, the crude diol **23** was converted directly to derivatives for further study, such as spiro[4.4]nona-1,3-diene-7,8-diol bis(*p*-toluenesulfonate) (**24**), obtained in 40% yield (overall from **17**) by treatment with *p*-toluenesulfonyl chloride and pyridine at −5°.

The spirodiol **23** was considered an attractive precursor of both **1** and **2** *via* any of several well-precedented elimination pathways. To test pyrolytic cis elimination leading directly to spiro[4.4]nonatetraene (**1**), the spirodiacetate **25** was prepared from acetic anhydride, isolated in *ca.* 95% purity, and characterized from spectral data. The technique chosen for thermal elimination involved injection of a sample of **25** onto

24, $X = p$-toluenesulfonate
25, $X = $ acetate
26, $X = CS_2CH_3$
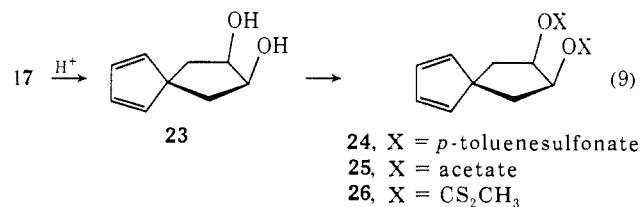
the top of a glass column held vertically, packed with glass helices, and heated by means of nichrome wire. The sample vapors were carried down the tube by a flow of argon introduced at the point of injection. The products collected at the bottom and were analyzed by glpc and pmr. With the tube at 350°, complete conversion of the diacetate **25** occurred, but among the several products, no species could be found with the properties expected for **1**. The only C_9H_8 isomer detected was indene, present in amounts corresponding to a yield of *ca.* 20%. The formation of indene indicated that loss of 2 mol equiv of acetic acid had occurred, and it is tantalizing to presume spiro[4.4]nonatetraene had formed and immediately rearranged to indene, a process with some precedent.[11] With a view toward achieving elimination at lower temperature, spirodiol **23** was treated with carbon disulfide and methyl iodide to produce the spirodixanthate **26**. When the crude dixanthate **26** was exposed to 130–200°, under conditions of short path distillation, complete conversion occurred but, again, no evidence for

$$25 \text{ or } 26 \xrightarrow{\Delta} \left[\text{?} \right] \longrightarrow \text{indene} \qquad (10)$$
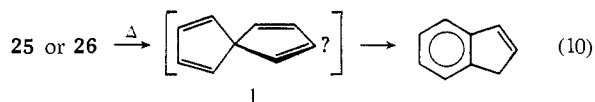
the formation of **1** was obtained; indene was the only C_9H_8 isomer detected.

Base-promoted elimination reactions of the spiro-ditosylate **24** also failed to produce **1** or any C_9H_8 isomer; however, **24** reacted with excess iodide ion at 100° in acetone (pressure bottle) to produce a single product, spiro[4.4]nona-1,4,7-triene (**2**) in 60–80% yield. This route (**17** → **24** → **2**) is longer than the alternative known scheme (eq 4), but provides an easily isolated product, uncontaminated with isomers. Spiro-triene **2** is of interest in comparison of chemical and spectral properties with the parallel data for **1**, and it is also an obvious potential precursor of **1** by usually reliable methods for converting an olefinic unit into a 1,3-diene, for example, allylic substitution of a hetero-atom followed by 1,4-elimination.

Allylic bromination–elimination had been used by Cram[1a] in the preparation of spiro[4.4]nona-1,3-diene (**10**) according to eq 2. In the case of spirotriene **2**, reaction with N-bromosuccinimide in refluxing carbon tetrachloride proceeded slowly and produced a mixture of products, including indene (20–25% yield). A pure monobromide (*e.g.*, **27**) was not isolated; treatment of the crude mixture with a variety of strong bases produced no detectable amounts of **1**. Related reactions beginning with selenium dioxide, *tert*-butyl perbenzoate (Cu⁺), or dichlorodicyanoquinone failed to provide spiro-[4.4]nonatetraene (**1**). The formation of indene during reaction of **2** with N-bromosuccinimide may occur *via* spontaneous elimination of hydrogen bromide from **27** and thermal (or acid catalyzed) rearrangement of transient **1** (eq 11).

$$\mathbf{2} \xrightarrow{\text{NBS}} \left[\mathbf{27} \right] \longrightarrow \qquad (11)$$
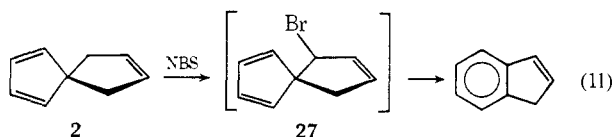
Because the 1,3-diene unit in **2** appeared to be leading to interference, either by preferential reaction or by promoting rearrangements under the reaction conditions, it was modified by reaction with dimethyl azo-dicarboxylate (**28a**) at 80° for 3.0 hr in carbon tetrachloride, giving **29a**. This dienophile was chosen because of abundant precedent for regeneration of 1,3-diene units under low temperature conditions.[25] The second 1,3-diene unit was introduced by allylic bromination (to give **30a**)[26] followed by dehydrobromination using potassium *tert*-butoxide in anhydrous ether at

(25) (a) S. G. Cohen and R. Zand, *J. Amer. Chem. Soc.*, **84**, 586 (1962); (b) N. Rieber, J. Alberts, J. A. Lipsky, and D. M. Lemal, *ibid.*, **91**, 5668 (1969).

(26) The structure of **30a** is tentative; no information is available to distinguish it from the equally reasonable allylic bromination product, i.


i
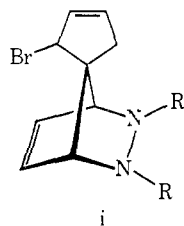
low temperature (eq 12). A single product was ob-

$$\mathbf{28} + \mathbf{2} \longrightarrow \mathbf{29} \longrightarrow \mathbf{30} \longrightarrow$$

$$\qquad (12)$$

31
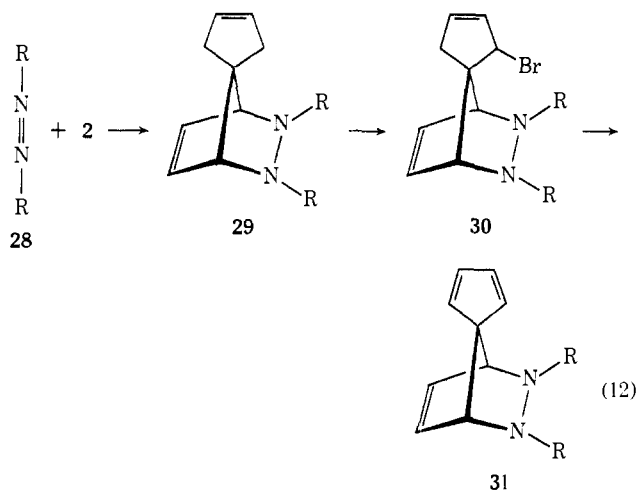
series a, $R = CO_2CH_3$
series b, $CO_2CH_2CCl_3$

tained which was reactive toward oxygen during preparation and storage, and was characterized as structure **31a** primarily by spectral analysis; the pmr spectrum showed a multiplet due to six vinyl protons (δ 6.10–6.70), a broad triplet for the two bridgehead protons (δ 4.72), and a singlet for the two equivalent methoxyl groups (δ 3.80). The new cyclopentadiene unit was confirmed by uv spectroscopy [uv max (EtOH), 250 nm ($\epsilon \approx 3000$)], while mass spectroscopy confirmed the molecular weight and the composition of the parent ion.

Many examples are known for the conversion of 2,3-diaza-2,3-dicarbomethoxybicyclo[2.2.n]alk-5-ene derivatives such as **29** and **31** into cyclo-1,3-dienes using the sequence: ester hydrolysis, decarboxylation, oxidation, and loss of nitrogen in a retro-Diels–Alder reaction.[25] In related substrates, the driving force for expulsion of the nitrogen atoms is often strong enough to result in formation of the cyclo-1,3-diene concomitant with hydrolysis, without the necessity of separate oxidation.[25a] The generation of **1** from **31a** (eq 13) is

$$\mathbf{31} \xrightarrow[R]{CO_2} \left[\text{NH} \right] \xrightarrow{[O]} \left[\text{N} \right] \longrightarrow \mathbf{1} \qquad (13)$$
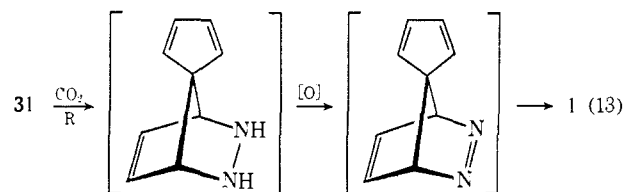
then a matter of choosing an efficient method of ester cleavage. Simple basic hydrolysis was not successful; treatment of **31a** with 15% potassium hydroxide in methyl alcohol gave rapid darkening at 25° and produced a complex reaction mixture. Other bases gave similar results, leading to the conclusion that **31a** is surprisingly sensitive to base. The unique spirocyclo-pentadiene construction in **31a** may be responsible for the base-promoted side reactions *via* ring-opening elimination of a cyclopentadienide anion; one possibility is outlined in eq 14. Other reagents for ester cleavage, such as lithium n-propylmercaptide in hexa-methylphosphoric triamide[27] and lithium iodide in di-

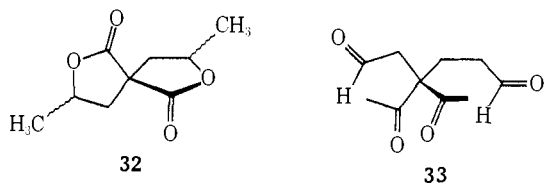(27) P. A. Bartlett and W. S. Johnson, *Tetrahedron Lett.*, 4459 (1970).

31a
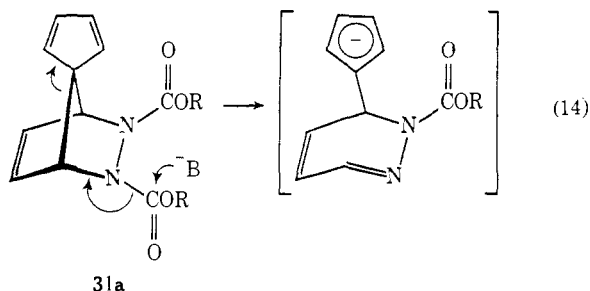
methylformamide, also led to complex product mixtures.

The corresponding derivatives (**29b** and **30b**) from bis(2,2,2-trichloroethyl) azodicarboxylate (**28b**) were prepared in order to initiate decarboxylation under reductive, nonbasic conditions.[28] Yellow, crystalline **28b** was obtained from 2,2,2-trichloroethyl chloroformate and hydrazine in a sequence parallel to the preparation of **28a**.[29] It reacts with **2** somewhat faster than **28a** to give the noncrystalline adduct, **29b**. The easy regeneration of the 1,3-diene unit was demonstrated by the conversion of **29b** back to spirotriene **2**. The best conditions involved simply stirring a solution of **28b** in methyl alcohol with a mixture of zinc-copper couple and mercuric oxide; decarboxylation and oxidation occurred spontaneously to provide **2** in 25-30% yield.

Allylic bromination of **29b** proceeded smoothly, but serious side reactions were observed during base-promoted dehydrobromination of **30b**. The base (potassium tert-butoxide or diazabicyclononene) appears to promote elimination of hydrogen chloride from the 2,2,2-trichloroethoxy unit faster than elimination of hydrogen bromide from the ring; the desired 1,3-diene **31b** was not detected.

Successful Synthesis of Spiro[4.4]nonatetraene. With continuing failures to utilize the cyclopentadienyl anion as a key synthon in the synthesis of **1**, we turned our attention to pathways which involve generation of both rings of **1** simultaneously, with functionality appropriate for introduction of the two 1,3-diene units. With many general approaches now available for the synthesis of cyclopent-2-en-1-ones,[30] the dienedione **35** was chosen as a key intermediate. Obvious precursors of **35** by well-precedented routes are dilactone **32**, diketo-dialdehyde **33**, and diallylmalonyl dichloride **34**. In

32

33

principle, cyclization of dilactone **32** under acidic, dehydrating conditions would provide **35** directly,[31] while **33** ought to give **35** upon warming with dilute

base. General precedent, summarized as the Darzen's reaction,[32] supported the hypothesis that powerful Lewis acids, such as aluminum chloride, would bring about direct cyclization of the diacid chloride **34** to **35**. The route via **34** proved successful with moderate efficiency; the alternate routes have not been pursued.

Diethyl malonate is converted to the anion using 2.2 mol equiv of sodium hydride in tetrahydrofuran solution. An amount of allyl bromide in slight excess of 2.0 mol equiv is added, giving rapid dialkylation. Saponification in alcoholic sodium hydroxide, followed by acidification and crystallization from water, produces diallylmalonic acid which is converted with thionyl chloride to the bis(acid chloride) **34** in 56% overall yield.

Treatment of **34** with aluminum chloride in dichloromethane at 0° led to rapid reaction as evidenced by a heavy yellow precipitate, but none of the desired dienedione **35** was detected after aqueous hydrolysis. The modification of Brown for the Darzens reaction,[33] employing a few molar equivalents of nitromethane as solubilizing agent, proved more successful. The bis(acid chloride) **34** was added slowly to a homogeneous mixture of aluminum chloride. nitromethane. and methylene chloride at 25°. A rapid reaction occurred without precipitation and spiro[4.4]nona-2.7-diene-1,6-dione (**35**) was obtained in 30-50% yield, after purification by sublimation or crystallization, mp 111-112° (eq 15).

(15)

34   35
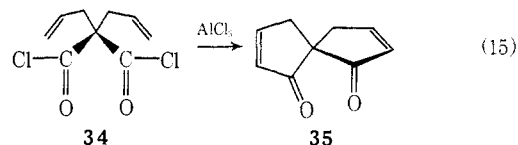
The final conversion of enone units into 1,3-diene units was accomplished by reduction of **35** to the diol **36**, exchange of hydroxyl for chlorine with thionyl chloride, and base-promoted dehydrochlorination (eq 16). Of the several techniques[34] for selective reduction

36   37

(16)

1

of cyclopentenone to cyclopentenol, only the procedure of Brown,[34a] employing aluminum hydride from lithium aluminum hydride and sulfuric acid, afforded any of the isomers of the desired product. With this reagent, a single racemic diol was isolated in 30% yield by careful crystallization from acetone (mp 127-129°). Spiro-[4.4]nona-2,7-diene-1,6-diol (**36**) can exist as three pairs of enantiomers (**36a-c**). The gross structure of the diol is ascertained from spectral data (ir, mass spec-

(28) (a) Removal with zinc: R. D. G. Cooper and F. L. José, J. Amer. Chem. Soc., **94**, 1022 (1972), and references therein; (b) electrolytic removal, M. F. Semmelhack and G. E. Heinsohn, ibid., **94**, 5139 (1972).

(29) Cf. "Organic Syntheses," Collect. Vol. IV, Wiley, New York, N. Y., 1963, p 411.

(30) The many preparations of cis-jasmone involve a few of the different approaches to cyclopentenones. For leading references, see J. E. McMurry and J. Melton, J. Amer. Chem. Soc., **93**, 5309 (1971).

(31) For a recent application and improved procedure, see P. E. Eaton and R. H. Mueller, ibid., **94**, 1014 (1972).

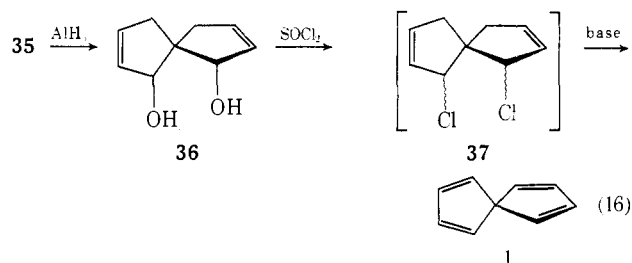(32) (a) G. Darzens, C. R. Acad. Sci., **139**, 1214 (1904); (b) M. S. Newman, Org. React., **5**, 413 (1949).

(33) We are indebted to Professor C. A. Brown (Cornell) for his suggestions concerning this reaction.

(34) (a) H. C. Brown and H. M. Hess, J. Org. Chem., **34**, 2206 (1969); (b) K. E. Wilson, R. T. Seidner, and S. Masamune, Chem. Commun., 213 (1970), and references therein.
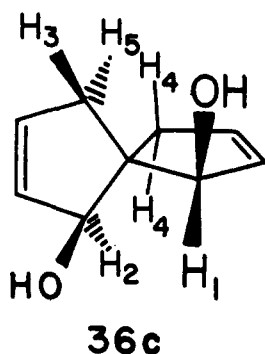
36c

Figure 1. Pmr spectrum of **36c** in DMSO-d_6–D_2O: vinyl H(4), δ 5.60–6.08 (broad multiplet), H₁, 4.72 (broad singlet), H₂, 3.94 (multiplet, small splittings), hydroxyl H(2), δ 3.82 (singlet), H₃, 2.85 (doublet of multiplets, J = 17 Hz, H₄(2), 2.13 (narrow multiplet), H₅, 1.96 (doublet of multiplets, J = 17 Hz).

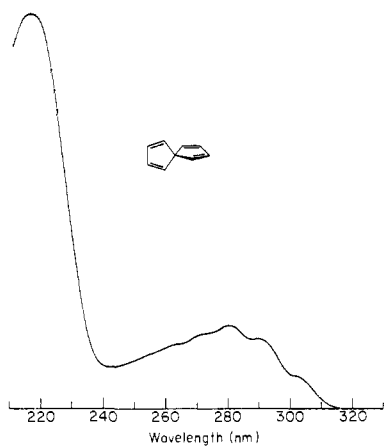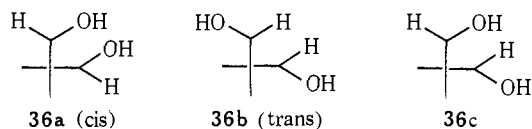Figure 2. Uv spectrum of spirononatetraene **1**.

36a (cis)　　**36b** (trans)　　**36c**

troscopy) while the configurational assignment follows from the very revealing pmr spectrum (Figure 1). Excluding the vinyl and hydroxyl protons, isomers **36a** and **36b** can show only four different pmr absorptions, while **36c** (Figure 1) can show six different absorptions; fortuitous overlap of signals from protons labeled H₄ in Figure 1 leads to five distinct absorptions, consistent with the actual spectrum.

The dichloride **37** has not been obtained pure and probably exists as a mixture of positional and/or configurational isomers. The mixture can be distilled in a short path apparatus (bp *ca.* 30° (0.01 Torr)), and used without further purification. Experimental conditions for the elimination reaction were chosen so as to minimize possible thermal decomposition of the desired product, spirotetraene **1**. To this end, the mixture of dichloride isomers was added to a flask containing excess potassium *tert*-butoxide in tetraglyme at 25° and the system was immediately evacuated to 0.01 Torr. The volatile products (spirotetraene **1** and *tert*-butyl alcohol) were collected over 2–3 hr in a trap (−196°) placed between the reaction mixture and the vacuum pump. Pure spiro[4.4]nonatetraene (**1**) was isolated by preparative glpc in 23% overall yield from the diol. A
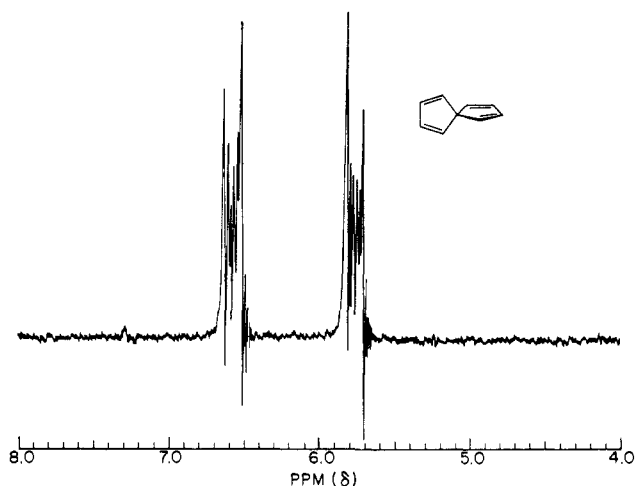

Figure 3. Pmr spectrum of spirononatetraene **1**.

sample of **1** in >95% purity can be obtained in 43% yield directly from the reaction mixture through the use of potassium 2,2-dimethyl-2-phenylethoxide, since the resulting carbinol is not distilled under the reaction conditions.

The structure of **1** was established through a combination of chemical and spectral studies. The mass spectrum was superimposable with that of indene: the ir spectrum (neat) was very similar to that of spiro[4.4]-nona-1,3-diene (**10**),[35] including a weak absorption at 1840 cm⁻¹, and strong bands at 1662 and 1528 cm⁻¹ due to olefinic stretching modes. The uv spectrum consisted of two broad absorption bands (276 nm (ε 1120) and 218 (5350)) in ethyl alcohol solution, and additional maxima superimposed on the long wavelength band in isooctane solution (Figure 2); the positions of the bands are consistent with the proposed structure, assuming the validity of spiroconjugation theory (see below). The pmr spectrum showed two symmetrical multiplets of equal area centered at δ 5.80 and 6.58 (Figure 3). In the ¹³C nmr spectrum, three peaks are observed, C₅ at δ 77.0 (*vs.* internal tetramethylsilane) and the two sets of sp²-hybridized carbons giving two peaks of equal intensity at δ 150.5 and 151. For further discussion of these assignments, see below.

Spiro[4.4]nonatetraene is highly reactive toward oxidation and polymerization; it decomposes within a few days when stored neat at −30°. It reacts completely with a saturated solution of tetracyanoethylene in chloroform within 15 min at 25°. The monoadduct **38** is obtained as the only product, a colorless solid, and is characterized primarily from spectral data, especially the pmr spectrum: H₁ at δ 3.54 (triplet with J = 2.0 Hz), H₂ at 5.9–6.2 (multiplet), H₃–H₅ at 6.5–7.1. Similarly, both the mono- (**31a**) and bisadducts (**39**) of **1** with dimethyl azodicarboxylate were prepared; both are oils and are characterized from spectral data, including high resolution mass spectra. Adduct **31a** was also obtained from spirotriene **2** as described above (eq 12), a sequence which provided a useful internal check on the structural assignments.

Consistent with the 1,3-diene structural features, spirononatetraene reacts with diiron nonacarbonyl to

(35) C. F. Wilcox, Jr., and R. Craig, *J. Amer. Chem. Soc.*, **83**, 3866 (1961).
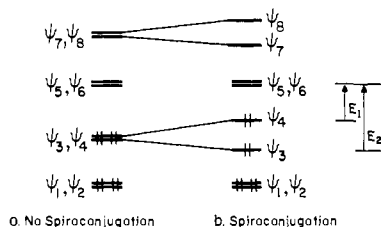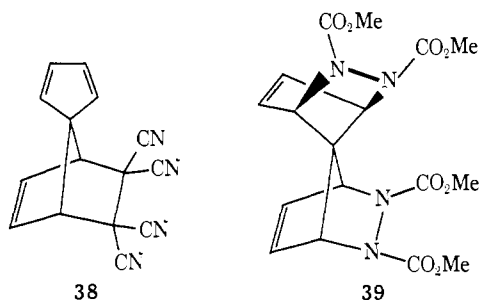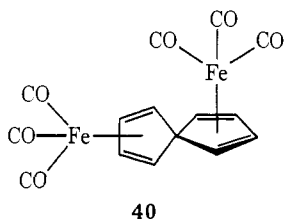
Figure 4. π orbitals in spiro[4.4]nonatetraene.

produce the crystalline bisiron complex **40**. The com-

40

plex is isolated in 42% yield by column chromatography on silica gel, and recrystallized from *n*-pentane, mp 111–112°. Solutions of **40** are stable at 100° for several hours and provide spectral data completely consistent with the structure.

Spiroconjugation in Spiro[4.4]nonatetraene. A simple analysis based on symmetry considerations led to the prediction that molecules in the spirogeometry with p orbitals on the radial atoms might show special effects in ground-state or excited-state stabilization due to homoconjugation across the spiro carbon atom (spiroconjugation).[3,4] In the special case of spiro[4.4]nonatetraene, the theory predicts splitting of the highest filled (and highest unfilled) diene π orbitals (π* orbitals) due to the spirointeraction. Assuming no interaction between the rings, the Hückel molecular orbital picture for **1** is represented in Figure 4a. Considering the symmetry of each of the π orbitals with respect to the perpendicular planes which contain the carbon atoms of **1**, four orbitals (ψ_3, ψ_4, ψ_7, and ψ_8) are of like symmetry (antisymmetric to both planes).[4] Interaction of orbitals with the same symmetry and similar (identical) energy produces a new molecular orbital scheme, Figure 4b. The net result is no significant change in bonding energy, but a narrowing of the gap ψ_4–ψ_5. Thus it was predicted that the lowest energy absorption in the electronic spectrum of **1** would appear at unusually long wavelength, due to spiroconjugation.[3,4] In addition, it was pointed out without elaboration that the effect of spiroconjugation on oscillator strength would be such as to lower the intensity of this absorption.[3] The electronic spectral data for **1** in comparison with **2** and **10** are presented in Figure 5. The comparison compounds, for which no spiroconjugative

effects are possible, show essentially identical spectra: the structural change due to the additional double bond in **2** compared to **10** has no effect on the electronic spectrum. Introduction of the fourth double bond, going to **1**, brings about a dramatic change, completely consistent with theoretical predictions. The gap between ψ_4 and ψ_5 is narrowed by 0.39 eV, giving rise to an absorption maximum at 276 nm: the intensity of this band is reduced by half, also as predicted. A new absorption, not observed in routine spectra of **2** or **10**, appears at 218 nm and is tentatively assigned to excitation indicated as E_2 in Figure 4b. Then the magnitude of the splitting due to spiroconjugation is $E_2 - E_1$, or 1.23 eV. Photoelectron spectroscopy has corroborated this assignment and has provided a precise measure of the orbital energy levels for **1**.[36]

Simmons and Fukunaga[3] suggested that spiroconjugation in **1** would lead to unequal charge densities among the carbon atoms in the π system, with $q = 0.987$ for carbons attached to the spiro atom (radial atoms) and $q = 1.013$ for the peripheral atoms (positions 2, 3, 7, and 8). The cmr spectral data (Table I)

276nm (1120)   254nm (2750)   254nm (2250)
218nm (5350)

Figure 5. Uv spectral data (EtOH).

Table I. [13]C Nmr Spectral Data for Spirocycles and Cyclopentadiene

Spirocycle	C_1,C_4	C_2,C_3	C_5	C_6,C_9	C_7,C_8
10	143.9[b]	127.9[b]	64.1	32.4	26.0
2	144.8[b]	127.9[b]	62.0	36.6	130.4
1	150.5[c]	151.0[c]	77.0	150.5[c]	151.0[c]
	132.8[d]	132.2[d]	41.6[d]		

[a] Positions are given in ppm downfield from internal tetramethylsilane at zero. [b] The assignments are based on the known shielding effects of carbon substituents.[37] [c] The closely spaced absorptions at δ 150.5 and 151.0 have been assigned arbitrarily; the first two entries for **1** could be reversed. [d] J. B. Strothers. "Carbon-13 NMR Spectroscopy," Academic Press, New York, N. Y., 1972, pp 72 and 82.

provide preliminary evidence that the charge distribution in spirotetraene **1** is very different from that of spirotriene **2** and spirodiene **10**.

In general, the chemical shifts of carbon atoms in a diene system are very sensitive to α and β substituents.[37]

(36) E. Heilbronner, M. F. Semmelhack, and C. Batich, manuscript in preparation.

(37) G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists," Wiley-Interscience, New York, N. Y., 1972, Chapter 3.

In spirodiene 10, the olefinic carbons at positions 1 and 4 would be more strongly affected than C-2 and C-3 by the ring attached at C-5 (compare 1,3-cyclopentadiene, Table I), and thus are assigned to the signal at δ 143.9. Little difference appears in the positions of the absorption bands due to the 1,3-diene carbons (1, 2, 3, and 4) with introduction of the C_7-C_8 π bond, in the spirotriene 2. In spirotetraene 1, all absorptions are moved to lower field, and the effect is greatest for C-2 and C-3 (change from δ 130 in 2 and 10 to δ 151 in 1). The relationship between electronic factors and ^{13}C nmr chemical shifts seems not yet fully understood.[38] It is tempting to suggest that at least part of the strong deshielding of the peripheral carbon atoms in 1 results from significant changes in π-electron densities due to spiroconjugation. The effect is opposite to that predicted;[3] the deshielding is consistent with lower π-electron density at the peripheral carbon atoms than at the radial carbons.[38b]

The obvious effect of spiroconjugation on the uv spectrum of 1 and the confirmation of a bonding π orbital pushed to higher energy (ca. 0.5 eV higher than in 2, from photoelectron spectroscopy)[36] lead to the question of what effects spiroconjugation might have on the reactivity of 1. Several recent papers[39,40] have proposed that changes in HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) in 1,3-dienes should have important consequences in the rate of Diels–Alder reactions for the dienes. In particular, a correlation has been drawn between substituent effects on orbital energies and substituent effects on Diels–Alder reactivity.[40] For the reaction of an electron-deficient dienophile bearing electron-withdrawing groups (such as dimethyl acetylenedicarboxylate) with a simple 1,3-diene, the dominant interaction is assumed to be between the HOMO (diene) and LUMO (acetylene); the alternative frontier orbital interaction, between LUMO (diene) and HOMO (acetylene), is neglected because of a larger estimated energy gap between these levels.[39]

These arguments lead to a prediction of enhanced rate of Diels–Alder reaction of 1 with an electron-deficient dienophile compared to the rates for spirodiene 2 and spirotriene 10 because of the higher HOMO in 1 compared to 2 and 10. However, inspection of Table II shows that *no rate enhancement* is observed in reactions of 1 with dimethyl acetylenedicarboxylate.

Possible explanations of the failure to observe rate enhancement include the following: (1) an unfavorable steric interaction selectively slows the Diels–Alder reaction of 1 compared to 2 and 10, thus exactly compensating for acceleration due to the higher HOMO in 1;[41] (2) the perturbation due to spiroconjugation may cause changes in the coefficients of the new molecular

Table II. Reaction of Dimethyl Acetylenedicarboxylate with **1**, **2**, and **10**

Spirocycle	Half-life[a] (34°), sec
1	320 ± 10[b]
2	320 ± 10
10	410 ± 10

[a] The half-life values are the average results of duplicate experiments; identical conditions of concentration were used in all runs. [b] A correction factor of 0.5 has been applied to compensate for two equivalent reaction sites in **1**.

orbital (ψ_4 in Figure 4b) compared to the HOMO's for 2 and 10, and the new distribution (smaller coefficients at carbons 1, 4, 6, and 9 in 1) could reduce interaction of ψ_4 with the dienophile;[42] (3) the assumption that the interaction of LUMO (diene) with HOMO (acetylene) can be neglected may be incorrect for Diels–Alder reactions of the spirocycles; if that were instead the dominant interaction, then changes in HOMO (diene) would have little effect on rate. The first possibility cannot be ruled out at this time; steric effects could operate to retard cycloaddition of 1 although contemplation of molecular models does not provide obvious support for a special steric effect. The third possibility cannot be evaluated without reliable values for the relative energies of LUMO (diene) and LUMO (acetylene); such data are not presently available.

The increase in energy of HOMO for 1 due to spiroconjugation has close parallel in the ethylene ketals of cyclopentadienone, where spiroconjugation produces a red shift of 30 nm in the lowest energy electronic transition.[43] The lone-pair oxygen orbitals interact with the 1,3-diene orbitals so as to provide a bonding orbital of higher energy, and no significant change in the LUMO.[3,43] The rates of Diels–Alder reaction of the cyclopentadienone ketals with electron-deficient dienophiles have not been reported in detail, but appear unexceptional[44] and may involve the same questions raised above for 1. On the other hand, the dimerization of the cyclopentadienone ketals by Diels–Alder reaction is strongly accelerated compared to cyclopentadiene, and this acceleration has been attributed to the higher HOMO (diene) due to spiroconjugation.[43] The same effects are present in spirotetraene 1; it polymerizes to a brittle solid on standing at 25°, whereas spirocycles 2 and 10 are stable for days at 25°. The results of a study of the dimerization reaction of 1 compared to 2 and 10 clearly reveal the remarkable reactivity of 1. The rate of dimerization of 1 at 50° is approximately 200 times the rate of dimerization of spirodiene 10 (extrapolated from two rates measured at higher temperatures, see Table III); spirodiene 10 and spirotriene 2 show nearly identical rates of dimerization at 103° (Table III).

At the present time, we can offer no consistent explanation of the acceleration of the Diels–Alder dimerization of spiroconjugated dienes and the absence of

(38) (a) For a related example with the absence of correlation between cmr chemical shift and π-electron density, see A. J. Jones, T. D. Alger, D. M. Grant, and W. M. Litchman, *J. Amer. Chem. Soc.*, **92**, 2386 (1970). (b) We feel further discussion of the cmr data will be useful only after a better understanding is achieved of structural and electronic effects on cmr chemical shifts. The referees have pointed out that a simple interpretation in terms of charge density alone is not justified; alternate explanations such as increase in the paramagnetic term due to decrease in the excitation gap can be given.

(39) (a) R. Sustmann and R. Schubert, *Angew. Chem., Int. Ed. Engl.*, **11**, 840 (1972), and references therein; (b) R. Sustmann, *Tetrahedron Lett.*, 2721 (1971).

(40) K. N. Houk, *J. Amer. Chem. Soc.*, **95**, 4094 (1973).

(41) This suggestion was prompted by the comments of a referee.

(42) K. L. Houk, private communication based on his manuscript in preparation. We are grateful to Professour Houk for his suggestion.

(43) E. W. Garbisch, Jr., and R. F. Sprecher, *ibid.*, **88**, 3433, 3434 (1966).

(44) P. E. Eaton and R. A. Hudson, *ibid.*, **87**, 2769 (1965).

Table III. Rates of Dimerization of Spirocycles **1, 2,** and **10**

Spirocycle	Temp, °C	k, M^{-1} sec^{-1} × 10^5
1	50 ± 1	4.4 ± 0.3
10	50 ± 1	0.021 ± 0.007[a]
10	78.1 ± 0.5	0.23 ± 0.03
10	103 ± 2	1.9 ± 0.3
2	103 ± 2	2.6 ± 0.3

[a] This value was obtained by an extrapolation of two experiments at higher temperatures.

acceleration in the Diels–Alder addition of the same dienes with electron-deficient dienophiles.

Spiro[4.4]nonatetraene (**1**) also differs from spiro-[4.4]nona-1,3-triene (**2**) and spiro[4.4]nona-1,3-diene (**10**) in rates of unimolecular rearrangement. The spirotetraene rearranges to indene with an activation energy of 26 kcal/mol, approximately 10 kcal/mol lower than the activation energies for exactly parallel reactions of **2** and **10**.[45] However, it does not seem likely that spiroconjugation can account for these differences; alternative explanations have been proposed.[46]

Experimental Section

General. All solvents used were ACS reagent grade and were not further purified except tetrahydrofuran (freshly distilled from lithium aluminum hydride), tetraglyme (distilled *in vacuo* from calcium hydride and stored over molecular sieves), and dimethylformamide (distilled at 50° (20 Torr) from calcium hydride and stored over molecular sieves). Boiling points and melting points are uncorrected. Infrared spectra were obtained using a Perkin-Elmer Infracord Model 137 spectrophotometer on samples prepared as neat films between sodium chloride plates unless otherwise specified. Pmr spectra were obtained using a Varian A-60A or a Perkin-Elmer R-24 spectrometer; ^{13}C nmr data were collected using a Bruker HX-90 spectrometer with Digilab computing accessory, deuteriochloroform as solvent. All nmr chemical shifts are expressed in parts per million downfield from internal tetramethylsilane. Ultraviolet spectra were obtained on Cary Model 14 or Model 16 spectrophotometers. All mass spectral data were obtained from an Associated Electrical Industries Model MS-902 spectrometer. Microanalytical data were obtained from Scandanavian Microanalytical Laboratory. The terms "under argon" (or "under nitrogen") imply that the reaction system is alternately evacuated to aspirator pressure and filled with argon (nitrogen) at least three times. All organic extracts were dried over anhydrous magnesium sulfate and filtered. Vapor phase chromatography was carried out on an F&M Model 609 (flame detector, 0.25-in. diameter columns) or an Aerograph Model A-90P3 (thermal conductivity detector, 0.375-in. diameter columns).

Reaction of Cyclopentadienide Anion with *cis*-1,4-Dichlorobut-2-ene. A 500-ml, three-necked flask was fitted with a 100-ml addition funnel, a reflux condenser topped with an exit bubbler to monitor gas evolution, and a three-way stopcock for evacuating and filling the system with argon. Sodium hydride (10.0 g of 57% suspension in mineral oil, 0.24 mol) was placed in the reaction flask and washed three times with *n*-pentane, and 50 ml of tetrahydrofuran was added. Then a solution of cyclopentadiene (6.64 g, 0.10 mol) and *cis*-1,4-dichlorobut-2-ene (12.6 g, 0.10 mol) in 125 ml of tetrahydrofuran was added over 1 hr, with the sodium hydride suspension at 25°. After addition, 75 ml of water and 50 ml of *n*-pentane were added and the organic layer was separated and washed sequentially with water (three times), 4% aqueous hydrochloric acid, 10% aqueous sodium carbonate, and water (three times). The organic solution was dried and concentrated by rotary evaporation; the residue was distilled to give a fraction of bp 58–67° (18 Torr), 4.64 g. Glpc (20 ft × 0.375 in., 5% Carbowax on Chromosorb W, 90°) analysis revealed two main components in a 5:1 ratio. The major isomer (retention time 5.8 min) was collected and identified as 1-vinylspiro-[2.4]hepta-4,6-diene (**10**) from spectral data.[2] The minor isomer (retention time 4.3 min) was identified as spiro[4.4]nona-1,4,7-triene (**2**) by comparison of spectral data.[2]

Preparation of *trans*-2,3-Di(bromomethyl)oxirane. A solution of *trans*-1,4-dibromo-2-butene (Aldrich Chemical Co., 93 g, 0.44 mol) and *m*-chloroperbenzoic acid (Aldrich Technical, 85% pure, 100 g, 0.58 mol) in 750 ml of chloroform was stirred for 20 hr at reflux. After being cooled to 25°, the mixture was filtered (benzoic acid precipitate), washed with 0.8 *M* sodium bisulfite solution (until moist starch–iodine paper remains colorless when the chloroform extract is applied), dried, concentrated by rotary evaporation, and fractionally distilled to give *trans*-2,3-di(bromomethyl)oxirane, bp 52–53° (0.09 Torr) (lit.[19] bp 87.5–88° (5 Torr)), 74 g, 74% yield; pmr (CDCl₃) complex multiplet between δ 3.0 and 3.6.

Preparation of *cis*-4,5-Di(bromomethyl)-2,2-dimethyl-1,3-dioxolane (16). To a solution of stannic chloride (Fisher, 11 g, 0.042 mol) in 50 ml of carbon tetrachloride (dried over anhydrous magnesium sulfate and decanted) was added acetone (120 g, 2.1 mol, Mallinckrodt Reagent, dried over calcium sulfate and decanted) and then *trans*-2,3-di(bromomethyl)oxirane (71 g, 0.32 mol). The reaction mixture was heated at 50° for 4 hr, cooled, and washed with 10% aqueous potassium hydroxide and then with water until the white solid was dissolved. The organic layer was dried, concentrated by rotary evaporation, and fractionally distilled to give a center cut of bp 69–79° (0.1 Torr), 85 g (95% yield). The distillate was a mixture of **16** (81%) and the corresponding trans isomer (**18**, 19%). Careful fractional distillation produced a sample of pure cis isomer (**16**): bp 69–71° (0.1 Torr) (lit.[19] bp 108–109° (5.5 Torr)); pmr (CDCl₃) δ 1.35 (s, 3 H, CH₃), 1.47 (s, 3 H, CH₃), 3.5–3.7 (m, 4 H), 4.3–4.8 (m, 2 H). The trans isomer was not obtained pure; it was assigned to the single methyl resonance at δ 1.42.

Preparation of *cis*-4,5-Di(chloromethyl)-2,2-dimethyl-1,3-dioxolane (22). Exactly as above for the corresponding dibromo analog. *trans*-1,4-dichloro-2-butene (Aldrich Chemical Co.), was converted to *trans*-2,3-di(chloromethyl)oxirane (**21**)[22] in 72% yield (bp 75–78° (10 Torr)) (lit.[22] bp 78–79° (13 Torr)) using *m*-chloroperbenzoic acid. The distilled epoxide (82 g, 0.58 mol) was mixed with stannic chloride (20 g, 0.076 mol) and acetone (220 g, 200 ml, 3.85 mol) in 90 ml of carbon tetrachloride. After being stirred at 40–45° for 4 hr, the mixture was cooled and washed with cold 10% aqueous potassium hydroxide solution (500 ml) and water (300 ml). The organic layer was dried, concentrated by rotary evaporation, and fractionally distilled to give a center cut of bp 88–92° (5.0 Torr), 72.4 g (60% yield), >95% pure **22** by pmr: pmr (CCl₄) δ 1.34 (s, 3 H, CH₃), 1.44 (s, 3 H, CH₃), 3.4–3.7 (m, 4 H, CH₂Cl), 4.16–4.52 (m, 2 H, CHO); a barely distinguishable singlet was present at δ 1.39, corresponding to the trans isomer **20** (<5%); mass spectral mol wt, 208, with isotope pattern characteristic of two chlorine atoms.

Anal. Calcd for C₇H₁₂Cl₂O₂: C, 42.21; H, 6.08; Cl, 35.63. Found: C, 42.20; H, 6.22; Cl, 35.10.

Preparation of *trans*-4,5-Di(chloromethyl)2,2-dimethyl-1,3-dioxolane (20). Exactly as immediately above, 1,4-dichloro-*cis*-2-butene reacted with *m*-chloroperbenzoic acid to give *cis*-2,3-di(chloromethyl)oxirane (**19**) in 82% yield after fractional distillation (bp 78–80° (10 Torr)); reaction of the oxirane with stannic chloride and acetone gave a single product. *trans*-4,5-di(chloromethyl)2,2-dimethyl-1,3-dioxolane (**20**), in 86% yield: bp 92–94° (5.0 Torr), pmr (CCl₄) δ 1.39 (s, 6 H, CH₃), 3.4–3.7 (m, 4 H, CH₂Cl), 3.9–4.2 (m, 2 H, CHO); mass spectral mol wt: 208, with isotope pattern characteristic of two chlorine atoms.

Anal. Calcd for C₇H₁₂Cl₂O₂: C, 42.21; H, 6.08; Cl, 35.63. Found: C, 42.06; H, 6.12; Cl, 35.64.

Preparation of Spirodioxolane 17. In a 1-l., three-neck flask fitted with two addition funnels (capped with serum caps) and a reflux condenser (capped with a three-way stopcock) was placed a suspension of sodium hydride (32 g of 57% suspension in mineral oil, 0.75 mol) in 500 ml of tetrahydrofuran. In one addition funnel was placed a solution of *cis*-4,5-di(bromomethyl)-2,2-dimethyl-1,3-dioxolane (**16**, 89 g containing 5% of the trans isomer, 0.30 mol) in 100 ml of tetrahydrofuran, and in the other was 100 ml of tetrahydrofuran. After placing the system under argon, cyclopentadiene (28.5 ml, 0.345 mol) was injected into the addition funnel containing tetrahydrofuran. Then the solutions were added simultaneously to the sodium hydride suspension over 2 hr at 25°. Spontaneous heating occurred. After addition, an additional 8 ml of cyclopentadiene was added all at once, and the mixture was allowed to stir at 25° for 1 hr. Then water and ether were added, and the organic layer was washed with water, dried, concentrated by rotary evaporation, and fractionally distilled to give 25.8 g (56% yield) of a colorless liquid with bp 80–84° (3.0 Torr): pmr (CCl₄) δ 1.28 (s, 3 H, CH₃), 1.54 (s, 3 H, CH₃), 1.80 (br s, 2 H, one H from each –CH₂– unit), 1.90 (d of d, 2 H, *J* = 4 and 1.5 Hz, one H from

(45) L. M. Dane, J. W. de Haan, and H. Kloosterziel, *Tetrahedron Lett.*, 2755 (1970).

(46) M. F. Semmelhack and J. S. Foos, submitted for publication.

each $-CH_2-$ unit), 4.65–4.80 (multiplet, 2 H, CHO), 5.8–6.4 (br m, 3 H, vinyl H), 6.68–6.86 (m, 1 H, H_1 in structure 17); mass spectral mol wt, 192.1141 (calcd for $C_{12}H_{16}O_2$, 192.1150); uv max (EtOH) 254 nm (ϵ 3750).

Nuclear Overhauser Effect in 17. A pure sample of **17** was placed in a 5-mm nmr sample tube. Deuteriochloroform (0.3 ml) was added; the solution was degassed by means of several freeze–evacuate–thaw cycles and sealed under argon. The pmr spectrum was observed using a Bruker HX-90 spectrometer in the frequency sweep mode with tetramethylsilane providing the lock signal. An external oscillator signal was applied at 10 Hz downfield of the methyl signal at δ 1.54, and swept in 2.0-Hz increments through the methyl resonance region to 10 Hz beyond the high field methyl resonance (δ 1.28). After each incremental shift, the integral of the two multiplets in the vinyl proton region was measured six times and an average value was obtained. By this means the following observations were made. Irradiation at the downfield methyl proton frequency (δ 1.54) produced an enhancement of 22% in the area of the multiplet from δ 6.68 to 6.86 (due to H_1, structure **17**) and no other change. Irradiation at the upfield methyl proton frequency (or at any other frequency in the range studied) produced no significant change ($\pm 2\%$) in the areas of the downfield multiplets. A second sample prepared in identical fashion gave identical results.

Preparation of Spiro[4.4]nona-1,3-diene-7,8-diol Di-p-toluenesulfonate (24) *via* **the corresponding Diol, 23.** A solution of spirodioxolane **17** (1.66 g, 8.7 mmol), 25 ml of water, 25 ml of methyl alcohol, and 8 drops of 0.1 M hydrochloric acid was heated at 90° for 3 hr in an open flask from which the vapors escaped slowly. Anhydrous methyl alcohol was added periodically to maintain a constant volume. The mixture was cooled and partitioned between ether and water, and the organic layer was dried and concentrated to give 0.89 g (68% yield) of crude diol **23**, >95% pure by pmr analysis. Attempted purification by distillation or chromatography led to loss of material and no significant improvement in purity: pmr (CDCl₃) δ 1.8–2.2 (m, 4 H, CH₂), 3.7 (br s, 2 H, OH), 4.30 (t, 2 H, CHO, J = 6 Hz), 6.1–6.5 (m, 4 H, vinyl H).

The crude diol **23** (0.98 g, 7.0 mmol) and p-toluenesulfonyl chloride (5.0 g, 25 mmol, Aldrich) were dissolved in 15 ml of pyridine (Fisher Certified ACS reagent grade) and allowed to stand at −5° for 3 days. The mixture was poured into ice–water and washed three times with ether. The combined organic layer was washed with cold 5% aqueous hydrochloric acid, then with water, and finally dried and concentrated to leave 1.67 g of solid residue. Recrystallization from ether at low temperature gave a colorless solid of mp 124–126° (40% yield overall from **17**): pmr (CDCl₃) δ 2.08 (4 H, t of d, -CH₂-), 4.92 (2 H, m, CHO), 2.45 (6 H, s, aromatic CH₃), 6.0–6.5 (4 H, m, vinyl H), 7.57 (8 H, quart, aromatic H); mass spectral mol wt, 428.

Anal. Calcd for $C_{23}H_{24}O_6S_2$: C, 59.98; H, 5.25; S, 13.92. Found: C, 60.09; H, 5.26; S, 13.68.

Preparation of Spiro[4.4]nona-1,3-diene-7,8-diol Diacetate (25). The crude spirodiol **23** (0.43 g, 2.8 mmol), acetic anhydride (3.0 ml, 4.1 mmol), pyridine (10 ml), and anhydrous ether (20 ml) were mixed and heated at reflux for 1 hr. The mixture was allowed to cool, and 50 ml of ice–water was added. The mixture was washed with ether and the ether solution was washed sequentially with aqueous sodium carbonate and 2% aqueous hydrochloric acid (until aqueous solution remained acidic), dried, and concentrated to give 0.33 g (43% yield) of crude diacetate **25**: pmr (CDCl₃) δ 2.00 (6 H, S, COCH₃) superimposed on multiplet (δ 1.9–2.2, 4 H, -CH₂-), 5.4 (2 H, br m, CHO), 6.0–6.5 (4 H, m, vinyl H). This product was used directly in the pyrolytic studies.

Pyrolysis of Diacetate 25. The crude diacetate (0.15 g, 0.81 mmol) was injected into the top of a vertical Pyrex column (15-cm long, 1.3 cm o.d.). The column was packed with 3/32-in. glass helices and wrapped with a coil of nichrome wire, with asbestos as an outer covering. A thermocouple was placed against the outer wall of the column to monitor the temperature. Argon was introduced at the top of the column to sweep the material through the heated region. At 350°, the effluent at the bottom of the column, collected at −78°, was analyzed by pmr and glpc. The characteristic peaks for indene at δ 3.33 (2 H), 6.50 (1 H), 6.82 (1 H), and 7.0–7.6 (4 H) were the major signals observed. The yield of indene was *ca.* 20%; no other constituents were identified. Higher temperatures (400 and 450°) increased the amount of indene.

Preparation of Spiro[4.4]nona-1,3-diene-7,8-diol Dixanthate (26). To a suspension of sodium hydride (0.60 g of 57% suspension in mineral oil, 14 mmol) in 40 ml of tetrahydrofuran was added the crude diol **23** (0.80 g, 5.0 mmol) over 10 min at 25°. After hydrogen evolution was complete (10 min), carbon disulfide (0.80 ml, 13

mmol) was added all at once. The mixture was allowed to stir for 2 hr at 25°, at which time methyl iodide (0.80 ml, 13 mmol) was added all at once. After 30 min at 25°, the mixture was partitioned between water and ether, and the organic layer was washed four times with water, dried, and concentrated to leave a liquid residue, 1.72 g (99% yield) of crude dixanthate **26**. Rapid chromatography on Florisil (30 g), eluting with n-pentane, gave a fraction of impure material (0.66 g) followed by a fraction (ether eluent) of material homogeneous by tlc (benzene–silica gel. R_f 0.7). The second fraction weighed 0.86 g (51% yield), and showed pmr absorption consistent with structure **26**: pmr (CDCl₃) δ 2.34 (4 H, d of d, J_1 = 2 Hz, J_2 = 5 Hz), 2.59 (6 H, s, SCH₃), 6.0–6.5 (6 H, m, vinyl H and CHO). The second fraction solidified to provide colorless crystals of mp 65–69°.

Pyrolysis of Dixanthate 26. A sample of dixanthate **26** (0.54 g, 1.7 mmol) was heated at 0.1 Torr in a short path distillation apparatus with the receiver cooled at −78°. Upon heating at 130°, decomposition was evident and a clear liquid distillate collected. The temperature was slowly raised to 200°. The distillate (0.10 g) was analyzed by pmr. Essentially all of the absorption downfield of δ 5.0 was attributable to indene, with the very characteristic vinyl and aryl proton pattern from δ 6.5 to 7.6.

Preparation of Spiro[4.4]nona-1,3,7-triene (2). A sample of ditosylate **24** (6.0 g, 13 mmol) and sodium iodide (12 g, 80 mmol) were dissolved in 50 ml of acetone and heated at 100° for 14 hr in a sealed Parr pressure bottle. The dark brown mixture was diluted with n-pentane and washed with 10% aqueous sodium sulfite until the iodine color disappeared. The organic layer was dried, concentrated at 25° (80 Torr) to a small volume, and then distilled in a short path apparatus (25° (0.1 Torr)) to give 1.1 g, 72% yield. Spiro[4.4]nona-1,3,7-triene (2) was identified by comparison with material prepared according to the method of Schönleber.[2]

Preparation of Diels–Alder Adduct 29a from Spirotriene 2. A solution of spiro[4.4]nona-1,3,7-triene (**2**, 182 mg, 1.54 mmol) and dimethyl azodicarboxylate (**28a**, 225 mg, 1.54 mmol, Aldrich Chemical Co., used directly) in 0.3 ml of carbon tetrachloride (in pmr sample tube) was heated on the steam bath for 3 hr. The solution (now colorless) was distilled in a short path apparatus to give a fraction of bp *ca.* 100° (0.01 Torr) (380 mg, 93% yield) which was homogeneous by tlc (ethyl acetate–silica gel, R_f 0.4): mass spectral mol wt 264; pmr (CCl₄) δ 2.20 (br s, 4 H, -CH₂-), 3.72 (s, 6 H, OCH₃), 4.70 (poorly resolved triplet, 2 H, bridgehead H, J = 2 Hz), 5.57 (m, 2 H, vinyl H in cyclopentene ring), 6.50 (t, 2 H, vinyl H in bicycloheptene. J = 2 Hz).

Preparation of 31a *via* **Bromination of 29a and Elimination of Hydrogen Bromide from 30a.** A solution of Diels–Alder adduct **29a** (480 mg, 1.82 mmol), N-bromosuccinimide (324 mg, 1.82 mmol, Eastman Organic Chemicals), and 20 mg of dibenzoyl peroxide in 20 ml of carbon tetrachloride was heated at reflux under irradiation with a 75-W tungsten lamp at a distance of 5 cm. After 2 hr, the end of the reaction was signaled by a precipitate floating at the surface. The mixture was cooled to 0°, filtered, and concentrated to leave a yellow residue, 630 mg, 100% yield. The crude bromide was not characterized except for pmr (CDCl₃): δ 2.1–2.6 (2 H, br m, -CH₂-). 3.74 (6 H, s, OCH₃), 5.0 (1 H, m. CHBr), 5.6 (1 H, m, vinyl H), 5.9–6.2 (1 H, m, vinyl H), 6.5–6.8 (2 H, m, vinyl H). Traces of succinimide were removed by filtration through Florisil, eluting with ether.

A sample of bromide **30a** (512 mg, 1.49 mmol) was dissolved in 10 ml of anhydrous ether and cooled to −78° in a flask capped with a drying tube. The drying tube was removed momentarily and solid potassium *tert*-butoxide (188 mg, 1.65 mmol) was added all at once. The mixture was then allowed to warm to −30° over 35 min (fine brown suspension). Then 10 ml of cold 5% aqueous hydrochloric acid was added, followed by 10 ml of water and 20 ml of ether. After vigorous shaking, the organic layer was dried, concentrated by rotary evaporation, and filtered through Florisil (eluting with ether) to give a yellow oil, 374 mg, 89% yield. The product was homogeneous by tlc (R_f 0.35, ethyl acetate–silica gel): pmr (CDCl₃) δ 3.80 (s, 6 H, OCH₃), 4.72 (t, 2 H, bridgehead H, J = 2 Hz), 5.75–6.0 (m, 1 H, vinyl H), 6.1–6.7 (br m, 5 H, vinyl H); mass spectral mol wt, 262; uv max (cyclohexane) 250 nm (ϵ *ca.* 3000; appears as shoulder on intense end absorption). The compound decomposed within a few hours upon standing at 25° exposed to air, and could not be recovered efficiently from preparative layer chromatography.

Preparation of Bis(2,2,2-trichloroethyl) Azodicarboxylate (28b).[47]

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(47) H. Leuchs and H. Lemcke, *Ber.*, 47, 2584 (1914).

In a sequence exactly parallel with the procedure for the preparation of diethyl azodicarboxylate,[29] 2,2,2-trichloroethyl chloroformate (Aldrich Chemical Co.) was converted to bis(2,2,2-trichloroethyl) hydrazodicarboxylate: pmr (CDCl₃) δ 5.82 (4 H, s), 7.41 (2 H, broad s); which was, in turn, oxidized with fuming nitric acid[29] to give yellow, crystalline bis(2,2,2-trichloroethyl) azodicarboxylate (28b), mp 110–112°; pmr (CDCl₃) singlet at δ 5.07.

Preparation of Diels–Alder Adduct 29b. Exactly according to the preparation of 29a, spirotriene 2 was converted to 29b; 88% yield after isolation by preparative layer chromatography: pmr (CDCl₃) δ 2.27 (br s, 2 H, –CH₂–), 2.38 (broad s, 2 H, –CH₂–), 4.82 (s, 4 H, –OCH₂–), 4.91 (br s, 2 H, bridgehead H), 5.63 (br s, 2 H, vinyl H), 6.64 (t, 2 H, vinyl H, J = 2 Hz).

Bromination of 29b to give 30b. Exactly as described for the conversion 29a → 31a, the adduct 29b was brominated with N-bromosuccinimide and isolated by filtration through Florisil (eluting with ether) in 68% yield: pmr (CDCl₃) δ 2.1–2.7 (br m, 2 H, –CH₂–), 4.81 (br s superimposed on a broad multiplet, OCH₃, CHBr, and bridgehead H). 5.5–5.7 (m, 1 H, vinyl H), 5.9–6.2 (m, 1 H, vinyl H), 6.5–6.8 (m, 2 H, vinyl H): the pattern of the vinyl proton absorption was superimposable on that for 30a. Signals assigned to small amounts of impurities were observed (δ 4.1, 4.6), but all attempts to further purify the compound resulted in substantial loss of material.

A variety of bases (potassium *tert*-butoxide in ether or tetrahydrofuran, diazabicyclononane in ether at –78°, pyridine in acetonitrile, pyridine in acetonitrile containing silver fluoroborate, and collidine in ether) failed to provide the desired product, 31b.

Regeneration of Spirotriene 2 from 29b. A heterogeneous mixture of zinc–copper couple[48] (3.17 g), mercuric oxide (1.10 g, 5.1 mmol), adduct 29b (602 mg, 1.21 mmol), and 30 ml of anhydrous ether was stirred at 25° for 18 hr. The solution was filtered, concentrated by distillation through a 10-cm Vigreux column at atmospheric pressure, and finally distilled in a short path apparatus at 50° (10 Torr), collecting the distillate at –78°. The distillate was analyzed for 2 by quantitative glpc using an internal standard. The yield of 2 was 27 ± 3%.

Preparation of Diethyl Diallylmalonate. A flask containing a suspension of sodium hydride (26.2 g of a 57% suspension in mineral oil, 0.57 mol) in 500 ml of tetrahydrofuran was cooled in an ice bath while diethyl malonate (32 ml, 0.2 mol) was added dropwise at a rate controlled to maintain an internal temperature of *ca.* 25°; total time of addition was 45 min. Then, with the solution at 25°, allyl bromide (52 ml, 0.6 mol) was added neat, dropwise, at a rate controlled to provide gentle reflux. After addition was complete (1.5 hr), the mixture was heated at reflux for 30 min, cooled to 0°, and 5% aqueous hydrochloric acid was added cautiously (150 ml, total). The water layer was washed with 2 × 100 ml portions of ether; the combined organic extracts were dried, concentrated by rotary evaporation, and fractionally distilled by means of a 30-cm Vigreux column. The center cut of bp 88–91° (1.0 Torr) amounted to 41.7 g (87%) of pure diethyl diallylmalonate (lit.[44] bp 120–122° (12 Torr): pmr (CCl₄) δ 1.24 (t, 6 H, CH₃, J = 7 Hz), 2.57 (d, 4 H, CH₂C=C, J = 7 Hz), 4.18 (quartet, 4 H, CH₂O, J = 7 Hz), 4.8–6.0 (typical vinyl group pattern, 6 H, CH=CH₂).

Preparation of Diallylmalonic Acid. Diethyl diallylmalonate (60 ml, 0.25 mol) and sodium hydroxide (48 g, 1.2 mol) were mixed at 25° and heated at 95° in a 1000-ml flask fitted with a Vigreux column and overhead stirring. As the temperature reached 95°, ethyl alcohol (5 ml) was added. Within a few minutes, a vigorous reaction began, with ethyl alcohol being distilled, and a heavy solid formed. Enough water was added to allow smooth stirring, and the suspension was stirred at 90° for 20 min. After being cooled to 25°, the solution was made acidic (concentrated hydrochloric acid, cooling) causing first dissolution of the solid and then precipitation of a new solid which was collected and recrystallized from hot water (<70°). The colorless needles of diallylmalonic acid (34.5 g, 69% yield) had mp 134–135° (lit.[47] mp 135–137°): pmr (acetone-d_6) δ 2.72 (d, 4 H, –CH₂–, J = 7 Hz), 4.7–6.0 (typical vinyl pattern, 6 H, CH=CH₂), 7.4 (br s, variable position, 2 H, CO₂H).

Preparation of Diallylmalonyl Dichloride 34. A mixture of diallylmalonic acid (34.5 g, 0.19 mol, dry!), thionyl chloride (54 ml, freshly distilled), and carbon tetrachloride (500 ml) in a 1000-ml flask was heated at reflux for 24 hr, using a calcium chloride filled tube to protect the mixture from atmospheric moisture. The mixture was concentrated by rotary evaporation and then fractionally distilled (10-cm Vigreux column) to give a center cut of bp 44–45°

(48) E. LeGoff, *J. Org. Chem.*, **29**, 2048 (1964).

(0.30 Torr), 38.6 g, 92% yield: pmr (CCl₄) δ 2.87 (d, 4 H, –CH₂–, J = 7 Hz), 5.0–6.0 typical vinyl pattern, 6 H, CH=CH₂); ir (CCl₄) 3020 (w), 2940 (w), 1790 (s, –CO–), 1645 (m), 1460 (m), 1450 (w), 1025 (s), 992 (m), 950 (s), 925 (s), 900 (s), 865 (s) cm⁻¹.

Preparation of Spiro[4.4.]nona-2,7-diene-1,6-dione (35). In a 1000-ml flask equipped with an overhead-drive stirrer and addition funnel was mixed 300 ml of dichloromethane and 10 ml of nitromethane, and the system was placed under nitrogen. Solid aluminum chloride (35.9 g, 0.269 mol) was added by momentarily opening the system, with 10 ml of nitromethane used to rinse in the aluminum chloride. With the homogeneous yellow solution stirring at 25° (water bath), diallylmalonyl dichloride (24.6 g, 0.11 mol) was added dropwise over 1 hr. The resulting brown solution was stirred for 30 min at 25°, then cooled to 0° and a solution of 10% aqueous ammonium chloride (40 ml) was added rapidly. The resulting precipitate was filtered, and the green filtrate was washed sequentially with 5% aqueous hydrochloric acid and water, then dried, and concentrated by rotary evaporation, and the residue was dissolved in 450 ml of anhydrous ether. Upon slow cooling to –78°, brown crystals of spiro[4.4]nona-2,7-diene-1,6-dione (35) appeared; mp 100–108°, 8.15 g, 51.5% yield. The pmr spectrum showed >95% purity. Sublimation (70° (0.01 Torr)) followed by recrystallization from benzene provided the analytical sample as colorless needles: mp 111–112°; pmr (CDCl₃) ABX pattern centered at δ 2.81 (quart of t, 4 H, –CH₂–, J_{AB} = 19 Hz, J_{AX} = J_{BX} = 2.5 Hz). 6.14 (d of t, 2 H, CH=C, J_1 = 7 Hz, J_2 = 2.5 Hz), 7.86 [overlapping d of t (5 lines), 2 H, CH=C, J_1 = 7 Hz, J_2 = 2.5 Hz]; ir (CHCl₃) 1724 (C=O) s, 1696 (C=O) s, 1601 (C=C) m, 1420 (m), 1335 (m), 1300 (m), 1165 (s), 1095 (m), 100 (w), 968 (w), 948 (w), 843 cm⁻¹ (m): mass spectral mol wt, 148.

Anal. Calcd for C₉H₈O₂: C, 72.96; H, 5.44. Found: C, 72.95; H, 5.49.

Preparation of Spiro[4.4]nona-2,7-diene-1,6-diol (36). In a 500-ml flask fitted with an overhead-drive stirrer and serum cap was placed a solution of spiro[4.4]nona-2,7-diene-1,6-dione (35, 4.25 g, 28.8 mmol) in tetrahydrofuran (100 ml). The system was placed under nitrogen and cooled in an ice bath, and a solution of aluminum hydride[34a] (50 ml of 0.77 M) in tetrahydrofuran was added at a rate of 1.4 ml/min. After addition, the mixture was stirred at 0° for 45 min and then was washed with 200 ml of ice-cold saturated aqueous potassium tartrate solution until the organic layer was clear. The aqueous washes were shaken with 100 ml of tetrahydrofuran, and the combined organic solution was dried and concentrated by rotary evaporation, and the residue was crystallized from acetone at low temperature. Collected was 1.24 g (30% yield), mp 127–129°. For the pmr spectrum, see Figure 1. Mass spectral mol wt, 152.

Anal. Calcd for C₉H₁₂O₂: C, 71.03; H, 7.94. Found: C, 70.70; H, 7.94.

Preparation of Spiro[4.4]nonatetraene (1) *via* Dichloride 37. To a magnetically stirred solution of the diol 36 (3.3 g, 21 mmol) dissolved in 200 ml of dry tetrahydrofuran in a 500-ml three-necked flask fitted with a drying tube and cooled in ice, was injected simultaneously thionyl chloride (3.66 ml, 6.1 g, 51 mmol) and dry pyridine (4.11 ml, 4.0 g, 51 mmol) over 5 min. The reaction mixture was allowed to stir for an additional 20 min at 0° and then it was added to 5% aqueous hydrochloric acid (100 ml) and pentane (100 ml), and shaken. The organic layer was washed sequentially with dilute sodium bicarbonate solution and water, dried, and concentrated by rotary evaporation to afford a viscous liquid. Distillation in a short-path apparatus at 25–35° (0.01 Torr) for 2.5 hr, with a receiver cooled with Dry Ice, gave a yellow liquid distillate. 1.74 g (43%). The mixture of dichloride isomers was used without further purification for the preparation of 1. Pmr (CCl₄): δ 5.95 (4 H, broad m, vinyl H), 4.5–5.2 (2 H, multiplets at 4.61, 4.96; ratio 1:3, two dichloride isomers), 2.4 (4 H, broad m, –CH₂–).

A one-neck, 50-ml round bottom flask was fitted with a three-way stopcock connected to an argon supply and to a trap to be cooled with liquid nitrogen. An exit from the trap leads to a vacuum pump. To the flask was added a magnetic stirring bar, 20 ml of tetraglyme, and potassium *tert*-butoxide (0.80 g, 7.1 mmol). The system including the trap was evacuated and filled with argon three times, then the flask was opened briefly to add the mixture of dichlorides (37, 0.42 g, 2.2 mmol), the system was evacuated to 0.2 Torr, and the trap was cooled to –196°. The contents of the flask was warmed at 35–40° for 2 hr. The colorless liquid which collected in the trap (mixture of *tert*-butyl alcohol and spiro[4.4]-nonatetraene) was injected into the gas chromatograph in 100-μl portions (10 ft × 0.375 in. 10% DC200 on Gas Chrom Z column at 75°). The slower component (retention time 5.0 min), spiro[4.4]-nonatetraene (1), amounted to 59 mg, 23% yield: for the pmr

spectrum, see Figure 3; uv spectrum in isooctane (see Figure 2) uv max 281 nm (ϵ 1350), 217 (ϵ 6500); in ethanol, uv max 276 nm (ϵ 1120), 218 (5350); ir 3820 (w), 1840 (w), 1662 (m), 1528 (s), 1280 (m), 1075 (s), 972 (s), 816 cm^{-1} (s); mass spectral mol wt, 116.0643 (calcd for C_9H_8, 116.0626).

An alternate procedure is identical with the above except that potassium 2-methyl-1-phenyl-2-propoxide, generated by the addition of excess 2-methyl-1-phenyl-2-propanol to potassium hydride in dry tetraglyme, is used in place of potassium *tert*-butoxide. This procedure offers the advantage of eliminating the alcohol by-product in the distillate from the reaction. By this technique, without preparative glpc, spiro[4.4]nonatetraene has been isolated in yields up to 43%.

Preparation of the Bis(iron tricarbonyl) Complex (40) of Spiro-[4.4]nonatetraene (1). A solution of diiron nonacarbonyl (1.50 g, 4.1 mmol) in 10 ml of anhydrous ether was degassed by means of three freeze–pump–thaw cycles, releasing the vacuum with argon. Then spiro[4.4]nonatetraene (1, 160 mg, 1.38 mmol) was added to the mixture at 25°, by means of a syringe. After being stirred for 24 hr at 25° under argon, the crude reaction mixture was concentrated and applied to a 2 cm × 30 cm column of Florisil. Elution with *n*-hexane gave a bright yellow solid, 0.32 g (58%). Recrystallization from *n*-hexane afforded yellow cubes (0.23 g, 42%): mp 111–112°; pmr (CDCl$_3$) δ 2.40 (m, 2 H), 3.43 (m, 2 H), 5.25 (m, 2 H), 5.43 (m, 2 H); uv max (isooctane) 228 nm (ϵ 45,000), 288 (8,200); ir (CDCl$_3$) 2060 (C≡O, S), 1990 (C≡O, S), 1356 (m), 1080 (w), 1055 (w), 1027 (w), 1000 (w) cm^{-1}; mass spectral mol wt (chemical ionization), 408.

Diels–Alder Reactions of Spiro[4.4]nonatetraene (1). **(a) One Mole Equivalent of Dimethylazodicarboxylate.** A mixture of spiro[4.4]nonatetraene (*ca.* 0.20 mmol, containing 1 equiv of *tert*-butyl alcohol) and dimethyl azodicarboxylate (added in small portions until 1.0 mol equiv was present by pmr analysis, *ca.* 50 μl) in carbon tetrachloride (0.3 ml) was allowed to stand at 25° for 4.0 hr (pmr indicated complete disappearance of 1). The volatiles were removed by rotary evaporation, and the residue was purified by preparative layer chromatography (silica gel–ethyl acetate): the adduct **31a** (R_f 0.6) was isolated in *ca.* 40% yield, and was identical in tlc, pmr, and mass spectral behavior with the material prepared by bromination–dehydrobromination of **29a** (above).

(b) With Excess Dimethylazodicarboxylate. A mixture of spiro[4.4]nonatetraene (*ca.* 0.40 mmol, containing 1 equiv of *tert*-butyl alcohol) and dimethyl azodicarboxylate (250 μl, 1.2 mmol) in 0.3 ml of carbon tetrachloride was allowed to stand at 25°, monitoring the reaction by pmr. Formation of the monoadduct, **31a**, proceeded to completion within 30 min: when the mixture was concentrated by rotary evaporation, further reaction occurred to produce a mixture of diadduct **39** and excess dimethyl azodicarboxylate. Preparative layer chromatography gave a pure sample of diadduct, 225 mg (R_f 0.4, 68% yield), as a colorless viscous oil: pmr (CDCl$_3$) δ 3.76 (12 H, s, OCH$_3$) 4.60 (4 H, m, bridgehead), 6.53 (4 H, m, vinyl H); mass spectral mol wt, 408.1286 (calcd for $C_{17}H_{20}N_4O_8$, 408.1281). The sample was homogeneous on analytical tlc (silica gel–ethyl acetate; R_f 0.36).

(c) With Excess Tetracyanoethylene. A suspension of excess tetracyanoethylene (recrystallized, sublimed) in carbon tetrachloride (0.3 ml) containing spiro[4.4]nonatetraene (1, *ca.* 1.7 mmol) at 25° was shaken periodically over 15 min. The solution was filtered and concentrated, and the residue was crystallized from chloroform or

benzene: mp *ca.* 200° dec; pmr (CDCl$_3$) δ 3.55 (t, 2 H, bridge-head H, J = 2 Hz), 5.9–6.2 (m, 1 H, vinyl H), 6.5–7.0 (m, 5 H, vinyl H); mass spectral mol wt, 244.0761 (calcd for $C_{15}H_8N_4$, 244.0749).

Rate Studies of the Addition of Dimethyl Acetylenedicarboxylate to 1, 2, and 10. In a series of exactly parallel experiments, 10 μl (*ca.* 0.1 mmol) each of three spirocycles (1, 2, and 10) was added to a mixture of deuteriochloroform (0.150 ml) and dimethyl acetylenedicarboxylate (100 μl, 125 mg, 0.88 mmol). The disappearance of 1 was monitored by observation of the integrated area of the δ 5.80 absorption. The disappearance of 2 and 10 was monitored by observation of the diene vinyl absorptions. These signals disappear cleanly during reaction. Duplicate runs were made for each spirocycle. The half-lives for the reactions are presented in Table IV. A least-squares analysis of the plot log pmr integral area *vs.*

Table IV

Spiro-cycle	Temp, °C	Slope (S)	Inter-cept (I)	k, M^{-1} sec^{-1} × 10^5	Corr coeff
2	103 ± 1	0.0088	1.59	2.3	0.990
2	104 ± 1	0.0104	1.48	2.9	0.989
1	50 ± 1	0.0127	1.13	4.7	0.9995
1	50 ± 1	0.0119	1.24	4.0	0.9864
10	78.1 ± 0.5	0.00084	1.71	0.20	0.995
10	78.1 ± 0.5	0.00091	1.55	0.24	0.998
10	78.1 ± 0.5	0.00094	1.50	0.26	0.999
10	103 ± 1	0.0066	1.75	1.6	0.994
10	104 ± 1	0.0089	1.73	2.1	0.998

time provided a correlation coefficient of ≥ 0.99 for each experiment.

Rate Studies of the Dimerization of Spirocycles 1, 2, and 10. In a series of exactly parallel experiments, 1:1 mixtures of toluene and spirocycles 1, 2, and 10 were heated in small sealed vials. For spirotetraene 1, small samples (*ca.* 1–2 μl) were withdrawn periodically and analyzed by glpc on a 3 ft × 0.375 in. column packed with 10% DC 200 on Gas Chrom 2, column at 75°. Retention times: toluene, 3.5 min; spirotetraene 1, 6.5 min. The samples of 2 and 10 were monitored by pmr integration, comparing the area of the vinyl region with the aromatic absorption. All initial concentrations are assumed identical, *ca.* 4.0 *M*. The second-order rate constant, k, was calculated from the expression

$$k = S/IM_i$$

where S = slope of the line from a plot of log pmr integral area *vs.* time; I = intercept; M_i = initial concentration of spirocycles (approximate).