The Bishomoconjugative Rearrangement Pathway. Structural Bond Relocation Attending the Dehydrohalogenation of Unsaturated Cyclic α-Halo Ketones and Sulfones[1,2]

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Abstract: Reaction of 7-bromo-*cis*-bicyclo[4.3.0]nona-2,4-dien-8-one (**1a**) as well as its 1,6-dimethyl (**1b**) and 1,6-tetramethylene derivatives (**2**) with potassium *tert*-butoxide in dimethyl sulfoxide for short periods of time at 25° results in dehydrobromination with structural bond reorganization to give bicyclo[4.2.1]nona-2,4,7-trien-9-ones (**19, 21,** and **26**). Direct irradiation of these bridged ketones causes decarbonylation and cyclooctatetraenes are produced. When these molecules experience triplet sensitization, photoisomerization to barbaralones operates. 7-Chloro-8-thiabicyclo[4.3.0]nona-2,4-diene 8,8-dioxides rearrange in analogous fashion when treated with strong base in a polar aprotic solvent. The resulting bridged sulfones (**34, 38,** and **43**) can be made to extrude sulfur dioxide by thermal or photochemical methods. These striking and unprecedented reactions provide a useful synthetic entry to functionalized [4.2.1]bicyclics. It is suggested that the α-halo ketones behave as in analogous Favorskii situations by deprotonation and subsequent π-assisted C–Br ionization to give a dipolar ion which undergoes intramolecular cycloaddition to the proximate diene system. The α-chloro sulfones probably experience 1,3-displacement of chloride ion with intermediate episulfone formation. The highly strained nature of these species and the DMSO solvent are believed to promote C–C bond heterolysis to afford a zwitterion with a chemical reactivity comparable to that seen for the oxyallyls.

A common process of fundamental importance to the chemistry of α-halo ketones and sulfones is their rearrangement in the presence of strong base (the Favorskii[4] and Ramberg–Bäcklund reactions,[5] respectively). Recent investigations have established that the mechanism of the Favorskii reaction involves initial reversible enolate anion formation.[6] Subsequent extensive stretching of the C–X bond leads to a highly ionic rate-determining transition state as revealed by relatively large Br/Cl rate ratios,[7] appreciable salt and solvent effects,[8] and the highly negative ρ's observed for loss of halide ion.[7,8] However, the ejection of halide is seemingly not the result of intramolecular SN2 displacement; actually, electron-withdrawing substituents attached to the carbon atom of the C–X bond retard the rearrangement rate, whereas electron-donating substituents have the reverse effect.[7] Rather, a substantial body of data supports the concept that C–X ionization assisted by π participation from the proximate enolate anion function leads to a delocalized dipolar intermediate. Disrotatory collapse of this zwitterion to a cyclopropanone probably then occurs.[7]

The 1,3 elimination of hydrogen halide from α-halo sulfones differs significantly in certain mechanistic details. For example, although this reaction again involves rapid and reversible carbanion formation,[5a,9] no comparable delocalized intermediate is involved. Large Br/Cl leaving group effects are likewise noted,[9] but the positive ρ value and the accelerating effect of substituents which enhance positive charge at the C–X carbon atom require that C–C bond formation be quite extensive. These data provide strong evidence for direct rate-controlling internal halide displacement by the neighboring α-sulfonyl carbanion with formation of intermediate episulfones.[5]

Although dipolar intermediates do not intervene in the Ramberg–Bäcklund rearrangement, it has been recognized that subsequent carbon–carbon bond cleavage of episulfones to generate such zwitterions can be made to operate in certain cases where strain factors gain importance.[10] That such dissociations should be energetically realizable is supported by the experimentally determined C–C bond length in *cis*-2-butene episulfone (1.60 Å) which is exceedingly long[11] and the facility with which suitably constructed episulfones undergo kinetically controlled C–C bond rupture under very mild valence isomerism conditions.[12]

Accordingly, we reasoned at the outset of this study that 1,3-dipolar ketone and sulfone intermediates were accessible from appropriate α-halo precursors. At the same time, the high reactivity of related zwitterion types[13] in intermolecular cycloaddition to homomultiple and heteromultiple bonds[14] suggested that geometrically well-defined *intramolecular* variants of this reaction could perhaps provide new dimension to the

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(1) α-Halo Sulfones. XXI. Part XX of this series: L. A. Paquette, R. E. Wingard, Jr., and R. H. Meisinger, *J. Amer. Chem. Soc.*, **93**, 1047 (1971).

(2) We thank the National Cancer Institute and Eli Lilly and Co. for funds used in partial support of this research.

(3) National Institutes of Health Predoctoral Fellow, 1969–1971.

(4) A. S. Kende, *Org. React.*, **11**, 261 (1960).

(5) (a) L. A. Paquette, *Accounts Chem. Res.*, **1**, 209 (1968); (b) L. A. Paquette, "Mechanisms of Molecular Migrations," Vol. I, B. S. Thyagarajan, Ed., Interscience, New York, N. Y., 1968, pp 121–156; (c) F. G. Bordwell, *Accounts Chem. Res.*, **3**, 281 (1970).

(6) F. G. Bordwell, R. R. Frame, R. G. Scamehorn, J. G. Strong, and S. Meyerson, *J. Amer. Chem. Soc.*, **89**, 6704 (1967).

(7) F. G. Bordwell and R. G. Scamehorn, *ibid.*, **90**, 6751 (1968).

(8) F. G. Bordwell, R. G. Scamehorn, and W. R. Springer, *ibid.*, **91**, 2087 (1969).

(9) F. G. Bordwell and J. W. Williams, Jr., *ibid.*, **90**, 435 (1968).

(10) L. A. Paquette and R. W. Houser, *ibid.*, **93**, 4522 (1971).

(11) R. Desiderato and R. L. Sass, *Acta Crystallogr.*, **23**, 430 (1967).

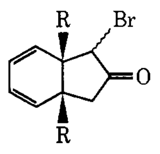
(12) (a) W. L. Mock, *Chem. Commun.*, 1254 (1970); (b) L. A. Paquette and S. Maiorana, *ibid.*, 313 (1971).

(13) For leading references, see (a) J. W. Lown and K. Matsumoto, *J. Org. Chem.*, **36**, 1405 (1971); (b) R. Huisgen and H. Mader, *J. Amer. Chem. Soc.*, **93**, 1777 (1971); (c) W. C. Agosta and A. B. Smith, III, *Chem. Commun.*, 685 (1970).

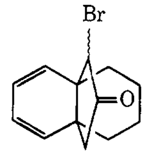
(14) Recent reviews of this topic have appeared: (a) R. Huisgen, *Angew. Chem.*, **75**, 604, 742 (1963); (b) R. Huisgen, *J. Org. Chem.*, **33**, 2291 (1968); (c) R. Huisgen, R. Grashey, and J. Sauer in "The Chemistry of Alkenes," S. Patai, Ed., Interscience, New York, N. Y., 1964, p 806.

synthetic utility of α-halo ketones[15] and sulfones. The present paper details a rearrangement reaction of broad scope in which bi- and tricyclic substrates of suitable molecular design are readily converted to [4.2.1]bicyclic products. Because these fascinating skeletal-bond reorganizations likely occur *via* bishomobenzene intermediates, the various transformations have been termed "bishomoconjugative rearrangements" for simplicity.[16]

The Bishomoconjugative α-Halo Ketone Rearrangement. The systems chosen for study were two bicyclo α-bromo ketones of general structure **1** and 11-bromo-12-oxo[4.4.3]propella-2,4-diene (**2**). Key intermediates in the synthesis of **1a** and **1b** were the imino nitriles **5a** and **5b** which were readily accessible from anhydrides **3a** and **3b** through lithium aluminum hydride reduction, tosylation, and Thorpe–Ziegler cyclization of the derived dinitriles (Scheme I). Alkaline hydrolysis of **5** afforded the diacids **6** which when heated with barium oxide gave the bicyclic ketones **7a** and **7b** in 55 and 70% yields, respectively. Monounsaturated ketal derivatives **8**, upon treatment with 1 equiv of bromine followed by dehydrobromination with anhydrous lithium chloride and lithium carbonate in dry hexamethylphosphoramide,[17] led most conveniently to diene ketals **9**. Mild acid hydrolysis of **9** and selective bromination of **10** with pyrrolidone hydrotribromide in the presence of 2-pyrrolidone[18] afforded **1a** and **1b** as unstable oils which were employed directly without purification.



1a, R = H
b, R = CH_3



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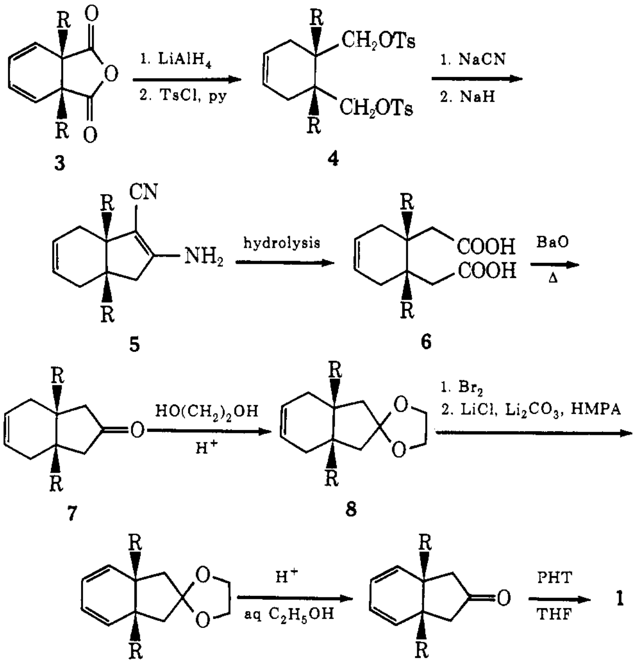
Scheme I

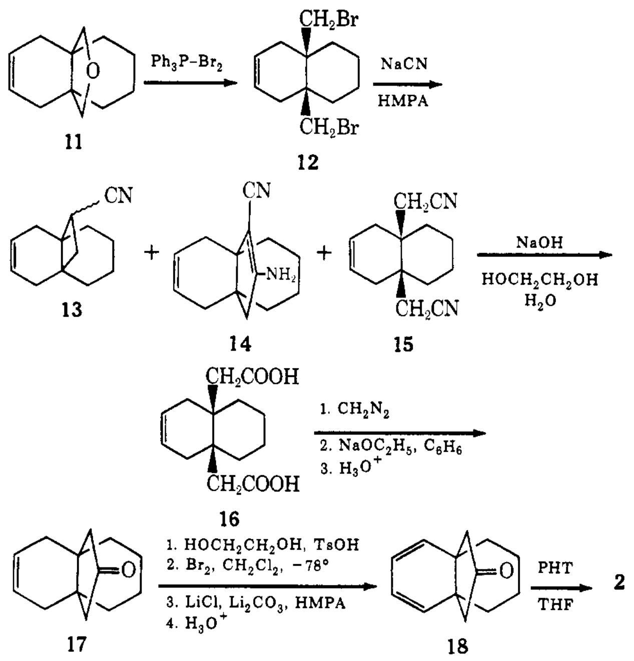


a, R = H; b, R = CH_3

The nmr and uv spectra of **10a** and **10b** left no doubt as to the presence and position of the cyclohexadiene ring. Thus, **10a** exhibited the symmetrical features expected for this structure in the olefinic (δ 5.53–6.10 (m, 4)) and allylic (2.93–3.27 (m, 2)), as well as α-carbonyl (2.23–2.48 (m, 4)) regions. Its electronic spectrum [$\lambda_{max}^{isooctane}$ 257 sh nm (ε 2360), 265 (3240), and 276 (2930)] is characteristic of the chromophore.

In the synthesis of **2** (Scheme II), access to ketone **17** was based upon a procedure developed by Ginsburg, *et al.*, for somewhat related compounds.[19] Extensive modification of the experimental details became necessary, and these are outlined in a later section of this paper. Upon treatment with sodium cyanide in dry hexamethylphosphoramide for 36 hr at 125°, octalin dibromide **12** gave rise in 30% yield to a crystalline mixture of **14** and **15** (*ca.* 1:1 by nmr analysis). Each of these isomers was obtained pure by careful column chromatography. The major product (69%) of the reaction was found to be cyano[4.4.2]propellene **13**, resulting from intramolecular cyclization of the intermediate bromo nitrile. Interestingly, the fully saturated counterpart of dibromide **12** yields only 11-cyano-[4.4.2]propellane when similarly treated with sodium cyanide, but the $\Delta^{2,6}$-hexalin system affords none of the corresponding cyano[4.4.2]propelladiene and gives exclusively the unsaturated counterparts of **14** and **15**.[19] This phenomenon, in which the facility of intermolecular nucleophilic displacement at the neopentyl positions in these systems increases in the order decalin < Δ^2-octalin < $\Delta^{2,6}$ hexalin, can be interpreted in terms

Scheme II



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[15] α-Halo ketones have been utilized to generate zwitterionic intermediates for the purpose of independently establishing their intervention in excited state processes: H. E. Zimmerman and G. R. Epling, *J. Amer. Chem. Soc.*, **94**, 3245 (1972); H. E. Zimmerman, D. S. Crumrine, D. Döpp, and P. S. Huyffer, *ibid.*, **91**, 434 (1969).

[16] Preliminary reports of this work may be found in ref 1 and L. A. Paquette, R. H. Meisinger, and R. E. Wingard, Jr., *ibid.*, **94**, 2155 (1972).

[17] J. F. Normant and H. Deshayes, *Bull. Soc. Chim. Fr.*, 2455 (1967).

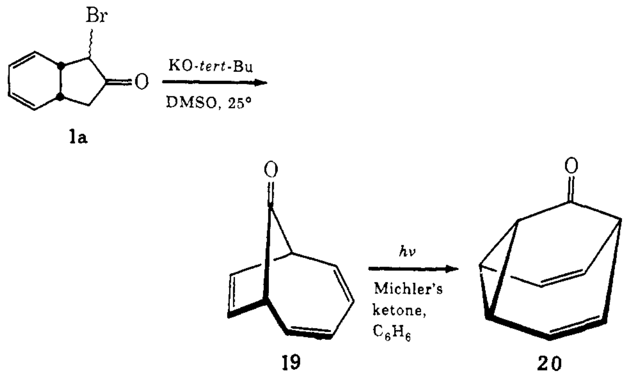
[18] D. V. C. Awang and S. Wolfe, *Can. J. Chem.*, **47**, 706 (1969).

[19] J. Altman, E. Babad, J. Itzchaki, and D. Ginsburg, *Tetrahedron Suppl.*, **8**, 279 (1966).

of steric factors which are reduced upon incremental introduction of unsaturation. Molecular models attest to the incursion of considerable flattening of the four-carbon bridges with replacement of tetrahedral by trigonal carbon. Not unexpectedly, therefore, the alkaline hydrolysis of **14** and **15** required forcing conditions to realize even acceptable (28%) yields. However, this low conversion is offset to a large measure by the fact that unreacted **14** (**15** is converted to **14** under the reaction conditions) may be recovered and recycled.

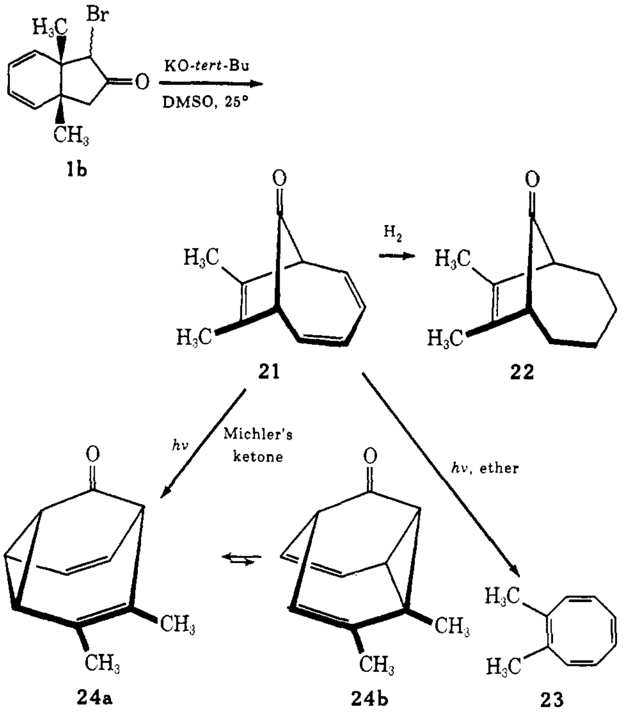
The proximity of the acetic acid side chains in **16** lends itself well to Dieckmann cyclization in high yield. Standard hydrolysis and decarboxylation conditions give rise to **17** which by the predescribed sequence can be transformed to **18**. Maxima are present in the uv spectrum of this ketone at 266 and 277 nm with shoulders at 257 and 294 nm. An intense carbonyl band at 1740 cm^{-1} is displayed in the infrared region, while the nmr spectrum exhibits an AA′BB′ multiplet of area 4 centered at δ 5.68, a pseudosinglet at 2.28 for the four α-carbonyl protons, and a second pseudosinglet (8 H) for the methylene hydrogens. When **2** was prepared, it likewise was found to be unstable to storage and was utilized in unpurified form.

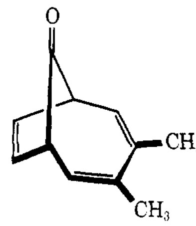
Dissolution of **1a** in dry dimethyl sulfoxide and treatment with excess potassium *tert*-butoxide at room temperature for 15 min gave bridged bicyclic ketone **19** in 30% yield after preparative scale gas chromatographic purification. The product ($\nu_{\max}^{\text{neat}}$ 1760 cm^{-1}) was identified by direct comparison with an authentic sample prepared according to the method of Shechter,[20] photosensitized isomerization with Michler's ketone in benzene solution to barbaralone (**20**), and direct photodecarbonylation to cyclooctatetraene.[20]



Similar treatment of **1b** afforded **21** in 16% overall yield from **10b**. The structure of **21** was established on the basis of its nmr spectrum in $CDCl_3$ in which is seen a four-proton multiplet at δ 5.68–5.97 (olefinic), a two-proton multiplet in the 2.80–3.17 region (bridgehead), and a singlet of area 6 at 1.77 for the methyl groups, its ultraviolet spectrum (isooctane) which is characteristic of this chromophore[20] [$\lambda_{\max}$ 218 nm (ϵ 2040), 273 (1910), 283 (1840), and 322 (580)], and its accurate mass analysis of *m/e* 160.0885 (calcd 160.0888). Chemical confirmation of the assignment was derived from catalytic hydrogenation to **22**, direct photolysis (2537 Å, ether) to 1,2-dimethylcyclooctatetraene (**23**) in 85% yield, and sensitized photoisomerization to dimethylbarbaralone **24**. The formation of **22**, the nmr spectrum of which is characterized by two allylic bridgehead protons (δ 2.58–2.70 (m)), a singlet of area 6 at 1.65 ($-CH_3$), and a broad eight-proton envelope at 1.25–1.83, is particularly informative since it serves to exclude from further consideration **25** and related positional isomers as alternate structural possibilities for **21**.

Scheme III





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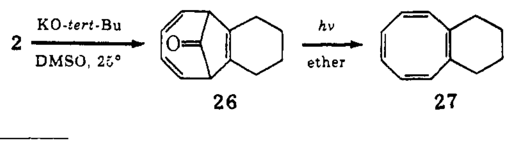
Equilibrium data as derived from nmr spectra of barbaralone **24** over the temperature range −80 to +40° have established that isomer **24a** is substantially (>85%) preferred over **24b**. This observation demonstrates again substantial preference of a methyl substituent for bonding to sp^2 hybridized rather than cyclopropyl carbon.[21,22]

It was immediately clear from inspection of analytical vpc traces obtained from reaction mixtures in which **2** had been similarly exposed to the action of potassium *tert*-butoxide in dry dimethyl sulfoxide at 25° that rapid rearrangement was again operative. This impression was confirmed by isolation of **26** in 24% over-



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(20) T. A. Antkowiak, D. C. Sanders, J. B. Trimitsis, J. B. Press, and H. Shechter, *J. Amer. Chem. Soc.*, **94**, 5366 (1972); see also K. Kurabayashi and T. Mukai, *Tetrahedron Lett.*, 1049 (1972); M. Sakai, R. F. Childs, and S. Winstein, *J. Org. Chem.*, **37**, 2517 (1972).

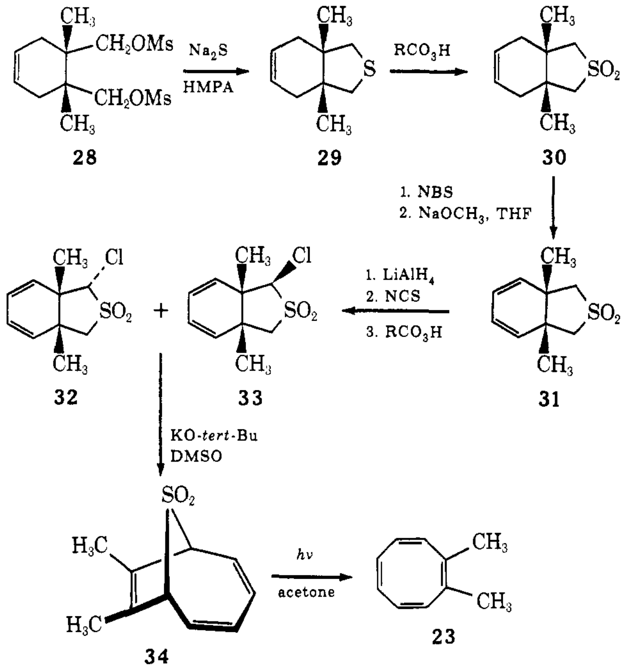
(21) J. C. Barborak, S. Chari, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **93**, 5275 (1971).

(22) G. Schröder and J. F. M. Oth, *Angew. Chem., Int. Ed. Engl.*, **6**, 414 (1967); L. A. Paquette, J. R. Malpass, G. R. Krow, and T. J. Barton, *J. Amer. Chem. Soc.*, **91**, 5296 (1969).

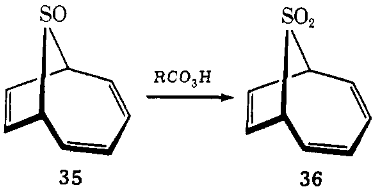
all yield after preparative scale vpc purification. The assignment of structure to **26** rests firmly on both spectroscopic and chemical evidence. The substance was shown to possess extended conjugation by the ultraviolet spectrum (see Experimental Section) and the presence of a strained bicyclic carbonyl group by an intense band at 1780 cm^{-1} in the infrared region. The nmr spectrum exhibits four absorptions of appropriate chemical shift, multiplicity, and area for the four inherently distinguishable proton types. Ketone **26** begins to show signs of decomposition when kept at room temperature for several hours; it can, however, be stored at 0° for several days before discoloration becomes evident. This innate instability is shared by **19** and **21**. Direct irradiation of **26** in ether solution at 2537 Å readily affords a single volatile compound identified as bicyclo[6.4.0]dodeca-1,3,5,7-tetraene (**27**). In agreement with its cyclooctatetraene character, this pale yellow oil shows only a shoulder on intense end absorption in the ultraviolet region.

The Bishomoconjugative α-Halo Sulfone Rearrangement. Preparation of the epimeric chloro sulfone mixture **32** and **33** was effected by a method modeled on the synthesis of related molecules developed earlier in this laboratory (Scheme IV).[23,24] Treatment of dimesylate **28** with anhydrous sodium sulfide in dry hexamethylphosphoramide solution at 120° gave the sulfide **29** (93% yield), which after conversion to its sulfone (**30**) could be readily oxidized to diene **31** by an allylic bromination–dehydrobromination sequence. Most efficient access to **32** and **33** was gained by initial lithium aluminum hydride reduction of **31** to its sulfide, α-chlorination with *N*-chlorosuccinimide, and reoxidation. By manual integration of suitably expanded 60-MHz nmr spectra, the ratio of **32** to **33** was determined to be 63:37.

Scheme IV

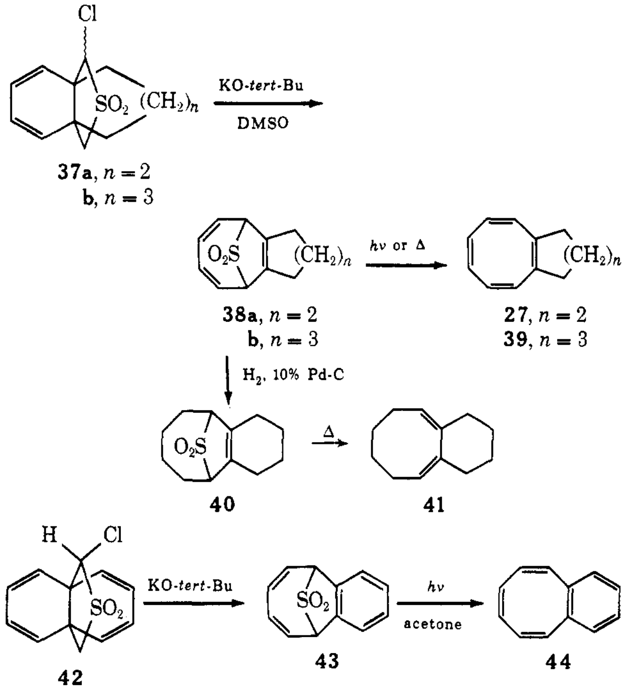


The substance which was produced rapidly when this α-chloro sulfone mixture was treated briefly with potassium *tert*-butoxide in dimethyl sulfoxide displays nmr absorptions (CDCl$_3$) at δ 5.83–6.08 (m, 4), 3.62–3.95 (m, 2), and 1.88 (s, 6), and an ultraviolet maximum in ethanol at 282 nm (ε 2100). These data indicated this new sulfone to be **34**, a conclusion supported further by a direct comparison with sulfone **36** of analogous structure, prepared by oxidation of the known sulfoxide **35**.[25,26] Furthermore, photolysis of **34** in acetone solution led again to the exclusive formation of 1,2-dimethylcyclooctatetraene (**23**).



Compelling evidence for the generality of this rearrangement was derived from the analogous behavior of chloro sulfones **37a**, **37b**, and **42** (Scheme V). Tetramethylene bridged sulfone **37a** was rapidly (20 min) converted to **38a** (56% yield) when treated as above with strong base in a dipolar aprotic medium. Only a trace amount of the normal Ramberg–Bäcklund product, [4.4.2]propella-2,4,11-triene,[24] was produced under these conditions. The spectral features of **38a** were fully compatible with the structural assignment. Chemical confirmation was achieved by catalytic hydrogenation over 10% palladium on carbon in ethyl acetate solution at atmospheric pressure. Under these conditions, rapid uptake of only 2 equiv of hydrogen occurred to yield tetrahydro derivative **40**. Vapor phase pyrolysis of this sulfone at 500° and 10 mm (contact time ≤ 1 sec) produced a hydrocarbon of formula

Scheme V



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(23) L. A. Paquette, R. E. Wingard, Jr., J. C. Philips, G. L. Thompson, L. K. Read, and J. Clardy, *J. Amer. Chem. Soc.*, **93**, 4508 (1971).

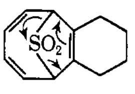
(24) L. A. Paquette, J. C. Philips, and R. E. Wingard, Jr., *ibid.*, **93**, 4516 (1971).

(25) A. G. Anastassiou and Y.-H. Chao, *Chem. Commun.*, 979 (1971).

(26) A vastly superior synthesis of **36** has recently been described by J. Gasteiger and R. Huisgen, *J. Amer. Chem. Soc.*, **94**, 6541 (1972).

$C_{12}H_{18}$ which exhibited all the spectral properties (uv, ir, and nmr) of the expected bicyclo[6.4.0]dodeca-1,7-diene structure (**41**).[27] Further structural proof was provided by catalytic reduction of **41** under 1 atm of hydrogen over platinum oxide in ethyl acetate to a mixture of *trans*- and *cis*-bicyclo[6.4.0]dodecanes in a 5:1 ratio, respectively. The same mixture of saturated hydrocarbons was obtained by hydrogenation of benzocyclooctene over rhodium on alumina in glacial acetic acid solution at 60°.

When a sample of **38a** was passed through a quartz tube packed with quartz chips heated to 400° at 10-mm pressure, a 92% yield of **27** was realized. The formation of **27** is an example of a (4 + 2) cycloreversion, and, if orbital symmetry is allowed, should involve the six-electron motion illustrated in I. Symmetry considerations also predict that photoextrusion of sulfur dioxide from **38a** should be possible in the (4 + 4) mode given by II. In point of fact, photolysis of **38a** in acetone solution through Corex with a 200-W Hanovia lamp source also afforded **27** in 75% yield. Irradiation of ether solutions of **38a** in the absence of sensitizer and of benzene solutions containing Michler's ketone gave analogous results.



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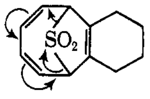
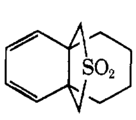


II

Numerous experiments utilizing a wide range of bases, solvents, temperatures, and reaction times have been conducted in an effort to determine those conditions under which **37a** would exhibit rearrangement to bridged sulfone **38a**. The desired transformation occurs in dimethyl sulfoxide solutions containing either potassium *tert*-butoxide or alcohol-free sodium methoxide at 25°, but unchanged starting chloro sulfone is returned upon substitution with potassium hydroxide even with prolonged heating (100°, 2 hr). When dimsyl anion was employed, only tarry material was isolated. Tetrahydrofuran solutions containing potassium *tert*-butoxide or sodium amide also afford **38a**, but sodium methylate and diazabicyclononene (DBN) had no effect. All four of the successful reactions lead to good yields of product, but the KO-*tert*-Bu–DMSO combination is the one of choice, in that quite pure crystalline sulfone is obtained directly from the reaction mixture. It has been noted that when the **37a** → **38a** conversion is conducted on a large scale (5–10 g), the longer times required for addition result in attack by excess base on the intermediate bridged sulfone **38a** to give annelated cyclooctatetraene **27** directly.[28]

No chemical change was encountered when **37a** was treated with sodium methoxide in diglyme (100°, 1 hr) or methanol (reflux, 24 hr) and sodium hydroxide in aqueous dioxane (reflux, 24 hr). Phenyllithium in benzene (25°, 20 min) afforded only dark intractable substances. The noneffectiveness of protic solvents was not surprising since their capability for hydrogen bonding to the derived α-sulfonyl carbanion has been noted previously to attenuate markedly the normal Ramberg–Bäcklund rearrangement.[24,29] Attempts to convert sulfone **45** directly to **38a** by direct reaction with powdered potassium hydroxide in carbon tetrachloride–*tert*-butyl alcohol[30] were likewise unsuccessful; 87% of **45** was recovered.



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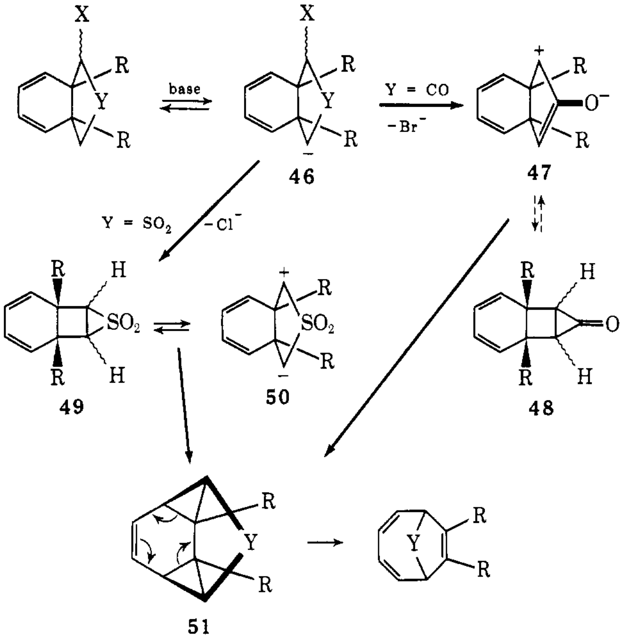
Discussion

In the introduction to this paper, the possibility was considered that carbonyl and sulfonyl 1,3-dipolar ions could arise as transient intermediates in the bishomoconjugative rearrangement, followed by intramolecular trapping of the zwitterions by the proximate diene unit, and retro Diels–Alder reactions of the resulting bishomobenzene (Scheme VI). Although the weight of combined experimental evidence presently does not provide confirmation of this mechanism, it remains the most likely pathway for reasons to be considered herein.

Scheme VI



The wealth of analogy available from extensive past studies of the Favorskii reaction suggests that α-bromo ketones **1** and **2** undergo initial deprotonation to give **46** and subsequent π-assisted dissociation of the C–Br bond with formation of **47**. In particular, the recognized capability of polar media to promote zwitterion production[31] is in agreement with the especially favorable nature of dimethyl sulfoxide as solvent. In fact, findings of this sort have led to the suggestion that the detailed nature of the Favorskii process as it relates to the generation of specific intermediates will vary with conditions.[32] In the present instance, not only should solvation by DMSO favor **47** over **48**, but the severe ring strain associated with the bicyclopentanone part

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(27) D. J. Cram and N. L. Allinger, *J. Amer. Chem. Soc.*, **78**, 2518 (1956).

(28) R. S. Beckley, private communication.

(29) L. A. Paquette and J. C. Philips, *Tetrahedron Lett.*, 4545 (1971).

(30) C. Y. Meyers, A. M. Malte, and W. S. Matthews, *J. Amer. Chem. Soc.*, **91**, 7510 (1969).

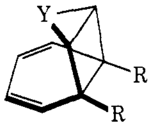
(31) H. O. House and G. A. Frank, *J. Org. Chem.*, **30**, 2948 (1965), and pertinent references cited therein; see also F. G. Bordwell and M. W. Carlson, *J. Amer. Chem. Soc.*, **92**, 3377 (1970).

(32) N. J. Turro and W. B. Hammond, *ibid.*, **87**, 3258 (1965).

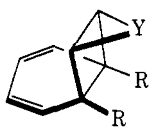
structure in the latter species will certainly demand relief, particularly in view of the resonance energy which can be maintained by remaining in form **47**. No evidence for cyclopropanone intervention has been obtained. Should such intermediates arise, mobile equilibrium with the corresponding planar oxyallyls (**47**) is fully expected.[33] An interesting, but as yet unresolved, question concerns the possibility that the oxyallyl zwitterions (**47**) may experience intramolecular cycloaddition to **51** more rapidly than disrotatory closure to **48**.

Assuming that the base-initiated elimination of HCl from α-chloro sulfones **32**, **33**, **37**, and **42** proceeds to give episulfones **49**, which because of ring strain undergo C–C bond cleavage with generation of **50**,[10] it is possible to account for the formation of bridged sulfones **34**, **38**, and **43**. In this eventuality, intramolecular capture of zwitterion **50** is required to be appreciably more efficient than loss of sulfur dioxide from **49**. As before, the highly polar aprotic DMSO solvent should facilitate the intervention of **50**. Some measure of confirmation of this proposal was gained by reaction of **42** with potassium *tert*-butoxide in ether. Under these conditions, [4.4.2]propella-2,4,6,8,11-pentaene was isolated in preparatively useful quantities.[24] Evidently, the diene moiety does not intercept the loss of sulfur dioxide in this solvent. It may be argued that diethyl ether is not a medium conducive to zwitterion formation, with the result that sulfur dioxide extrusion from **49** regains its customary position as the kinetically dominant pathway.

A somewhat extreme mechanistic alternative consists of direct intramolecular cycloaddition from intermediates **48** and **49**. Two stereoisomers of these structures are possible (III and IV), but if the recognized reactivity preference of bicyclo[2.1.0]pentanes is to hold true with these structures, inside approach to the bicyclopentane flap is necessary.[34] This stereoalignment is available only to III. However, not only does this intramolecular variant suffer from geometrical restraints which cause poor overlap of the internal bond of the three-membered ring with the diene p orbitals, but molecular models indicate that the situation is significantly inferior to that existing in **47** and **50**. Also, the electrophilic character of oxyallyl (a 2π component) appears to be far superior to that of a neutral strained C–C bond.[35]



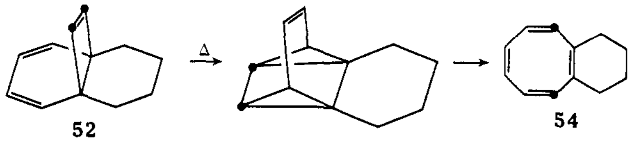
III



IV

The bishomobenzene intermediate **51** could conceivably also arise by vinylogous SN2′ intramolecular displacement of halide ion, *i.e.*, by a formal 1,8 loss of HX. Were such a process to operate, the driving force would presumably arise from the formation of two highly strained cyclopropane bonds. In view of Bordwell's recent reanalysis of simple SN2′ reactions,[36] it would seem clear that the loss of chloride ion could not arise from a concerted transformation in which many bonds are formed and broken. We do not favor the SN2′ mechanism because of the inherent unattractiveness of stepwise carbanion attack on a diene system, the lack of an energetically favorable driving force, and the requisite structural reorganization which, because it is unusually large, should prove costly in energy.[37] In contrast, the direct conversion of zwitterions **47** and **50** to **51** is orbital symmetry allowed and proceeds with charge annihilation.

The intramolecular (4 + 2) cycloaddition mechanism parallels in a rather direct way the pathway utilized by a number of unsaturated propellanes such as **52** when



52 **53** **54**

these are heated in the gas phase.[38] Appropriate deuterium labeling studies attest to the intervention of tetracyclo[4.2.0.0^{2,8}.0^{5,7}]octenes (**53**) on the way to the isomeric cyclooctatetraene structures. An analogous scheme may be followed in the degenerate thermal rearrangements of certain disubstituted cyclooctatetraenes.[39]

Once access is gained to **51**, its rapid conversion to [4.2.1]bicyclic products by ($_{\sigma}2_s$ + $_{\sigma}2_s$ + $_{\pi}2_s$) bond reorganization is fully expected.[40] Further experimental support for the intervention of **51** is found in a recent report by Vedejs[41] who treated bromo ketone **55** with potassium *tert*-butoxide in *tert*-butyl alcohol and observed its conversion to **19** as the sole product. Since the epimeric bromo ketone did not give **19**, the mechanism suggested by the illustrated chemical transformation involves 1,3 displacement of bromide ion from enolate **56** to give tetracyclic ketone **51**, retro Diels–Alder reaction of which affords **19**.

From the synthetic viewpoint, the bishomoconjugative α-halo ketone and sulfone rearrangements can be expected to permit access to bicyclo[4.2.1]nonatrienones, 9-thiabicyclo[4.2.1]nona-2,4,7-triene 9,9-dioxides, barbaralones, and cyclooctatetraene derivatives whose preparation cannot be realized readily by other methods. By utilizing the principle of intercepting reactive intermediates by appropriate positioning of olefinic centers to insure intramolecular capture, considerable

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(33) For a theoretical discussion of this point, see R. Hoffmann, *J. Amer. Chem. Soc.*, **90**, 1475 (1968).

(34) P. G. Gassman, *Accounts Chem. Res.*, **4**, 128 (1971).

(35) J. G. Burr, Jr., and M. J. S. Dewar, *J. Chem. Soc.*, 1201 (1954); R. Hoffmann and R. B. Woodward, *J. Amer. Chem. Soc.*, **87**, 2046 (1965).

(36) F. G. Bordwell, *Accounts Chem. Res.*, 3, 281 (1970); F. G. Bordwell, D. A. R. Harper, and G. D. Cooper, *Tetrahedron Lett.*, 2759 (1972); F. G. Bordwell and T. G. Mecca, *J. Amer. Chem. Soc.*, **94**, 5825, 5829 (1972).

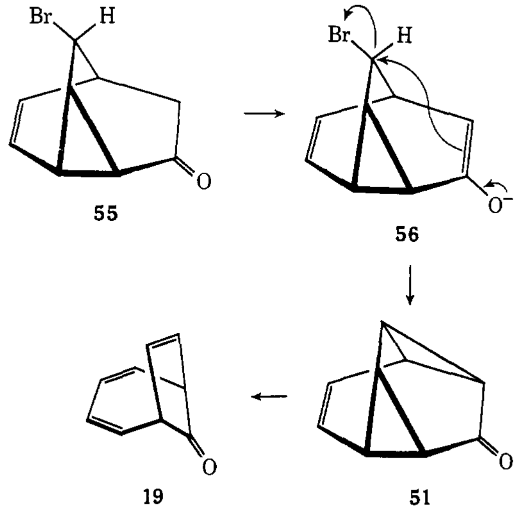
(37) J. Hine, *J. Org. Chem.*, **31**, 1236 (1966); *J. Amer. Chem. Soc.*, **88**, 5525 (1966).

(38) L. A. Paquette and R. E. Wingard, Jr., *ibid.*, **94**, 4398 (1972).

(39) L. A. Paquette, R. H. Meisinger, and R. E. Wingard, Jr., *ibid.*, **94**, 9224 (1972).

(40) For analogous structural bond organizations, see (a) H. W. Whitlock, Jr., and P. F. Schatz, *ibid.*, **93**, 3837 (1971); (b) W. von E. Doering and J. Rosenthal, *ibid.*, **88**, 2078 (1966); (c) W. Grimme, H. J. Riebel, and E. Vogel, *Angew. Chem., Int. Ed. Engl.*, **7**, 823 (1968); (d) M. Jones, Jr., and B. Fairless, *Tetrahedron Lett.*, 4881 (1968); (e) L. A. Paquette, G. R. Krow, and J. R. Malpass, *J. Amer. Chem. Soc.*, **91**, 5522 (1969); (f) R. T. Seidner, N. Nakatsuka, and S. Masamune, *Can. J. Chem.*, **48**, 187 (1970); (g) W. von Philipsborn, J. Altman, E. Babad, J. J. Bloomfield, D. Ginsburg, and M. B. Rubin, *Helv. Chim. Acta*, **53**, 725 (1970), and additional references cited in these papers.

(41) E. Vedejs, R. A. Gabel, and P. D. Weeks, *J. Amer. Chem. Soc.*, **94**, 5842 (1972).



mechanistic insight into a variety of reactions should be accessible. Additionally, the attendant molecular reorganizations will quite likely give rise to new classes of polyunsaturated carbocyclic and heterocyclic molecules. Such phenomena are presently under active investigation.

Experimental Section

Melting points are corrected. Proton magnetic resonance spectra were obtained with a Varian A-60A spectrometer and apparent coupling constants are cited. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

cis-**8-Amino-7-cyanobicyclo[4.3.0]nona-3,7-diene (5a).** A stirred mixture containing 109.4 g (0.243 mol) of ditosylate **4a**[42] and 35.8 g (0.729 mol) of sodium cyanide in 400 ml of freshly distilled dimethyl sulfoxide was cautiously heated to 100° under an atmosphere of dry nitrogen. After 1.5 hr, the homogeneous solution was cooled to 25° and 10.73 g (0.255 mol) of sodium hydride dispersion (57% in mineral oil washed thoroughly with anhydrous benzene) was added.[43] Slow warming to 100° was followed by a 45-min period of heating at this temperature. The cooled reaction mixture was poured onto ice, diluted with ice-water to a volume of 3 l., cooled, and filtered. The precipitated solid was washed with additional small portions of ice-water and thoroughly dried to give 35.2 g (90.5%) of **5a** as an off-white solid: mp 96.5-97.5° (lit.[43] mp 195.4-196°, perhaps a typographical error); $\nu_{\max}^{\text{Nujol}}$ 3380, 3310, 3220, 2180, 1660, and 1600 cm^{-1}; $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 5.78-5.97 (m, 2, olefinic), 4.68 (br s, 2, NH_2), and 1.67-3.25 (m, 8).

Cyclohex-4-ene-*cis*-1,2-diacetic Acid (6a). A solution of 32.0 g (0.20 mol) of sodium hydroxide in 200 ml of ethylene glycol and 275 ml of water was refluxed under a nitrogen atmosphere for 12 hr, at which time it was cooled and diluted to a volume of 1.25 l. with water. Nonhydrolyzed organic material was removed by extraction with methylene chloride. The aqueous layer was acidified with cold 6 *N* hydrochloric acid and cooled at 0° for several hours before the product was collected by filtration. This material, together with additional diacid obtained from ether extraction of the filtrate, furnished 33.8 g (85.5%) of **6a**, mp 157-158° (lit.[42a] mp 157°); $\nu_{\max}^{\text{Nujol}}$ 2900 and 1685 cm^{-1}.

cis-**Bicyclo[4.3.0]non-3-en-8-one (7a).** A stirred mixture of 4.95 g (0.025 mol) of **6a** and 256 mg (1.07 mmol) of barium oxide contained in a short-path distillation apparatus equipped with an ice-cooled collector was heated at 275° and 100 mm for 5 hr. The distillate was taken up in 100 ml of hexane, filtered, washed with brine, dried, and evaporated. Distillation of the residue afforded 1.86 g (55%) of **7a**, bp 41.5-42.5° (0.25 mm). Spectral characteristics were consistent with reported data.[44]

Anal. Calcd for $C_9H_{12}O$: C, 79.37; H, 8.88. Found: C, 79.13; H, 8.99.

cis-**8,8-Dioxyethylenebicyclo[4.3.0]non-3-ene (8a).** A solution of 2.75 g (0.0189 mol of **7a**, 2.5 ml of ethylene glycol, and 100 mg of *p*-toluenesulfonic acid in 80 ml of dry benzene was refluxed in a Dean-Stark apparatus for 90 hr, at which time it was cooled to 25°, washed with saturated sodium bicarbonate solution and brine, and dried. The solution was concentrated and the residue distilled to afford 3.21 g (94%) of **8a**: bp 57-60° (0.25 mm); $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 5.67 (t, $J = 1.5$ Hz, 2, olefinic), 3.87 (s, 4, $-OCH_2-$), and 1.6-2.5 (m, 10).

Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.11; H, 8.92.

cis-**Bicyclo[4.3.0]nona-2,4-dien-8-one (10a).** To a stirred solution of 2.40 g (13.3 mmol) of **8a** in 40 ml of methylene chloride cooled to −70° was added 1 mol equiv of bromine during 40 min. The reaction mixture was then diluted with 200 ml of methylene chloride, washed with 0.5 *N* sodium hydroxide, water, and brine, dried, and evaporated. There was obtained 4.17 g (92%) of crystalline dibromide.

This material was heated with 2.82 g (67 mmol) of dry lithium chloride and 4.96 g (67 mmol) of dry lithium carbonate in 50 ml of freshly distilled anhydrous hexamethylphosphoramide at 90-95° for 40 hr under nitrogen. The cooled mixture was diluted with 250 ml of ice-water and extracted numerous times with pentane. The combined organic extracts were washed thoroughly with water, dried, and evaporated.

The residual oil was hydrolyzed by stirring in 160 ml of ethanol-water (3:1) containing 200 mg of *p*-toluenesulfonic acid at 25° for 26 hr. The solution was diluted with 500 ml of a saturated sodium bicarbonate solution and extracted with ether. The combined organic layers were processed in the customary fashion to provide 1.31 g of crude **10a**. Pure ketone was obtained by preparative scale vpc isolation from a 5 ft × 0.25 in. column packed with 5% SE-30 at 150°: 269 mg (16.5%); $\nu_{\max}^{\text{neat}}$ 1740 cm^{-1}; $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 5.53-6.10 (m, 4, olefinic), 2.93-3.27 (m, 2, allylic), and 2.23-2.48 (m, 4, $-CH_2CO-$); $\lambda_{\max}^{\text{isooctane}}$ 257 sh nm (ϵ 2360), 265 (3240), and 276 (2930); *m/e* 134.0729 (calcd 134.0731).

The semicarbazone of **10a** was obtained as white crystals, mp 186.5-188.5° dec, from aqueous ethanol.

Anal. Calcd for $C_{10}H_{13}N_3O$: C, 62.80; H, 6.85; N, 21.98. Found: C, 62,80; H, 6.97; N, 22.52.

cis-**1,2-Bis(hydroxymethyl)-1,2-dimethylcyclohex-4-ene.** To a refluxing suspension of 6.0 g (0.158 mol) of lithium aluminum hydride in 400 ml of dry tetrahydrofuran was added 21.81 g (0.12 mol) of **3b**[45] dissolved in 200 ml of the same solvent over a period of 2.5 hr. The mixture was refluxed for 3 days, cooled to 0°, and treated dropwise with 90 ml of ice-water followed by dilution with 600 ml of an ice cold 5% sulfuric acid solution. The diol was separated by repeated extraction of the acidic solution with methylene chloride and evaporation of the combined dried organic layers. Sublimation at 130° and 0.2 mm furnished 19.3 g (94%) of white crystals: mp 198.5-201.5°, upon recrystallization from hexane; $\nu_{\max}^{\text{Nujol}}$ 3090 cm^{-1}; $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 5.55 (t, $J = 1.5$ Hz, 2, olefinic), 5.02 (s, 2, OH), 3.45 (s, 4, $-CH_2O-$), 1.52-2.43 (m, 4, allylic), and 0.90 (s, 6, methyls).

Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.54; H, 10.66. Found: C, 70.47; H, 10.57.

Ditosylate **4b** was obtained in 83% yield (stirred solution, 7°, 7 days) as a white crystalline solid, mp 83.5-84°, from absolute ethanol.

Anal. Calcd for $C_{24}H_{30}O_6S_2$: C, 60.22; H, 6.32; S, 13.40. Found: C, 60.32; H, 6.36; S, 13.27.

cis-**8-Amino-7-cyano-1,6-dimethylbicyclo[4.3.0]nona-3,7-diene (5b).** Reaction of 16.7 g (0.035 mol) of **4b** with 5.15 g (0.105 mol) of sodium cyanide in 175 ml of hexamethylphosphoramide (110-115°, 70 hr) and subsequent exposure to sodium hydride (1.50 g, 53.6 mmol) in the predescribed manner gave rise to 5.24 g (80%) of **5b** as an off-white solid: mp 131-131.5° dec, from carbon tetrachloride: $\nu_{\max}^{\text{Nujol}}$ 3400, 3325, 3215, 2180, 1650, and 1600 cm^{-1}; $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 5.67-5.83 (m, 2, olefinic), 4.58 (br s, 2, NH_2), 1.88-2.37 (m, 6, methylenes), 1.08 and 1.05 (s, 3 each, methyls).

Anal. Calcd for $C_{12}H_{16}N_2$: C, 76.55; H, 8.75. Found: C, 76.97; H, 8.53.

cis-**1,2-Dimethylcyclohex-4-ene-1,2-diacetic Acid (6b).** When 11.0 g (58.5 mmol) of **5b** was hydrolyzed as before (50 g of NaOH, 100 ml of ethylene glycol, and 120 ml of water, 91 hr), there was obtained 10.87 g (82.5%) of **6b**; $\nu_{\max}^{\text{Nujol}}$ 1695 cm^{-1}. A portion of

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[42] (a) D. C. Ayres and R. A. Raphael, *J. Chem. Soc.*, 1779 (1958); (b) E. Casadevall, C. Largeau, and P. Moreau, *Bull. Soc. Chim. Fr.*, 1514 (1968); (c) B. P. Mundy and R. D. Otzenberger, *J. Org. Chem.*, 37, 677 (1972).

[43] This procedure has been adapted from the method described by J. J. Bloomfield and P. V. Fennessey, *Tetrahedron Lett.*, 2273 (1964).

[44] J. C. Jallageas and E. Casadevall, *C. R. Acad. Sci., Ser. C*, 268, 449 (1969).

[45] R. B. Woodward and R. B. Loftfield, *J. Amer. Chem. Soc.*, 63, 3167 (1941).

this material was esterified with excess diazomethane to generate the volatile dimethyl ester which was isolated in pure form by vpc isolation from the SE-30 column at 190°: $\nu_{\mathrm{max}}^{\mathrm{neat}}$ 1750 cm^{-1}; $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.61 (t, J = 1.5 Hz, 2, olefinic), 3.63 (s, 6, OCH_3), 2.31 (s, 4, $-CH_2$-CO–), 2.0–2.5 (m, 4, allylic), and 1.0 (s, 6, methyls).

Anal. Calcd for $C_{14}H_{22}O_4$: C, 66.11; H, 8.72. Found: C, 65.92; H, 8.67.

cis-**1,6-Dimethylbicyclo[4.3.0]non-3-en-8-one (7b).** An intimate mixture of 8.40 g (44.2 mmol) of **6b** and 452 mg (2.95 mmol) of barium oxide was heated at 235–260° under 55 mm pressure until no additional material was seen to distill. Sublimation of the distillate at 90–95° and 0.2 mm afforded 5.07 g (70%) of **7b** as a low melting white solid: $\nu_{\mathrm{max}}^{\mathrm{Nujol}}$ 1740 cm^{-1}; *m/e* 164.1199 (calcd 164.1201); $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.65 (t, J = 1.5 Hz, 2, olefinic), 2.15 (s, 4, $-CH_2$-CO–), 2.0–2.58 (m, 4, allylic), and 1.05 (s, 6, methyl).

Its semicarbazone was obtained in 76% yield as colorless crystals, mp 215.5–216.5° dec, from aqueous ethanol.

Anal. Cald for $C_{12}H_{19}N_3O$: C, 65.12; H, 8.65; N, 18.99. Found: C, 64.73; H, 8.62; N, 18.88.

Ketalization of **7b** in standard fashion led to the isolation of **8b** in 71% yield: bp 69° (0.3 mm); $\delta_{\mathrm{TMS}}^{\mathrm{CDCL_3}}$ 5.55 (t, J = 1.3 Hz, 2, olefinic), 3.82 (s, 4, $-CH_2O-$), 1.40–2.48 (m, 8, methylenes), and 0.97 (s, 6, methyls).

Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 74.84; H, 9.68.

cis-**1,6-Dimethylbicyclo[4.3.0]nona-2,4-dien-8-one (10b).** When 5.20 g (25 mmol) of **8b** was brominated, dehydrobrominated, and deketalized by the procedure outlined above, there was isolated 3.04 g of impure colorless liquid. This material was purified by preparative scale vpc isolation from the SE-30 column at 140° again with considerable losses to afford 1.07 g (26.5%) of **10b**: $\nu_{\mathrm{max}}^{\mathrm{neat}}$ 1740 cm^{-1}; $\lambda_{\mathrm{max}}^{\mathrm{isooctane}}$ 255 sh nm (ε 2510), 263 (3450), and 272 (3110); *m/e* 162.1043 (calcd 162.1044); $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.37–6.03 (m, 4, olefinic), 2.53 and 2.13 (center of AB doublets, J = 18 Hz, 4, $-CH_2-$) and 1.07 (s, 6, methyls). A 14% recovery of unchanged **7b** was also realized.

The semicarbazone of **10b** was obtained in 73% yield as colorless crystals, mp 205.5–206.5° dec, from ethanol–water.

Anal. Calcd for $C_{12}H_{17}N_3O$: C, 65.72; H, 7.81; N, 19.16. Found: C, 65.69; H, 7.74; N, 19.13.

cis-**9,10-Bis(bromomethyl)-Δ²-octalin (12).** To an ice-cold magnetically stirred solution of 11.5 g (44 mmol) of triphenylphosphine in 25 ml of dry chlorobenzene under nitrogen was added dropwise 7.05 g (44 mmol) of bromine in 25 ml of chlorobenzene. After addition was complete, the temperature of the slurry was raised to 120° and 7.00 g (39.4 mmol) of 12-oxa[4.4.3]propell-3-ene (**11**)[46] in 10 ml of chlorobenzene was added dropwise. The bath temperature was maintained at 120–130° for 15 hr. The solvent was removed *in vacuo* and the resulting dark oil was triturated with hot petroleum ether (65–110°) and filtered to remove triphenylphosphine oxide. The filtrate was passed through an alumina column (elution with 5% ether in petroleum ether) to give 10.1 g (79.5%) of **12**, mp 88.0–89.0°, from high boiling petroleum ether: $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.62 (m, 2, olefinic), 3.43, 3.60, 3.65 and 3.82 (AB pattern, J = 10 Hz, 4, CH_2Br), 2.18 (br s, 4, allylic), and 1.55 (br s, 8, methylenes).

Anal. Calcd for $C_{12}H_{18}Br_2$: C, 44.75; H, 5.63. Found: C, 44.71; H, 5.66.

Reaction of 12 with Sodium Cyanide. A mechanically stirred slurry of 644 g (13.1 mol) of sodium cyanide in 1.5 l. of hexamethylphosphoramide was heated under vacuum (~15 mm) until the temperature of the distillate reached 120°. After cooling to room temperature, 136 g (0.422 mol) of **12** dissolved in 500 ml of the same solvent was added and the slurry was stirred at 125° for 36 hr. The solvent (1 l.) was distilled from the reaction under vacuum after which the dark reaction mixture was diluted with 2 l. of water and extracted three times with ether. The combined ethereal extracts were washed well with water and saturated sodium chloride solution and dried. Removal of the solvent *in vacuo* gave a dark oil which was triturated with hot petroleum ether (65–110°) and allowed to stand at 0° overnight. Filtration of the yellowish crystalline precipitate gave 27.4 g (30.4%) of a mixture of **14** and **15** in the approximate ratio of 45:55 (nmr analysis).

The two isomeric nitriles were separated by column chromatography on silica gel. Octalin dinitrile **15** was the first to elute and an analytical sample was obtained after recrystallization from ether: mp 126–127°; $\nu_{\mathrm{max}}^{\mathrm{CHCl_3}}$ 2240 cm^{-1}; $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.65 (m, 2, olefinic), 2.45 (center of AB pattern, J = 17 Hz, 4, CH_2CN), 2.10–2.35 (m, 4, allyl), and 1.62 (br s, 8, methylenes).

Anal. Calcd for $C_{14}H_{18}N_2$: C, 78.46; H, 8.47. Found: C, 78.30; H, 8.50.

Pure **14** was obtained by recrystallization from methylene chloride–petroleum ether: mp 113–115°; $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.65 (m, 2, olefinic), 4.62 (br s, 2, NH_2), 2.28 (s, 2, CH_2CN), 1.9–2.2 (m, 4, allyl), and 1.47 (br s, 8, methylenes); $\nu_{\mathrm{max}}^{\mathrm{CHCl_3}}$ 2180 cm^{-1}.

Anal. Calcd for $C_{14}H_{18}N_2$: C, 78.46; H, 8.47. Found: C, 78.42; H, 8.49.

The solvent was removed from the mother liquor *in vacuo* to give a dark oil which was dissolved in ether and passed through an alumina column to give 54.5 g (69.4%) of the epimeric 11-cyano-[4.4.2]propell-3-enes (**13**) as a light yellow viscous oil. An analytical sample was obtained by preparative vapor phase chromatography (6 ft × 0.25 in., 5% SF-96 on Chromosorb G, 160°); $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.82–6.05 (complex multiplet with sharp singlets at 5.88 and 5.95, 2, olefinic), 1.3–3.5 (broad envelope with singlet at 1.50, 15).

Anal. Calcd for $C_{13}H_{17}N$: C, 83.37; H, 9.15. Found: C, 83.48; H, 9.13.

cis-**Δ²-Octalin-9,10-diacetic Acid (16).** Into a 1-l. flask were placed 26.9 g (0.126 mol) of nitrile mixture **14** and **15**, 60 g (1.5 mol) of sodium hydroxide, 300 ml of water, and 240 ml of ethylene glycol. The slurry was refluxed with magnetic stirring for 84 hr. After cooling to room temperature, the solution was diluted with water and extracted three times with chloroform (chloroform extracts contain unreacted starting material which may be recycled). The aqueous solution was acidified with concentrated hydrochloric acid and extracted five times with ethyl acetate. The combined extracts were washed with water and saturated salt solution and dried, and the solvent was removed to afford 9.08 g (28.6%) of crude **16**. An analytical sample was obtained after three recrystallizations from ethanol–water: mp 225–227° dec; $\nu_{\mathrm{max}}^{\mathrm{Nujol}}$ 2880, 1710, and 1650 cm^{-1}; $\delta_{\mathrm{TMS}}^{\mathrm{pyr\text{-}d_6}}$ 5.63 (m, 2, olefinic), 2.53 (center of AB quartet, J = 13 Hz, 4, CH_2CO_2H), 2.35 (br, s, 4, allyl), and 1.62 (br s, 8, methylenes).

Anal. Calcd for $C_{14}H_{20}O_4$: C, 66.64; H, 7.99. Found: C, 66.38; H, 8.07.

cis-**9,10-Bis(carbomethoxymethyl)-Δ²-octalin.** A solution of *ca.* 100 mmol of diazomethane in ether was distilled into a magnetically stirred solution of 4.12 g (16.3 mmol) of **16** in 300 ml of dry glyme at 0°. The yellow solution was allowed to warm to ambient temperature and the excess diazomethane was destroyed with formic acid. Evaporation gave a quantitative yield (4.67 g) of diester as a clear viscous oil. Preparative vpc (6 ft × 0.25 in., 5% SF-96 on Chromosorb G, 200°) gave an analytical sample: $\nu_{\mathrm{max}}^{\mathrm{neat}}$ 1730 cm^{-1}; $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.60 (m, 2, olefinic), 3.63 (s, 6, methyl), 2.42 (center of AB quartet, J = 13 Hz, 4, $CH_2CO_2CH_3$), 2.18 (br s, 4, allyl), and 1.55 (br s, 8, methylenes).

Anal. Calcd for $C_{16}H_{24}O_4$: C, 68.54; H, 8.63. Found: C, 68.77; H, 8.63.

12-Oxo[4.4.3]propell-3-ene (17). To 18.2 g (63.7 mmol) of the above diester in 220 ml of dry benzene was added 24 ml (19 g, 0.41 mol) of absolute ethanol and 8.3 g (0.36 g-atom) of sodium metal. This magnetically stirred solution was refluxed for 5 hr, diluted with water, and acidified with concentrated hydrochloric acid. The solution was extracted with ether and the etheral extract was washed with water and brine and dried. Removal of the solvent *in vacuo* gave 15.7 g (94.0%) of β-keto ester as a slightly yellow viscous oil; $\nu_{\mathrm{max}}^{\mathrm{neat}}$ 2890, 2840, 1760, 1720, and 1040 cm^{-1}.

To a magnetically stirred solution of 15.7 g (59.8 mmol) of β-keto ester in 210 ml of glacial acetic acid was added 30 ml of water and 30 ml of concentrated hydrochloric acid and the solution was refluxed for 5 hr. The solution was diluted with water (750 ml) and extracted with ether (3 × 300 ml), and the extracts were washed with 0.5 *N* sodium hydroxide solution until the wash solutions were alkaline, then with saturated salt solution and dried. Removal of the solvent gave 9.72 g (85.3%) of **17** as an oil. An analytical sample, mp 54.5–56.0°, was obtained after preparative vpc (6 ft × 0.25 in., 5% SF-96 on Chromosorb G, 160°): $\nu_{\mathrm{max}}^{\mathrm{CHCl_3}}$ 1740 cm^{-1}; nm $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.62 (m, 2, olefinic), 2.18 (center of AB quartet, J = 18 Hz, 4, $-CH_2CO-$), 2.02 (m, 4, allyl), and 1.47 (br s, 8, methylenes).

Anal. Calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.54. Found: C, 82.06; H, 9.60.

12,12-Dioxyethylene[4.4.3]propell-3-ene. To a magnetically stirred solution of 9.06 g (47.7 mmol) of **17** in 250 ml of dry benzene was added 0.5 g of *p*-toluenesulfonic acid and 22 g (0.35 mol) of ethylene glycol and the mixture was refluxed for 48 hr in a Dean–Stark apparatus whose receiver contained anhydrous sodium sulfate. Over the period of reflux, the solvent was removed slowly

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(46) W. B. Scott and R. E. Pincock, *J. Org. Chem.*, **32**, 3374 (1967).

through the water separator and the sodium sulfate was replaced every 12 hr. Additional dry solvent was added as needed. The solution was diluted with ether, washed with 10% potassium carbonate solution, water, and saturated sodium chloride solution, and dried. Removal of the solvent gave a dark oil which was distilled to afford 7.44 g (67.0%) of ketal as a clear viscous oil, bp 94–96° (0.05 mm). Preparative vpc (6 ft × 0.25 in., 5% SF-96 on Chromosorb G, 175°) gave an analytical sample: $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.58 (m, 2, olefinic), 3.83 (s, 4, $-CH_2O-$), 1.63, 1.87, 1.95, and 2.18 (AB pattern, $J = 14$ Hz, 4, five-membered ring methylene), 1.98 (br s, 4, allyl), and 1.45 (br s, 8, cyclohexane ring).

Anal. Calcd for $C_{15}H_{22}O_{22}$: C, 76.88; H, 9.46. Found: C, 76.62; H, 9.38.

12-Oxo[4.4.3]propella-2,4-diene (18). To a magnetically stirred solution of 97 mg (0.41 mmol) of ketal in 45 ml of dry methylene chloride under nitrogen at −78° was added dropwise over a period of 5 min 66 mg (0.41 mmol) of bromine in 6 ml of dry methylene chloride. After addition was complete, stirring was continued for 30 min and the solution was allowed to warm to room temperature. The solvent was removed *in vacuo* (no heat) to afford 162 mg of a clear waxy solid. To a magnetically stirred solution of this dibromide in 50 ml of hexamethylphosphoramide was added 420 mg (10 mmol) of lithium chloride and 740 mg (10 mmol) of lithium carbonate (both salts were dried prior to use) and the slurry was stirred at 90–95° for 20 hr under a dry nitrogen atmosphere. After cooling to room temperature, the solution was diluted with water and extracted three times with pentane. The combined extracts were washed with water (3×), 20% hydrochloric acid solution (3×), water and saturated sodium chloride solution and dried. Evaporation of the solvent gave a yellow liquid which was chromatographed on alumina. Elution with pentane and ether–pentane (1:1) gave a small amount of a volatile oil which was discarded. Elution with ether and then chloroform–ether (1:1) gave a light yellow oil which showed two volatile components by vpc in a ratio of ∼95:5. The minor peak was isolated by preparative vpc (6 ft × 0.25 in., 5% SF-96 on Chromosorb G, 125°) to yield *ca.* 2 mg of unreacted **17**. Isolation of the major component (shortest retention time) afforded 19 mg (0.10 mmol, 25%) of diene ketone **18** as a colorless oil: $\nu_{\max}^{\mathrm{neat}}$ 1740 cm^{-1}; $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.68 (A_2B_2 pattern, 4, olefinic), 2.28 (s, 4, $-CH_2CO-$), and 1.45 (s, 8, methylenes); $\lambda_{\max}^{\mathrm{isooctane}}$ 315 nm (ϵ 130), 304 (280), 294 sh (510), 277 (2300), 266 (2500), and 257 sh (1800); *m/e* 188.1197 (calcd 188.1201).

Anal. Calcd for $C_{13}H_{16}O$: C, 82.93; H, 8.57. Found: C, 82.67; H, 8.61.

Bicyclo[4.2.1]nona-2,4,7-trien-9-one (19). To a stirred solution containing 58 mg (0.43 mmol) of **10a** and 37 mg (0.43 mmol) of 2-pyrrolidone in 2.5 ml of freshly distilled tetrahydrofuran was added dropwsie 215 mg (0.43 mmol) of pyrrolidone hydrotribromide dissolved in 10 ml of the same solvent during 30 min at 25° in the absence of light. As reaction proceeded, insoluble pyrrolidone hydrobromide precipitated as a white solid. After 1.5 hr, the mixture was filtered and concentrated *in vacuo*. The residual material was taken up in ether, refiltered, washed with water and brine, dried, and evaporated.

To the unpurified α-bromo ketone dissolved in 5 ml of dry dimethyl sulfoxide was added with stirring 58 mg (20% excess) of freshly sublimed potassium *tert*-butoxide in one portion at 25°. The mixture which immediately developed a dark color was treated dropwise after 15 min with 20 ml of ice-water and extracted exhaustively with pentane. The combined organic layers were washed several times with water, dried, and evaporated. The product ketone (**19**) was isolated by preparative scale vpc purification on the SE-30 column at 95°, 17 mg (30%). The spectral characteristics were identical with those of an authentic sample.[20] There was also isolated 10% of unchanged **10a**.

Photoisomerization of 19. A solution of 2.4 g of **19** and 3.0 g of Michler's ketone in 800 ml of benzene was purged with nitrogen and photolyzed through Pyrex with a 450-W Hanovia lamp for 2.5 hr. The solution was concentrated and the residue was extracted with pentane. The combined pentane solutions afforded upon evaporation a solid which when sublimed (40–60°, 8 mm) furnished 1.88 g (78.5%) of barbaralone (**20**) as colorless crystals, mp 50–51°, identical with known samples.[47]

7,8-Dimethylbicyclo[4.2.1]nona-2,4,7-trien-9-one (21). To a solution containing 602 mg (3.72 mmol) of **10b** and 368 mg (3.72 mmol) of 2-pyrrolidone dissolved in 100 ml of dry tetrahydrofuran was added dropwise a solution containing 1.84 g (3.7 mmol) of pyrrolidone hydrotribromide in 100 ml of the same solvent. After 4 hr at 25°, this mixture was processed as above to give crude α-bromo ketone **1b** which was exposed for 30 min to the action of 1.70 g (15.2 mmol) of sublimed potassium *tert*-butoxide in 100 ml of dry dimethyl sulfoxide. Vpc purification of **21** furnished 97 mg (16%) of low melting solid: $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.68–5.97 (m, 4, olefinic), 2.80–3.17 (m, 2, bridghead), and 1.77 (s, 6, methyls); $\lambda_{\max}^{\mathrm{isooctane}}$ 218 nm (ϵ 2040), 273 (1910), 283 (1840), and 322 (580); *m/e* 160.0885 (calcd 160.0888).

The semicarbazone of **21** was obtained as colorless crystals, mp 212.5–214° dec, from aqueous ethanol.

Anal. Calcd for $C_{12}H_{15}N_3O$: C, 66.34; H, 6.96; N, 19.34. Found: C, 66.12; H, 7.13; N, 19.17.

7,8-Dimethylbicyclo[4.2.1]non-7-en-9-one (22). Hydrogenation of **21** (26 mg) was effected by the use of 10% palladium on carbon in ethyl acetate at atmospheric pressure. The solution was filtered through a pad of Celite, concentrated *in vacuo*, and subjected to vpc purification on the SE-30 column at 130° to afford 7 mg of **22**: $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 2.58–2.70 (m, 2, bridgehead), 1.65 (s, 6, methyls), and 1.25–1.83 (m, 8, methylenes); *m/e* 164.1200 (calcd 164.1201). A 2,4-dinitrophenylhydrazone was prepared, mp 114–116°.

Anal. Calcd for $C_{17}H_{20}N_4O_4$: C, 59.29; H, 5.85. Found: C, 59.29; H, 5.99.

1,2-Dimethylcyclooctatetraene (23). A solution of 10 mg of **21** in 9 ml of dry ether previously purged with nitrogen was irradiated in a quartz vessel with 2537 Å light (Rayonet reactor) for 15 min. The solution was concentrated and the hydrocarbon product was isolated by vpc methods; 7 mg (85%). The spectra of this material were identical with those of an authentic sample.[39]

3,4-Dimethyltricyclo[3.3.1.0^{2,8}]nona-3,6-dien-9-one (24). A solution of 65 mg (0.406 mmol) of **21** and 65 mg of 4,4′-bis(dimethylamino)benzophenone (Michler's ketone) in 30 ml of dry benzene was purged with nitrogen and irradiated through quartz at 0° for 2 hr with a 450-W Hanovia arc. The resultant yellow solution was filtered and evaporated to give 67 mg of crude mixture. Separation of **24** was effected by preparative scale vpc on the SE-30 column. There was obtained 17 mg (26%) of colorless liquid: $\nu_{\max}^{\mathrm{neat}}$ 1700 cm^{-1}; $\lambda_{\max}^{\mathrm{isooctane}}$ 271 nm (sh on end absorption, ϵ 3580); $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ (40°) 5.17–5.83 (m, 2, olefinic), 1.92–2.95 (m, 4), 1.78 and 1.75 (s, 3 each, methyls); *m/e* 160.0885 (calcd 160.0888).

1,2,3,4,5,10-Hexahydro-5,10-methanobenzocycloocten-11-one (26). To a magnetically stirred solution of 104 mg (0.553 mmol) of **18** in 20 ml of tetrahydrofuran in the dark was added dropwise over a period of 3.5 hr 274 mg (0.553 mmol) of pyrrolidone hydrotribromide in 50 ml of the same solvent. The solution was allowed to stir for 12 hr in the dark at room temperature. The solvent was removed *in vacuo* (no heat) and the residue was triturated with ether and filtered to remove the white crystalline insoluble hemihydrobromide. The ethereal solution was washed with water (3×) and brine and dried. Evaporation of the solvent (no heat) gave α-bromo diene ketone **2** as a viscous yellow oil. To a magnetically stirred solution of this oil in 50 ml of dry dimethyl sulfoxide under dry nitrogen was added in one portion 560 mg (5.0 mmol) of potassium *tert*-butoxide, and the crimson solution was stirred at ambient temperature for 30 min. The mixture was diluted with cold water (100 ml) and extracted with pentane (3 × 100 ml). The combined extracts were washed with water (3×) and saturated salt solution and dried. Evaporation of the solvent gave 98 mg of a yellow oil which showed two volatile components by vpc. Preparative vpc (6 ft × 0.25 in., 5% SF-96 on Chromosorb G, 125°) afforded a small amount of unreacted diene ketone **18** (first peak) and 23 mg (24%) of **26** as a colorless liquid: $\nu_{\max}^{\mathrm{neat}}$ 1780 cm^{-1}; $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.75 (br s, 4, olefinic), 2.82–3.07 (m, 2, bridgehead), 1.85–2.35 (m, 4, allyl), and 1.67 (br s, 4, methylene); $\lambda_{\max}^{\mathrm{isooctane}}$ 318 nm (ϵ 390), 283 (1380), 273 (1410), and 217 sh (2590); *m/e* 186.1042 (calcd 186.1044).

Bicyclo[6.4.0]dodeca-1,3,5,7-tetraene (27). A solution of 22 mg (0.18 mmol) of **26** in 10 ml of ether contained in a quartz test tube was irradiated employing a Rayonet reactor fitted with a bank of 2537-Å germicidal lamps. After 15 min, vpc analysis of the reaction mixture indicated complete loss of starting material and formation of a lone photoproduct. The solvent was removed with a gentle stream of nitrogen and the residue was subjected to preparative vpc (4 ft × 0.25 in., 5% SF-96 on Chromosorb G, 80°) to give 5 mg (30%) of **27**: $\nu_{\max}^{\mathrm{neat}}$ 2910, 2850, 2780, 1430, 795, 785, 745, 714, and 685 cm^{-1}; $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ 5.50–5.97 (m, 6, olefinic), and 1.5–2.5 (br m, 8); $\lambda_{\max}^{\mathrm{isooctane}}$ 280 sh nm (ϵ 290).

Anal. Calcd for $C_{12}H_{14}$: C, 91.08; H, 8.92. Found: C, 91.02; H, 9.07.

***cis*-1,2-Bis(methanesulfonyloxymethyl)-1,2-dimethylcyclohex-4-ene**

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[47] The authors are indebted to Dr. M. J. Broadhurst for this experiment.

(28). To an ice-cold stirred solution of *cis*-1,2-bis(hydroxymethyl)-1,2-dimethylcyclohex-4-ene (19.3 g, 0.114 mol) in 300 ml of dry pyridine was added 71.5 g (0.625 mol) of methanesulfonyl chloride at a rate such that the solution temperature remained below 5°. The mixture was stirred an additional 2 hr at 5°, poured onto ice, and treated with 300 ml of 10% hydrochloric acid solution (total volume 1 l.). After several hours at 0°, the crystalline dimesylate was separated by filtration and recrystallized from 95% ethyl alcohol to give 31.9 g (86%) of white crystals: mp 85–86°; $\nu_{\max}^{\text{Nujol}}$ 1350 and 1170 cm^{-1}; $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 5.63 (t, J = 1.5 Hz, 2, olefinic), 4.17 (s, 4, $-CH_2O-$), 3.05 (s, 6, CH_3SO_2), 2.03 (t, J = 1.5 Hz, 4, allylic), and 1.07 (s, 6, CH_3).

Anal. Calcd for $C_{12}H_{22}O_6S_2$: C, 44.15; H, 6.79; S, 19.65. Found: C, 44.17; H, 6.72; S, 19.35.

***cis*-1,6-Dimethyl-8-thiabicyclo[4.3.0]non-3-ene 8,8-Dioxide (30).** A mechanically stirred slurry of 72 g (0.3 mol) of sodium sulfide nonahydrate and 200 ml of freshly distilled hexamethylphosphoramide was heated under vacuum (~15 mm) until the temperature of the distillate reached 130° and was then cooled to 25°. Dimesylate **28** (31.9 g, 0.098 mol) was introduced in one portion and the mixture was heated at 120° under nitrogen for 17 hr. After cooling, ice water (1 l.) was added and this solution was extracted with ether (5 × 200 ml). The combined organic layers were washed with water, dried, and evaporated. Chromatography of the residue on neutral alumina (elution with petroleum ether–ether 95:5) afforded 15.2 g (93%) of **29** as a white, low melting, crystalline solid.

Oxidation of 15.2 g (0.09 mol) of **29** with 268 ml of 0.69 *M* monoperphthalic acid (0.185 mol) in 175 ml of ether gave 15.2 g (84%) of **30** as shiny white leaflets: mp 152–153°; $\nu_{\max}^{\text{Nujol}}$ 1325, 1135, and 1115 cm^{-1}; $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 5.63 (t, J = 1.5 Hz, 2, olefinic), 3.08 (s, 4, $-CH_2SO_2-$), 1.78–2.72 (m, 4, allylic), and 1.22 (s, 6, methyl).

Anal. Calcd for $C_{10}H_{16}O_2S$: C, 59.96; H, 8.05; S, 16.01. Found: C, 59.93; H, 7.92; S, 15.83.

***cis*-1,6-Dimethyl-8-thiabicyclo[4.3.0]nona-2,4-diene 8,8-Dioxide (31).** A mixture of 15.1 g (0.075 mol) of **30**, 14.8 g (0.083 mol) of *N*-bromosuccinimide, and a catalytic quantity of benzoyl peroxide in 700 ml of carbon tetrachloride was refluxed with stirring for 15 min under nitrogen. The mixture was cooled to 10°, filtered, and evaporated. To a solution of the residue in 100 ml of dry tetrahydrofuran was added 10 g of sodium methoxide and the mixture was heated at reflux for 24 hr under nitrogen. After cooling to 0°, ice–water (25 ml) was added dropwise, the layers were separated, and the aqueous phase was extracted with ether–methylene chloride (3:1). The combined organic layers were washed with brine, dried, and evaporated to give a yellow oil, sublimation of which at 110° and 0.2 mm furnished 1.94 g (84%) of sulfone **31** as white crystals; mp 93–94.5°, from ethyl ether; $\nu_{\max}^{\text{Nujol}}$ 1110 and 1290 cm^{-1}; $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 5.45–6.20 (m, 4, olefinic), 3.33 (d, J = 13 Hz, 2, $>CHSO_2-$), 3.02 (d, J = 13 Hz, second half of AB pattern, 2, $>CHSO_2$), and 1.25 (s, 6, methyl).

Anal. Calcd for $C_{10}H_{14}O_2S$: C, 60.59; H, 7.12; S, 16.15. Found: C, 60.31; H, 7.04; S, 15.98.

7-Chloro-1,6-dimethyl-8-thiabicyclo[4.3.0]nona-2,4-diene 8,8-Dioxide (32 and 33). Reduction of **31** (2.5 g, 12.6 mmol) with 2.40 g (63.0 mmol) of lithium aluminum hydride in 150 ml of ether (reflux 63 hr), followed by an alkaline work-up and chromatography on alumina, afforded 1.57 g (76%) of diene sulfide as a white low melting crystalline solid: $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 5.28–6.03 (m, 4, olefinic), 3.03 and 2.75 (center of AB doublets, J = 10 Hz, 4, $-CH_2S-$), and 1.03 (s, 6, methyl).

A solution of 889 mg (5.35 mmol) of this sulfide in 20 ml of carbon tetrachloride was heated at reflux for 2 hr in the presence of *N*-chlorosuccinimide (786 mg, 5.89 mmol) under a nitrogen atmosphere. The crude product was directly oxidized with 11.8 mmol of monoperphthalic acid in 20 ml of ether (25°, 24 hr) and yielded 1.08 g (87%) of epimeric α-chloro sulfone mixture (ratio of **32**:**33** was determined to be 63:37 by nmr methods).

Chromatography of the mixture on silica gel (gradient elution with 1–20% ether in hexane) caused the minor isomer (**33**) to be eluted first: mp 91.5–92°, from ether–hexane; $\nu_{\max}^{\text{Nujol}}$ 1320 and 1120 cm^{-1}; $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 5.25–6.25 (m, 4, olefinic), 4.90 (s, 1, $>CHCl$), 3.33 and 3.05 (center of AB doublets, J = 13.5 Hz, 2, $-CH_2SO_2-$), 1.47–1.12 (s, 3 each, methyls).

Anal. Calcd for $C_{10}H_{13}ClO_2S$: C, 51.62; H, 5.63; Cl, 15.24. Found: C, 51.58; H, 5.65; Cl, 15.38.

Isomer **32** eluted somewhat later: mp 90–91°, from ether–hexane; $\nu_{\max}^{\text{Nujol}}$ 1325 and 1125 cm^{-1}; $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 5.42–6.25 (m, 4, olefinic), 5.18 (s, 1, $>CHCl$), 3.43 and 3.12 (center of AB doublets, J = 13.5 Hz, 2, $-CH_2SO_2-$), and 1.32 and 1.16 (s, 3 each, methyl).

Anal. Calcd for $C_{10}H_{13}ClO_2S$: C, 51.62; H, 5.63; Cl, 15.24. Found: C, 51.33; H, 5.61; Cl, 15.48.

7,8-Dimethyl-9-thiabicyclo[4.2.1]nona-2,4,7-triene 9,9-Dioxide (34). To a solution of 3.32 g (0.0144 mol) of an unpurified mixture of **32** and **33** in 100 ml of dry dimethyl sulfoxide was added in one portion 1.61 g (14 mmol) of potassium *tert*-butoxide. The temperature slowly rose from 25 to 35°. After 10 min, the solution was cooled to 20° and 300 ml of ice–water was cautiously added and the mixture was extracted with ether (5 × 100 ml). Normal processing afforded 230 mg (17%) of **34** as white crystals: mp 202° dec, from methylene chloride–ether; $\nu_{\max}^{\text{Nujol}}$ 1600, 1290, and 1100 cm^{-1}; $\lambda_{\max}^{\text{C}_2\text{H}_5\text{OH}}$ 282 nm (ϵ 2100); $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 5.83–6.08 (m, 4, olefinic), 3.62–3.95 (m, 2, bridgehead), and 1.88 (s, 6, methyl). Additional material, obtained by acidifying the aqueous layers and extraction with ether, brought the total quantity of isolated **34** to 509 mg (27%).

Anal. Calcd for $C_{10}H_{12}O_2S$: C, 61.19; H, 6.16; S, 16.34. Found: C, 61.21; H, 6.41; S, 16.08.

Photolysis of 34. A solution of **34** (68 mg) in 6 ml of acetone was irradiated with a 450-W Hanoria lamp through a Vycor filter for 4 hr. The solution was concentrated and preparative scale vpc purification was employed to obtain 5 mg (11%) of 1,2-dimethylcyclooctatetraene (**23**), identical in all respects with the material obtained earlier.

9-Thiabicyclo[4.2.1]nona-2,4,7-triene 9,9-Dioxide (36). To a stirred solution of 1.485 g (9.64 mmol) of 9-thiabicyclo[4.2.1]nona-2,4,7-triene 9-oxide[25] in 100 ml of methylene chloride was added dropwise during 1 hr at 0° 1.86 g (9.65 mmol) of *m*-chloroperbenzoic acid (89.5%) dissolved in 50 ml of the same solvent. The solution was stirred overnight at 25° and then washed with 25 ml portions of 0.5 *M* sodium hydroxide solution until alkaline and with water until neutral. Evaporation of the dried organic phase afforded 1.23 g (75%) of **36** as shiny white crystals: mp 193.5° dec, from methylene chloride–ether; $\nu_{\max}^{\text{Nujol}}$ 1390, 1125, and 1100 cm^{-1}; $\lambda_{\max}^{\text{C}_2\text{H}_5\text{OH}}$ 279 nm (ϵ 2340); *m/e* calcd 168.0244, found 168.0242; $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 5.80–6.37 (m, 6, olefinic), and 3.78–4.15 (m, 2, bridgehead).

Anal. Calcd for $C_8H_8O_2S$: C, 57.12; H, 4.79. Found: C, 56.90; H, 4.79.

1,2,3,4,5,10-Hexahydro-5,10-epithiobenzocyclooctene 11,11-Dioxide (38a). To a magnetically stirred solution of 109 mg (0.970 mmol) of potassium *tert*-butoxide in 50 ml of dry dimethyl sulfoxide under nitrogen was added 92.1 mg (0.356 mmol) of α-chloro sulfone **37a**,[23] and the intensely green solution was stirred for 20 min. With cooling, water (50 ml) was added and the solution was extracted with ether (3 ×). The combined extracts were washed with water and saturated salt solution, dried, and evaporated to afford 43.8 mg of crude **38a** as a yellow solid. Recrystallization from ether–hexane gave 32.1 mg (56.4%) of white crystals: mp 167.5–169.0° dec; $\nu_{\max}^{\text{CHCl}_3}$ 1310, 1145, 1135, and 1100 cm^{-1}; $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 5.95 (m, 4, olefinic), 3.68 (br s, 2, $>CHSO_2-$), 2.13 (br s, 4, allyl), and 1.74 (br s, 4, methylene); $\lambda_{\max}^{\text{C}_2\text{H}_5\text{OH}}$ 282 nm (ϵ 2100).

Anal. Calcd for $C_{12}H_{14}O_2S$: C, 64.85; H, 6.35; S, 14.10. Found: C, 64.72; H, 6.33; S, 14.33.

1,2,3,4,5,6,7,8,9,10-Decahydro-5,10-epithiobenzocyclooctene 11,11-Dioxide (40). A magnetically stirred solution of 38.7 mg (0.174 mmol) of **38a** in 25 ml of ethyl acetate was hydrogenated at atmospheric pressure over *ca.* 100 mg of 10% palladium on charcoal. After the uptake of 2 equiv of hydrogen (15 min), the reaction mixture was filtered through a silica gel column and the solvent evaporated to yield 38.9 mg (99.5%) of **40** as white crystals: mp 138.0–139.0° from ether–hexane; $\nu_{\max}^{\text{CHCl}_3}$ 1290, 1160, and 1110 cm^{-1}; $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 3.55 (br s, 2, $>CHSO_2-$) and 1.6–2.4 (envelope, 16, allyl and methylene).

Anal. Calcd for $C_{12}H_{18}O_2S$: C, 63.70; H, 8.02; S, 14.14. Found: C, 63.62; H, 8.01; S, 14.15.

Bicyclo[6.4.0]dodeca-1,7-diene (41). A 208 mg (0.923 mmol) sample of **40** was passed through a quartz chip packed quartz tube heated at 500° at 10 mm with a slow stream of nitrogen. There was obtained 110.2 mg (78.8%) of diene **41** as a pale yellow oil. Preparative vpc (5 ft × 0.25 in., 5% Carbowax 20M on Chromosorb G, 130°) gave an analytical sample of the hydrocarbon as a clear oil: $\nu_{\max}^{\text{neat}}$ 2910, 2850, 2800, 1445, 830, and 740 cm^{-1}; $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 5.6 (br s, 2, olefinic), 2.0 (br s, 8, allyl), and 1.2–1.7 (envelope, 8, methylene); $\lambda_{\max}^{\text{isooctane}}$ 228 nm (ϵ 5500) [lit.[27] $\lambda_{\max}^{\text{C}_2\text{H}_5\text{OH}}$ 221 (6640)].

Anal. Calcd for $C_{12}H_{18}$: C, 88.82; H, 11.18. Found: C, 88.60; H, 11.12.

***cis*- and *trans*-Bicyclo[6.4.0]dodecanes. A. From Reduction of Bicyclo[6.4.0]dodeca-1,7-diene (41).** A solution of 13.5 mg (0.084 mmol) of **41** in ethyl acetate was hydrogenated at atmospheric pressure over platinum oxide for 60 hr. Filtration and vpc analysis showed that two products had been formed in a 5:1 ratio. The isomers were separated by preparative vpc (12 ft × 0.25 in., 10% Carbowax 6000 on Chromosorb G, 160°).

The major isomer had the longest vpc retention time: $\nu_{\max}^{\text{neat}}$ 2850, 2800, 2660, 1470, 1450, 1345, and 1000 cm^{-1}; $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 1.22 and 1.53 (centers of two broad overlapping singlets, high field signal has greater height).

Anal. Calcd for $C_{12}H_{22}$: C, 86.66; H, 13.34. Found: C, 86.75; H, 13.34.

The minor isomer had the shortest retention time: $\nu_{\max}^{\text{neat}}$ 2850, 2800, 2660, 1480, 1460, 1445, and 1355 cm^{-1}; $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 1.19 and 1.59 (centers of two broad overlapping singlets, low field signal has greatest height).

Anal. Calcd for $C_{12}H_{22}$: C, 86.66; H, 13.34. Found: C, 86.74; H, 13.22.

B. Reduction of Benzocyclooctene. A solution of 1.56 g (9.65 mmol) of benzocyclooctene in 100 ml of glacial acetic acid was hydrogenated for 72 hr over 250 mg of 5% rhodium on alumina at 60° under 50 psi hydrogen in a Paar hydrogenation apparatus. The solution was diluted with water (600 ml) and extracted with pentane (3 × 250 ml). The extracts were washed with water, dried, and evaporated through a metal helix-packed column. Analysis of the clear residue by vpc showed two products were present in a 5:1 ratio. The isomers were separated by preparative vpc (12 ft × 0.25 in., 10% Carbowax 6000 on Chromosorb G, 160°) and were identical in every respect with those obtained above.

Pyrolysis of 38a. A 120 mg (0.540 mmol) sample of **38a** was passed through a quartz chip packed quartz tube heated at 400° at 10 mm with a slow stream of nitrogen. There was obtained 78.3 mg (91.5%) of tetraene **27** as a yellow oil. An analytical sample of the yellow liquid obtained by preparative vpc was identical in all respects with that isolated above.

Photolysis of 38a. A solution of 10.7 mg (0.048 mmol) of **38a** in 3 ml of acetone was irradiated with a 200-W Hanovia lamp equipped with Corex optics. Monitoring of the photolysis by tlc showed no sulfone remained after 30 min. Preparative vpc (5 ft × 0.25 in., 5% Carbowax 20M on Chromosorb G, 130°) was used to isolate the sole volatile component. It was spectrally identical with authentic **27**.

2,3,4,5,6,11-Hexahydro-6,11-epithio-1*H*-cycloheptacyclooctene 12,12-Dioxide (38b). To a magnetically stirred solution of 666 mg (2.44 mmol) of α-chloro sulfone **37b**[23] in 75 ml of dry dimethyl sulfoxide under nitrogen was added 863 mg (7.70 mmol) of potassium *tert*-butoxide, and the dark green solution was stirred for 15 min. With cooling, 25 ml of ice–water was added and the solution was extracted three times with ether. The combined extracts were washed, and dried, and the solvent was removed to afford 322 mg (55.8%) of **38b**: mp 149.5–150.5°, from ether–methylene chloride; $\nu_{\max}^{\text{CHCl}_3}$ 1310, 1130, and 1110 cm^{-1}; $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 5.90–6.10 (m, 4, olefinic), 3.73–3.97 (m, 2, >$CHSO_2$–), 2.22–2.58 (m, 4, allyl), and 1.35–1.95 (m, 6, methylene).

Anal. Calcd for $C_{13}H_{16}O_2S$: C, 66.08; H, 6.83; S, 13.55. Found: C, 66.06; H, 6.94; S, 13.32.

Bicyclo[6.5.0]trideca-1,3,5,7-tetraene (39). A solution of 87.0 mg (0.368 mmol) of **38b** in acetone was irradiated with a 450-W Hanovia lamp through a Corex filter for 60 min. By preparative vpc (6 ft × 0.25 in., 5% SF-96 on Chromosorb G, 130°) there was isolated 23.0 mg (37%) of **39** as a yellow oil: $\nu_{\max}^{\text{neat}}$ 2960, 2890, 2820, 1450, and 690 cm^{-1}; $\lambda_{\max}^{\text{isooctane}}$ 285 sh nm (ε 123); $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 5.53–5.90 (m with sharp singlet at 5.75, 6, olefinic), 2.0–2.5 (m, 4, allyl), and 1.57 (br s, 6, methylene).

Anal. Calcd for $C_{13}H_{16}$: C, 90.64; H, 9.36. Found: C, 90.60; H, 9.52.

5,10-Dihydro-5,10-epithiobenzocyclooctene 11,11-Dioxide (43). To a magnetically stirred solution of 234 mg (0.931 mmol) of α-chloro sulfone **42**[23] in 30 ml of dry dimethyl sulfoxide under nitrogen was added 112 mg (1.00 mmol) of potassium *tert*-butoxide, and the deep green solution was stirred for 30 min. With cooling, 50 ml of water was added and the solution was acidified with concentrated hydrochloric acid. The aqueous solution was extracted with chloroform and the extract was washed with water and brine and dried. Evaporation of the solvent and recrystallization from methanol–chloroform gave 137 mg (68.4%) of **43** as a white crystalline solid: mp 269.0–271.0° dec, from ether–chloroform; $\nu_{\max}^{\text{KBr}}$ 1310, 1190, and 1100 cm^{-1}; $\delta_{\text{TMS}}^{\text{DMSO-}d_6}$ 7.43 (s, 4, aromatic), 5.93 (br s, 4, olefinic), and 4.90–5.07 (m, 2, >$CHSO_2$–); $\lambda_{\max}^{C_2H_5OH}$ 267 sh (ε 2280), 273 (2470), and 278 sh (2280).

Anal. Calcd for $C_{12}H_{10}O_2S$: C, 66.05; H, 4.62; S, 14.66. Found: C, 65.77; H, 4.61; S, 14.82.

Benzocyclooctatetraene (44) from 43. A solution of 25.0 mg (0.116 mmol) of **43** in acetone was irradiated for 3 hr with a 200-W Hanovia lamp equipped with a Vycor filter. Analysis of the photolysis solution showed only one volatile component. Preparative vpc (6 ft × 0.25 in., 5% SF-96 on Chromosorb G, 120°) gave 16.2 mg (91%) of crystalline benzocyclooctatetraene (**44**), mp 49–50°, identical upon spectral comparison with an authentic sample.[48]

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(48) L. B. Anderson and L. A. Paquette, *J. Amer. Chem. Soc.*, **94**, 4915 (1972); L. Friedman and D. F. Lindow, *ibid.*, **90**, 2329 (1968).

Olefin Isomerizations Accompanying the Hydroformylation of 3-Methyl-1-hexene-*3*-d_1[1]

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Abstract: The dicobalt octacarbonyl catalyzed hydroformylation of 3-methyl-1-hexene-*3*-d_1 (**1**-*d*) followed by oxidation and esterification gives 3.1% methyl 3-(ethyl-*1*-d_1)hexanoate (**3**-*d*) in addition to the normal hydroformylation products. The Eu(DPM)$_3$-shifted nmr spectra of **3**-*d* demonstrated that a 1,2 migration of deuterium had occurred in the hydroformylation of **1**-*d*. This result taken together with Pino's observation that the hydroformylation of optically active **1** gives **3** with 70% retention of optical activity demonstrates that **3**-*d* is formed by multiple isomerizations of the complexed alkene which immediately precede hydroformylation. The rate of isomerization of the complexed alkene consequently must be greater than the rate of decomplexation. A mechanism, previously proposed by Pino, involving direct insertion of cobalt into a carbon–hydrogen bond of a methyl group, is directly refuted by the results obtained here.

Hydridotetracarbonylcobalt is the active catalyst in the dicobalt octacarbonyl catalyzed hydroformylation of olefins.[2] Depending on the reaction conditions employed, olefin isomerization accompanying hydro-

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(1) Some of the results described in this paper have appeared in preliminary form: C. P. Casey and C. R. Cyr, *J. Amer. Chem. Soc.*, **93**, 1280 (1971).

(2) For reviews of hydroformylation, see (a) A. J. Chalk and J. F. Harrod, *Advan. Organometal. Chem.*, **6**, 119 (1968); (b) R. F. Heck, *ibid.*, **4**, 243 (1966); (c) C. W. Bird, "Transition Metal Intermediates in Organic Synthesis," Academic Press, New York, N. Y., 1967, Chapter 6.