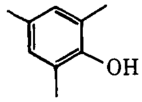
The second route developed to system **3** involves the intramolecular Diels–Alder reaction of a 6-acryloxy-2,4-cyclohexadienone formed by a novel variant of the Wessely oxidation. The feasibility of this pathway was investigated by treatment of mesitol (**12**) in acrylic acid with lead tetraacetate at room temperature. This gave the dienone **13**, which was not isolated, but was converted at 70° to **14**, mp 111–112° [$\lambda_{\max}^{\mathrm{CCl_4}}$ 5.58, 5.74 μ; $\lambda_{\max}^{\mathrm{MeOH}}$ 312 (ϵ 180) nm; $\delta^{\mathrm{CDCl_3}}$ 1.26 (s, 3 H), 1.44 (s, 3 H), 1.93 (d, J = 2 Hz, superimposed on m, 5 H), 2.84 (d of d of d, J = 9, 5, 2 Hz, 1 H), 3.30 (d of d, J = 5, 2 Hz, 1 H), 5.79 (br s, 1 H)]. The structure of the latter was established by its spectra and its conversion on treatment with aqueous base followed by periodic acid to the lactol **15** [$\lambda_{\max}^{\mathrm{CHCl_3}}$ 3–4, 5.71, 5.86 μ; $\delta^{\mathrm{C_5H_5N}}$ 1.50 (s, 3 H), 1.82 (s, 3 H), 2.23 (br s, 3 H), 2.45 (m, 1 H), 3.15 (m, 2 H), 3.53 (m, 1 H), 6.07 (br s, 1 H)]; this was converted by lead tetraacetate to **16**, mp 56–57.5° [$\lambda_{\max}^{\mathrm{CHCl_3}}$ 5.64 μ; $\delta^{\mathrm{CDCl_3}}$ 1.40 (s, 3 H), 1.42 (s, 3 H), 1.90 (d, J = 2 Hz, 3 H), 2.0–2.6 (m, 3 H), 3.19 (d of d, J = 4, 2 Hz, 1 H), 6.12 (br s, 1 H)], which on treatment with palladium/charcoal in refluxing 2-methoxyethanol gave 3,5-dimethylbenzoic acid.

The xanthene **17**[7] on treatment in acrylic acid with lead tetraacetate at room temperature gave the dienone **18**, which was not isolated but was converted at 80° to **19**, mp 116–118° [$\lambda_{\max}^{\mathrm{CHCl_3}}$ 5.58, 5.72 μ; $\lambda_{\max}^{\mathrm{MeOH}}$ (ϵ) 271 (1410), 275 (1380), 310 (200) nm; $\delta^{\mathrm{CDCl_3}}$ 1.39 (s, 3 H), 1.84 (d of d of d, J = 13, 11, 2 Hz, 1 H), 2.26 (d of d of d, J = 13, 3.5, 1.5 Hz, 1 H), 2.70 (d of d, J = 11, 1.5 Hz, 1 H), 3.42 (d of d of d, J = 7, 3.5, 2 Hz, 1 H), 3.59 (d, J = 2 Hz, 2 H), 6.28 (d of t, J = 7, 2 Hz, 1 H), 7.14 (m, 4 H)].



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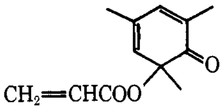

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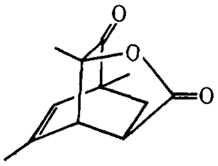

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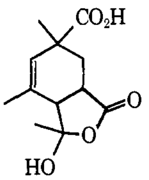

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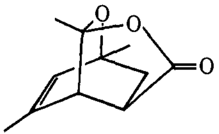

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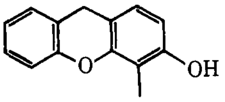

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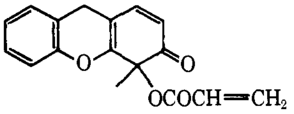

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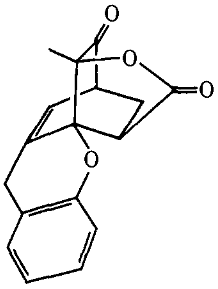

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(7) Prepared by reduction of 3-hydroxy-4-methylxanthone[8] with lithium aluminum hydride; *cf.* A. Mustafa and O. H. Hishmat, *J. Org. Chem.*, **22**, 1644 (1957).

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Acknowledgment. We thank the National Research Council of Canada for support of this work.

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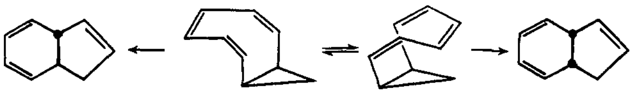
Received March 2, 1972

Epimerization at the 9 Position in Substituted Bicyclo[6.1.0]nona-2,4,6-trienes[1]

Sir:

Compounds containing the bicyclo[6.1.0] skeleton display a wide variety of rearrangements and have posed particularly vexing problems of mechanism.[2] The unsubstituted molecule[3–5] and 9-monosubstituted compounds[6–8] rearrange mainly to *cis*-dihydroindenes. 9,9-Dialkyl-substituted compounds, by contrast, give predominantly *trans*-dihydroindenes.[9–11] When the 9 position is substituted with a cyano group,[12,13] a spirofluorene[14] or a spirocyclopentadiene,[15] bicyclo-[4.2.1]nonatrienes are produced.

It has been suggested[9,10] that the *cis*-dihydroindenes are formed from the coiled arrangement (**1**) and the *trans*-dihydroindenes from the extended form (**2**).



2 **1**

This explains the reluctance of the 9,9-disubstituted compounds to give the cis product as the coiled form should be severely destabilized by endo-9 substitution.[16]

A long-standing problem has been the behavior of *endo*-9-methylbicyclo[6.1.0]nonatetraene (**3a**). Although one might reasonably expect this compound to mimic the 9,9-dimethyl substance, which also possesses an endo methyl group, it does not. Like its epimer **3b**, the products of rearrangement are mainly *cis*-dihydroindenes.[8] The recent report[17] that the products of thermal rearrangement of **3a** are not identical with

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(1) Support of this work by the National Science Foundation through Grants GP-12759 and 30797X is warmly acknowledged. We also express our appreciation for helpful comments by Professor Paul von R. Schleyer and Dr. F.-G. Klärner.

(2) For a review, see: S. W. Staley, *Intra-Sci. Chem. Rep.*, **5**, 149 (1971).

(3) E. Vogel, W. Wiedemann, H. Kiefer, and W. F. Harrison, *Tetrahedron Lett.*, 673 (1963).

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(5) W. Grimme, *Chem. Ber.*, **100**, 113 (1967).

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(7) G. J. Fonken and W. Moran, *Chem. Ind. (London)*, 1841 (1963).

(8) P. Radlick and W. Fenical, *J. Amer. Chem. Soc.*, **91**, 1560 (1969).

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(10) S. W. Staley and T. J. Henry, *ibid.*, **91**, 7787 (1969).

(11) W. Grimme, private communication, 1970.

(12) A. G. Anastassiou, R. P. Cellura, and E. Ciganek, *Tetrahedron Lett.*, 5267 (1970).

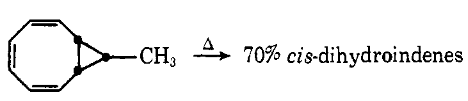
(13) F.-G. Klärner, *ibid.*, 3611 (1971).

(14) M. E. Hendrick, unpublished observation.

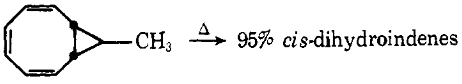
(15) D. Schönleber, *Chem. Ber.*, **102**, 1789 (1969).

(16) Conrotatory opening of the extended form to a cyclononatetraene containing a trans double bond followed by disrotatory closure allows formation of *trans*-dihydroindene. No mechanism has yet been proposed which accounts for the conversion of the coiled form to *cis*-dihydroindene without the intrusion of an orbital symmetry forbidden step or the intervention of diradicals.

(17) A. G. Anastassiou and R. C. Griffith, *Chem. Commun.*, 1301 (1971).



3a

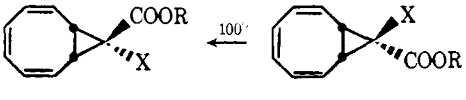


3b

those of **3b**, but merely similar, does little to resolve the difficulty which revolves around the relative absence of *trans*-dihydroindenes, the expected products of any compound bearing an endo methyl group.

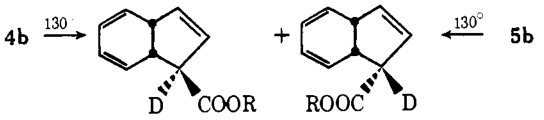
An attractive resolution of the problem would involve epimerization of **3a** to **3b** prior to rearrangement. This process has not been observed previously. We provide here a particularly clean example of such a reaction and suggest a mechanism.

Epimers **4a** and **5a** and **4b** and **5b** were prepared by



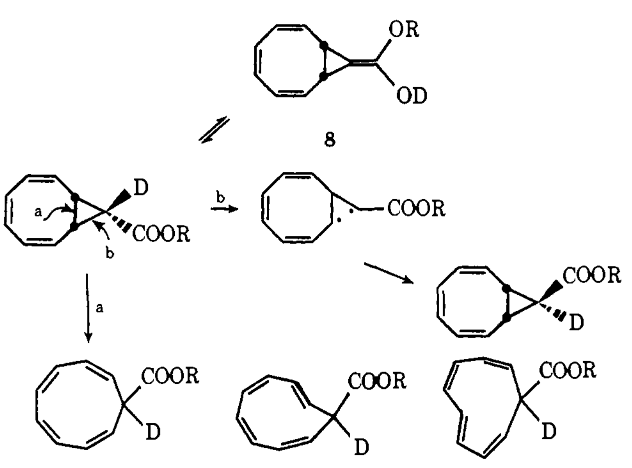
4a, X = H　　**5a**, X = H
4b, X = D　　**5b**, X = D

addition of methyl or ethyl diazoacetate and their deuterated analogs to cyclooctatetraene. Separation was achieved by careful column chromatography. At 130°, **4b** and **5b** were converted with half-lives of *ca.* 1 hr to an 86:14 mixture of **6** and **7**. The major isomer corresponding to that proved to have the carboalkoxy group cis to the bridgehead hydrogens,[6] and both **6** and **7** could be shown to possess a cis ring junction from determination of the coupling constant between the two bridgehead hydrogens. Both **6** and **7** had $J = 12.5$ Hz. For comparison, a value of 12 Hz was quoted for other *cis*-8,9-dihydroindenes[8] and 20 Hz for *trans*-.[9] Integration of the spectra revealed that the deuterium atom and the ester group remained attached to the same carbon. This shows that shifts of the 9 substituents are not occurring in this system.[18] At 100°, at which temperature **6** and **7** were not formed, **5a** and **5b** were transformed into **4a** and **4b**, respectively, with a half-life of *ca.* 4 hr.



6　　**7**

Inversion at the 9 position can occur by three mechanisms; cleavage of either bond a or bond b or through formation of enol **8** followed by regeneration of the ester with stereospecific transfer of the deuterium atom from carbon to oxygen and back again. The epimerization of **4a** also proceeds readily in the gas phase, and pyrolysis of **4b** in CH_3OH (100° for 38 hr) results in no apparent exchange of deuterium for hydrogen. Moreover, 9-methyl-9-carbomethoxybicyclo[6.1.0]nonatriene (**9a**) is converted to the isomeric **9b** on heating to 160°.[22] In **9a**, formation of an enol is impossible.



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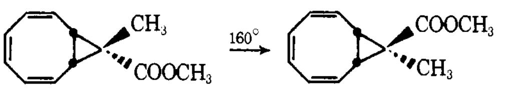
10　　**11**　　**12**



9a　　**9b**

Cleavage of bond a would lead to cyclononatetraenes **10**, **11**, and/or **12**. Precedent exists for the assumption that these would close directly to dihydroindenes without re-forming starting material.[23–26] Therefore we favor a mechanism dependent upon breaking bond b. Variations of this mechanism in which the eight-membered ring is closed to a bicyclic structure prior to cleavage of a cyclopropane bond can be constructed, but the basic arguments are not changed.

We cannot comment on the precise extent to which epimerization complicates the case of the monomethyl compounds, but such a process must now be explicitly considered. 9,9-Dialkyl-substituted compounds are reported not to undergo interconversion before rearrangement to dihydroindenes,[9–11] and at first sight this might seem to make epimerization in a 9-monomethyl compound unlikely. However, 9-alkyl groups should weaken the internal cyclopropane bond (bond a), and two alkyl groups should be more effective than one.[27–29] Perhaps this allows bond a to break first in the disubstituted compounds, while bond b breaks first in the monomethyl cases. We suggest a close reexamination of the rearrangements of *exo*- and *endo*-9-methylbicyclo[6.1.0]nonatriene.

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[18] Such a rearrangement has been shown not to occur in the parent system,[5,19] but does take place in several chlorinated compounds.[20,21]

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[22] Compound **9b** can be isolated in 20% yield from a crude reaction mixture. We thank Dr. F. O. Klärner for help in assigning the structures of **9a** and **9b**.

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Received September 29, 1971