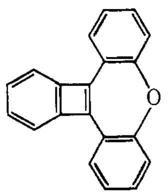
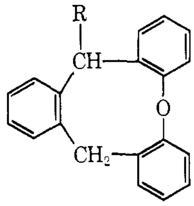
the benzenoid rings of biphenylene has been replaced by a $4n + 2$ five-membered or nine-membered heterocyclic ring. We now report the first example of a biphenylene analog (**1**) in which a benzenoid ring has been replaced by a $4n$ heterocyclic ring, namely an oxepin.

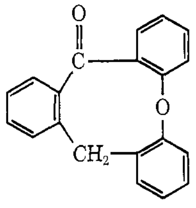
Oxidation of 10*H*,15*H*-tribenzo[*b*,*e*,*h*]oxonin (**2**)[3] by chromic acid in warm acetic acid gave, in 80% yield, the corresponding monoketone **3**, mp 197–199°.[4] Sodium borohydride reduction of **3** gave, in 89% yield, the alcohol **4**, mp 165–166°. Reaction of **4** with thionyl chloride followed by direct treatment of the resulting chloride **5** with a refluxing solution of potassium *tert*-butoxide in *tert*-butyl alcohol afforded, in 32% yield, the condensed benzocyclobutene **6**, mp 131–133°. The cis configuration for compound **6** is assigned on the basis of its benzylic proton signal at δ 5.08, a value close of that (δ 5.20) observed for *cis*-1,2-diphenylbenzocyclobutene.[5] Bromination of **6** by NBS in CCl$_4$ gave, in 70% yield, the corresponding dibromide **7**, mp 214–216° dec.



1



2, R = H
4, R = OH
5, R = Cl



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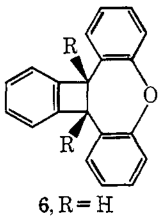
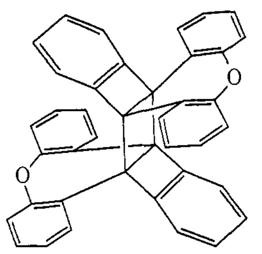


6, R = H
7, R = Br

Reaction of dibromide **7** with zinc–silver couple[6] in warm tetrahydrofuran afforded an orange-red solution (λ_{max} 496 nm) of the oxahomobiphenylene **1**. Solutions of **1** could be preserved unchanged for several hours at $-78°$; at room temperature, however, the red color vanished within 1 min with the formation of a colorless dimer **8**, mp 347–349° dec (80% based upon **7**). When **1** was generated in the presence of 1,3-diphenylisobenzofuran, it was trapped efficiently to give, in 76% yield, the Diels–Alder adduct **9**, mp 264–266°.[7] Attempts to effect a cycloaddition of **1** to 4-phenyltriazoline-3,5-dione were unsuccessful, but these reactions afforded (~12% yield) the oxidation product of **1**, 10*H*,15*H*-tribenzo[*b*,*e*,*h*]oxonin-10,15-dione (**10**), mp 179–181°, identical with material prepared by an independent synthesis.[8]



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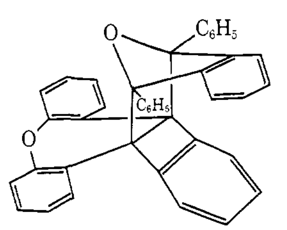
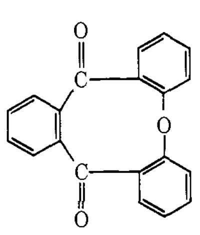


9



10

Red solutions of **1** gave no esr signal at $-195°$, indicating a singlet ground state for **1**. The observed high reactivity of **1**, however, is indicative of an antiaromatic ring system. A comparison of the stability of **1** with that of related compounds in which the oxygen of **1** has been replaced by other atoms would be of considerable interest; the synthesis of such compounds is under active investigation in our laboratory.

Acknowledgment. We thank the National Science Foundation for a grant (GP 24057X) in support of this research.

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(3) T. Sato, K. Uno and M. Kainosho, *J. Chem. Soc., Chem. Commun.*, 579 (1972).

(4) Satisfactory analyses and spectral data were obtained for all new compounds.

(5) L. A. Carpino, *J. Amer. Chem. Soc.*, **84**, 2196 (1962).

(6) J. M. Denis, C. Girard, and J. M. Conia, *Synthesis*, 540 (1972). We thank Professor B. M. Trost for suggesting this reagent.

(7) Compounds **8** and **9** are assigned the most likely stereochemistry. A head-to-head structure for **8** and an endo structure for **9** cannot, however, be excluded on current experimental evidence.

(8) M. Schaaf, Ph.D. Dissertation, Wayne State University, 1969. Addition of the Grignard reagent from 2-iodophenyl phenyl ether to phthalic anhydride and acid-catalyzed cyclization of the product gave **10** in good yield.

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Mass Spectrometry in Structural and Stereochemical Problems. CCXXXIII.[1] On the Stereochemical Dependence of the Retro-Diels–Alder Reaction

Sir:

Recent investigations in this laboratory have shown that the retro-Diels–Alder (RDA) reaction in the mass spectral decomposition of some Δ^7 steroidal olefins exhibits a high degree of stereospecificity with A/B cis compounds decomposing significantly more readily by this route than the corresponding trans compounds.[2] This observation is *a priori* surprising, since RDA processes have frequently been observed in trans-fused polycyclic hydrocarbons.[3] A comparison of the relative importance of the RDA reaction in cis–trans isomeric polycyclic hydrocarbons has, however, not been made so far. To study this problem more fully we have

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(1) For paper CCXXXII in this series, see P. J. Derrick, A. M. Falick, A. L. Burlingame, and C. Djerassi, submitted to *J. Amer. Chem. Soc.* for publication.

(2) I. Midgley and C. Djerassi, unpublished results.

(3) For examples of RDA reactions in A/B trans Δ^2 steroids and B/C trans Δ^{12} triterpenes see: (a) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Structure Elucidation of Natural Products by Mass Spectrometry," Vol. 2, Holden-Day, San Francisco, Calif., 1964; (b) H. Budzikiewicz, J. I. Brauman, and C. Djerassi, *Tetrahedron*, **21**, 1855 (1965).

begun an investigation of the mass spectra of various pairs of cis–trans isomeric model compounds.

Mandelbaum and coworkers[4] have very recently shown that certain unsaturated cyclic diketones, *e.g.*, **1**, decompose in the mass spectrometer by a RDA reaction if cis at the central ring junction, but not if trans. They point out that this is the behavior expected if the mass spectral RDA reaction is concerted and follows symmetry rules analogous to those established for thermal reactions.[5]

We wish here to give a preliminary account of our results, since our data with regard to the mass spectral retro-Diels–Alder reaction in simple bicyclic Δ^2 olefins (compounds **2**, **3**, and **4**) show that the occurrence of abundant ions formed by this reaction is not generally dependent upon the stereochemistry at the central bond.

The relative abundance at 70 eV of the molecular ions and the ions associated with the RDA process in the mass spectra of the isomers of **2**, **3**, and **4** is given in Table I.[6]

Table I. Relative Abundance of RDA Ions[a]

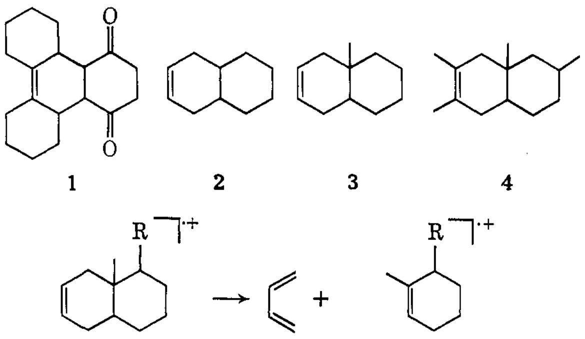
Compd	M	$[M - C_4H_6]\cdot^+$	$[M - C_4H_6 - CH_3]^+$
2, cis	15.1[b]	5.3	12.1
2, trans	17.8[b]	2.1	9.8
3, cis	10.4	20.4[b]	11.0
3, trans	11.0	29.9[b]	11.7
4a	7.6	11.3	14.8[b]
4b	8.2	8.2	12.0[b]
4c	10.1	7.8	12.1[b]

[a] Measured at 70 eV on an AEI MS-9 mass spectrometer by Mr. R. G. Ross and expressed in per cent of Σ_{40}. [b] Base peak.

In **3**, the RDA reaction gives rise to the base peak in the cis as well as in the trans isomers, and only a slight difference appears between the propensity of the cis and trans isomers of **2**, **3**, and **4** to decompose *via* this process. Spectra obtained at low ionizing voltage show the same pattern, even though the relative abundance of the RDA product ions at 12 eV is increased slightly in the cis compounds relative to the trans. To further study the behavior at low energies we have examined the relative intensities of the $[M - C_4H_6]\cdot^+$ peaks in a mixture of *cis*-9-methyl-2-octalin and labeled *trans*-9-methyl-2-octalin (see Scheme I) while decreasing the ionizing voltage to less than the appearance potential of these ions. Within the limits of detectability the abundance of both ions decreased to below measurable values simultaneously, showing that even at onset no significant difference exists in this respect between the cis and trans compounds.[7]

Comparison of the RDA decomposition of cis and trans isomers in the field-free regions is not possible, since neither of the spectra exhibit measurable metastable peaks corresponding to the RDA process.[8] Rather than taking this to imply that the reaction occurs from an excited state[5] we believe that the absence of metastable peaks in both field-free regions shows that nearly all the reactive molecular ions either fragment or undergo double bond migration in the ion source. The latter process is likely on the basis of the recently described[9] results in cyclohexene in which such double bond migration was shown to be operative before the molecules reach the field-free regions of the mass spectrometer.

Scheme I



m/*e* 96 for R = H
m/*e* 97 for R = D

These results thus show that the mass spectral retro-Diels–Alder reaction of the simplest polycyclic olefins is not dependent in any marked fashion on the stereochemistry at the ring junction and therefore lend support to the earlier suggestion[3b] that this process is stepwise rather than concerted.

Acknowledgments. We are indebted to the National Institutes of Health (Grants AM 04257 and GM 06840) and to Statens Naturvidenskabelige Forskningsraad, Copenhagen (Grant 511-1224 to S. H.), for financial support.

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(4) A. Karpati, A. Rave, J. Deutsch, and A. Mandelbaum, *J. Amer. Chem. Soc.*, **95**, 4244 (1973); we thank Dr. Mandelbaum (Technion, Haifa, Israel) for making his manuscript available to us prior to publication.

(5) R. C. Dougherty, *J. Amer. Chem. Soc.*, **90**, 5780, 5788 (1968).

(6) Only three of the possible four isomers of **4** have been examined; the stereochemical identity of each of these has not yet been unambiguously determined, but at least one must be cis and at least one trans at the ring junction; they are given in Table I in the order they were collected by preparative glc (10% SE-30 on Chromosorb W at 175°).

(7) This procedure allows us to assess the difference in appearance potentials while avoiding the pitfalls of attempting to measure the exact numerical values.

(8) Confirmed by metastable defocusing experiments on the $[M - C_4H_6]\cdot^+$ ions of *cis*- and *trans*-**3**.

(9) P. J. Derrick, A. M. Falick, and A. L. Burlingame, *J. Amer. Chem. Soc.*, **94**, 6794 (1972).

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On Homoaromatic Stability

Sir:

The concept of homoaromaticity, proposed over a decade ago by Winstein and his collaborators,[1] provided a plausible explanation for the unusually high stability of a large class of cyclic molecules and ions. In the original formulation of the theory a homoaromatic molecule was pictured as being a cyclic $(4n + 2)$ "aromatic" polyene in which the ring conjugation had been interrupted in one or more places by aliphatic chains of varying lengths. In certain instances the π-electron structure of the original polyene was envisioned to be only slightly perturbed and to maintain a signifi-

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(1) For reviews see: (a) S. Winstein, *Quart. Rev., Chem. Soc.*, **23**, 141 (1969); (b) P. R. Story and B. C. Clark, Jr., in "Carbonium Ions," G. A. Olah and P. v. R. Schleyer, Ed., Vol. III, Wiley-Interscience, New York, N. Y., 1972, p 1007.