(10) D. Seyferth, C. Sarafidis, and A. B. Evnin, *J. Organomet. Chem.*, **2**, 417 (1964).

(11) R. Weiss and S. Andrae, in preparation.

(12) Benzene derivatives **5**, **6**, and **8** are photostable under our irradiation conditions.

(13) Professor R. Breslow has kindly informed us that prompted by our results he reinvestigated his earlier work[2] and was indeed able to confirm his original results. At present the reasons for the discrepancy between his and our results are not fully understood.

(14) D. M. Lemal and J. P. Lokensgard, *J. Am. Chem. Soc.*, **88**, 5934 (1966).

(15) Attempts to observe **3** directly in the photolysis of **9** were unsuccessful.

(16) R. Weiss and H. Kölbl, following paper in this issue.

Robert Weiss,* Heinz Kölbl
Institut für Organische Chemie der Universität München
8 München 2, Germany

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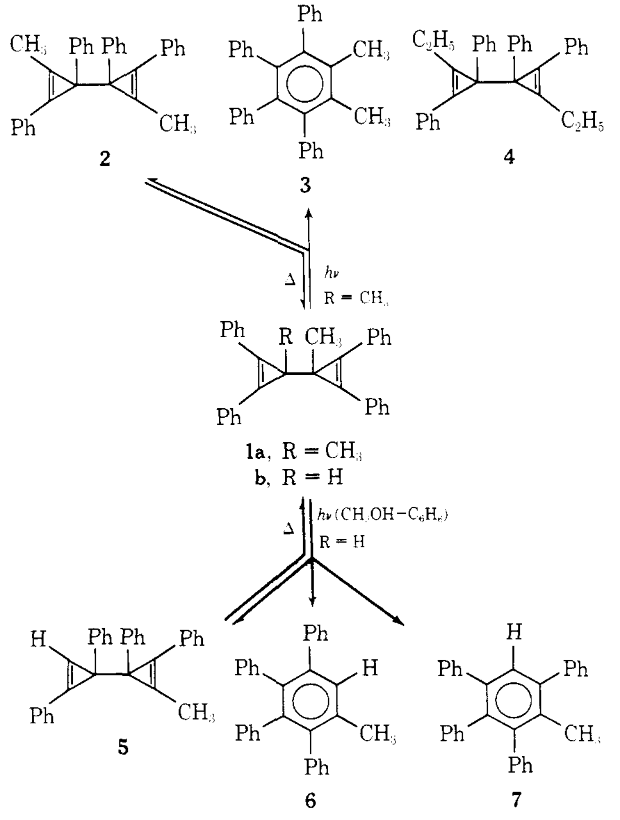
The Bicyclopropenyl Cope Rearrangement[1,2]

Sir:

So far there have been no reports of Cope rearrangements involving cyclopropene moieties. In this communication we wish to report the first examples, both photochemical and thermal, of bicyclopropenyl → bicyclopropenyl rearrangements which, apart from adding new mechanistic and structural facets to the Cope rearrangement, also allow some insight into bicyclopropenyl → benzene rearrangement pathways.

Direct 320-nm irradiation of **1a**[3] (see Scheme I) in 3:1 CH_3OH-C_6H_6 (Graentzel reactor 400, 600 W, substrate concentration $\sim 10^{-3}$ mol/l., irradiation time 7 hr) gave two new products, **2** (95%) and **3** (5%), which after total conversion of **1a** could be separated by fractional crystallization. The structure of **3** (mp 230°) follows from spectral comparison with an authentic sample.[4] The structural assignment of **2** (mp 173°) as a bicyclopropenyl isomeric with **1a** is based on the following data: ir (KBr) 1845 cm^{-1} (ν >C=C<); uv (CH_2Cl_2) λ_{max} 270 nm (ϵ 23,600); NMR ($CDCl_3$) τ 7.58 (6 H, s); MS 410 (M^+), 205.

Scheme I



Ir and UV characteristics of **2** are completely analogous to the spectra of bicyclopropenyl **4** synthesized by Breslow via reductive coupling of the ethyldiphenylcyclopropenium ion.[5]

2 is photostable under 320-nm irradiation because the transformation **1a** → **2** is connected with a pronounced blue shift in the longest wavelength absorption (331 → 270 nm).

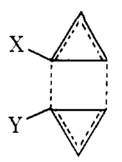
Similarly, under the same irradiation conditions, photolysis of **1b** gave a mixture of **5** (65%), **6** (30%), and **7** (5%).[2] **5** was isolated by low-temperature fractional crystallization from ether and had the following: mp 128–130°; ir (KBr) 1845, 1755 cm^{-1} (ν >C=C<); uv (CH_2Cl_2) λ_{max} 269 nm (ϵ 21,400); NMR ($CDCl_3$) τ 7.58 (3 H, s); MS 396 (M^+), 205, 191. Typically, the two cylopropene >C=C< absorptions in the ir spectrum of **5** reflect the different substitution patterns of the two double bonds. Like **2**, **5** is fairly photostable at 320 nm (and for the same reasons).

While the interconversions **1a** → **2** and **1b** → **5** constitute the first examples of photochemically induced Cope rearrangements in the bicyclopropenyl series, the thermal counterpiece was discovered in the thermolysis of **2** and **5** (see Scheme I).

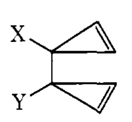
It was found that both **2** and **5** under rather mild conditions were reconverted exclusively[6] to the starting bicyclopropenyl systems, this reaction being accompanied by formation of benzene derivatives (**2** $\tau_{1/2}^{150^\circ}$ (*o*-dichlorobenzene) 15 min with product composition, **1a** (50%), **3** (50%); **5** $\tau_{1/2}^{80^\circ}$ (benzene) 30 min with product composition, **1** (85%), **6** (10%), **7** (5%).

The driving force of these thermal Cope rearrangements is probably provided by restoration of conjugation between the phenyl substituents. Evidently the photo-Cope rearrangements furnish the more endothermic of the two equilibrium partners—a feature which it shares with some of the few known photo-Cope rearrangements in the open-chain series.[7] This fact allows the conclusion[8] that in all probability **2** and **5** are formed in a true photoreaction and not in a hot ground state reaction.

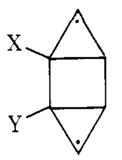
Our observations immediately provoke some mechanistic comments. (1) As concerns stereochemistry our results strongly suggest that both **2** and **5** arise via a *chair* transition state (and hence in the case of **2** should possess *d,l* rather than mesoconfiguration). This follows from the observed *mutually stereospecific* **1a** ⇌ **2** (**1b** ⇌ **5**) interrelationships which imply *that either both thermal and photochemical Cope rearrangements proceed via a boat or both via a chair transition state.*[9] As it is totally unreasonable in view of the rotational flexibility and the mild reaction conditions that the *thermal* Cope rearrangement should exclusively proceed via a boat transition state, the above conclusion concerning the photochemical case follows. (2) Pericyclic vs. two-step process. In view of the continuing discussion of whether open-chain Cope rearrangements proceed as a pericyclic or as a two-step process,[10] we wish to point out that a two-step process in the case of **9** should be inherently more favorable. This arises because the introduction of a single bond between the two cyclopropene moieties to yield the *anti*-1,4-tricyclohexylene (biradicaloid[10]) intermediate **10** is connected with some 25 kcal relief of total strain



8



9



10

energy as compared to **9**,[11] whereas the pericyclic transition state **8** maintains the cyclopropene level of ring strain.

In the preceding paper[2] we have shown that a prismane intermediate is unlikely to occur in photochemically induced bicyclopropenyl → benzene rearrangements. Although we cannot at present exclude an alternative involving initial retrocarbene fission of one cyclopropene ring,[12] it is tempting to consider intermediates of type **10** as common intermediates for both Cope rearrangement (corresponding to fission of one peripheral cyclobutane bond) and aromatization (corresponding to electrocyclic collapse of the inner cyclobutane bonds) to yield ortho x,y-substituted benzene derivatives. If this latter process is a stepwise one then as a further local energy minimum down the bicyclopropenyl → benzene energy cascade "pre-fulvene" intermediates will have to be considered with their possibility of ortho-meta scrambling of x,y-substituents.[13]

We feel that this possibility may well form a basis for understanding the photochemical behavior of **1b** and are presently elaborating on this point. Our further research is aimed at mechanistic details of the photo-Cope process and at the implications of the thermal counterpart for the mechanism of *thermal* bicyclopropenyl → benzene rearrangements.[14]

Acknowledgment. Support of this work by the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

References and Notes

(1) Reactions of coupled three-membered rings, part VIII; presented in part at the Chemiedozententagung, Stuttgart, April 1–4, 1974.
(2) For part VII of this series see: R. Weiss and H. Kölbl, *J. Am. Chem. Soc.*, preceding paper in this issue.
(3) **1a** was synthesized from **1b** following a procedure described in ref 2 for the synthesis of **1b** from 1,2,1′,2′-tetraphenyl-bicyclopropenyl-3,3′ (mp 170°; NMR ($CDCl_3$) τ 8.44 (6 H, s)).
(4) Ir and NMR spectra kindly provided by Professor G. Maier, Marburg.
(5) R. Breslow, P. Gal, H. W. Chang, and L. J. Altman, *J. Am. Chem. Soc.*, **87,** 5139 (1965). The configuration of **4** could not be determined.
(6) No other isomeric bicyclopropenyl systems could be detected.
(7) R. C. Cookson, V. N. Gogte, J. Hudec, and N. A. Mirza, *Tetrahedron Lett.*, 3955 (1965).
(8) N. J. Turro, "Molecular Photochemistry", W. A. Benjamin, New York, N.Y., 1967, p 186.
(9) For instance the combination

$$\mathbf{1a} \xrightarrow[\text{(boat)}]{h\cdot\nu} \mathbf{2} \xrightarrow[\text{(chair)}]{\Delta}$$

would not regenerate **1a** but give rise to a structural isomer with one methyl group at a bridgehead position and one at a double bond.
(10) For a leading reference see M. J. S. Dewar, S. Kirschner, H. W. Kollmar, and L. E. Wade, *J. Am. Chem. Soc.*, **96,** 5242 (1974).
(11) Assuming that the strain energy of **10** is equal, or nearly so, to *anti*-tricyclohexane.
(12) R. Weiss and S. Andrae, *Angew. Chem., Int. Ed. Engl.*, **12,** 150 (1973).
(13) As is easily verified this could happen via the benzvalenes which can be derived from a prefulvene precursor.
(14) Note Added in Proof. A further example of a thermal bicyclopropenyl–Cope rearrangement has just been published: W. H. de Wolf, I. J. Laudheer, and F. Bickelhaupt, *Tetrahedron Lett.*, 179 (1975).

Robert Weiss,* Heinz Kölbl
Institut für Organische Chemie der Universität München
8 München 2, Germany

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Helium(I) Photoelectron Spectrum of *p*-Quinodimethane

Sir:

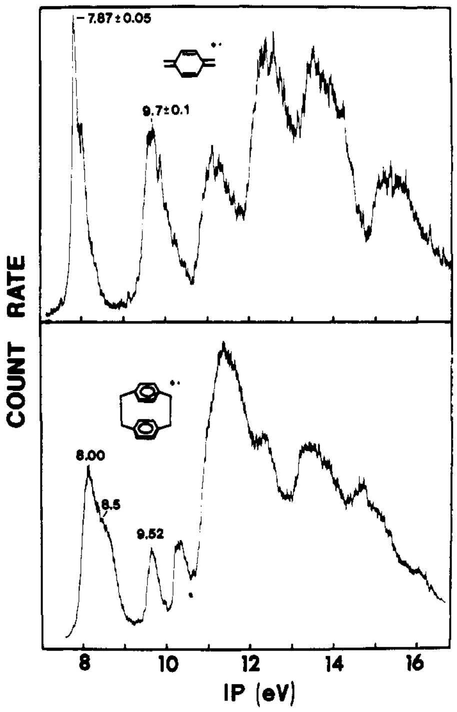
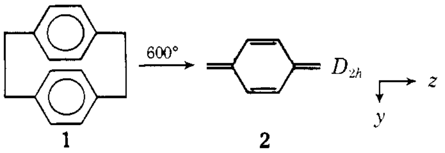


Figure 1.



1 **2**

We wish to report our observation of the He(I) photoelectron spectrum of *p*-quinodimethane[1] (**2**) formed from the flash vacuum pyrolysis[2] of [2.2]paracyclophane (**1**), and our analysis of the first three ionic states in terms of the structure representation (SR)[3] method. The spectra were obtained using a modified Perkin-Elmer PS-18 photoelectron spectrometer. The basic modifications include the insertion of a pyrolysis tube between the He(I) light source and the target chamber as described previously.[4] The sample was introduced from a sublimation chamber, directly attached to the furnace base, which was heated by a separate induction coil. The experimental spectra of the [2.2]paracyclophane (**1**) precursor[5] and the transient (**2**) are shown as Figure 1.

Chemical evidence that the observed transient species is **2** is the fact that a film of its polymer was isolated from the liquid nitrogen trap after warming to room temperature. Previous investigations[6] of the PMR, ir, and uv spectra of **2**, obtained by a similar pyrolysis and collection at low temperature, indicate clean formation of **2** in the pyrolysis. The present PES spectrum (Figure 1) is like the PMR, ir, and uv spectra in that its appearance is entirely consistent with formation of essentially pure **2**.

The position of the second band maximum in the observed spectrum of **2** (9.7 eV) is strikingly close to that observed[7] for the related 1,4-cyclohexadiene, 1,4-dihydropyridine, and *N*-methyl-1,4-dihydropyridine. This result is predicted by the SR analysis, offered for interpretation of the spectra of the latter three compounds, if this band is the antisymmetric combination of the ionic structures derived from the two endocyclic double bonds ($^2B_{1g}$, $1/\sqrt{2}(\Psi_{III} - \Psi_{IV})$, Figure 2) with inductive effects being ignored. The position of this band is thus entirely determined by the direct interaction across the ring ($S_{1,4} = 0.74$ eV).[7]

The same method predicts the first band should be assigned to the mixed symmetric combination of the endocyclic and exocyclic ion structures ($^2B_{3u}{}^{(-)}$, $N_1(\Psi_I + \Psi_{II}) - N_2(\Psi_{III} + \Psi_{IV})$, Figure 2) and should be observed near 7.98 (obsd 7.87 eV). This band position is mainly determined by the interaction constant between the ionic struc-