

Figure 3. Plot of the rate constants of Figure 2 using eq 5.

mol,  $\Delta S^\ddagger = -9.5 \pm 1.5$  eu. These data correspond to the barrier of valence isomerization,  $1 \rightarrow 2$ , because acetic acid turned out to be a "plateau solvent" in Figure 1.

The mechanistic scheme above is plausible. It has been established that valence tautomerism of cyclooctatetraene leads to a 0.01% equilibrium concentration of bicyclo[4.2.0]octatriene (dioxane,  $100^\circ$ ).<sup>7,8</sup> The ionization tendency of the 1-bromo derivative stems from the formation of a homocyclopropenium ion.<sup>9</sup> That ion recombination takes place on the same side of the four-membered ring, *i.e.*, to form **4**, may be due to an ion-pair phenomenon; it is also the least-hindered side for nucleophilic addition. The benzenoid character of **5** ensures the irreversibility of the *conrotatory* ring cleavage of **4**. The small amount of *cis*- $\beta$ -bromostyrene in the product results probably not from a *disrotatory* ring opening of **4**, but rather from ion recombination on the opposite side of **3**, leading to the epimer of **4**.

Further evidence for this rearrangement mechanism—to our knowledge without precedence in cyclooctatetraene chemistry—is presented in the following communications. Criegee, *et al.*,<sup>10</sup> recently assumed an analogous reaction path by studying the thermal rearrangement of halobenzobicyclo[4.2.0]octatrienes.

(7) R. Huisgen and F. Mietzsch, *Angew. Chem., Int. Ed. Engl.*, **3**, 83 (1964).

(8) R. Huisgen, F. Mietzsch, G. Boche, and H. Seidl, *Chem. Soc., Spec. Publ.*, **19**, 3 (1965).

(9) T. J. Katz and E. H. Gold, *J. Amer. Chem. Soc.*, **86**, 1600 (1964).

(10) R. Criegee, C. Schweickhardt, and H. Knoche, *Chem. Ber.*, **103**, 960 (1970).

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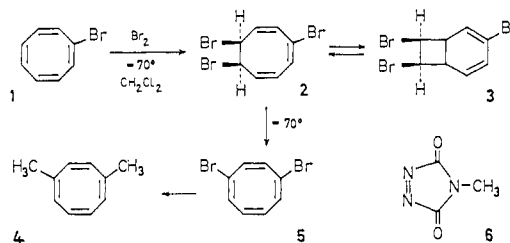
#### Further Contributions to the Mechanism of the Halocyclooctatetraene Rearrangement

Sir:

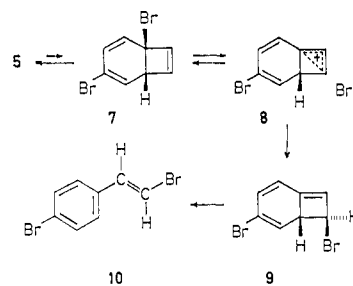
On viewing the mechanistic path proposed for the conversion of bromocyclooctatetraene (**1**) to *trans*- $\beta$ -bromostyrene,<sup>1</sup> one becomes aware of the fact that

the bromine in the product is no longer attached to the original carbon atom but has undergone a 1,3 migration.

By the bromination of **1**, we obtained, *via* **2**, the 1,4-dibromo compound **5** in  $\geq 92\%$  purity. Evidence for the intermediacy of **2** came from the nmr spectra



of the Diels–Alder adducts of the bicyclic tautomer **3** with tetracyanoethylene or **6**. Elimination of HBr to give **5** was effected by potassium *t*-butoxide in dichloromethane. To establish the position of the two bromine atoms, **5** was converted to 1,4-dimethylcyclooctatetraene (**4**, 95%, bp  $60\text{--}62^\circ$  (12mm);  $n_D^{25}$ , 1.5206; nmr ( $\text{CDCl}_3$ )  $2\text{CH}_3$ , s,  $\tau$  8.30) by lithium dimethylcopper.<sup>2</sup> Catalytic hydrogenation of **4** gave 1,4-dimethylcyclooctane (nmr ( $\text{CDCl}_3$ )  $2\text{CH}_3$ , d,  $\tau$  9.11,  $J = 6.4$  Hz), which was identical with a specimen prepared by the hydrogenation of 1,6-dimethylcycloocta-1,3,5-triene.<sup>3</sup>



On injecting **5** onto a glpc column (Apiezon L, 2 m,  $180^\circ$ , 30 lb/in.<sup>2</sup> of  $\text{N}_2$ ), one observed, besides three minor components, up to 92% of *p*- $\beta$ -dibromostyrene (**10**). Preparative glpc made possible the isolation of **10**, its characterization (mp  $67\text{--}68^\circ$ ; uv (methanol)  $265\text{ m}\mu$ ,  $\log \epsilon$  4.40; nmr ( $\text{CDCl}_3$ ) olefinic AB spectrum,  $\tau$  2.99 and 3.24,  $J = 14.2$  Hz), and its oxidation to *p*-bromobenzoic acid. The aforementioned facts were supplemented by the independent synthesis of **10**. Thus, the expected shift of bromine is established by the 1,6 positions of the bromine atoms in **10**.

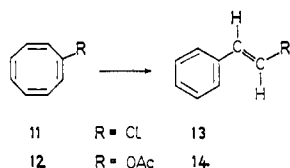
Cope and Burg<sup>4</sup> obtained  $\beta$ -chlorostyrene from chlorocyclooctatetraene (**11**) at  $200^\circ$  and assigned the *cis* configuration to it. The nmr (AB  $\tau$  3.23 and 3.42,  $J = 13.8$  Hz), however, leaves no doubt that it is *trans*- $\beta$ -chlorostyrene (**13**) that is formed. As in the case of bromocyclooctatetraene,<sup>1</sup> the conversion,  $11 \rightarrow 13$ , is strongly catalyzed by Lewis and Brønsted acids; rearrangement in the presence of  $\text{D}_2\text{O}$  or DOAc does not lead to deuterium incorporation in **13**. Also here the rate of rearrangement depends on solvent polarity. The rate constant at  $120^\circ$  in the neat state

(1) R. Huisgen and W. E. Konz, *J. Amer. Chem. Soc.*, **92**, 4102 (1970).

(2) E. J. Corey and G. H. Posner, *ibid.*, **89**, 3911 (1967).

(3) We gratefully acknowledge an authentic specimen obtained from Professor E. Vogel, Köln.

(4) A. C. Cope and M. Burg, *J. Amer. Chem. Soc.*, **74**, 168 (1952).



is  $2.1 \times 10^{-6}$ , whereas in acetonitrile it is  $2.1 \times 10^{-4}$  ( $\text{sec}^{-1}$ ).

Acetoxycyclooctatetraene (**12**)<sup>1</sup> rearranges slowly at  $200^\circ$  to *trans*- $\beta$ -acetoxystyrene (**14**), undergoing some decomposition as well. Acetic acid accelerates the process so much that at  $120^\circ$  kinetics are measurable and the yield of **14** is quantitative. Bromo- (**1**), chloro- (**11**), and acetoxycyclooctatetraene (**12**) undergo the rearrangement to  $\beta$ -substituted styrenes in the rate ratio 4000:2200:1, as shown by the first-order rate constants in HOAc at  $120^\circ$ : **1**,  $1.11 \times 10^{-2}$  ( $\text{sec}^{-1}$ ); **11**,  $6.32 \times 10^{-3}$  ( $\text{sec}^{-1}$ ); **12**,  $2.81 \times 10^{-6}$  ( $\text{sec}^{-1}$ ). Acetic acid is a "plateau solvent" for the rearrangement of **1**; *i.e.*, only the initial valence tautomerization is rate determining.<sup>1</sup> The same is not true for **11** and **12** where ionization is still the limiting step. Thus, the difference in the ionization rates of the bicyclic tautomers of **1** and **11** is probably much larger than indicated by the data above, and the expected dependence of leaving groups on the rate is substantiated.

Kinetic measurements of the process, **11**  $\rightarrow$  **13**, with increasing concentration of the acid catalyst reveals that even trichloroacetic acid does not give rise to a "plateau phenomenon" in the rate constants as found for **1**.<sup>1</sup> The linear relation of  $k$  and  $[\text{Cl}_3\text{C}-\text{CO}_2\text{H}]$  is compatible with a mobile valence-tautomeric equilibrium of **11** followed by a slow ionization step. It is only with the stronger acid,  $\text{F}_3\text{C}-\text{CO}_2\text{H}$ , that  $k$  values of the rearrangement of **11**, in acetonitrile at  $100^\circ$ , approach a plateau. Using steady-state treatment<sup>1</sup> furnished  $k_1 = 1.5 \times 10^{-3}$  ( $\text{sec}^{-1}$ ) for the isomerization constant of chlorocyclooctatetraene to 1-chlorobicyclo[4.2.0]octatriene.

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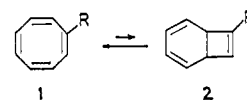
### Evidence for Different Valence Tautomers of Bromocyclooctatetraene

Sir:

Cyclooctatetraene (**1**, R = H) must surmount an energy barrier possessing a  $\Delta H^\ddagger = 28.1$  kcal/mol in tautomerizing to bicyclo[4.2.0]octatriene (**2**, R = H); the small equilibrium concentration of **2** has been trapped by dienophiles to give Diels-Alder adducts.<sup>1,2</sup> Phenylcyclooctatetraene (**1**, R =  $\text{C}_6\text{H}_5$ ) combines with maleic anhydride or TCNE to give adducts which are exclusively derived from the bicyclic tautomer **2**, R =  $\text{C}_6\text{H}_5$ ,<sup>2</sup> even though four structural isomers are conceivable. We have found that ethyl-, bromo-, chloro-, acetoxy-, and methoxycarbonylcyclooctatetraene likewise form TCNE adducts which stem from the 7-substituted bicyclic tautomer **2** to the extent of 92–99%.<sup>3</sup>

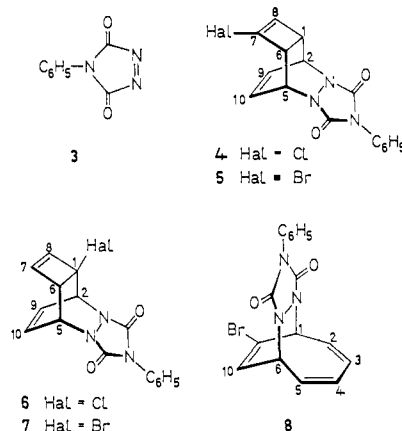
(1) R. Huisgen and F. Mietzsch, *Angew. Chem., Int. Ed. Engl.*, **3**, 3 (1964).

(2) R. Huisgen, F. Mietzsch, G. Boche, and H. Seidl, *Chem. Soc., Spec. Pub.*, **19**, 3 (1965).



Is the formation of **2** from **1** kinetically or thermodynamically favored over the other three possible monosubstituted bicyclo[4.2.0]octatrienes or does **2** simply add dienophiles faster?

The latter turned out to be correct. With 4-phenyl-1,2,4-triazoline-3,5-dione (**3**) as a more reactive dienophile,<sup>4</sup> the *1-* as well as the *7-*substituted bicyclic tautomers of bromo- and chlorocyclooctatetraene were intercepted. This formation was the "missing link" in the series of arguments which point to 1-halobicyclo[4.2.0]octatrienes as being key intermediates in the rearrangement of halocyclooctatetraenes to *trans*- $\beta$ -halostyrenes.<sup>5,6</sup>



A solution of chlorocyclooctatetraene and **3** in ethyl acetate after 48 hr at  $60^\circ$  yielded, after thick-layer chromatography on silica gel using chloroform as eluent, 27% **4** and 30% **6**.<sup>7</sup> Adduct **4** showed the following: mp  $208-210^\circ$ ; nmr ( $\text{CDCl}_3$ )<sup>8</sup> 8-H  $\tau$  4.12 (s);<sup>9</sup> 9- and 10-H 3.72 (t); 2- and 5-H 4.7–5.1 (m); 1- and 6-H 6.46 and 6.75 (2t). Adduct **6** showed the following: mp  $214-216^\circ$ ; nmr ( $\text{DMSO}-d_6$ ) 7- and 8-H, AB spectrum,  $\tau$  3.84 and 3.79 ( $J = 2.5$  Hz); 2- and 5-H 4.6–5.0 (m); 6-H 6.56 (d,  $J = 4.1$  Hz).

Bromocyclooctatetraene combines with **3** in boiling ethyl acetate (48 hr) to give—after thick-layer chromatography—12% **5** (mp  $217-218^\circ$ ),<sup>3</sup> 25% **7** (mp  $216-217^\circ$ ),<sup>3</sup> 10% **8**, and, in addition, bromostyrene as rearrangement product; nmr ( $\text{CDCl}_3$ ) of **8**, vinyl-H in 1:4 ratio, 10-H  $\tau$  3.33 (d,  $J = 8.0$  Hz); 2- to 5-H 3.6–4.1 (m);  $\text{C}_6\text{H}_5$  2.55 (s). Thus, bromocyclooctatetraene (**9**), although a poor diene, competes with 1- and 7-bromobicyclo[4.2.0]octatriene (**10** and **11**, respectively) for the potent dienophile **3**.

Quantitative competition experiments between rearrangement of **9** *via* **10** and Diels-Alder reaction with TCNE *via* **11** confirmed the above scheme and allowed the following numerical evaluation. **9** and TCNE,

(3) The description and structural discussion of these adducts will be published elsewhere.

(4) R. C. Cookson, S. S. H. Gilani, and I. D. R. Stevens, *J. Chem. Soc. C*, 1905 (1967).

(5) R. Huisgen and W. E. Konz, *J. Amer. Chem. Soc.*, **92**, 4102 (1970).

(6) W. E. Konz, W. Hechtl, and R. Huisgen, *ibid.*, **92**, 4104 (1970).

(7) Satisfactory elementary analyses have been obtained.

(8) Spectra measured on Varian A-60 with TMS as internal standard.

(9) 1- and 2-H of cyclobutene do not couple with 3- and 4-H: K. B. Wiberg and B. J. Nist, *J. Amer. Chem. Soc.*, **83**, 1226 (1961).