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°).[7,8] The ionization tendency of the 1-bromo derivative stems from the formation of a homocyclopropenium ion.[9] 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-β-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.,[10] 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).

Rolf Huisgen, Will Elmar Konz
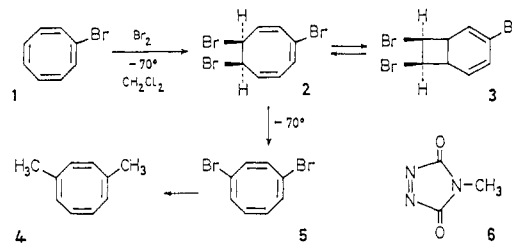Institut für Organische Chemie der Universität
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## Further Contributions to the Mechanism of the Halocyclooctatetraene Rearrangement

Sir:

On viewing the mechanistic path proposed for the conversion of bromocyclooctatetraene (1) to trans-β-bromostyrene,[1] 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 60–62°(12mm); n^{25}D, 1.5206°; nmr (CDCl$_3$) 2CH$_3$, s, τ 8.30) by lithium dimethylcopper.[2] Catalytic hydrogenation of 4 gave 1,4-dimethylcyclooctane (nmr (CDCl$_3$) 2CH$_3$, d, τ 9.11, J = 6.4 Hz), which was identical with a specimen prepared by the hydrogenation of 1,6-dimethylcycloocta-1,3,5-triene.[3]
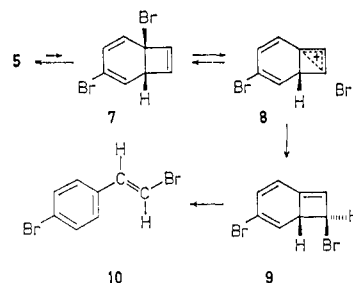
On injecting 5 onto a glpc column (Apiezon L, 2 m, 180°, 30 lb/in.^{2} of N$_2$), one observed, besides three minor components, up to 92% of p-β-dibromostyrene (10). Preparative glpc made possible the isolation of 10, its characterization (mp 67–68°; uv (methanol) 265 mμ, log ϵ 4.40; nmr (CDCl$_3$) olefinic AB spectrum, τ 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[4] obtained β-chlorostyrene from chlorocyclooctatetraene (11) at 200° and assigned the cis configuration to it. The nmr (AB τ 3.23 and 3.42, J = 13.8 Hz), however, leaves no doubt that it is trans-β-chlorostyrene (13) that is formed. As in the case of bromocyclooctatetraene,[1] the conversion, 11 → 13, is strongly catalyzed by Lewis and Brønsted acids; rearrangement in the presence of D$_2$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° 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).

11   R = Cl   13
12   R = OAc   14
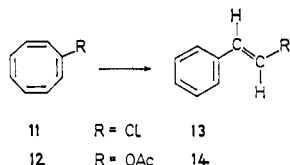
is 2.1×10^{-6}, whereas in acetonitrile it is 2.1×10^{-4} (sec^{-1}).

Acetoxycyclooctatetraene (12)[1] rearranges slowly at 200° to trans-β-acetoxystyrene (14), undergoing some decomposition as well. Acetic acid accelerates the process so much that at 120° kinetics are measurable and the yield of 14 is quantitative. Bromo- (1), chloro- (11), and acetoxycyclooctatetraene (12) undergo the rearrangement to β-substituted styrenes in the rate ratio 4000:2200:1, as shown by the first-order rate constants in HOAc at 120°: 1, 1.11×10^{-2} (sec^{-1}); 11, 6.32×10^{-3} (sec^{-1}); 12, 2.81×10^{-6} (sec^{-1}). Acetic acid is a "plateau solvent" for the rearrangement of 1; i.e., only the initial valence tautomerization is rate determining.[1] 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 → 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.[1] The linear relation of k and [Cl$_3$C–CO$_2$H] is compatible with a mobile valence-tautomeric equilibrium of 11 followed by a slow ionization step. It is only with the stronger acid, F$_3$C–CO$_2$H, that k values of the rearrangement of 11, in acetonitrile at 100°, approach a plateau. Using steady-state treatment[1] furnished $k_1 = 1.5 \times 10^{-3}$ (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 $\Delta H^{\pm} = 28.1$ 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.[1,2] Phenylcyclooctatetraene (1, R = C$_6$H$_5$) combines with maleic anhydride or TCNE to give adducts which are exclusively derived from the bicyclic tautomer 2, R = C$_6$H$_5$,[2] 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%.[3]

(1) R. Huisgen and F. Mietzsch, Angew. Chem., Int. Ed. Engl., 83, 3 (1964).
(2) R. Huisgen, F. Mietzsch, G. Boche, and H. Seidl, Chem. Soc., Spec. Pub., 19, 3 (1965).

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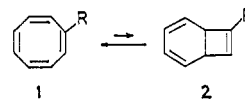
Is the formation of 2 from 1 kinetically or thermodynamically favored over the other three possible monosubstituted bicyclo[4.2.0]octatrienes or does 2 simply add dienophiles faster?

The latter turned out to be correct. With 4-phenyl-1,2,4-triazoline-3,5-dione (3) as a more reactive dienophile,[4] 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-β-halostyrenes.[5,6]

3

4 Hal = Cl
5 Hal = Br

6 Hal = Cl
7 Hal = Br

8
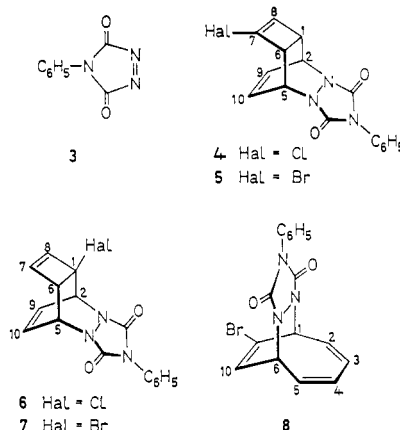
A solution of chlorocyclooctatetraene and 3 in ethyl acetate after 48 hr at 60° yielded, after thick-layer chromatography on silica gel using chloroform as eluent, 27% 4 and 30% 6.[7] Adduct 4 showed the following: mp 208–210°; nmr (CDCl$_3$)[8] 8-H τ 4.12 (s);[9] 9- and 10-H 3.72 (t); 2- and 5-H 4.7–5.1 (m); 1- and 6-H 6.46 and 6.75 (2t). Adduct 6 showed the following: mp 214–216°; nmr (DMSO-d_6) 7- and 8-H, AB spectrum, τ 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°),[3] 25% 7 (mp 216–217°),[3] 10% 8, and, in addition, bromostyrene as rearrangement product; nmr (CDCl$_3$) of 8, vinyl-H in 1:4 ratio, 10-H τ 3.33 (d, $J = 8.0$ Hz); 2- to 5-H 3.6–4.1 (m); C$_6$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).