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 $\Delta H^{\ddagger} = 28.1$ 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.[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
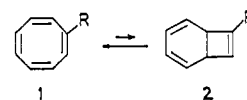
Is the formation of 2 from 1 kinetically or thermodynamically favored over the other three possible monosubstituted bicyclo[4.2.0]octatrienes or does 2 simply add dienophiles faster?

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
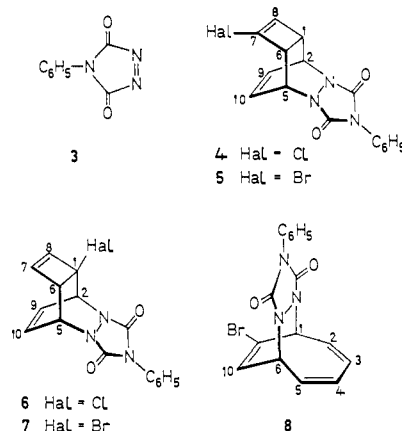
A solution of chlorocyclooctatetraene and 3 in ethyl acetate after 48 hr at 60° yielded, after thick-layer chromatography on silica gel using chloroform as eluent, 27% 4 and 30% 6.[7] Adduct 4 showed the following: mp 208–210°; nmr (CDCl$_3$)[8] 8-H τ 4.12 (s);[9] 9- and 10-H 3.72 (t); 2- and 5-H 4.7–5.1 (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).
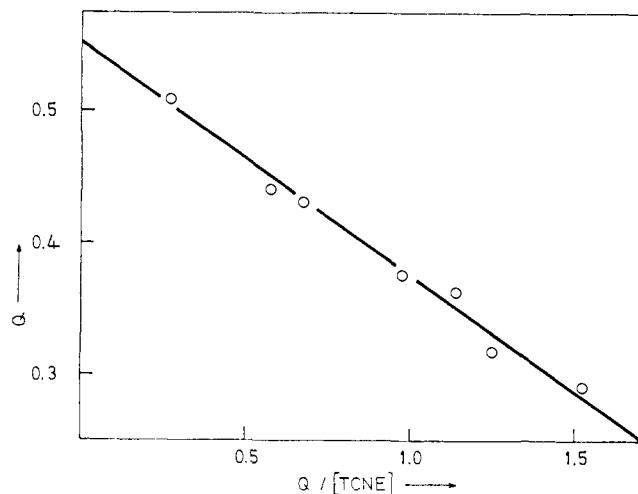
Figure 1. Competition between rearrangement and TCNE addition. Results of Table I are plotted using eq 3.

The 50-fold excess of TCNE makes it possible to use the product ratio instead of the differential quotient; also, assuming $k_{-1} \ll k_i$ in acetonitrile leads to

$$\frac{\%12}{\%13} = \frac{1}{Q} = \frac{k_1(k_{-1}' + k_2'[TCNE]}{k_1'k_2'[TCNE]} \qquad (2)$$

and after transformation to the equation for a straight line, we have

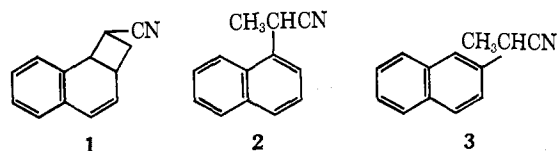$$Q = \frac{k_1'}{k_1} - \frac{k_{-1}'}{k_2'}\frac{Q}{[TCNE]} \qquad (3)$$

The results of Table I are plotted in Figure 1. From the intercept, $k_1'/k_1 = 0.544$ is calculated. Thus, the tautomerization rate constants of bromocyclooctatetraene to 10 and to 11 are in the ratio 65:35 (acetonitrile, 70°). The absolute value of k_1 has been previously reported.[5]

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in the constant ratio of 1:50, were allowed to react in acetonitrile (in this polar solvent k_1 is rate determining for the formation of 12[5]) in increasing dilution; 12 was
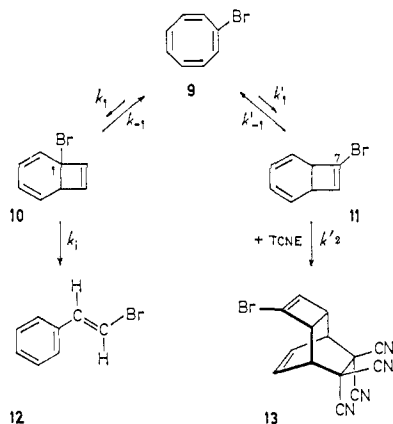
analyzed by glpc using methylnaphthalene as internal standard, and 13 was determined by gravimetry. Table I shows satisfactory total yields and the expected

Table I. Reaction of Bromocyclooctatetraene with TCNE (1:50)[a]

[TCNE], mM	% 12 + 13	Mol % 12	13	13/12
1914	96	63.5	32.8	0.517
765	99	68.7	30.2	0.440
639	95	66.1	28.6	0.433
383	99	72.0	27.0	0.375
319	95	69.5	25.2	0.363
255	97	73.7	23.5	0.319
191	97	75.0	21.8	0.291

[a] In acetonitrile at 70°; competition between rearrangement and adduct formation.

increase of the rearrangement product with decreasing concentration of TCNE.

Applying the steady-state treatment[5] to 10 and 11, one obtains

$$\frac{d[12]}{d[13]} = \frac{k_1 k_i (k_{-1}' + k_2'[TCNE])}{(k_{-1} + k_i)k_1'k_2'[TCNE]} \qquad (1)$$

Solvent Effects on the Photoaddition of Naphthalene and Acrylonitrile. Evidence for an Exciplex as Intermediate

Sir:

We previously reported that the photoaddition of naphthalene and acrylonitrile in alcohol solution affords cycloaddition products,[1,2] e.g., 1, together with naphthylpropionitriles 2 and 3. We have de-

termined[2] that the cycloadducts are formed from the lowest singlet excited state of naphthalene. We now wish to report that the formation of the naphthyl-propionitriles involves the solvent, acting as a proton source. The proton acceptor is very probably the exciplex of naphthalene singlet and acrylonitrile.

The evidence is as follows. First, it was found that the ratio of cycloaddition:substitution depended on the solvent used, and the ratios for some solvents are given in Table I. While several parameters undoubtedly contribute to the solvent effect, the results show that the fraction of substituted naphthalenes increases with acidity and polarity of the protic medium. It is interesting that neither type of adduct is formed in aprotic solvents, even those with a high dielectric constant, e.g., acetonitrile.

Second, it was shown that the most acidic proton of the solvent is incorporated into the methyl groups of 2 and 3. Thus, when deuterium acetate (CH_3CO_2D) or deuteriomethanol[3] (CH_3OD) was employed as solvent, the naphthalene derivatives contained one deuterium label in the methyl groups.[4] The simul-

(1) J. J. McCullough, C. Calvo, and C. W. Huang, *Chem. Commun.*, 1176 (1968); J. J. McCullough and C. W. Huang, *Can. J. Chem.*, 47, 757 (1969).
(2) R. M. Bowman and J. J. McCullough, unpublished results.
(3) We thank Dr. N. H. Werstiuk for this material.
(4) Deuterium assay was by nmr and mass spectra.