

RELATIVE REACTIVITIES OF THE 5-HALOCYCLOPENTADIENES IN DIELS-ALDER  
AND 1,5 SHIFT REACTIONS

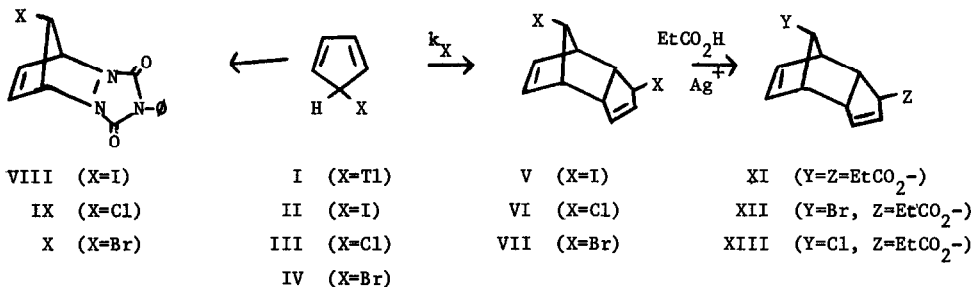
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(Received in USA 23 May 1973; received in UK for publication 7 August 1973)

Recently we have prepared a series of 5-halocyclopentadienes as precursors of the antiaromatic cyclopentadienyl cation. Thus, 5-iodocyclopentadiene (II) was synthesized<sup>1</sup> by reaction of thallos cyclopentadienide (I) with  $I_2$  and used in solvolytic studies of the stability of cyclopentadienyl cation. 5-Chlorocyclopentadiene (III) and 5-bromocyclopentadiene (IV) were prepared<sup>2</sup> by reacting thallos cyclopentadienide with the N-halosuccinimide; the compounds were used in the successful generation<sup>2</sup> of  $C_5H_5^+$  as a ground-state triplet. The availability of this series has also made it possible to study the effect of the halogens on the Diels-Alder reactivity of these cyclopentadienes and on the relative rates of the characteristic 1,5 hydrogen shift in these compounds.

All three of the halocyclopentadienes are much more reactive than is unsubstituted cyclopentadiene in the simple Diels-Alder dimerization. The kinetics were conveniently monitored by removing aliquots and reacting them with an excess of N-phenyltriazolinedione. With this reagent, II forms the previously reported adduct VIII, IV forms a similar adduct X, while the chlorocyclopentadiene III forms a mixture of IX and its chlorine epimer.<sup>3</sup> At 20° in  $CH_2Cl_2$  solution the iodo compound II has a second order dimerization rate constant of  $2.28 \times 10^{-3} M^{-1} sec^{-1}$  and the chloro compound III under the same conditions has a second order rate constant of  $3.5 \times 10^{-3} M^{-1} sec^{-1}$ . For the bromo compound IV the rate was comparable but good data could not be obtained because of the presence of catalytic materials whose effect could be suppressed only irreproducibly with added base (no such effect was observed with compounds II or III). These rate constants should be compared with the observation for cyclopentadiene itself at 25° in various solvents of second order rate constants<sup>4</sup> of  $2-2.5 \times 10^{-6} M^{-1} sec^{-1}$ . Thus, the halogens accelerate the dimerization process by a factor of more than  $10^3$ .



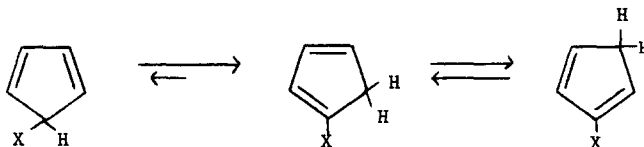
Apparently, the halogen activates both the diene and dienophile in this reaction, since even in the presence of a twelve-fold excess of unsubstituted cyclopentadiene the chloro compound III affords only its dimer with no evidence for reaction with the unsubstituted cyclopentadiene. Rough competitive studies on the dimerization reaction in mixtures of the halocyclopentadienes show that the relative rate of disappearance is III>IV>II. In a competition reaction with the chlorocyclopentadiene (III) and iodocyclopentadiene (II) the unequal rate of disappearance of these materials indicates that there is no strong preference for one of these compounds to act as a diene while the other one acts as dienophile.

We reported previously<sup>1</sup> that the dimerization of II is strikingly accelerated by Ag<sup>+</sup> and we find that this is also true with III and IV. With silver ion in propionic acid II afforded the bis-propionate XI by a process which we have shown<sup>1</sup> to involve a solvolytic Cope rearrangement. Under these conditions, IV afforded both XI and the 8-bromo-1-propionate dimer XII, while III affords only the 8-chloro-1-propionate XIII. These products are also formed under the same conditions from the halodimers V, VI, and VII, in line with our suggestion<sup>1</sup> that they result from subsequent solvolysis of halodimers whose formation is catalyzed by Ag<sup>+</sup>.

The high reactivity of the 5-halocyclopentadienes as diene components in a Diels-Alder reaction probably reflects spiroconjugation<sup>5</sup> of the halogen.<sup>6</sup> In the case of a halocyclopentadiene acting as a dienophile, two factors can be invoked. One is the spiroconjugation effect and the other is an expected effect of the electronegative halogen in withdrawing electrons from the cyclopentadiene system so as to produce, by negative hyperconjugation, a system which resembles cyclopentadienyl cation to a small extent and which should accordingly be reactive as an electron-accepting dienophile. This latter effect is presumably promoted by coordination of Ag<sup>+</sup> with the halogen in the silver catalyzed reactions.

The halocyclopentadienes are not more reactive toward all dienophiles, however. In competition experiments using *N*-phenylmaleimide as the dienophile, the order of reactivity is cyclopentadiene>III>IV>II, with relative reactivities of 1.00, 0.67, 0.64, and 0.17 by careful competitive kinetics. *N*-Phenylmaleimide is a much more electrophilic dienophile than is a halocyclopentadiene. If the transition state for Diels-Alder reaction has appreciable charge-transfer character with an electrophilic dienophile, then the electronegativity of the halogens apparently deactivates the 5-halocyclopentadienes as diene components. It is thus apparent that in the dienes these halogens can be either activating or deactivating in the Diels-Alder reactions depending on the precise character of the dienophile.

At high dilution ( $10^{-3}M$  in toluene) the dimerization processes could be suppressed and we were able to study hydrogen tautomerization of II, III, and IV. Whereas cyclopentadiene-5-D is reported<sup>7</sup> to equilibrate to a mixture of its three possible isomers in one hour at 60°, we find that III requires 2 hr at 75° to reach an equilibrium mixture containing only the 1- and 2-isomers, IV requires 2 hr at 100° to come to this equilibrium, while II has not been completely equilibrated after 6 hr at 100°. These rough quantitative data reveal the striking fact that halogen slows the 1,5-hydrogen shift reaction, even though it stabilizes the product of the reaction. One might have thought<sup>7</sup> that the transition stage for this hydrogen shift would have cyclopentadienyl anion character, and that the halogen would stabilize it. Apparently the converse is true: the 1,5 hydrogen shift must involve local positive, not negative, charge on carbon in its transition state.<sup>8,9</sup>



#### References

1. R. Breslow and J.M. Hoffman, Jr., *J. Amer. Chem. Soc.*, **94**, 2110, 2111 (1972).
2. M. Saunders, R. Berger, A. Jaffe, J.M. McBride, J. O'Neill, R. Breslow, J.M. Hoffman, Jr., C. Perchonock, E. Wasserman, R.S. Hutton, and V.J. Kuch, *ibid.*, **95**, 3017 (1973).
3. Stereochemical assignments are by nmr: VIII has a signal at  $\delta 4.40$ , X at  $\delta 4.48$ , IX at  $\delta 4.53$  and the IX epimer at  $\delta 4.18$  for the proton  $\alpha$  to halogen. The competitive Diels-Alder kinetics were monitored by quenching with excess *N*-phenyltriazolinedione to afford these same

adducts, and nmr analysis.

4. H. Kaufmann and A. Wasserman, J. Chem. Soc., 1939, 870.
5. H.E. Simmons and T. Fukunaga, J. Amer. Chem. Soc., 89, 5208 (1967); P.E. Eaton and R.A. Hudson, ibid., 87, 2769 (1965).
6. There is evidence for unusual magnetic anisotropy in these compounds in the observation that the C-5 proton nmr signals ( $\text{CDCl}_3$ ) occur at  $\delta$ 5.54, 5.07, and 4.91 respectively for compounds II, IV and III; this order is the reverse of that ordinarily seen in alkyl halides.
7. V.A. Mironov, E.V. Sobolev and A.N. Elizanova, Tetrahedron, 19, 1939 (1963); cf. also W.R. Roth, Tetrahedron Lett., 1009 (1964).
8. S. McLean, C.J. Webster, and R.J.D. Ruthford, Can. J. Chem., 47, 1555 (1969) report that methyl on C-5 accelerates the 1,5-H shift. This is consistent with our opposite effect for halogen, although both kinds of substituents stabilize the product. An alternate explanation is that methyl favors, and halogen disfavors, the rehybridization of C-5 toward (more electronegative)  $\text{sp}^2$ . In the product, this effect is overbalanced by the newly-developed conjugation.
9. Support of this work by the National Institutes of Health, and an NIH Postdoctoral Fellowship to C.P., are gratefully acknowledged.