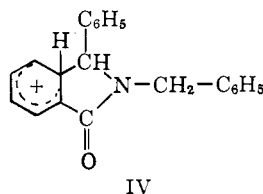


availability of the rather stable σ -complex IV as an intermediate. This species, which could be formed by an "insertion"⁹ of the benzene carbonium ion into the C-H bond, is of course the same intermediate that would be involved if III were formed from II. It is in fact conceivable that the cation II could also be formed from IV rather than by a more direct 1,5-hydride ion transfer. The possibility of such an "insertion" reaction takes cognizance of the similarity between benzene carbonium ions and carbenes.^{11,15}



The independent preparation of the cation II⁴ now makes it possible to study its intramolecular electrophilic substitution reactions. In dry ethylene chloride, II has been found to be stable with respect to five-member ring formation for 24 hr. at room temperature. In the presence of the base tribenzylamine, the phthalimidine III is formed in detectable quantities (n.m.r.) at the end of 10 min. at the same temperature.¹⁷ This remarkable finding probably indicates that the proton removal from the presumed intermediate IV is the rate-determining step in this electrophilic substitution.

In the absence of added base, phthalimidine III was produced in 6% yield at the end of 1 week at room temperature and in 14% yield when the solution was heated at 70° for 1.5 hr. None of the 1-phenyl-2-benzoylisoindoline² which would result by substitution into the benzyl ring could be detected by gas chromatography. Thus, it is evident that this electrophilic ring closure reaction is controlled exclusively by the stereoelectronically imposed proximity of the reacting centers rather than by the electron availability on the ring in which substitution occurs.

The low rate of the intramolecular electrophilic substitution makes it appear doubtful that ring closure could compete with solvolytic cleavage of the cation II. A direct study of this competition was performed by injecting 1 ml. (0.7 mmole) of an ethylene chloride solution of the hexachloroantimonate salt of II into the acetic-sulfuric acid reaction mixture (50 ml.) at the temperature (steam bath) of the previous² diazonium

ion decomposition in this solvent and examining the hydrolysis product by gas chromatography for the phthalimidine III. None was found. If III were indeed formed from the cation II in the diazonium ion decomposition, a simple calculation based on the previous data² indicates that about 9% of this cation should be converted to phthalimidine III under these conditions.

Although this cannot be taken as rigorous proof that the phthalimidine is formed by direct attack of the benzene carbonium ion on the benzylic carbon atom (or on the C-H bond), it is certainly suggestive of this type of mechanism.¹⁸ Experiments now under way should throw more light on this question.

(18) Many of the products that have been reported in diazonium ion decompositions can be explained, although not uniquely, by the "insertion" process. For example, this path is much more attractive than a radical combination mechanism for the production of *m*- and *p*-nitrophenylethanols in the photolytic decomposition of the corresponding diazonium ions in ethanol.¹⁹ The formation of fluorenes, in one case quantitatively, upon deamination of 2-amino-2'-alkylbiphenyls²⁰ is another example. Finally, the reductions that frequently occur when diazonium ions are heated in alcohol solutions could be brought about by insertion of the benzene carbonium ion into the carbinol C-H bond to form a σ -complex followed by loss of a proton and an aldehyde or ketone.

(19) W. E. Lee, J. G. Calvert, and E. W. Malmberg, *J. Am. Chem. Soc.*, **83**, 1928 (1961).

(20) L. Mascarelli and B. Longo, *Gazz. chim. ital.*, **67**, 812 (1937); *Chem. Abstr.*, **32**, 4564 (1938); L. Mascarelli and A. Angeletti, *Gazz. chim. ital.*, **68**, 29 (1938); *Chem. Abstr.*, **32**, 4565 (1938); L. Mascarelli and B. Longo, *Gazz. chim. ital.*, **68**, 121 (1938); *Chem. Abstr.*, **32**, 6235 (1938).

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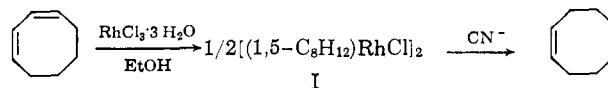
RECEIVED APRIL 6, 1964

The Isomerization of 1,3-Cyclooctadiene to 1,5-Cyclooctadiene via the Rhodium(I) π -Complex

Sir:

Recent reports on the isomerization of cyclooctadiene by iron carbonyl¹ and by potassium *t*-butoxide in dimethyl sulfoxide² have demonstrated that 1,3-cyclooctadiene is thermodynamically the most stable of the isomeric cyclooctadienes. By each method, 1,5-cyclooctadiene is isomerized quantitatively to 1,3-cyclooctadiene.

We wish to report that $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$, which forms π -complexes preferentially with chelating 1,5 dienes,³ under conditions which isomerize other olefins,⁴ isomerizes 1,3-cyclooctadiene to I, the dimer of rhodium(I) chloride-1,5-cyclooctadiene.^{5,6} Analytically pure 1,5-cyclooctadiene is obtained by treating I with aqueous KCN.



(1) J. E. Arnet and R. Pettit, *J. Am. Chem. Soc.*, **83**, 2954 (1961).

(2) D. Devaprabhakara, C. G. Cardenas, and P. D. Gardner, *ibid.*, **85**, 1553 (1963).

(3) E. W. Abel, M. A. Bennett, and G. Wilkinson, *J. Chem. Soc.*, 3178 (1959).

(4) R. E. Rinehart, H. P. Smith, H. S. Witt, and H. Romeyn, Jr., *J. Am. Chem. Soc.*, **84**, 4145 (1962).

(9) This "insertion" reaction would require attack of the cationic carbon on the carbon-hydrogen bond in a direction perpendicular to it. This would presumably involve a transition state of the very same type as that suggested¹⁰ on experimental and theoretical grounds for hydride transfer reactions.

(10) M. F. Hawthorne and E. S. Lewis, *J. Am. Chem. Soc.*, **80**, 4296 (1958).

(11) Both have only two σ -bonds and are thus capable of forming two more. Both are very unselective.¹² The existence of both singlet and triplet carbenes¹³ might also have an analogy in this system since evidence has recently been put forth that such cations may exist in triplet states.¹⁴

(12) E. S. Lewis, *J. Am. Chem. Soc.*, **80**, 1371 (1958); W. E. Doering, R. G. Buttery, R. G. Laughlin, and N. Chaudhuri, *ibid.*, **78**, 3224 (1956).

(13) G. Herzberg and J. Shoosmith, *Nature*, **183**, 1801 (1959).

(14) R. W. Taft, *J. Am. Chem. Soc.*, **83**, 3350 (1961).

(15) The benzene carbonium ion may or may not be associated with a molecule of nitrogen.¹⁶

(16) E. S. Lewis and J. M. Insole, *J. Am. Chem. Soc.*, **86**, 34 (1964).

(17) Competing with phthalimidine formation in this case is a hydride transfer from tribenzylamine to II.⁴

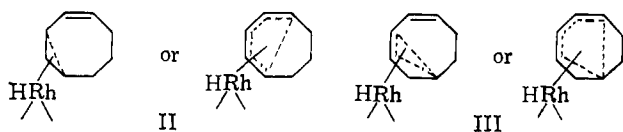
Except for an induction period, I forms from 1,3-cyclooctadiene at a rate comparable to the formation from 1,5-cyclooctadiene (Fig. 1).

In a typical procedure, from 2 g. of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ and 1 ml. of 1,3-cyclooctadiene (97% pure, 2.4% 1,5-isomer, by v.p.c.) in 20 ml. of absolute ethanol, there was obtained, after 24 hr. at 50° , 1.24 g. (66% yield) of I, identical in the X-ray diffraction powder pattern, in the n.m.r. spectrum, and in the infrared spectrum with authentic I prepared by the method of Chatt and Venanzi.⁵

Recrystallized I (0.2 g.) prepared from 1,3-cyclooctadiene was suspended in 20 ml. of 10% aqueous KCN. The orange complex dissolved rapidly giving a colorless solution plus a small amount of insoluble hydrocarbon. The hydrocarbon was extracted into pentane. The pentane solution was dried over anhydrous CaCl_2 , filtered, and concentrated by evaporation. Analysis by v.p.c. (300-ft. capillary column, coated with squalane) revealed only one principal peak (in addition to pentane) at the retention time observed for 1,5-cyclooctadiene. The 1,5-cyclooctadiene was greater than 99 mole % pure; no 1,3-isomer was detected.

No isomerization of hydrocarbon, other than that involved in complex formation, was observed. Excess olefin in the reaction mixture from the preparation of I from 1,3-cyclooctadiene was separated by steam distillation and dried over anhydrous CaCl_2 . Analysis by v.p.c. showed 1,3-cyclooctadiene of 98% purity.

A reasonable mechanism for the isomerization must provide for a rapid hydrogen transfer from the 5,6-position to the 3,4-position of 1,3-cyclooctadiene. We propose π -complex formation, followed by a hydrogen transfer assisted by the metal atom through formation of a rhodium hydride bond,^{7,8} resulting in a π -allyl complex⁹ (e.g., II or III).



An alternative mechanism,¹⁰ involving successive substitutions of one double bond by a hydridic rhodium species,^{10a} we find unattractive. Any stepwise mechanism¹¹ would require formation of substantial quantities of 1,4-cyclooctadiene (at a rate comparable to π -complex formation from 1,5-cyclooctadiene in the absence of isomerization), which in turn would be isomerized to

(5) J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 4735 (1957).
 (6) J. A. Ibers and R. G. Snyder, *J. Am. Chem. Soc.*, **84**, 495 (1962).
 (7) S. S. Bath and L. Vaska, *ibid.*, **85**, 3500 (1963).
 (8) J. Chatt and B. L. Shaw, *Chem. Ind.* (London), 290 (1963).
 (9) For recent references on π -allyl complexes, cf. (a) S. D. Robinson and B. L. Shaw, *J. Chem. Soc.*, 4806 (1963); (b) J. E. Mahler and R. Pettit, *J. Am. Chem. Soc.*, **85**, 3955 (1963).
 (10) T. A. Manuel, *J. Org. Chem.*, **27**, 3941 (1962), has proposed as alternative mechanisms for the isomerization of olefins by iron carbonyl either formation of isomeric π -allyl complexes, or formation of σ -alkyliron compounds.

(10a) NOTE ADDED IN PROOF.—After this communication had been submitted, J. F. Harrod and A. J. Chalk, *J. Am. Chem. Soc.*, **86**, 1776 (1964), proposed a mechanism for the isomerization of n -olefins by group VIII metal salts, including $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$, involving substitutions by metal hydride. Their experimental results can be explained equally well by a mechanism involving π -allyl complexes.

(11) M. Johnson, *J. Chem. Soc.*, 4859 (1963), has discussed the stepwise isomerization observed in hydroformylation reactions.

complexed 1,5-cyclooctadiene. The formation of 1,4-cyclooctadiene (with a configuration stabilized neither by conjugation nor by chelation) is not supported by experimental evidence.

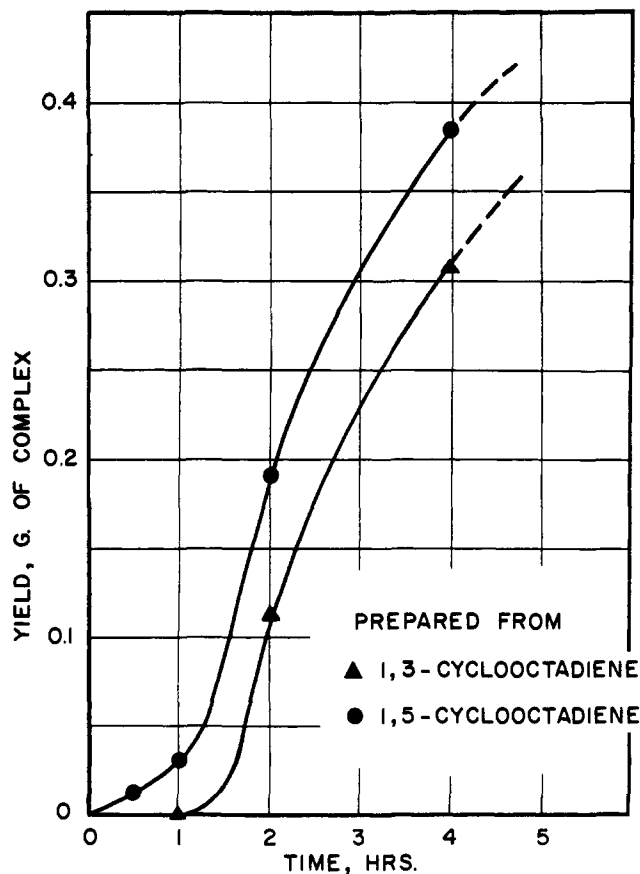


Fig. 1.—Formation of $(1,5\text{-C}_8\text{H}_{12}\text{RhCl})_2$ from 1 g. of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ in 20 ml. of EtOH at 50° with 1 ml. of 1,5-cyclooctadiene and with 1 ml. of 1,3-cyclooctadiene.

Observations on metal halides other than rhodium have shown that under the above conditions isomerization of 1,3-cyclooctadiene to a complex of 1,5-cyclooctadiene cannot be effected by PdCl_2 . A different complex is formed by PdCl_2 from each cyclooctadiene; only the complex from 1,5-cyclooctadiene releases 1,5-isomer upon treatment with aqueous KCN.

"Ruthenium trichloride trihydrate" forms an insoluble complex from 1,3-cyclooctadiene, similar in the infrared spectrum to $(\text{RuCl}_2\text{C}_8\text{H}_{12})_n$ prepared from 1,5-cyclooctadiene.

$\text{IrCl}_3 \cdot 4\text{H}_2\text{O}$ can be used in a manner comparable to $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ to isomerize 1,3-cyclooctadiene to the 1,5-isomer. A low yield of iridium complex, $(\text{IrHCl}_2\text{-C}_8\text{H}_{12})_2$,¹² forms after several days at 50° in ethanol from 1,3-cyclooctadiene (a complex identical in the infrared spectrum, n.m.r. spectrum, and X-ray diffraction powder pattern is formed from 1,5-cyclooctadiene¹³

(12) NOTE ADDED IN PROOF.—Based on appearance, analysis, method of preparation, and an infrared band at 1260 cm^{-1} , this complex is probably identical with the complex prepared from chloroiridic acid and 1,5-cyclooctadiene in ethanol reported independently while this paper was in proof by S. D. Robinson and B. L. Shaw, *Tetrahedron Letters*, No. 20, 1301 (1964).

(13) Chatt and Venanzi⁵ failed to obtain a complex from iridium chloride and 1,5-cyclooctadiene in ethanol, probably because of insufficient reaction time.

