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TRANSFORMATION OF CYCLOOCTA-1,5-DIENE THROUGH ITS PALLADIUM COMPLEX.

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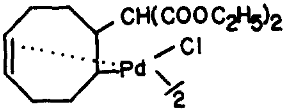
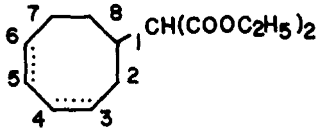
Tsuji and Takahashi(1) reported that the complex I undergoes various transformations at the cyclooctenyl ligand on treatment with borohydride, alkoxide, and alkali to give 2-(cyclooctyl)-malonate(II), 2-(cyclooct-5-enyl)-malonate(III), and 2-(cycloocta-3,5-dienyl)-malonate(IV) respectively.

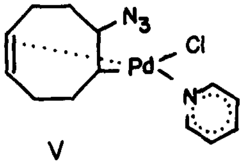
In this paper we wish to describe a few transformations at the cyclooctenyl ligand of the complex VII and VIII which were easily synthesized from dichloro-(cycloocta-1,5-diene)-palladium (VI) by treatment with equivalent amount of sodium azide in methanol and with excess ammonia gas in benzene respectively(2).



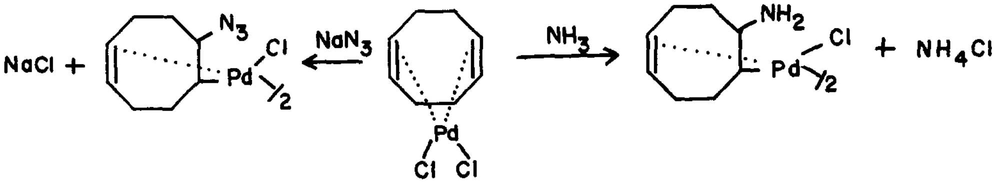
I



II: saturated
III: Δ56, IV: Δ34,56



V



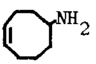
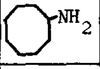
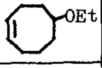
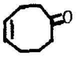
VII VI VIII

Complex VII, pale yellow, mp. 170°(dec.), has two azide bands at 2050 and 2090 cm^{-1} which suggest the complex being the mixture of stereoisomers. Treatment of the complex VII with pyridine gives the monomeric complex V (3) which has the single absorption at 2020 cm^{-1}.

Complex VIII, white, mp. ca.100°(dec.), 3450, 3240, 1620, and 1583 cm^{-1}, decomposes to precipitate metallic palladium on further treatment with ammonia in methanol or chloroform.

Products from the reductive decomposition of the complex VII and VIII are listed in the table. In any reactions the total yield of the products is reasonably high(70 - 90%) though some part of hydrocarbon escaped from the product-mixture during work up.

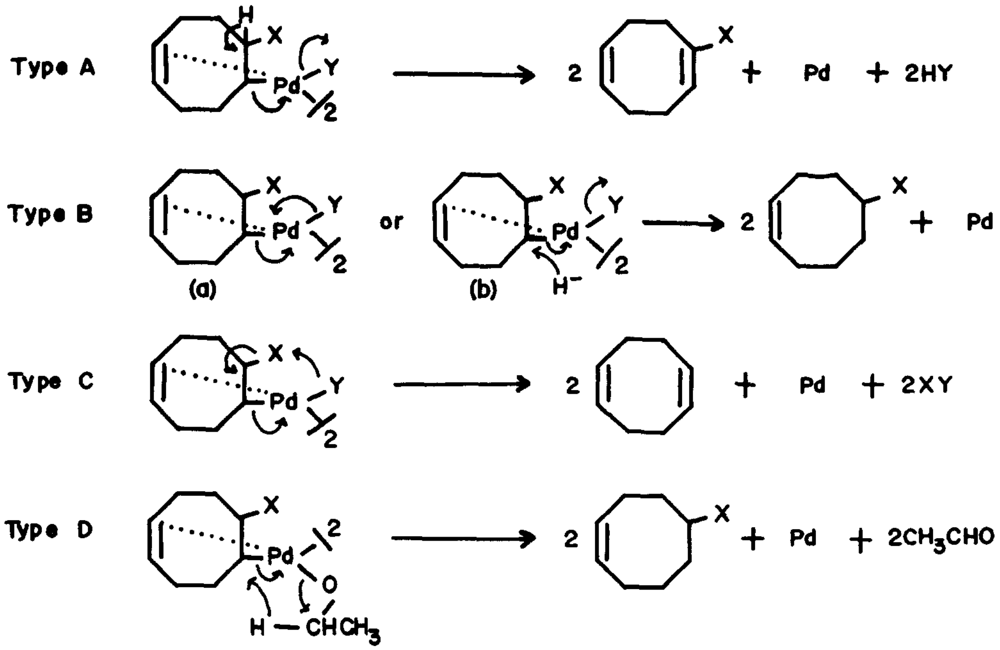
Table; The composition of products.*

		reaction condition							unknown
$NaBH_4$	VII	room temperature, 2 hr.			70%	30%			
	VIII		5%	60%	27%	8%			
Na_2CO_3	VII	70°						80%	20%
	VIII	40 hr.						70%	30%
$NaOC_2H_5$	VII	70°					100%		
	VIII	10 hr.						80%	20%

*Percentage of each components was determined by v.p.c. analysis.

The complex VII looses a nitrogen function completely on treatment with sodium borohydride, sodium carbonate, and sodium ethoxide to give unsaturated cyclooctanes, cyclooct-4-enone, and ethoxy cyclooct-4-ene respectively. This feature can be accounted for by the high "leaving efficiency" of azide group (4) which is easily replaced by hydride, hydroxide, and alkoxide before cleavage of carbon palladium bond. On the other hand, amino group has a poor "leaving efficiency" in nucleophilic substitution(4) and the complex VIII retains amino group on treatment with sodium borohydride to give cyclooct-4-enyl amine and cyclooctyl amine. Though the complex VIII partly looses amino group on borohydride reduction to afford cycloocta-1,5-diene and cyclooctene, this feature can preferentially be interpreted in other way than substitution of amino group with hydride(described later). Formation of cyclooct-4-enone from the complex VIII on treatment with sodium carbonate(THF-H_2O) and sodium ethoxide must involve the initial formation of enamine intermediate.

We classified these reactions into four types as shown in the equations on next page, though the arrow may not represent the real movement of electron.



In type A reaction the cleavage of the carbon-palladium bond accompanies the loss of hydrogen attached to the carbon bearing the substituent X. This type of reaction gives cycloocta-1,5-diene and cyclooct-4-enone from the complex VII after replacement of azide group with hydride and hydroxide(X=H, Y=H, and X=OH, Y=OH). Cyclooctene is presumably formed by hydrogenation of cycloocta-1,5-diene with palladium hydride existing in the reaction mixture(1). The same process must operate for the production of cyclooct-4-enone from the complex VIII with sodium carbonate(THF-H_2O)and the sodium ethoxide <u>via</u> the enamine intermediate which hydrolyses to the ketone(X=NH_2, Y=OH, and X=NH_2, Y=OC_2H_5).

Formation of cyclooct-4-enyl amine -- also cyclooctyl amine on further hydrogenation -- from the complex VIII on treatment with sodium borohydride must be accounted for by the type B reaction(X=NH_2, Y=H). The type B process involves the intramolecular hydride shift from the palladium to next carbon depicted as (a) or the hydride may originate from another molecule of borohydride depicted as (b).

The third type of the reaction(type C) must be responsible for the formation of cycloocta-1,5-diene from the complex VIII on borohydride reduction(X=NH_2, Y=H). The initial substitution of amino group with hydride is hardly possible and the loss of amino group can be rationalized by the type C process.

The formation of ethoxy cyclooct-4-ene from the complex VII, whose azide group is initially replaced by alkoxy group, must be reffered to type D process. In this process the cleavage of palladium-carbon bond accompanies the hydrogen transfer from the carbinol carbon to the cyclooctene moiety(5).

Though we need more information for the discussion of the reaction mechanism, the reductive cleavage of the complex VII and VIII can be classified into four types A,B,C, and D. Two types of the reactions compete in some reaction.

REFERENCES

1) J. Tsuji and H. Takahashi; J. Am. Chem. Soc., 87, 3275 (1965). ibid, 90, 2387 (1968).

2) A similar reaction with primary amine has been reported. G. Pairo, A. De Rengi and R. Palumbo; Chemical Communication, 1150 (1967).

3) J. K. Stille and R. A. Morgan; J. Am. Chem. Soc., 88, 5135 (1966).

4) The basicity of substituent is the measure of "leaving efficiency". The less basic group is the better leaving group. cf. E. S. Gould; MECHANISM and STRUCTURE in ORGANIC CHEMISTRY, Henry Holt and Company, New York (1959), p. 261.

5) This reaction mechanism was initially proposed by Tsuji and Takahashi. cf. reference 1.