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Organic Synthesis by Means of Noble Metal Compounds. L.[1] Palladium Catalyzed Reactions of Enamines with Butadiene and Allyl Acetate

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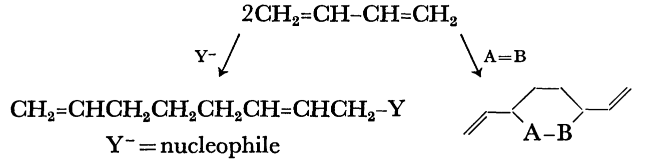
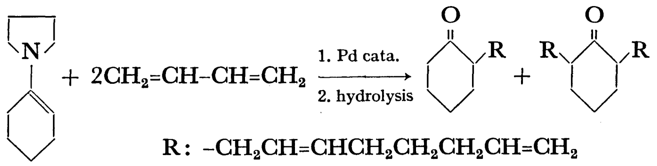
Recently extensive studies have been carried out on the palladium catalyzed dimerization reactions of butadiene, which can be classified into two types.[3] The first one is the dimerization reaction, especially with incorporation of a nucleophile such as water, alcohols, carboxylic acids, ammonia, amines, and some active methylene compounds to give 1-substituted 2,7-octadienes. Another one is the cocyclization reaction with a dipolar double bond such as aldehydes and isocyanates to give six-membered heterocyclic compounds.



We have investigated a reaction of enamine with butadiene in the presence of a palladium catalyst based on the following considerations. Enamines are considered to be a strong nucleophile and their nucleophilic reactions are well known.[4] In addition, enamines have dipolar double bond, which takes part in cyclization reactions to form six- or four-membered rings. Thus with these dual reactivities of butadiene and enamines in mind, we have carried out the reaction of enamine with butadiene in the presence of a palladium catalyst in order to determine which type of the reaction, namely nucleophilic attack or cocyclization of enamine, takes place. Concerning the interaction of enamine with a palladium complex, we have shown before that enamines are allylated with π-allylpalladium chloride.[5]

Pyrrolidine enamine of cyclohexanone was allowed to react with butadiene by using palladium acetate combined with triphenylphosphine as the catalyst. The reaction observed was not the cocyclization, but the introduction of 2,7-octadienyl moiety at the α position of cyclohexanone took place. In addition, 2,6-disubstituted cyclohexanone was obtained as a minor product. Pyrrolidine enamine of cyclopentanone behaved similarly giving 2-(2,7-octadienyl)cyclopentanone as a main product, accompanied by 2,5-di(2,7-octadienyl)-cyclopentanone.



R: $-CH_2CH=CHCH_2CH_2CH_2CH=CH_2$

The reaction undoubtedly proceeds through nucleophilic attack of the enamine on an intermediate π-allylic palladium complex formed from butadiene and the palladium compound. Formation of the intermediate π-allylic complex was proposed by Hagihara and his co-workers for dimerization of butadiene in the presence of nucleophiles.[6] Allyl acetate is known to form the most simple π-allylpalladium complex,

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[1] Part XLIX. T. Susuki and J. Tsuji, This Bulletin, **46**, 655 (1973).

[2] The content of this paper was presented with other reactions at the 23rd Intern. Congr. Pure Appl. Chem., July 1971, Boston, *Pure Appl. Chem. Suppl.*, **2**, 107 (1972).

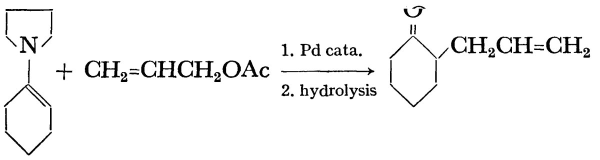
[3] For references: J. Tsuji, *Accounts Chem. Res.*, **6**, 8 (1973).

[4] A. G. Cook, "Enamines", Marcel Dekker, Inc., New York, N. Y. (1969).

[5] J. Tsuji, H. Takahashi, and M. Morikawa, *Tetrahedron Lett.*, 1965, 4387.

[6] S. Takahashi, H. Yamazaki, and N. Hagihara, This Bulletin, **41**, 254 (1968).

which is expected to react with enamines in the presence of the palladium catalyst. Thus we carried out the reaction of allyl acetate with the enamine of cyclohexanone, and 2-allylcyclohexanone was obtained as expected.[7]



Experimental

Reaction of the Cyclohexanone Enamine. A solution of 1-pyrrolidinocyclohexene (15 g), palladium acetate (100 mg), triphenylphosphine (200 mg) in acetonitrile (40 ml) was placed in an autoclave, and butadiene (12 g) was introduced. The autoclave was shaken for 3 hr at 80 °C. Two layers were formed, which were subjected to hydrolysis with hydrochloric acid at 50 °C for 30 min. Dichloromethane (100 ml) was added and the solution was washed with water. After being dried, the solvent was evaporated. The residue was distilled to give 2-(2,7-octadienyl)cyclohexanone (13.5 g) and 2,6-di(2,7-octadienyl)cyclohexanone (6.8 g), which were identified by the following data.

2-(2,7-Octadienyl)cyclohexanone. Bp 130—135 °C/3 mmHg, IR (neat); 993, 911 (CH=CH_2), 968 cm^{-1} (*trans* olefin). The NMR spectrum (CCl_4) showed complex olefin bands at τ 3.5—4.8 (=CH–) and τ 4.8—5.4 (=CH_2), which were identical with the olefin bands of the NMR spectrum of the known methyl 2,7-octadienyl ether.[8]

Found: C, 81.66; H, 10.73%; mol wt (mass spectrum), 206. Calcd for $C_{14}H_{22}O$: C, 81.50; H, 10.75%; mol wt, 206.32.

2,4-Dinitrophenylhydrazone, mp 93—94 °C. Found: C, 62.54; H, 6.81; N, 14.51%. Calcd for $C_{20}H_{26}O_4N_4$: C, 62.16; H, 6.78; N, 14.50%.

2,6-Di(2,7-octadienyl)cyclohexanone. Bp 170—175 °C/1 mmHg, showed the similar NMR olefinic bands as those of the above-shown monoderivative. Found: mol wt, 314. Calcd for $C_{22}H_{34}O$: 314.49. Hydrogenation over platinum oxide absorbed 4 mol of hydrogen to give 2,6-dioctylcyclohexanone, bp 160—165 °C/0.5 mmHg, mp 37—38 °C (from methanol–ether).

Found: C, 82.16; H, 12.84%; mol wt, 322. Calcd for $C_{22}H_{42}O$: C, 81.91; H, 13.13%; mol wt. 322.56.

Reaction of Cyclopentanone Enamine. A mixture of the enamine (10 g), butadiene (9 g), dimethylformamide (30 ml), palladium acetate (100 mg), and triphenylphosphine (200 mg) was allowed to react at 85 °C for 5 hr. After the usual work-up, 2-(2,7-octadienyl)cyclopentanone (8.2 g) and 2,5-di(2,7-octadienyl)cyclopentanone (4.2 g) were obtained.

2-(2,7-Octadienyl)cyclopentanone. Bp 100—105 °C/3 mmHg. The NMR spectrum showed the similar olefinic pattern as that of the corresponding cyclohexanone derivative.

Found: C, 81.36; H, 10.60%; mol wt. 192. Calcd for $C_{13}H_{20}O$: C, 81.20; H, 10.48%; mol wt. 192.29.

2,5-Di(2,7-octadienyl)cyclopentanone. Bp 155—165 °C/2 mmHg.

Found: C, 83.76; H, 10.68%; mol wt. 300. Calcd for $C_{21}H_{32}O$: C, 83.94; H, 10.73%; mol wt. 300.47.

Hydrogenation gave 2,5-dioctylcyclopentanone, mp 45—47 °C.

Found: C, 81.86; H, 12.90%; mol wt. 308. Calcd for $C_{21}H_{40}O$: C, 81.75; H, 13.07%; mol wt. 308.53.

Reaction of Allyl Acetate and Cyclohexanone Enamine. A mixture of 1-pyrrolidinocyclohexene (18 g), allyl acetate (15 g), acetonitrile (30 ml), palladium acetate (100 mg), and triphenylphosphine (200 mg) was stirred at 80 °C for 5 hr. Then 10 ml of concd hydrochloric acid and 10 ml of water were added and the mixture was stirred for 30 min. After the usual work-up, distillation gave 2-allylcyclohexanone (7.2 g, 70—73 °C/3 mmHg) and 2,6-diallylcyclohexanone (3 g, 85—95 °C/3 mmHg). They were identified with authentic samples prepared by the known method[9] by NMR and IR spectra and mixed mp determination of 2,4-dinitrophenylhydrazones (148—150 and 113—115 °C).

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7) The same reaction was reported recently by; H. Onoue, I. Moritani, and S. Murahashi, *Tetrahedron Lett.*, **1973**, 121.

8) S. Takahashi, T. Shibano, and N. Hagihara, This Bulletin, **41**, 454 (1968).

9) G. Opitz, H. Mildenberger, and H. Suhr, *Ann.*, **649**, 47 (1961).