REACTION OF DIAZOALKANES WITH UNSATURATED COMPOUNDS. COMMUNICATION 2. CYCLOPROPANATION OF OLEFINS BY DIAZOMETHANE IN THE PRESENCE OF PALLADIUM COMPOUNDS\*

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Derivatives of metals of the nickel subgroup, especially, palladium, serve as specific catalysts for the cyclopropanation of olefins by diazo compounds. Thus, palladium diacetate and bis( $\pi$ -allylpalladium) dichloride have been used in the cyclopropanation of styrene [3], norbornene (NB), norbornadiene (NBD) [4], other strained cyclic olefins [5], and  $\alpha$ , $\beta$ -unsaturated ketones [6]. The selective cyclopropanation of terminal olefins by diazomethane in the presence of palladium compounds has also been noted [1, 7]. In this regard, palladium catalysts behave identically in the cyclopropanation of olefins by both diazomethane and, for example, alkyl diazoacetates [8], which indicates a common mechanism for these reactions.

In the present work we studied the cyclopropanation of some olefins by  $CH_2N_2$  in the presence of palladium compounds. We first established that the use of different palladium compounds such as  $PdCl_2$ ,  $Pd(OAc)_2$ ,  $[\pi-C_3H_5PdCl]_2$ , or  $(PhCN)_2 \cdot PdCl_2$  does not have a significant effect on the nature of the transformation of these or other olefins, while the yields of the corresponding cyclopropanation products under identical conditions are largely a function of the nature of the double bonds. Nevertheless, the use of  $[\pi-C_3H_5PdCl]_2$  and  $(PhCN)_2 \cdot PdCl_2$  is favored in light of the good solubility of these complex catalysts in  $CH_2Cl_2$  which is employed as the solvent. Thus, the reaction of NB or NBD with  $CH_2N_2$  at from  $-10^\circ$  to  $0^\circ C$  in the presence of 0.3-0.4 mole %  $(PhCN)_2 \cdot PdCl_2$  (relative to the starting olefin) leads to tricyclo[ $3.2.1.0^{2}, 4$ ]octane (I) and tetracyclo[ $3.3.1.0^{2}, 4.0^{6}, 8$ ]nonane (II), respectively, in ~100% yields. This requires virtually stoichiometric amounts of  $CH_2N_2$ 



Cyclohexene (CHX), cycloheptene (CHP); and cyclooctene (COC) in the presence of ~0.4 mole % palladium catalyst are converted at from  $-10^{\circ}$  to  $0^{\circ}$ C by the action of CH<sub>2</sub>N<sub>2</sub> to the corresponding products (III), namely, bicyclo[4.1.0]heptane (IIIa) in ~15% yield, bicyclo-[5.1.0]octane (IIIb) in 80-82% yield, and bicyclo[6.1.0]nonane (IIIc) in 90-93% yield, respectively.



n = 4 (a), 5 (b), 6 (c).

\*A partial report on the results of this work was given at the Twelfth Mendeleev Congress on General and Applied Chemistry in Baku [1]. For communication 1, see [2].

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The low yield of (IIIa) is related to the rapid decomposition of the catalyst in the case of CHX which will be discussed below. This apparently accounts for the previous failure to cyclopropanate CHX by diazomethane in the presence of palladium compounds [4]. However, in the present work, we demonstrated the feasibility of obtaining (IIIa) by this reaction by selection of optimal conditions. Thus, the addition of  $(PhCN)_2 \cdot PdCl_2$  in three or four 10-mg portions to CHX at -15°C and the use of a ~20% molar excess of  $CH_2N_2$  increased the yield of (IIIa) to 60%.

The reaction of 1,5-cyclooctadiene (COD) with  $CH_2N_2$  at from  $-10^{\circ}$  to 0°C in the presence of a palladium catalyst leads directly to the accumulation of the products of exhaustive cyclopropanation, namely, tricyclo[7.1.0.0<sup>4,6</sup>]decanes (V) which is seen, for example, in the use of equimolar amounts of COD and  $CH_2N_2$ . The major product is the crystalline trans isomer; the trans/cis ratio is about 7:1 (the structure assignments were carried out according to Fieser and Sachs [9]). The cyclopropanation of this diene by  $CH_2N_2$  in the presence of CuCl [2] gives both isomers in approximately equal amounts



The intracyclic bonds in cyclopentadiene (CPD) and 6-methyl-6-cyclopropylfulvene (MCPF) are cyclopropanated with equal success by  $CH_2N_2$  in the presence of  $(PhCN)_2 \cdot PdCl_2$ 



The PMR spectrum of tricyclo[4.1.0.0<sup>2,4</sup>]heptane (VII) obtained from CPD fully supports its trans configuration [10]. In the case of MCPF, only the endocyclic double bonds undergo cyclopropanation. The PMR spectrum of 5-(1'-cyclopropylethylidene)tricyclo[4.1.0.0<sup>2,4</sup>]heptane (IX) has only one methyl group proton signal, which may be taken as evidence of the formation of only the trans isomer.

The addition of methylene in the cyclopropanation of a mixture of 1- and 2-methylcyclopentadienes (in ~0.83:1 ratio) by  $CH_2N_2$  in the presence of  $(PhCN)_2 \cdot PdCl_2$  occurs only at the unsubstituted double bond of the starting dienes and leads to a mixture of 2- and 3-methylbicyclo[3.1.0]hex-2-enes in ~1:0.8 ratio and 78% yield.



The highly regioselective action of the palladium catalysts is very evident in the  $CH_2N_2$  cyclopropanation of dienic hydrocarbons with a terminal vinyl group such as cis-piperylene, isoprene, and 4-vinylcyclohexene (VCH); in all three cases, there is predominant reaction at the unsubstituted vinyl group and the greatest regioselectivity is found in the cyclopropanation of piperylene ( $\geq 30:1$  ratio).



Especially high selectivity in the cyclopropanation of various double bonds by the action of  $CH_2N_2$  in the presence of palladium catalysts is found in the cyclopropanation of olefins containing strained intracyclic double bonds. For example, only NBD is initially cyclopropanated upon passing  $CH_2N_2$  through a mixture of NBD and VCH in the presence of catalytic amounts of any of the palladium catalysts noted above; this selectivity is independent of the ratio of the starting dienes. The cyclopropanation of VCH, predominantly at the terminal vinyl group, begins only after the conclusion of the exhaustive cyclopropanation of NBD.

Anciaux et al. [8] have noted that the selective cyclopropanation of olefins by alkyl diazoacetates in the presence of palladium compounds may be the result of the initial formation of a complex of the olefin with the catalyst which then reacts with the diazo compound. The observed predominant cyclopropanation of olefins having enhanced double bond  $\pi$ -acidity indeed may be related to the participation of  $\pi$ -olefinic complexes with the palladium catalyst; the stability of these complexes is in accord with this behavior. Hence, we studied the reaction of CH<sub>2</sub>N<sub>2</sub> with previously prepared  $\pi$ -olefinic complexes of PdCl<sub>2</sub> with NBD and COC [11]. However, the treatment of these compounds at  $-10^{\circ}$ C led to the regeneration of the corresponding olefins and the separation of a black precipitate of metallic palladium. On the other hand, if this reaction is carried out in an excess of the olefins, we find decoloration of the initially yellow olefin•PdCl<sub>2</sub> complex upon the passage of the first portion of CH<sub>2</sub>N<sub>2</sub>, while the further introduction of CH<sub>2</sub>N<sub>2</sub> leads to the usual course of the reaction with the formation of cyclopropane hydrocarbons such as (IIIc) in the case of COC.

Since the formation of metallic palladium in these experiments undoubtedly is related to manifestation of the reductive properties of diazomethane, we assume that there is initial reduction of Pd(II) to Pd(0) in the cyclopropanation of olefins in the presence of various Pd(II) compounds. Pd(0) complexes with the olefin and participates in the formation of the cyclopropane compounds. Of course, such olefins as NBD, COC, COD, and, to a lesser extent, olefins with a terminal vinyl group, will stabilize the Pd(0) formed as  $\pi$ -olefinic complexes (XIX) when these olefins are present in excess. Such complexes require the presence of several ligands in the coordination sphere; their insufficiency or replacement by olefins with lower complexing capacity ( $\pi$ -acidity) would lead to the precipitation of metallic palladium.



Since olefinic complexes of zero-valent metals of the nickel triad are extremely reactive and exist mainly at temperatures below 0°C [12], confirmation of the zero-valent state of palladium in this reaction was found in its capacity to form more stable complexes with other ligands such as phenyl phosphite. For this purpose, after all the complex of PdCl<sub>2</sub> with the olefin was dissolved and the cyclopropanation of the olefin begun, we stopped passing  $CH_2N_2$  and added an excess of  $(PhO)_3P$  to the reaction mixture. In this case, a colorless crystalline complex  $[(PhO)_{3}P]_{4}Pd$  separated out. This complex was identical to that obtained previously by the reduction of  $[(PhO)_{3}P]_{2}PdCl_{2}$  by hydrazine in the presence of  $(PhO)_{3}P$  [13].

The high selectivity of the cyclopropanation of various double bonds by diazomethane in the presence of palladium compounds is apparently a result of their selectivity in the formation and stabilization of  $\pi$ -olefinic complexes of Pd(0) as well as the absence of dissociation of these complexes, which distinguish these complexes from olefinic complexes of Cu(I). While slight changes in the coordinated ligand relative to the starting olefin are characteristic for the olefinic complexes of the copper subgroup, extensive changes are found in the coordinated ligand, in isoelectronic complexes of formally zero-valent metals of the nickel subgroup: lengthening of the double bond, change in the olefin [14]. Hence, the reaction of olefinic complex (XIX) with CH<sub>2</sub>N<sub>2</sub> may occur either through the intermediate formation of a methylene coordination complex or lead to the direct nucleophilic cleavage of the Pd-C bond by the action of CH<sub>2</sub>N<sub>2</sub> with the elimination of nitrogen. The intermediate metallocyclic compound (XX) apparently immediately decomposes with the formation of a new olefinic complex and a cyclopropane compound.

It is interesting to note that the presence of free diazomethane in the reaction mass in some cases, for example, due to the high rate of its inlet or the reduced temperature of the reaction mixture does not have a deleterious effect on the cyclopropanation reaction, which, in the case of CuCl, leads to catalyst "poisoning" [2]. Thus, the success of the cyclopropanation of olefins by diazomethane in the presence of palladium compounds is primarily a factor of the capacity of the olefins to retain Pd(0) in solution in a complex form.

## EXPERIMENTAL

The analysis of the reaction mixtures was carried out by gas-liquid chromatography on an LKhM-8MD chromatograph with a flame-ionization detector and I-02 integrator on a  $300 \times 0.3$ -cm column packed with 5% SE-30 or 15% Carbowax 20M on Chromatone N-AW-DMCS using helium as the carrier gas. The flow rate was 20 ml/min. Preparative separation was carried out on an LKhP-7I chromatograph on a  $300 \times 1.2$ -cm column packed with 5% SE-30 on Chromatone N-AW-DMCS (0.25-0.36 mm) using nitrogen as the carrier gas. The flow rate was 200 ml/min. The PMR spectra were obtained on a Tesla BS-467 spectrometer at 60 MHz for chloroform solutions with TMS as the internal standard. The IR spectra were taken neat on a UR-20 spectrometer between KBr plates.

The olefin samples were distilled prior to use. The content of the major component was 98-99%. The samples of cyclopentadiene and isomeric methylcyclopentadienes containing up to 6% CPD, 42% 1-methyl- and ~50% 2-methylcyclopentadienes [15] were obtained by the monomerization of the corresponding dimeric adducts. A sample of 6-methyl-6-cyclopropylfulvene was obtained according to Olah et al. [16]. A sample of diazomethane was obtained by the alkaline hydrolysis of N-nitroso-N-methylurea (MNM) [2]. The yield of  $CH_2N_2$  according to acidometric titration was 60-65%. The identification of the cyclopropanation products and their yields were determined by gas-liquid chromatography using a control mixture of the starting olefin and the corresponding cyclopropane hydrocarbon as well as by PMR spectroscopy.

<u>Bicyclo[4.1.0]heptane (IIIa).</u> a) A sample of  $CH_2N_2$  obtained from 3.5 g (33 nmoles NMM) was passed through a solution of 1.65 g (20 mmoles) cyclohexene (CHX) and 0.03 g (PhCN)<sub>2</sub>PdCl<sub>2</sub> in 5 ml  $CH_2Cl_2$  at from  $-10^\circ$  to 0°C. The reaction mass became black and palladium separated out. The conversion of CHX to (IIa) was found by gas-liquid chromatography to be about 15%.

b) Four 8-mg portions of  $(PhCN)_2PdCl_2$  were added to a solution of 0.82 g CHX in 3 ml  $CH_2Cl_2$  at  $-15^{\circ}C$  with the continuous passage of  $CH_2N_2$  (from 2 g NMM). Foaming and diminution of the yellow color were observed. The yield of (IIIa) was about 60%.

<u>Bicyclo[5.1.0]octane (IIIb).</u> By a method analogous to method above, 1.0 g cyclopentene (CHP) in the presence of 0.02 g (PhCN)<sub>2</sub>PdCl<sub>2</sub> and CH<sub>2</sub>Cl<sub>2</sub> generated from 2 g NMM gave (IIIb) in 80-82% yield.

Bicyclo[6.1.0]nonane (IIIc). A sample of (IIIc) was obtained in 93% yield (according to gas-liquid chromatographic analysis) by methoda) from 1.1 g cyclooctene (COC) in the presence of 0.02 g (PhCN)\_2PdCl\_2 and  $CH_2N_2$  generated from 2 g NMM. Distillation yielded 1.1 g (~89%) (IIIc), bp 78-79°C (40 mm).

<u>Tricyclo[3.2.1.0<sup>2</sup>, 4]octane (I).</u> A sample of (I) was obtained in 96% yield according to method a) from 0.95 g norbornene (NB) in the presence of 0.01 g Pd(OAc)<sub>2</sub> (or 0.008 g  $[\pi-C_3H_5 \cdot PdCl]_2$ ) and CH<sub>2</sub>N<sub>2</sub> generated from 2 g NMM.

<u>Tetracyclo[3.3.1.0<sup>2,4</sup>.0<sup>6.8</sup>]nonane (II)</u>. A sample of  $CH_2N_2$  generated from 7 g NMM was introduced to a mixture of 1.85 g norbornadiene (NBD) and 0.03 g (PhCN)<sub>2</sub>PdCl<sub>2</sub> (or 0.015 g PdCl<sub>2</sub>) in 5 ml  $CH_2Cl_2$  at from -10°C to 0°C. Hexane was added to the mixture obtained. The reaction mixture was filtered through silica gel and distilled to yield 2.25 g (94%) (II) with bp 61-62°C (20 mm). The PMR spectrum corresponds to the exo, exo-isomer [17].

<u>Tricyclo[7.1.0.0<sup>4,6</sup>]decane (V).</u> An equimolar amount of  $CH_2N_2$  generated from 3.5 g NMM was passed into a mixture of 2.2 g 1,5-cyclooctadiene (COD), 2 ml  $CH_2Cl_2$ , and 0.03 g (PhCN)<sub>2</sub>PdCl<sub>2</sub> at from -10° to 0°C. The yields of bicyclo[6.1.0]non-4-ene (IV), trans-(V), and cis-(V) were ~5, 38, and 5.5%, respectively, as determined by gas-liquid chromatographic analysis. Then, the same amount of  $CH_2N_2$  (similarly generated from 3.5 g NMM) was introduced at from -10° to 0°C. The yields of the hydrocarbon products were increased to 6, 72, and 10%, respectively. Distillation gave 2.2 g of a mixture of the two isomers of (V), bp 79-82°C (20 mm). Preparative gas-liquid chromatography at 185°C gave pure trans-(V), mp 40-41°C [2].

<u>Tricyclo[4.1.0.0<sup>2,4</sup>]heptane (VII).</u> A mixture containing 10% starting CPD, 15% bicyclo-[3.1.0]hex-2-ene (VI), and 75% (VII) was obtained by analogy to method b) from 1.3 g cyclopentadiene (CPD) in the presence of (PhCN)<sub>2</sub>PdCl<sub>2</sub> added in three 8-mg portions and CH<sub>2</sub>N<sub>2</sub> generated from 7 g NMM. Distillation yielded 1.1 g (59%) (VII), bp 100-103°C (750 mm) with ~98% purity. The mixture distills virtually entirely; up to 15% (VII) remains in the predistillate. The PMR spectrum of (VII) is in full accord with the structure of the trans isomer [10].

 $\frac{5-(1-Cyclopropylethenylidene)tricyclo[4.1.0.0<sup>2,4</sup>]heptane (IX).}{(IX) with bp 95-98°C (16 mm) was obtained by analogy to method a) from 2.6 g 6-methyl-6-cyclo$ propylfulvene (MCPF) in the presence of 0.05 g (PhCN)<sub>2</sub>PdCl<sub>2</sub> and CH<sub>2</sub>N<sub>2</sub> generated from 7 g $NMM. PMR spectra (<math>\delta$ , ppm): 1.48 s (CH<sub>3</sub>) and 1.85-1.25 m (CH) (total of 8H), 1.0-0.16 m (8H, CH<sub>2</sub>). IR spectrum ( $\nu$ , cm<sup>-1</sup>): 1018, 1010, 3070, and 3075 (C-C and C-H in the cyclopropane fragment), 1620 w (C=C).

<u>2- and 3-Methylbicyclo[3.1.0]hex-2-enes (X).</u> By analogy with method b), a mixture was obtained containing 75-78% (X) from 1.6 g of a mixture of 1- and 2-methylcyclopentadienes containing 6% CPD in the presence of  $(PhCN)_2PdCl_2$  (added in four 7-mg portions) and  $CH_2N_2$  generated from 4 g NMM. Both isomers, which give a single gas-liquid chromatographic peak, were isolated using preparative gas-liquid chromatography at 110°C. The yield of (X) was 1.2 g (63%). PMR spectrum ( $\delta$ , ppm): 5.52 (0.55H),and 4.92 m (0.45H, C=CH), 2.35 m (2H, CH<sub>2</sub>), 1.8 q and 1.67 m (<sup>4</sup>J ~ 1 Hz, CH<sub>3</sub>) and 1.8-1.3 m (HC=CH) (total of 5 H), 0.78 m (1H, syn-H), -0.08 m (1H, anti-H).

<u>Propenylcyclopropane (XI)</u>. By analogy to method a), a sample of 1.3 g (90%) (XI) with bp 71-73°C was obtained from 1.35 g cis-piperylene in the presence of 0.02 g (PhCN)<sub>2</sub>PdCl<sub>2</sub> and CH<sub>2</sub>N<sub>2</sub> generated from 4 g NMM.

<u>Cyclopropanation of Isoprene</u>. A sample of 0.02 g  $[\pi-C_3H_5PdCl]_2$  or 0.02 g  $Pd(OAc)_2$  was added to 2.7 g isoprene in the absence of solvent and a sample of  $CH_2N_2$  generated from 8 g NMM was introduced. The reaction mixture was shown by gas-liquid chromatographic analysis to contain 70% isopropenylcyclopropane (XIII), 12% l-methyl-l-vinylcyclopropane (XIV), 9% l-cyclopropyl-l-methylcyclopropane (XV), and the starting diene.

<u>Cyclopropanation of 4-Vinylcyclohexene (VCH)</u>. By analogy to method b), amixture of 68-70% 4-cyclopropylcyclohexene (XVI), <4% 3-vinylnorcarane (XVII), 7% 3-cyclopropylnorcarane (XVIII), and starting VCH was obtained from 1.1 g VCH in the presence of 0.03 g (PhCN)<sub>2</sub>PdCl<sub>2</sub> and  $CH_2N_2$  generated from 2.1 g NMM. The ratio of the isomers of the mixture isolated by preparative gas-liquid chromatography at 180°C was found by analysis of the PMR spectrum to be about 20:1. The yield of this mixture was 0.8 g (65%). The signals for the olefin protons of the HC-CH fragments in (XVI) and C=CH<sub>2</sub> in (XVII) are seen in nonoverlapping regions of the spectrum at 5.58 and 5.0-4.7 ppm.

<u>Reaction of Norbornadienepalladium Dichloride and Cyclooctenepalladium Dichloride with</u> <u>CH<sub>2</sub>N<sub>2</sub>.</u> A sample of CH<sub>2</sub>N<sub>2</sub> was introduced into a sample of 0.27 g C<sub>7</sub>H<sub>8</sub>•PdCl<sub>2</sub> or 0.29 g C<sub>8</sub>H<sub>14</sub>• PdCl<sub>2</sub> [11] in 2-4 ml CH<sub>2</sub>Cl<sub>2</sub> in the presence of 0.10 g nonane taken as the internal standard for gas-liquid chromatographic analysis. Immediate precipitation of metallic palladium was noted. The solution contained about 75% of the starting olefins in complex form. A sample of  $CH_2N_2$  obtained from 0.7 g NMM was introduced into a suspension of 0.13 g  $C_7H_8 \cdot PdCl_2$  and 0.2 g NBD in 3 ml  $CH_2Cl_2$  at  $-10^{\circ}C$ . The complex dissolved and the solution became colorless. Then, 0.8 g  $(PhO)_3P$  and about 20 ml hexane were added at  $-10^{\circ}C$ . The colorless precipitate formed was filtered off, recrystallized from ethanol, and dried in an argon stream to yield 0.54 g  $(\sim 80\%)$  tetrakis(triphenylphosphite)palladium. Found: C 64.7; H 4.6; P 9.5; Pd 7.9%. Calculated for  $C_{72}H_{60}O_{12}P_4Pd$ : C 64.17; H 4.49; P 9.19; Pd 7.90%. PMR spectrum ( $\delta$ , ppm): 7.35-6.99 m and 6.97-6.68 m; the intensity of the multiplets was 3:2.

## CONCLUSIONS

1. In the cyclopropanation of mono- and polyolefins by diazomethane in the presence of palladium compounds, strained intracyclic and terminal double bonds are initially cyclopropanated with high selectivity.

2. The cyclopropanation of olefins proceeds through a step involving the reaction of diazomethane with a  $\pi$ -olefinic complex of zero-valent palladium formed upon the reduction of the palladium compounds introduced as the catalyst by diazomethane.

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