SBORNÍK
Vysoké školy chemickotechnologické v Praze C 26 (1980)
Organická chemie a technologie

СБОРНИК
Пражского химико-технологического института C 26 (1980)
Органическая химия и технология

SCIENTIFIC PAPERS
of the Prague Institute of Chemical Technology C 26 (1980)
Organic Chemistry and Technology

PALLADIUM COMPLEX CATALYZED LINEAR DIMERIZATION OF 2-METHYL-1,3-BUTADIENE

JAN BARTOŇ AND VLASTIMIL RŮŽIČKA

Department of Organic Technology

Received November 6, 1979

Linear dimerization of 2-methyl-1,3-butadiene using complex homogeneous catalyst has been studied. Homogeneous catalytic system consisted of palladium compounds (palladium(II)bis-2,4-pentadionate, palladium(II)acetate, or palladium(II)-nitrate), triphenylphosphine, potassium phenoxide, and 2-methyl-1,3-butadiene. It was found that the 2,7-dimethyl-1,3-trans-7-octatriene is the main product when this catalytic system is added to the mixture of 2-propen-1-ol and 2-methyl-1,3 butadiene. The study of the effect of different palladium compounds on the conversion and on the selectivity of reaction revealed that the highest values of both factors result if palladium (II)bis-2,4-pentadionate complex was used.

Untill now monoterpenes are obtained mostly form natural resources which could not secure any substantial increase of production in the near future. New possibilities of direct

synthesis of acyclic monoterpenes from 2-methyl-1,3-butadiene, which is the basic building block of terpenes, are therefore searched.

Direct synthesis of acyclic monoterpenes ocimene and myrcene has been announced recently in the patent [1]. According to this patent, ocimene and myrcene were obtained from 2-methyl-1,3-butadiene using homogeneous complex catalytic system prepared from $Pd(NO_3)_2$ (or $Pd(CH_3COO)_2$) and triphenylphosphine in the presence of allylic alcohols and MOR (where M=Na,K; and R=C_1-C_5 alk(en)yl, or phenyl). In this work we reexamined patented catalytic system described above. We used homogeneous catalytic systems prepared by mixing of palladium compound (palladium(II)bis-2,4-pentadionate, Palladium(II)acetate, or palladium(II)nitrate), triphenylphosphine, and potassium phenoxide in 2-methyl-1,3-butadiene. Catalysts prepared by this procedure were added to a mixtures of 2-methyl-1,3-butadiene and 2-propen-1-ol.

EXPERIMENTAL PART

Materials

2-Propen-1-ol (pure,Lachema Brno) and 2-methyl-1,3-butadiene (pure, stabilized, Fluka AG) were rectified and dried over molecular sieve, triphenylphosphine (puriss. Fluka AG) used as obtained commercially, potassium phenoxide was prepared from phenol and potassium in toluene, palladium(II)bis-2,4-pentadionate complex, palladium acetate and anhydrous palladium nitrate were prepared using literature procedures [2,3,4].

Apparatus

A glass autoclave of total volume 450 cm^3 consisted of two parts. Parts A and B were manufactured from thick-wall glass tubes of inner diameter 70 mm with spherical ground glass joints. In part A an other co-axial tube of inner diameter 20 mm was internally sealed to obtain two spaces for separated

preparation of catalytic systems. Appropriate sealing of both parts was achieved using bakelite ring flanges with four bolts. The best sealing material was plastic cement COLORPLAST (Matador, Bratislava). The flanges were equipped with steel bars cage which served as the carrying construction of glass autoclave.

Typical Experimental Procedure

A) Preparation of catalytic system at laboratory temperature:

The following chemical were introduced in the described sequence into 25 ml Erlenmayer flask: palladium(II)bis-2,4-pentadionate complex (0,8 mmol), triphenylphosphine (0,8 mmol), 2-methyl-1,3-butadiene (60 mmol), and potassium phenoxide (1,6 mmol). After an addition of potassium phenoxide the colour of reaction mixture changed to brownish violet. The mixture was left for 10 minutes with occasional shaking. Then it was poured into part B of glass autoclave to the already present 140 mmol of 2-methyl-1,3-butadiene and 40 mmol of 2-propen-1-ol. The autoclave was closed and put on 50°C bath. Mixture was stirred externally with magnetic stirrer. Revolutions of driving motor were set on 400 r.p.m. After selected reaction time the autoclave was cooled to laboratory temperature and carefully opened. The total loss of reaction mixture mass was generally about 2 - 8% of its starting value and was directly proportional to the reaction time. For the purposes of material balance this loss of mass was added to the amount of unreacted 2-methyl-1,3-butadiene.

Concentration of dimers in reaction mixtures was determined chromatographically and the dimers were isolated by preparative operations (distillation of unreacted 2-methyl-1,3-butadiene and column chromatography on silicagel (20 - 90 μ) for removal of catalyst). The resulting crude dimers were distilled with b.p. 55 - 58°C/2,8 kPa giving yields about 20 - 30% lower than expected on the basis of the chromatographic analysis.

B) Preparation of catalytic system at 50°C

Magnetic stirrer, $Pd(NO_3)_2$ (0,2 mmol), 2-methyl-1,3-buta-

diene (30 mmol), triphenylphosphine (0,2 mmol) and potassium phenoxide (0,8 mmol) were introduced into the inner tube of part A of glass autoclave. 2-Methyl-1,3-butadiene (70 mmol), and 2-propen-1-ol (20 mmol) were put into annular space together with a magnetic stirred. Assembled glass autoclave was put on water bath at 50°C with part A down. After 15 min the autoclave was turned bottom upwards (part B down) and the reaction started. A workup of reaction mixture was the same as described in preceding part.

Palladium(II)nitrate could not be transfered quantitatively into reaction space under conditions for preparation of catalytic system at reaction temperature (Table I, exp. No.6), as well as under laboratory temperature, because this palladium compound adhered firmly to the bottom of space for preparation of catalytic system.

The experiment No.5 was carried out by direct introduction of $Pd(NO_3)_2$ into reaction space without separate preparation of catalytic system.

During the course of reaction a black coating, formed probably by colloidal palladium, deposited on the wall of reactor.

Analytical Methods

Reaction mixtures of 2-methyl-1,3-butadiene dimers were analyzed chromatographically on gas chromatograph CHROM 4 (Laboratorní přístroje, Praha) with flame ionization detector. Glass column of 2,5 m length with 2 mm I.D. packed with 15% of Apiezon L on Chromaton N-AW-HMDS was used at 100°C working temperature.

Analysis shows that four isomers are present, the 2,7-dimethyl-1,3-trans-7-octatriene (DMOT) being formed with more than 50% selectivity. Molecular weight, determined by mass spectrometry, was 136. The mass spectrum of a dimer represented by a rider peak on a tail of the DMOT peak could not be reliably identified. The structure of DMOT was verified by means of NMR, IR, and mass spectrometry.

Table I

Results of 2-methyl-1,3-butadiene dimerization

No.	Ratio of $Pd(X)_2$:Ph_3P:PhOK:PROL:MBTD[a]	t_r (°C)	t (hr)	x_K	Dimers		Higher Oligomers %
					Total %	DMOT %	
X=acac							
1.	1:1:4:100:500[b,g]	50	17	0,3	75	82	25
2.	1:1:4:100:500[b,c,g]	50-62	12	0,6	66	93	34
3.	1:1:4:50:220[d,g]	50	10	0,6	60	85	40
X=AcO							
4.	1:1:4:100:500[b,g]	50	16	0,15	95	70	5
$X=NO_3$							
5.	1:1:4:100:500	50	16	0,1	95	80	5
6.	1:1:4:100:500[b,f]	50	10	0,01	100	65	-
X=acac							
7.	1:1:2:50:250[e,g]	50	17	0,5	66	87	34
8.	1:1:2:50:250[e,g]	50	12	0,43	84	86	16
9.	1:1:2:50:250[e,g]	50	9	0,36	90	85	10
10.	1:1:2:50:250[e,g]	50	5	0,22	93	80	7
11.	1:1:2:50:250[e,g]	50	2	0,08	99	40	1

a) Ph_3P = triphenylphosphine, PhOK = potassium phenoxide, PROL = 2-propen-1-ol, MBTD = 2-methyl-1,3-butadiene; molar ratio

b) catalytic system $Pd(X)_2$:Ph_3P:PhOK:MBTD 1:1:4:30

c) in rocking steel autoclave with frequency 600 min^{-1}

d) catalytic system $Pd(X)_2$:Ph_3P:PhOK:MBTD 1:1:4:75

e) catalytic system $Pd(X)_2$:Ph_3P:PhOK:MBTD 1:1:2:75

f) catalytic system prepared at 50°C

g) catalytic system prepared at laboratory temperature

Mass spectrum (70 eV):m/e (rel.intensity) = 136(7), 121(23), 107(15), (93(15), 81(100), 79(46), 55(15), 53(35), 41(37), 39(30).

RESULTS AND DISCUSSION

The results of palladium(II)complex catalyzed dimerization of 2-methyl-1,3-butadiene are presented in Table I. The selection of experimental conditions had only preliminary character, nevertheless some more generall conclusion can be proposed.

On the basis of comparison of the experiments Nos. 1 - 3 it can be stated that an increase in temperature 10°C had the similar effect on yield and selectivity of reaction as twofold increase in palladium(II)bis-2,4-pentadionate complex, triphenylphosphine, and potassium phenoxide concentration at temperature 50°C.

The catalytic system formed from $Pd(acac)_2$ had the highest activity under comparable conditions of 2-methyl-1,3-butadiene conversion as follows from experiments Nos. 1,4, and 5. With this catalytic system we measured the time-concentration dependence of reaction products and the selectivity of DMOT formation in dimer mixture on total concentration of dimers in reaction mixture (Fig. 1 and 2) at 50°C.

From Fig. 1 we can see that the DMOT concentration had a maximum (t = 12 hrs.) while the concentration of unidentified dimers remained constant from approx. t = 4 hrs. This results can be explained by assumption that the higher oligomers are formed predominantly from DMOT. The Fig. 2 shows that the selectivity of DMOT formation is going up to 90% with increasing concentration of dimers in reaction mixture (or with reaction time resp.).

The order of DMOT formation was practically zero for the 2-methyl-1,3-butadiene up to the conversion α_x = 0,3. Reaction velocity was $7,3.10^{-3}$ mol DMOT/$g_{Pd(acac)_2}$.hr.100 g of reaction mixture.

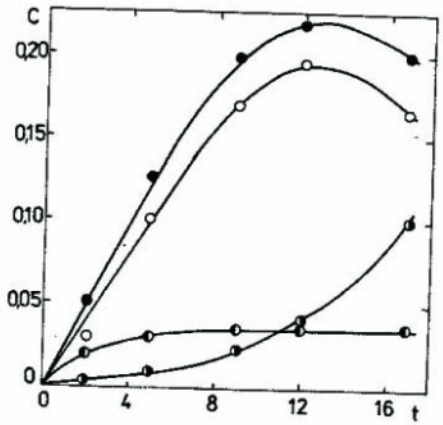

Fig.1 Concentration of Products versus Time
C=conc.,mol/100 g of reaction micture
t=time in hrs.
○ DMOT, ● dimers, ◐ unidentified dimers,
◑ higher oligomers expressed as dimers

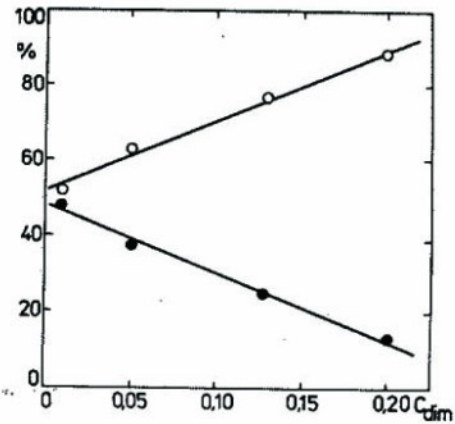

Fig.2 Dependence of DMOT selectivity on concentration of dimers
C_{dim}=conc.of dimers,mol/100g of react.mixt.
○ DMOT, ● unidentified dimers

As follows from comparison of experiments Nos. 3, 8, and 9 a decrease in an amount of reduction component of catalytic system from the ratio $Pd(acac)_2$: PhOK = 1 : 4 on 1 : 2, resulted in decreased activity of whole catalytic system. Consequently, this brought about a lower conversion of starting compound and an increase in selectivity on DMOT in the same time period.

The synthesis of DMOT from 2-methyl-1,3-butadiene is described in a number of papers or patents [5-9], from which the work of Josey [7] presented also a reaction mechanism. This work did not confirm the formation of myrcene and ocimene from 2-methyl-1,3-butadiene and catalytic system studie, but their presence could not be admittedly excluded as three dimers were not identified. But the fact that the 2,7-dimethyl-1,3-trans-7-octatriene is the main product shows a relation of our work with the papers mentioned above, [5-9].

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Lineární dimerizace 2-metnyl-1,3-butadienu působením homogenních komplexních palladiových katalyzátorů

Jan Bartoň a Vlastimil Růžička

Byla studována lineární dimerizace 2-metnyl-1,3-butadienu působením homogenních komplexních katalyzátorů. Homogenní komplexní katalytický systém byl vytvořen z palladiové sloučeniny (bis-2,4-pentadionato) palladnatý komplex, octan palladnatý nebo dusičnan palladnatý), trifenylfosfinu, fenolátu draselného a 2-metnyl-1,3-butadienu. Bylo zjištěno, že katalytický systém všech tří palladiových sloučenin přidaný do směsi 2-propen-1-olu a 2-metnyl-1,3-butadienu poskytuje zejména 2,7-dimetnyl-1,3-trans-7-oktatrien.

Byl studován vliv použitých palladiových sloučenin na stupeň konverze 2-metnyl-1,3-butadienu a selektivitu reakce. Nejvyššího stupně konverze a selektivity reakce bylo dosaženo použitím bis(2,4-pentadionato) palladnatého komplexu.