Tetrahedron Letters Vol. 21, pp 3787 - 3790
© Pergamon Press Ltd. 1980. Printed in Great Britain

0040-4039/80/0922-3787$02.00/0

SULFINATE AS COCATALYST 2[1]: PALLADIUM CATALYZED DIMERIZATION OF BUTADIENE WITH ACYLOINS

Y. Tamaru, R. Suzuki,[2] M. Kagotani, and Z. Yoshida*
Department of Synthetic Chemistry, Kyoto University,
Yoshida, Kyoto 606, Japan

Abstract. Toluenesulfinate serves as a cocatalyst for the selective formation of α-hydroxy α-octa-2,7-dienyl ketones (**2**, the products of C-C bond formation) in the reaction of palladium catalyzed dimerization of 1,3-butadiene with acyloins, while the same reaction using triphenylphosphine, instead of toluenesulfinate, as a cocatalyst provides a mixture of **2** and 2-oxy octa-2',7'-dienyl ethers (**3**, the products of C-O bond formation).

Previously we have reported that sodium salts of alkyl-, aryl-, and aralkylsulfinic acids serve as a cocatalyst for the palladium catalyzed dimerization of 1,3-butadiene with primary and secondary alcohols to give 2,7-octadienyl alkyl ethers in high yields.[1] Here we wish to report that the complex prepared in situ from palladium chloride and sodium toluenesulfinate[3] nicely catalyzes a dimerization reaction of butadiene with α-hydroxy ketones (i.e., acyloins). Making marked contrast to the ether formation reaction with alcohols as mentioned above, acyloins (**1a**~**1f**) reacted with butadiene at the carbon atom bearing a hydroxyl group to give rise to the α-hydroxy α-octa-2,7-dienyl ketones (**2**, the products of C-C bond formation reaction) selectively with a concomitant formation of small amounts of the C-O bond formation products (2-oxy octa-2',7'-dienyl ethers **3**) (equation 1).

Results of reactions with some typical acyloins are summarized in Table I, which shows the generality of the present reaction for acyloins with a variety of structures. An acyloin is one of the typical active methylene compounds and its alkali metal salt reacts with alkyl halide at the carbon bearing a hydroxyl group.[4] Therefore, the present reaction may be recognized as one example of the reactions of palladium catalyzed butadiene dimerization with active methylene compounds (such as diethyl malonate, acetylacetone, α-sulfonyl ketones, etc.). But, to our surprise, despite the extensive studies on this field,[5] no report has appeared on the reaction of butadiene with acyloin, which might partly be attributed to the non-selectivity for the reactions using triphenylphosphine as a cocatalyst. All the palladium-triphenylphosphine complexes examined (palladium complexes b, c, and d, Table I) turned out to catalyze the reaction to give an unpredictable mixture of products (**2** and **3**) in low yields. Among them, exceptionally high selectivity for the C-O bond

Table I. Palladium Catalyzed Dimerization of Butadiene with Acyloins[a)]

Entry	Acyloin	Palladium Complex[b)]	Conversion (%)[c)]	Isolated Yield (%)[d)]	Product Ratio[e)]	
					2[f)]	3[f)]
1	1a[f)]	a	100	87	89	11
2	1a	b	97	34[g)]	3	97
3	1a	c	24	(37)	5	95
4	1a	d	53	(28)	16	84
5	1b	a	100	47	100	∿ 0
6	1b	b	38	(8)	75	25
7	1c	a	90	42	98	2
8	1c	b	52	(6)	57	43
9	1d	a	93	44	100	∿ 0
10	1d	b	97	75	89	11
11	1e	a	98	(57)	93	7
12	1e	b	78	(26)	56	44
13	1f	a	95	88	100	0
14	1f	b	62	70	66	34

a) Molar ratio of reactant is as follows: For entries 1∿4, palladium complex (1 mmol), acyloin (160 mmol), butadiene (120∿140 mmol), and with (460 mmol, entry 1) or without H_2O (entries 2, 3, 4). For entries 5∿10 and 12∿14, palladium complex (1 mmol), acyloin (50∿100 mmol), butadiene (150∿300 mmol), and dimethyl sulfoxide (15∿30 ml). For entry 11, H_2O (470 mmol) was added to the above reaction mixture (entries 5∿10 and 12∿14).

b) Small letters a, b, c, and d are meant to refer to the palladium complexes $PdCl_2$ (1 mmol)+p-$CH_3C_6H_4SO_2Na \cdot 4H_2O$ (5 mmol), $Pd(PPh_3)_4$, $Pd(PPh_3)_2$(maleic anhydride), and $Pd(OAc)_2$ (1 mmol)+PPh_3 (4 mmol), respectively.

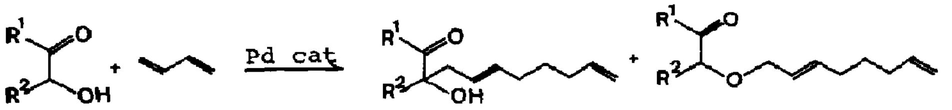
c) Conversion is determined either on the basis of butadiene recovered (entries 1∿4) or acyloin recovered (entries 5∿14).

d) The values in parentheses refer to the vpc yields taking bibenzyl as an internal standard.

e) Product ratio is determined on the basis of area intensities (vpc).

f) For the structures of 1, 2, and 3, see equation 1.

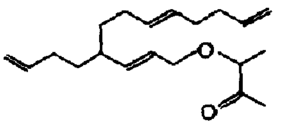
g) In addition to 2 and 3, 4 and 5 were isolated in 11 and 16% yields, respectively (see text).



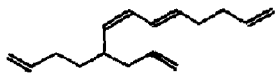
1 **2** **3**

1a	$R^1=R^2=CH_3$	1d	$R^1=PhCH_2$, $R^2=H$
1b	$R^1-R^2=(CH_2)_4$	1e	$R^1=Ph$, $R^2=H$
1c	$R^1-R^2=(CH_2)_3$	1f	$R^1=R^2=Ph$

formation was observed in the reaction with **1a** when $Pd(PPh_3)_4$ was used as a catalyst (entry 2, Table I). In the same run, in addition to **2** and **3** ($R^1=R^2=CH_3$), butadiene tetramers **4** and **5**[6] were also produced in 11 and 16% yields, respectively, whose structures were assigned tentatively as depicted.[7]



4



5

The reduced isolated yields encountered in the reactions with **1b**, **1c**, **1d**, and **1e** may be due to the propensity of self-dimerization of these acyloins to form 2,3,5,6-tetrasubstituted 2,5-dihydroxy-1,4-dioxanes.[8,9]

When an unsymmetric acyloin (**1**; $R^1=C_2H_5$, $R^2=CH_3$) was subjected to the reaction under the same conditions as entry 1, three kinds of products were isolated, two of which were the products of type **2** ($R^1=C_2H_5$, $R^2=CH_3$ and $R^1=CH_3$, $R^2=C_2H_5$ in 38 and 31% yields, respectively) together with **3** ($R^1=C_2H_5$, $R^2=CH_3$, 10%).[10] This result suggests that the present reaction proceeds via an enol-form of **1**.

Experiments typified with entry 1 are as follows. Magnetical stirring of $PdCl_2$ (185 mg, 1.04 mmol) and $p\text{-}CH_3C_6H_4SO_2Na\cdot 4H_2O$ (1.26g, 5.03 mmol) in 8 ml of H_2O at ambient temperature for 30 min forms yellow suspension of palladium complex. To the suspension in a screw capped test tube are added acetoin (**1a**, 14 g, 158 mmol) and 1,3-butadiene (6.5 g, 120 mmol) and the mixture was stirred vigorously at ambient temperature for 20h. After recovery of butadiene (no butadiene is recovered in this run), sat. NaCl was added to the reaction mixture and extracted with benzene twice. Benzene extracts were dried over Na_2SO_4, condensed and the residue was distilled under reduced pressure (~110°/35 mmHg) to give a mixture of **2** and **3** ($R^1=R^2=CH_3$) in a ratio of 89:11 as a colorless liquid (10.3 g, 87% yield based on butadiene), each of which was purified by preparative vpc. **2** ($R^1=R^2=CH_3$):

^{1}H NMR (δ in CCl_4) 1.31(s, 3H), 1.57∿2.20(m, 6H), 2.12(s, 3H), 2.32(d, J=6Hz, 2H), 3.45(s, 1H), 4.73∿6.18(m, 5H); IR (neat film, cm^{-1}) 3400m, 3100w, 1715s, 1645w, 1165m, 990w, 970m, 910m; mass spectrum (m/e, rel. intensity) 153(19), 109(18), 95(100), 88(54), 67(69), 55(57), 43(98). $\underset{\sim}{3}$ (R^1=R^2=CH_3): ^{1}H NMR (δ in CCl_4) 1.21(d, J=7Hz, 3H), 1.32∿2.43(m, 6H), 2.05(s, 3H), 3.76(q, J=7Hz, 1H), 3.95(d, J=5Hz, 2H), 4.85∿6.27(m, 5H); IR (neat film, cm^{-1}) 3060w, 1715s, 1640w, 1110s, 990w, 970m, 910m; mass spectrum (m/e, rel. intensity) 109(35), 67(100), 55(35), 43(71).

In conclusion, sodium toluenesulfinate proved to be a cocatalyst for the selective formation of $\underset{\sim}{2}$ in the palladium catalyzed dimerization of butadiene with acyloins. The efficiency of the present reaction is augmented by the ease with which it is performed (ambient temperature, neutral conditions, without care for moisture or air) and also by the interesting structural features of the products as a synthetic intermediate.[4,11]

Acknowledgement. We are grateful for the partial support for this research from the Ministry of Education, the Japanese Government (Grant-in-Aid for Scientific Research No. 475663).

References and Notes

1) Part 1: Y. Tamaru, M. Kagotani, R. Suzuki, and Z. Yoshida, Chem. Lett., 1329 (1978).
2) Research Fellow from Daicel Chemical Co. Ltd..
3) Sodium p-toluenesulfinate was purchased from Nakarai Chemical Co. and used without purification.
4) a) J. H. van deSande and K. R. Kopecky, Can. J. Chem., 47, 163 (1964);
   b) F. Chen, R. E. Robertson, and C. Ainsworth, J. Chem. Eng. Data, 16, 121 (1971).
5) B. M. Trost, Tetrahedron, 33, 2615 (1977).
6) W. Kein and H. Chung, J. Org. Chem., 37, 947 (1972).
7) The similar tetramerization of butadiene is observed in the reaction of butadiene with 2,3-dihydroxybutane when tetrakis(triphenylphosphine)palladium was used as a catalyst, where 3-hydroxy-2-butyl 2,7-octadienyl ether (dimer) and 3-hydroxy-2-butyl 4-(3',7'-octadienyl)-2,7-octadienyl ether (tetramer) were isolated in 62 and 22% yields, respectively.
8) No significant peaks, ascribable to products except for $\underset{\sim}{2}$ and $\underset{\sim}{3}$, were observed on vpc (except for the entry 2, see text).
9) J. C. Sheehan, R. C. O'Neill and M. A. White, J. Am. Chem. Soc., 72, 3376 (1950).
10) The regioisomer $\underset{\sim}{3}$ (R^1=CH_3, R^2=C_2H_5) was not detectable, probably being the result of steric prohibition of reaction around the moiety of the hydroxyl group.
11) T. Hase, Synthesis, 36 (1980).

(Received in Japan 30 June 1980)