CONCLUSIONS

1,2-Dichloroethane, 1,4-dichlorobutane, and bis (2-chloroethyl) ether were obtained by the reaction of ethylene and anodically generated chlorine radicals in methanol and in aqueous acetonitrile, and 1-methoxy-2-chloroethane was also obtained in methanol.

LITERATURE CITED

- 1. G. A. Tedoradze, V. A. Paprotskaya, and A. P. Tomilov, Elektrokhimiya, 10, 1292 (1974).
- 2. M. A. Kalinin and V. V. Stender, Zh. Prikl. Khim., 19, 1045 (1946).
- 3. G. A. Tedoradze, D. A. Ashurov, E. A. Ponomarenko, A. P. Tomilov, Yu. A. Yuzbekov, V. A. Paprotskaya, and B. N. Babaev, in: Electrochemical Synthesis of Monomers [in Russian], Nauka, Moscow (1980), p. 209.
- 4. A. P. Tomilov, Yu. D. Smirnov, and M. I. Kalitina, Zh. Prikl. Khim., <u>38</u>, 2123 (1965).
- 5. V. A. Grinberg, V. R. Polishchuk, L. S. Kanevskii, L. S. German, A. M. Skundin, and Yu. B. Vasil'ev, Izv. Akad. Nauk SSSR, Ser. Khim., 344 (1980).
- 6. F. Pattison, J. Stotchers, and R. G. Woolford, J. Am. Chem. Soc., 78, 2256 (1956).
- V. A. Grinberg, V. R. Polishchuk, E. I. Mysov, L. S. German, L. S. Kanevskii, V. V. Tsodikov, and Yu. B. Vasil'ev, Izv. Akad. Nauk SSSR, Ser. Khim., 2825 (1977).
- 8. C. D. Nenitescu, Organic Chemistry [Russian translation], Vol. 1, Inostr. Lit., Moscow (1962).
- 9. R. G. Woolford, J. Soong, and W. S. Lin, Can. J. Chem., 45, 1837 (1967).
- 10. L. Eberson and K. Nyberg, Tetrahedron, 32, 2185 (1976).
- 11. S. L. Kiperman, Introduction to the Kinetics of Heterogeneous Catalytic Reactions [in Russian], Nauka, Moscow (1974).
- 12. E. Stenhagen, S. Abrahamson, and F. W. McLafferty, Atlas of Mass Spectral Data, Vol. 1, New York (1969), p. 2.

SYNTHESIS OF UNSATURATED ALCOHOLS

BY TELOMERIZATION OF H₂O WITH 1,3-DIENES,

CATALYZED BY PALLADIUM COMPLEXES

U. M. Dzhemilev, V. V. Sidorova, and R. V. Kunakova UDC 542.97:547.36

The activation of H_2O molecules in their reaction with butadiene by means of low-valent phosphine complexes of palladium has provided the basis for a promising method for the preparation of 1,7- and 2,7-octadienols (I) and (II) [1-7]. It has been shown to be possible to prepare nonadienols by the concurrent telomerization of butadiene and isoprene with H_2O [8]. A necessary condition for the successful accomplishment of these reactions is the inclusion of CO_2 in the composition of the catalyst. The relatively high consumption of catalyst and the low selectivity of these reactions [1-8] renders them of little use for the preparation of unsaturated alcohols.

In order to develop a selective method for the synthesis of octadienols, and for the preparation of other unsaturated alcohols, the reaction of 1,3-dienes with complexed H_2O , catalyzed by palladium compounds, was first examined. It would be expected that H_2O present in crystalline hydrates of the type $MX_n(H_2O)_m$ would be activated by complexation with the central metal atom, and would react with 1,3-dienes more readily than free H_2O to give alcohols (I) and (II). Preliminary experiments showed that butadiene reacted with complexed H_2O over the catalyst $Pd(acac)_2 - PPh_3 - AlEt_3$ in the absence of CO_2 .

Thus, telomerization of butadiene with the complex $CuSO_4 \cdot 5H_2O$ in the presence of this catalyst (Pd : PPh₃:Al=1:3:4, 90°C, 6 h) in acetone gave a mixture of unsaturated alcohols consisting of (I), (II), and the ether (III) in an overall yield of ~50%, calculated on H₂O. The yields and compositions of the telomerization products varied considerably depending on the reaction conditions and the diene :H₂O ratio

Institute of Chemistry, Bashkir Branch, Academy of Sciences of the USSR, Ufa. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 3, pp. 584-588, March, 1983. Original article submitted May 21, 1982.

Time, b	Conver-	Yield of reaction products, %			H ₂ O:	Conver-	Yield of reaction products, %		
	H ₂ O,%	(1)	(II)	(111)	butadiene ratio	H ₂ O, %	(I)	(II)	(111)
4 6 10	30 41 50	74 73 59	17 12 20	9 15 21	1:1 1:2 1:4	47 30 12	48 79 61	14 9 9	38 12 5

TABLE 1. Effects of Ratios of Reactants and Reaction Time * on the Yields and Compositions of Products of the Telomerization of Butadiene with Complexed H₂O

*Reaction conditions: $CuSO_4 \cdot 5H_2O \ 0.05$ mole, butadiene 0.5 mole, 90 °C, Pd)acac)₂-PPh₃-AlEt₃ (1:3:4), Pd:H₂O=1:500, solvent - acetone.



As will be seen from Table 1, as the telomerization time increases the yields of (I)-(III) increase substantially, reaching 50% after 10 h. Increasing the concentration of butadiene in the catalysate reduces the overall yield of (I)-(III), but in these experiments the selectivity with respect to (I) was ~ 61%.

Of the phosphorus and nitrogen-containing ligands tested [(EtO)₃P, (PhO)₃P, Bu₃P, PPh₃, C₅H₅N, Et₃N, Et₂NH], the formation of (I)-(III) in satisfactory yields was only observed with PPh₃.

Since CO_2 has a promoting effect on the reaction of H_2O with butadiene [1-8], telomerization of the latter was carried out with complexed H_2O in the presence of the catalyst $Pd(acac)_2 - PPh_3 - AlEt_3$, activated by an excess of CO_2 . It became clear that under our experimental conditions CO_2 has virtually no effect on the yields and compositions of the telomerization products. These findings suggest that under the reaction conditions CO_2 not only functions as an activating ligand [1-8], but is also an intermediate playing a direct part in the formation of (I) and (II). It is likely that in the reaction of free H_2O with butadiene over the catalytic system $Pd(acac)_2 PPh_3 - AlEt_3 - (CO_2)_n$, H_2CO_3 is first formed, and this reacts readily with the diene to form ethers (IV) and (V). The latter break down in the presence of excess H_2O to give (I), (II), and H_2CO_3 . When complexes such as $MSO_4 \cdot$ $(H_2O)_n$ are used as sources of water, it is obvious that as a result of the absence of free H_2O , H_2CO_3 (which is responsible for the formation of (I)-(III)) cannot be formed. In all likelihood, like other carboxylic acids and H_3BO_3 [11], H_2CO_3 reacts much more readily than free H_2O with butadiene.

The nature of the solvent has a considerable effect on the yields of (I)-(III). For example, the yields of (I) and (II) can be increased up to 80% by carrying out the telomerization in DMF, HMPA, or pyrrolidone. It is noteworthy that in these experiments only (I) and (II) were formed. No telomerization whatsoever occurred in THF, dioxane, DMSO, or pyridine, owing to the formation of coordinately-saturated palladium complexes, which are inactive in telomerization



We next studied the possibility of using the sulfates of other transition and nontransition metals (Fe, Co, Ni, Mn, Cd, Ca, and Zn) containing water of crystallization (Table 2). In all the experiments, (I)-(III) were formed, in overall yields varying from 5~50% depending on the crystalline hydrate. The highest yields of (I)-(III) were obtained with Co and Cd salts. Replacement of the sulfates by the chlorides failed to give even traces of (I)-(III). The bulk of the butadiene in these experiments was converted into 4-vinylcyclohexene.

MX _n ·H ₂ O _m	Conver- sion of H_2O , % [†]	Composit products, (I)+(II)	ion of %	MX _n ·H ₂ O _m	Conver- sion of H ₂ O, %†	Composit products, (I)+(II)	ion of % (III)
$\begin{array}{c} CoSO_4\cdot 7H_2O\\ CdSO_4\cdot 7H_2O\\ NiSO_4\cdot 7H_2O\\ CuSO_4\cdot 5H_2O \end{array}$	50 40 35 35	60 80 75 80	40 20 25 35	$\begin{array}{c} ZnSO_4\cdot 7H_2O\\ FeSO_4\cdot 7H_2O\\ MnSO_4\cdot 5H_2O\\ CaSO_4\cdot 2H_2O\end{array}$	$ \begin{array}{r} 30 \\ 24 \\ 20 \\ 5 \end{array} $	86 72 57 56	14 28 43 44

TABLE 2. Effect of the Metal in Crystalline Hydrates on the Yields of Products of Telomerization of Butadiene with H_2O^*

*Reaction conditions: $Pd(acac)_2 - PPh_3 - AlEt_3$ (1:4:4), 90°C, 4 h, solvent - acetone, $Pd(acac)_2 : H_2O = 1.500$.

[†]The conversion of H_2O is adequate to account for the yields of products (I)-(III).

Following these highly promixing results for the telomerization of butadiene with complex-bound H_2O , we examined the reaction of isoprene, trans-piperylene, cyclopentadiene, and 1,3-cyclohexadiene with $CoSO_4 \cdot 7H_2O$ with the aim of obtaining higher straight-chain and cyclic unsaturated alcohols. It was found that these dienes failed to react with complex-bound H_2O , irrespective of the ratios of the catalyst components or changes in the reaction conditions. For this reason, it was of interest to try these conjugated dienes in the telomerization with free water, catalyzed by the system $Pd(acac)_2 - PPh_3 - AlEt_3$, activated by excess CO_2 .

Isoprene reacted with H_2O , being converted into 2,7-dimethyl-1,3,7-octatriene (VI) and a mixture of decadienols (VII)-(XI), which were isolated by preparative GLC. The structures of (VI)-(IX) were confirmed by comparison of their spectral characteristics and physicochemical constants with those of authentic samples [12, 13]. The structures of the unsaturated alcohols (X) and (XI) were proved by spectral methods.

Unlike isoprene, trans-piperylene gave (XII) in extremely high yields. The yields of (VII)-(XII) were 50 and 20% respectively. Under these conditions, cyclopentadiene and 1,3-cyclohexadiene failed to react with H_2O .



EXPERIMENTAL

The 1,3-dienes used were 99% pure. Products were analyzed on a Chrom-47 chromatograph, column 1.2 m, phase SE-30, carrier gas helium. Preparative separations were carried out on a Perkin-Elmer F-12, 2.7 m column with PEG-10M. PMR spectra were obtained on Tesla BS-487B and Tesla BS-467B instruments in $CDCl_3$ or CCl_4 , relative to TMS. ¹³C NMR spectra were recorded on a JEOL FX-90Q spectrometer with wide-band suppression for protons in the "homoresonance" mode, relative to TMS. IR spectra were recorded on a UR-20 spectrometer (film). Mass spectra were obtained on an MX-1306 at 70 eV and ionization chamber temperature 200°C.

<u>General Method for the Reaction of Complexed H₂O with Butadiene.</u> a) To a solution of 0.157 g of Pd(acac)₂ and 0.4 g of PPh₃ in 10 ml of dry toluene, cooled to $-15 \text{ to } -20^{\circ}\text{C}$ was added with stirring under argon 0.86 g of AlEt₃, and the mixture kept for 5-10 min at -15°C . In a 100 ml steel autoclave cooled to $-5 \text{ to } -10^{\circ}\text{C}$ were placed 0.05 mole of the appropriate crystalline hydrate $MX_n(H_2O)_m$ and 0.5 mole of butadiene in 25 ml of acetone, and the catalyst solution was then added followed by heating for 4 h at 90°C. The mixture was cooled, the solid salt filtered off, the organic layer diluted with 50 ml of benzene, washed with 5% HCl followed by water, and dried over Na₂SO₄. Removal of the solvent gave a mixture of alcohols (I) and (II) together with bis-2,7-octadienyl ether

(III), which were separated by vacuum distillation. The experimental results are shown in Table 2. The structures of (I) and (II) were confirmed by a comparison of their constants with those for authentic samples [6].

 $\begin{array}{l} \underline{\rm Bis-2,7-octadienyl\ Ether\ (III),\ bp\ 90-92\,^\circ\!C\ (1\ mm),\ n_D^{20}\ 1.4714. \ IR\ {\rm spectrum}\ (\nu,\ cm^{-1}):\ 920,\ 1000,\ 3080\ (CH=CH_2),\ 980,\ 1640,\ 3030\ (trans-CH=CH). \ PMR\ {\rm spectrum}\ (CCI_4,\ \delta,\ ppm):\ 1.47\ m\ (4H,\ CH_2),\ 2.0\ m\ (8H,\ CH_2=C),\ 3.78\ d\ (4H,\ CH_2O,\ J=5\ Hz),\ 4.9\ m\ (4H,\ =CH_2),\ 5.5\ m\ (6H,\ CH=CH). \ ^{13}C\ NMR\ {\rm spectrum}\ (\delta,\ ppm):\ 70.52\ t\ (C^1),\ 126.91\ d\ (C^2),\ 133.80\ d\ (C^3),\ 31.74\ t\ (C^4),\ 28.35\ t\ (C^5),\ 33.24\ t\ (C^6),\ 138.36\ d\ (C^7),\ 114.60\ t\ (C^8). \ M^+\ 232. \ {\rm Reaction\ of\ 10\ g\ of\ CoCl_2\cdot 6H_2O\ with\ 27\ g\ of\ butadiene\ as\ described\ above\ gave\ 10\ g\ of\ vinylcyclo-hexene\ and\ 10\ g\ of\ recovered\ CoCl_2\cdot 6H_2O. \end{array}$

Similar results were obtained when $CdCl_2 \cdot 6H_2O_1$, $CuCl_2 \cdot 2H_2O_2$, or $MnCl_2 \cdot 4H_2O$ were used.

b) When telomerization was carried out in DMF with the $Pd(acac)_2 - PPh_3 - AlEt_3 catalyst, 12.5 g of CuSO_4 \cdot 5H_2O and 27 g of butadiene afforded 24 g (80%) of a mixture of alcohols (I) and (II) in a ratio of 3:1.$

c) Similarly, 12.5 g of $CuSO_4 \cdot 5H_2O$ and 27 g of butadiene afforded 21 g (70%) of a mixture of alcohols (I) and (II) in a ratio of 9:1.

d) When telomerization was carried out in pyrrolidone under the conditions described above, 12.5 g of $CuSO_4 \cdot 5H_2O$ and 27 g of butadiene afforded 18 g (60%) of a mixture of alcohols (I) and (II) in a ratio of 7:1.

Reaction of H_2O with Isoprene and trans-Piperylene. In a 100 ml steel autoclave were placed 4.5 g of H_2O , 34 g of isoprene in 25 ml of DMF, and then the catalyst, obtained from 0.72 g of Pd(acac)₂ and 2 g of PPh₃ as described above, followed by CO_2 to a pressure of 40 atm. The mixture was heated for 20 h at 100-110°C, cooled, diluted with benzene (50 ml), the mixture washed with 5% HCl followed by water, and the organic layer dried over Na₂SO₄. Removal of the solvent gave 34 g of a mixture of 2,7-dimethyl-1,3,7-octatriene (VI) and alcohols (VII)-(XI). The ratio of (VI): (VII)-(XI), from GLC data, was 1:1. The alcohols (VII)-(XI) were separated by preparative GLC, the ratios being (VII): (VIII): (X): (X): (X) = 2:63:8:3:24. The structures of (VI)-(IX) were confirmed by comparison of their IR, PMR, and mass spectra, and their constants, with those given in the literature [12, 13].

 $\frac{2,6-\text{Dimethyl}-2,7-\text{octadien}-1-\text{ol} (IX), \text{ bp } 60-62^{\circ}\text{C} (2 \text{ mm}), n_D^{20} 1.4680. \text{ IR spectrum } (\nu, \text{ cm}^{-1}): 860, 1640}{(\text{CH}=\text{C}), 920, 1010, 1660, 3080 (\text{CH}=\text{CH}_2), 3200-3600 (\text{OH}). \text{ PMR spectrum } (\text{CCl}_4, \delta, \text{ppm}): 1.0 \text{ d} (3\text{H}, \text{CH}_3, \text{J}=9 \text{ Hz}), 1.6 \text{ s} (3\text{H}, \text{CH}_3\text{C}=), 1.4 \text{ m} (2\text{H}, \text{CH}_2), 2.0 \text{ m} (3\text{H}, \text{CH}_2\text{C}=, \text{CHC}=0, 3.8 \text{ s} (2\text{H}, \text{CH}_2\text{O}), 4.5-5.5 \text{ m} (4\text{H}, \text{CH}=\text{CH}_2, \text{CH}=\text{C}). \text{ M}^+ 154.$

 $\frac{2,6-\text{Dimethyl}-2,7-\text{octadien}-1-\text{ol} (XI), \text{ bp } 68-70^{\circ}\text{C} (2 \text{ mm}), n_{\text{D}}^{20} 1.4608. \text{ IR spectrum } (\nu, \text{ cm}^{-1}): 890, 1640, 3100 (=CH_2), 860, 1670, 3010 (CH=C), 3200-3600 (OH). PMR spectrum (CCl₄, <math>\delta$, ppm): 1.5 m (2H, CH₂), 1.63 s (3H, CH₃C=), 1.69 s (3H, CH₃C=), 2.0 m (4H, CH₂C=), 2.5 s (1H, OH), 3.95 s (2H, CH₂O), 4.67 s (2H, =CH₂), 5.4 m (1H, CH=C). ¹³C NMR spectrum (δ , ppm): 68.79 t (C¹), 126.0 d (C³), 27.52 t (C⁴), 27.26 t (C⁵), 37.45 t (C⁶), 145.72 s (C⁷), 109.92 t (C⁸), 22.41 q (CH₃C⁷), 13.65 q (CH₃C²). M⁺ 154.

Telomerization of 4.5 g of H_2O with 34 g of piperylene as described above gave 9.0 g (20%) of the alcohol (XII).

 $\frac{1,5-\text{Dimethyl}-2,7-\text{octadien}-1-\text{ol} (XII), \text{ bp } 65-67^{\circ}\text{C} (2 \text{ mm}), n_{D}^{20} 1.4669. \text{ IR spectrum } (\nu, \text{ cm}^{-1}): 920, 1010, \\ 3090 (CH=CH_2), 980, 1640, 3030 (trans-CH=CH), 3200-3600 (OH). PMR spectrum (CCl_4, <math>\delta$, ppm): 0.86 d (3H, CH_3C⁵, J=6.5 Hz), 1.23 d (3H, CH_3C¹, J=6.5 Hz), 1.5 m (1H, C⁵H), 2.0 m (4H, CH_2C=), 4.2 m (1H, CHO; 1H, OH), 4.9 m (2H, CH_2), 5.5 m (3H, CH=CH, CH=). M⁺ 152.

CONCLUSIONS

1. It has been shown possible to prepare unsaturated alcohols in satisfactory yields by the telomerization of butadiene, isoprene, and trans-piperylene with water in the presence of palladium catalysts.

2. Water, present in crystalline hydrates $MX_n(H_2O)_m$, reacts with butadiene in the presence of the catalytic system $Pd^{2+}-PPh_3-AlEt_3$ in the absence of CO_2 .

LITERATURE CITED

- 1. K. E. Atkins, W. E. Walker, and R. M. Manyik, Chem. Commun., 330 (1971).
- 2. Jap. Pat. No. 53~147013 (1978); Ref. Zh. Khim., 13N24P (1980).
- 3. Jap. Pat. No. 54-141712 (1979); Ref. Zh. Khim., 19N23P (1980).
- 4. Jap. Pat. No. 54-145605 (1979); Ref. Zh. Khim., 19 N20 P (1980).

- 5. Jap. Pat. No. 74-35603 (1974); Chem. Abstr., 82, 124743d (1975).
- 6. French Pat. No. 2045369 (1969); Chem. Abstr., 74, 41892p (1972).
- U. M. Dzhemilev, R. V. Kunakova, and V. V. Sidorova, Inventor's Certificate No. 3303652/23-04 (USSR), 18.06.1981.
- 8. J. -P. Blanchini, B. Waegel, and E. M. Gaydou, J. Mol. Cat., 10, 247 (1981).
- 9. W. E. Walker, R. M. Manyik, K. E. Atkins, and M. L. Farmer, Tetrahedron Lett., 3817 (1970).
- 10. E. J. Smutny, J. Am. Chem. Soc., 89, 6793 (1967).
- 11. U. M. Dzhemilev, R. V. Kunakova, D. L. Minsker, G. A. Tolstikov, and E. V. Vasil'eva, Izv. Akad. Nauk SSSR, Ser. Khim., 1466 (1978).
- 12. L. I. Zakharkin, S. A. Babich, and I. V. Pisareva, Izv. Akad. Nauk SSSR, Ser. Khim., 1616 (1976).
- 13. Eschinasi, Emile H., Isr. J. Chem., 6, 713 (1968); Chem. Abstr., 70, 78165x (1969).

TELOMERIZATION OF BUTADIENE AND ISOPRENE WITH SULFONES CONTAINING ACTIVE METHINE AND METHYLENE GROUPS, CATALYZED BY PALLADIUM COMPLEXES

G.	Α.	Tolstikov,	0. A.	Rozentsvet,	UDC 542,97:66.095.2:
R.	ν.	Kunakova,	and N.	N. Novitskaya	547.315.2

Synthesis involving sulfones have acquired great importance in the chemistry of alkenes in recent years. Special interest lies in sulfones as convenient starting materials for the preparation of polyenes including carotenoids, juvenoids, and other biologically significant compounds [1-5].

In a search for convenient pathways for the synthesis of compounds which hold potential interest as precursors for juvenoids and pheromones, we studied the catalytic telomerization of 1,3-dienes with sulfones. Bisphenylsulfonylmethane as well as esters and amides of arylsulfonylacetic acids react with butadiene to form mono- or bis-2,7-octadienyl derivatives [6-8]. This study was carried out for the reaction of butadiene and isoprene with β -sulfonoesters (I)-(IV), β -ketosulfones (V), and p-toluenesulfonylnitromethane (VI) (Table 1). A PdCl₂- (Ph₃P)₂-PhONa system was used as the catalyst. This system has high activity relative to the telomerization of dienes with β -dicarbonyl compounds [6].

Both aryl- and alkylsulfonoesters readily react with butadiene to yield monoalkylation products (VII) with yields up to 85% (Table 2). Their structure as 2,7-octadienyl derivatives was shown by spectral methods and chemical conversions (Table 3)



Sulfonoester (VIIh) upon epoxidation by p-carbomethoxyperpenzoic acid (CPA) yields dioxide (VIII), while its oxidation with atmospheric oxygen by the action of a palladium—copper catalyst according to Clement and Selwitz [10] led to ketoester (IXh). Telomers (VIIa) and (VIIg) are oxidized under analogous conditions to ketoesters (IXa) and (IXg) in almost quantitative yields:



Institute of Chemistry, Bashkir Branch, Academy of Sciences of the USSR, Ufa. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 3, pp. 589-597, March, 1983. Original article submitted March 1, 1982.