wise an alcoholic solution of 0.26 g (0.001 mole) $RhCl_3 \cdot 3H_2O$. The reaction mixture was stirred 5 h in an Ar atmosphere at ∿20°, then decomposed with an equal volume of water and extracted with benzene. After the usual treatment a bright blue powdery substance was obtained, which was recrystallized from a benzene–hexane (1:1) mixture. Yield 0.33 g (47%), mp (with dec.) 232°C. Found: C 78.00; H 8.70; N 6.13%. $C_{45}H_{60}N_3O_3$. Calculated: C 78.25; H 8.74; N 6.10%. M^+ 690.

0.3 g of the prepared blue substance was dissolved in acetone and an excess of an aqueous solution of $K_4Fe(CN_6)$ added. The reaction mixture was stirred for 4 h at ∿20° then stood overnight. After extraction with ether and removal of the solvent a yellow colored residue was obtained, which was recrystallized from hexane. Yield 100%, mp 134-136°C. Found: C 78.15; H 8.78; N 6.07%. $C_{45}H_{61}N_3O_3$. Calculated: C 78.16; H 8.83; N 6.08%. M^+ 691.

CONCLUSIONS

Complexes of palladium (II) and rhodium (III) with 4-hydroxy-3,5-di-tert-butylbenzonitrile have been synthesized and it has been found that during their oxidation the metal–ligand bond is broken to yield the free nitrilophenoxyl radical in solution which under the action of the transition metal salt undergoes cyclotrimerization with formation of the nonsymmetrical triazine.

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CHEMISTRY OF VINYLIDENE COMPLEXES.

COMMUNICATION 2.* CONVERSIONS OF PHENYLVINYLIDENE IN POLYNUCLEAR COMPLEXES OF OSMIUM AND MANGANESE

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I. Yu. Efremova, A. A. Ioganson, and S. P. Gubin

UDC 542.91:541.49:547.1'13:546.94

The most significant features of mononuclear vinylidene complexes of transition metals are the presence of the unsaturated M=C=C metalloallene grouping and the deficiency of electron density on the α-carbon atom [1]. The M=C=C group can take part in very diverse processes: the addition of carbenoid metal-complex fragments containing Mn, Re, Fe, or Pt across the M=C bond, the addition of nucleophilic reagents (CO, phosphites) to the α-carbon atom, hydrogenation, etc. [1-7].

In this communication we shall report the conversions of phenylvinylidene in a heteronuclear system of four metal atoms formed during the reaction between the phenylvinylidene complex of manganese $Cp(CO)_2Mn{=}C{=}CHPh$ (I) and the unsaturated carboyl hydride cluster of osmium $H_2Os_3(CO)_{10}$. As far as we know, reactions of mononuclear vinylidene complexes with clusters of metals have not previously been reported.

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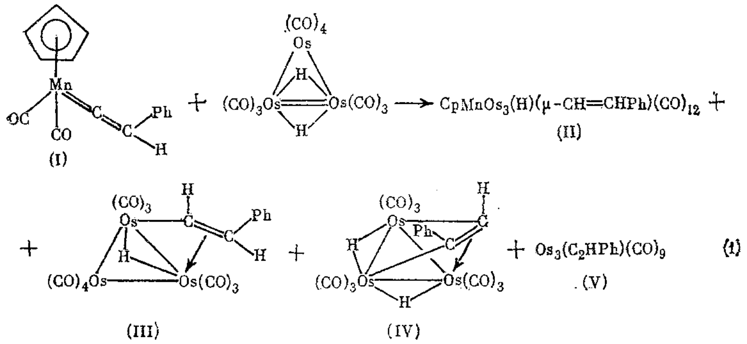
*For Communication 1, see [1].

Institute of Chemistry and Chemical Engineering, Academy of Sciences of the USSR, Siberian Branch, Krasnoyarsk. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 5, pp. 1146-1152, May, 1984. Original article submitted March 9, 1983.

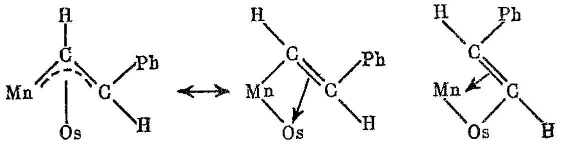
0568-5230/84/3305-1052\$08.50

The reaction of I with $H_2Os_3(CO)_{10}$ in CH_2Cl_2 at 20°C produces four polynuclear complexes (Table 1) with unsaturated organic ligands.



The main product of reaction (1) is the heterometallic cluster II, a dark red crystalline compound, which is highly soluble in polar organic solvents and moderately soluble in nonpolar organic solvents. The crystals of II are stable, its solutions in polar coordinating solvents (dioxane, THF) are comparatively stable, but it rapidly decomposes in nonpolar media (pentane, cyclohexane). According to the data from elemental analysis and the PMR and IR spectra, compound II contains three Os atoms and one Mn atom, to which the Cp ring, a bridging phenylvinyl ground, one bridging hydride atom (δ −22.2 ppm), and one bridging CC group (ν C=O = 1790 cm^{-1}) in addition to the terminal CO groups are bonded. The value of the spin–spin coupling constant J = 14.2 Hz between the protons of the olefin ligand CH=CHPh attests to its trans configuration. A peak for the molecular ion is not found in the mass spectrum of II. The peak with the greatest mass number m/z 956 corresponds to the $[Os_3C_2H_3Ph(CO)_{10}]^+$ ion, i.e., molecular ion III. The mass spectrum of II also contains intense peaks of the $[Os_3H_2(CH{\equiv}CPh)(CO)_9]^+$, $[CpMn(CO)_3]^+$, $[CpMn(CO)_2]^+$, $[PhCH{=}CH_2]^+$, and $[PhCH{=}CH]^+$ ions.

It is known [8] that the reactions of the allenes $R_2C{=}C{=}CR_2$ with hydride complexes of transition metals result in the hydrogenation of the central C atom of the allene and the formation of π-allyl complexes. Reaction (1) reveals some similarity between the behavior of a metalloallene system and organic allenes. Cluster II is obtained as a result of the addition of the Mn=C=C grouping in complex I at an Os–H bond in the hydride $H_2Os_3(CO)_{10}$ and the transfer of one of the hydride atoms to the α-carbon of the vinylidene. It was expected that cluster II would contain "π-allyl" fragment VII:



(VII) (II)

However, as was shown by x-ray diffraction analysis,* in cluster II the phenylvinyl group is σ-bonded to one of the Os atoms and π-coordinated by the Mn atom. Thus, extensive restructuring of the coordination sphere of the Mn atom, including an n–π rearrangement of the unsaturated ligand, occurs during reaction (1). A similar rearrangement of the n-vinylidene ligand to a π-olefinic ligand was previously observed in [1, 7].

Trinuclear osmium complexes III-V are obtained in comparatively small amounts during reaction (1) (see Table 1). The problem of the identification and establishment of the structure of trinuclear metallocarbonyl clusters with unsaturated organic ligands is greatly facilitated by the fact that the patterns of the νCO bands in the IR spectra are individual for each structural type of cluster. For example, the IR spectra of the types of clusters considered in the present work, viz., $H_2Os_3(\mu^3\text{-}C{=}CRR')(CO)_9$, $HOs_3(\mu^2\text{-}Cr{=}CHR')(CO)_{10}$, and $H_2Os_3[\mu^3\text{-}C(R){\equiv}CR'](CO)_9$, in the 2200-1900-$cm^{-1}$ region differ sharply from one another. At the same time, the analysis of the data in the literature [9] and our observations show that within each structural type the nature of the radicals R and R' (H, alkyl, aryl) only slightly influ-

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*The structure of II was established in the laboratory for x-ray diffraction analysis at the Institute of Organometallic Compounds of the Academy of Sciences of the USSR by Yu. T. Struchkov and A. I. Yanovskii.

TABLE 1. Physicochemical Characteristics of Complexes II–VI

Complex	Color	Yield, %[a]	mp, °C	IR spectrum: νCO, cm^{-1}[b]	PMR spectrum: δ, ppm[c]
(II) $CpMnOs_3(H)(CH{=}CHPh)(CO)_{12}$	Dark red	60	75–76[d]	2127 m 2073 s 2053 sh 2047 vs 2030 s 2010 s 1997 vs 1980 m 1950 sh 1933 m 1790 w	9.34 (d, 1H, CH, J = 14.2 Hz), 7.27 (m, br, 5H, C_6H_5), 4.39 (s, 5H, C_5H_5), 3.75 d (d, 1H, CH, J = 14.2 Hz), −22.2 s (1H, OsH)
(III) $HOs_3(\mu^2\text{-}CH{=}CHPh)(CO)_{10}$	Orange	5	106	2104 m 2062 vs 2053 s 2023 vs 2011 s 2005 m 1994 m 1982 m	7.90 dd (1H, CH, J = 14.4, J = 1.7 Hz), 7.30 s,br (5H, C_6H_5), 5.29 d (1H, CH, J = 14.4 Hz), − 18.3 d (1H, OsH, J = 1.7 Hz)
(IV) $H_2Os_3(\mu^3\text{-}CH{\equiv}CPh)(CO)_9$	Pale yellow	10	96–98	2108 m 2081 vs 2056 vs 2031 vs 2025 s 2011 vs 2000 m 1991 w 1982 m	8.84 (m, 1H, CH, J = 0.5 to 1.0 Hz), 7.21 s.br (s, br, 5H, C_6H_5), −17.7 (s.br (1H OsH), −21.1 (s, br, 1H, OsH)
(V) $Os_3(C_2HPh)(CO)_9$	Dark red	4,5	103–104	2114 w 2072 s 2057 s 2040 m 2029 s 2017 m 2001 m 1989 w,sh	7.26 (m, 5H, C_6H_5), 6.47 (s, 1H, CH)
(VI) $H_2Os_3(\mu^3\text{-}C{=}CHPh)(CO)_9$	Pale yellow			2107 w 2082 s 2059 s 2029 s 2019 s 2007 m 1991 w 1984 m	

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[a] Yields in reaction (1).

[b] In cyclohexane

[c] II in $CDCl_3$, III–VI in CCl_4.

[d] From dioxane.

ences the frequencies and has practically no influence on the ratio between the intensities of the νCO bands.

The complex $HOs_3(\mu^2\text{-}CH{=}CHPh)(CO)_{10}$ (III), which contains a bridging phenylvinyl group σ,π-bonded to two Os atoms, was previously obtained in [9] by reacting phenylacetylene with $H_2Os_3(CO)_{10}$. Compounds IV and V, which were obtained for the first time, are crystalline, highly soluble in organic solvents, and stable both in the solid state and in solutions.

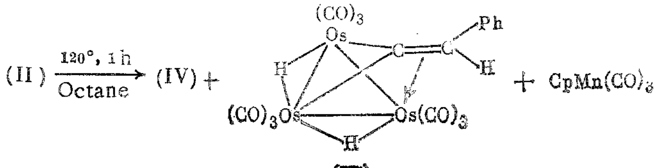
The IR spectrum of IV in the νCO region is identical to the spectra of the known [9] clusters of the type $H_2Os_3[\mu^3\text{-}C(R){\equiv}CR'](CO)_9$, in which the acetylenic ligand $C(R){\equiv}CR'$ (propyne, 2-butyne, or tolan) is σ-bonded to two Os atoms and π-bonded to the third Os atom. The chemical shifts of the signals of the bridging hydrides in the PMR spectrum of IV are close to the chemical shifts of the known μ^3-acetylenic clusters of this type. The signal of the proton in the alkyne ligand in the spectrum of IV is in the usual region for such compounds and is split into a multiplet due to the presence of the small vicinal spin–spin coupling constants with the hydride atoms. Thus, according to the data from the IR and PMR spectra, as well as on the basis of the elemental analysis, compound IV is triangulo-(μ-hydrido)(μ^3-phenylacetylene)enneacarbonyltriosmium $H_2Os_3(\mu^3\text{-}CH{\equiv}CPh)(CO)_9$.

According to the data from the PMR sepctrum at 20°C, dark red complex V does not contain hydride atoms. According to the IR spectrum, this complex cannot be assigned to any of the structural types of trinuclear clusters known to us. The composition of V, $Os_3(C_2HPh)(CO)_9$, was established with the aid of PMR and mass spectrometry. It is significant that the yield of V is greatly dependent on the ratio between the original reactants in reaction (1) and is proportional to the quantity of $CpMn(CO)_2(C_2HPh)$ (I).

Transfer of a vinylidene ligand from the Mn atom in I to a mononuclear complex of Re was previously realized [3]. In order to study the possibility of the transfer of phenylvinylidene from the Mn atom to the Os_3 metallocycle, as well as the paths for the appearance of complexes III and IV in reaction (1), we investigated the behavior of cluster II in solutions.

It was noted above that under the concentrations for the measurement of mass spectra, cluster II readily eliminates a $[CpMn(CO)_2]$ fragment. It was found that in solutions in aliphatic hydrocarbons II readily eliminates an Mn-containing fragment, being converted into osmium clusters containing unsaturated organic groups, the composition of the products formed being dependent on the decomposition conditions:

$$\text{(II)} \xrightarrow[\text{Pentane}]{20°,\ 24\ \text{h}} \text{(III)} + \text{(IV)} + CpMn(CO)_3 \qquad (2)$$



(VI)

(3)

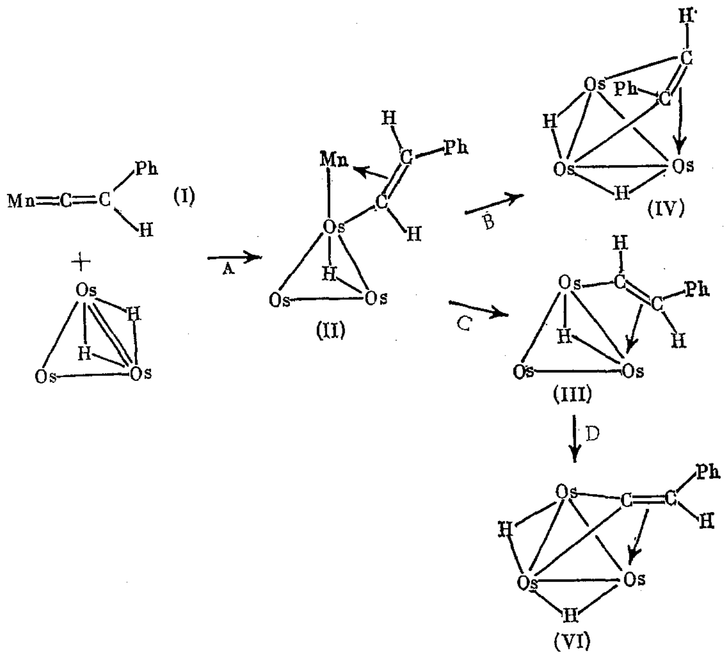
Both reactions are quantitative after the time indicated.

Complexes III and IV form in reaction (2) in a 1:2 ratio. These compounds were discovered in the same reaction in reaction (1). This probably attests to their formation in this reaction as a result of the partial decomposition of II in the reaction mixture.

When II is boiled in octane [reaction (3)], a mixture of the isomeric complexes IV and VI, which cannot be separated with the aid of TLC, forms in a 2.3:1 mole ratio. The products were identified on the basis of the PMR spectra. The cluster $H_2Os_3(\mu^3C{=}CHPh)(CO)_9$ (VI) with a bridging phenylvinylidene ligand, whose α-carbon atom is σ-bonded to two Os atoms and whose C=C bond is π-coordinated by the third metal atom, was previously obtained in [9] with an 88% yield by boiling III in octane. The formation of IV was not noted under these conditions. When this reaction was repeated, we found that the thermolysis of III affords a small quantity of μ^3-acetylenic cluster IV, although the main product is, in fact, μ^3-vinylidene complex VI.

The results presented allow us to describe the processes occurring in reactions (1)-(3) and resulting in the conversion of phenylvinylidene in the coordination sphere of the polynuclear systems and in the alteration of the type of coordination of the C=C fragment by the following scheme:

Scheme*



A heteronuclear $MnOs_3$ system (II) with a bridging μ^2-σ(Os):η(Mn)-phenylvinyl group, which forms as a result of the hydrogenation of the α-carbon atom of phenylvinylidene, is obtained in the first step (process A). This is followed by the elimination of the $[CpMn(CO)_2]$ fragment and the entrance of the unsaturated ligand into the coordination sphere of the remaining osmium atoms of the Os_3 system. The predominant process is the dehydrogenation of the olifinic ligand with cleavage of the C—H bond at the β-carbon and the formation of μ^3-acetylenic complex IV (process B). Summarizing processes A and B, we may treat the conversion of phenylvinylidene into phenylacetylene during the I → II → IV transition as isomerization of the unsaturated ligand.

Process B is accompanied by the parallel observation of the transfer of the hydrogenated ligand to the Os_3 system with the formation of μ^2-vinyl cluster III (process C). Finally, dehydrogenation of the olefinic group in complex III with the elimination of hydrogen from the α-carbon atom, which produces μ^3-vinylidene cluster VI (process D), occurs under severe conditions. The result of the chain of conversions I → II → III → VI is the transfer of the vinylidene ligand from the Mn atom to the osmium metallocycle.

Despite the tendency noted in [10] for the transfer of carbene ligands from one metal atom to another, the number of known examples of such transfer, especially in polynuclear systems, is very limited. There have only been reports of the transfer of alkoxycarbene ligands of the "Fischer" type during the formation of the trinuclear complexes $Pt_3[\mu^2\text{-}C(OMe)Ph]_{3-n}(CO)_n(PR_3)_3$ (n = 0 to 2) from $(CO)_5M[C(OMe)Ph]$ (M = Cr, W) and $Pt(C_2H_4)_2(PR_3)$ [10] and $Ni_3[\mu^2\text{-}C(OMe)PH]_3(CO)_3$ from $Cp(CO)(NO)Mo[C(OMe)Ph]$ and $Ni(CO)_4$ [11]. However, in all these cases, the carbene ligand is actually transferred to a mononuclear system, which is subsequently converted into a trinuclear system with μ^2-alkoxymethylene bridges.

The conversion which we discovered

$$(I) + H_2Os_3(CO)_{10} \rightarrow (II) \rightarrow (III) \rightarrow (VI)$$

is the first example of the direct transfer of an unsaturated carbene ligand from a mononuclear system to a trinuclear metallocycle.

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*The Cp and CO ligands have been omitted.

EXPERIMENTAL

Absolute solvents saturated with Ar were used. All the operations were carried out in an Ar atmosphere. Silica gel L100/400 were used for the chromatography in columns, and Silica gel L100/160 from Chemapol was used for the TLC. The IR sepctra were recorded on a Specord IR-75 instrument, and the PMR spectra were recorded on a Tesla BS-467 spectrometer (60 MHz) at 20°C. The mass spectra were obtained on an AEI MS-30 instrument with an energy of the ionizing electrons equal to 70 eV and an accelerating voltage equal to 2 kV.

Reaction of $Cp(CO)_2Mn{=}C{=}CHPh$ (I) with $H_2Os_3(CO)_{10}$. A mixture of 0.250 g (0.9 mmole) of I and 0.430 g (0.5 mmole) of $H_2Os_3(CO)_{10}$ in 15 ml of CH_2Cl_2 was stirred for 6 h at 20°C and evaporated in a vacuum. The oily residue was dissolved in 5 ml of $CHCl_3$ and chromatographed in a column with SiO_2. The following fractions were eluted: a violet fraction (1) by petroleum and then bright yellow (2), orange (3), and dark red (4) fractions by 50:1, 5:1, and 2:1 petroleum ether—$CHCl_3$ mixtures, respectively. Fraction 1 yielded 0.016 g (4%) unreacted $H_2Os_3(CO)_{10}$. Fractions 2 and 3 contained mixtures of several products, which were decomposed by TLC.

Four products were recorded from fraction 2 by elution with petroleum ether: traces of $CpMn(CO)_3$ and $Os_3(CO)_{12}$, which were identified according to their IR spectra and by TLC; 0.021 g (5%) of bright orange crystals of $HOs_3(CH{=}CHPh)(CO)_{10}$ (III) with mp 106°C, which was identical to a known sample obtained according to the method in [9] with respect to its PMR spectra and R_f values 0.042 g (10%) of pale yellow crystals of $H_2Os_3(CH{\equiv}CPh)(CO)_9$ (IV) with mp 96-98°C. Found: C 22.43; H 0.76; Os 60.97%. Calculated for $C_{17}H_8O_9Os_3$: C 22.00; H 0.86; Os 61.58%.

Unreacted I and 0.019 g (4.5%) of dark red crystals with a metallic shine of $Os_3(C_2HPh)(CO)_9$ (V) with mp 103-104°C (from hexane) were isolated from fraction 3 (the eluent was 5:1 petroleum ether—$CHCl_3$ mixture). Mass spectrum (for $^{192}Os^{190}Os_2$, m/z): 926 $[P]^+$, $[P - nCO]^+$ ions, where n = 1 to 8; 674 $[Os_3C_2HPh]^+$, 102 $[C_2HPh]^+$.

After crystallization from dioxane, 0.354 g (60%) of dark red crystals of $CpMnOs_3(H)(CH{=}CHPh)(CO)_{12}\cdot C_4H_8O_2$ (II) with mp 75-76°C were obtained from fraction 4. Found: C 28.20; H 1.92; Os 46.35%. Calculated for $C_{29}H_{21}O_{14}MnOs_3$: C 28.57; H 1.74; Os 46.80%. Mass spectrum (m/z): 956 $[Os_3C_2H_3Ph(CO)_{10}]^+$, $[Os_3C_2H_3Ph(CO)_n]^+$ ions, where n = 9 to 1; 676 $[Os_3C_2H_3Ph]^+$, 204 $[CpMn(CO)_3]^+$, 176 $[CpMn(CO)_2]^+$, 148 $[CpMnCO]^+$, 120 $[CpMn]^+$, 104 $[C_2H_3Ph]^+$, 103 $[C_2H_2Ph]^+$, 55 $[Mn]^+$.

Conversion of $CpMnOs_3(H)(CH{=}CHPh)(CO)_{12}$ (II) at 20°C in Pentane. A solution of 0.051 g of II in 80 ml of pentane was stirred for 24 h at 20°C, and the mixture obtained was separated by TLC, the eluent being petroleum. This gave 0.015 g (32%) of III and 0.029 g (64%) of IV and $CpMn(CO)_3$.

Conversion of II at 120°C. A solution of 0.051 g of II in 20 ml of octane was boiled for 40 min, and the yellow solution was evaporated to a volume of 5 ml and filtered through a layer of ∿3 cm of SiO_2. The filtrate was evaporated to dryness and the dry residue was dissolved in CCl_4. The PMR spectrum of the solution contains the signals of IV and VI, the ratio between IV and VI being ∿2.3:1. Both these compounds have identical R_f values, and they cannot be separated by TLC.

We express our sincerest thanks to Yu. S. Nekrasov, V. F. Sizoi, and D. V. Zagorevskii for obtaining and discussing the mass spectra, to N. I. Pavlenko for measuring the IR spectra, and to N. V. Ped'ko for taking part in the experiment.

CONCLUSIONS

1. It has been established that the heteronuclear cluster $CpMnOs_3(H)(CH{=}CHPh)(CO)_{12}$, which forms when $Cp(CO)_2Mn{=}C{=}CHPh$ reacts with $H_2Os_3(CO)_{10}$, readily dissociates in solutions with the elimination of an Mn-containing fragment and the formation of trinuclear osmium clusters with bridging vinyl, acetylenic, and vinylidene ligands.

2. The occurrence of the following processes with the participation of the phenylvinylidene ligand in the coordination sphere of several metal atoms has been demonstrated: hydrogenation with the formation of a phenylvinyl group and isomerization to phenylacetylene.

3. The transfer of a vinylidene ligand from a mononuclear system to a metallocycle has been realized for the first time.

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TRANSFORMED STROIDS.

COMMUNICATION 137. SYNTHESIS AND STEREOCHEMISTRY OF STEROID 23-METHOXYTETRAHYDROPYRANOLS

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V. S. Bogdanov, and E. G. Cherepanova

UDC 542.91:541.63:547.92

It has already been shown that steroids with dihydropyran E ring [1] can be used to synthesize steroid pyranosides [2, 3] with 17,20,22,23-hydroxyl groups. The present article deals with the synthesis of 22-desoxy analogs based on them.

Addition of methanol to $\Delta^{22(23)}$-bond of ketone (I) in the presence of MeONa proceeds regio- and stereospecifically from the α-region and quantitatively leads to 23α-methoxy ketone (II). However, during its reduction with $NaBH_4$, instead of the expected methoxydiol (III), diol (IV) (that we have already described in [3]) is formed, probably as a result of the elimination of methanol and the subsequent reduction of the 20-ketone (I) to a saturated alcohol. We therefore studied another path for the reaction, i.e., starting from allyl acetate (V), obtained in [3] as a minor component in the reduction of ketone (I) by $NaBH_4$.

It is known that the regiospecific reduction of α-enones into allyl alcohols is difficult to attain. We studied hydrides giving 1,2-addition products, but under mild conditions the use of $NaBH_4$ in the presence of $CeCl_3 \cdot 6H_2O$ [4], or $LiAlH_4$ was found to be unsuccessful. Only the reduction by sodium aluminohydride bis(2-methoxyethylate) [5] led to (V) in yield of ∿50%. The bromoalkoxylation of (V) was carried out by N-bromosuccinimide (NBS) in MeOH [6]. The two-component mixture of 22-bromo-23-methoxytetrahydropyranols obtained was subjected to hydrogenolysis over Ni-rhenium in the presence of Et_3N [7], and, as a result, after chromatographic separation, 23α- and 23β-methoxy derivatives (IIIa, b) were obtained in a ratio 5:4. The bromoalkoxylation reaction thus proceeds regioselectively, as in the monocyclic series [6], but not stereospecifically: through two isomeric 22(23)-bromonium ions (whose formation from α- and β-regions is clearly equally probable); the regiodirectiveness of their opening is explained by the preferred attack of the nucleophile at the site of a higher localization of the positive charge, i.e.,at the C^{23} atom

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0568-5230/84/3305-1058$08.50