Catalytic ring opening of acetylcyclopropane by water and alcohols under the action of copper or palladium salts

U. M. Dzhemilev,[a] R. I. Khusnutdinov,[a]★ A. M. Atnabaeva,[a] Z. S. Muslimov,[a] R. I. Parfenova,[a] and Yu. V. Tomilov[b]★

[a]Institute of Petrochemistry and Catalysis, Academy of Sciences of Republic Bashkortostan, Ufa Research Center of the Russian Academy of Sciences, 141 prosp. Oktyabrya, 450075 Ufa, Russian Federation. Fax: +7 (347 2) 31 2750. E-mail: ink@anrb.ru
[b]N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky prosp., 119991 Moscow, Russian Federation. Fax: +7 (095) 135 5328 E-mail: tom@cacr.ioc.ac.ru

The possibility of the cleavage of the C—C bond in acetylcyclopropane (ACP) under the action of water or alcohols in the presence of copper or palladium salts was demonstrated for the first time. At 175—180 °C, the reactions proceeded regioselectively with the cleavage of the C(1)—C(2) bond in the cyclopropane ring. The reaction of ACP with water afforded 5-hydroxypentan-2-one, bis(3-acetylpropyl) ether, and furan compounds, whereas the reactions with alcohols proceeded selectively to form 5-alkoxypentan-2-ones. The yields of the latter depend on the nature and structure of the alcohol, the maximum values (98%) being achieved in the case of primary alcohols.

Key words: acetylcyclopropane, catalysis, copper and palladium salts, hydrolysis, alcoholysis, 5-hydroxypentan-2-one and its derivatives.

It is known that the cyclopropane ring possessing partial π character can be coordinated to transition metals, which results in the activation of σ bonds of the ring and promotion of chemical transformations involving the cleavage of the C—C bonds. Because of this, examples of the preparation of cyclopropane complexes with transition metals stable under the normal conditions are scarce.[1] Generally, these complexes are unstable and either undergo cyclopropyl-allylic isomerization[2] (skeletal rearrangement in the case of polycyclic cyclopropane-containing structures[3]) or are converted into metallacyclobutanes.[4]

Studies on the cyclopropane ring opening by different organic reagents under the conditions of metal-complex catalysis have been carried out in recent years. In particular, ring opening by alcohols under the action of platinum complexes is of substantial synthetic interest.[5] Palladium complexes catalyze analogous reactions of silyloxycyclopropanes with acyl, aryl, and vinyl halides.[6] The reactions with trialkylalanes are catalyzed by nickel complexes.[7] The cyclopropane ring opening in acetylcyclopropane (ACP, **1**) and its derivatives performed under conditions of acid catalysis with addition of water[8] or hydrogen halides[9] resulted in derivatives of γ-acetopropyl alcohol, γ-halo ketones, and β,γ-dihalo ketones.

With the aim of developing a regioselective procedure for the cleavage of the C—C bond in cyclopropanes and constructing selective metal-complex catalysts for this reaction, we studied the reactions of ACP with water and alcohols under the action of Cu and Pd salts and complexes, which are widely used in homogeneous catalytic conversions of hydrocarbons and unsaturated compounds.

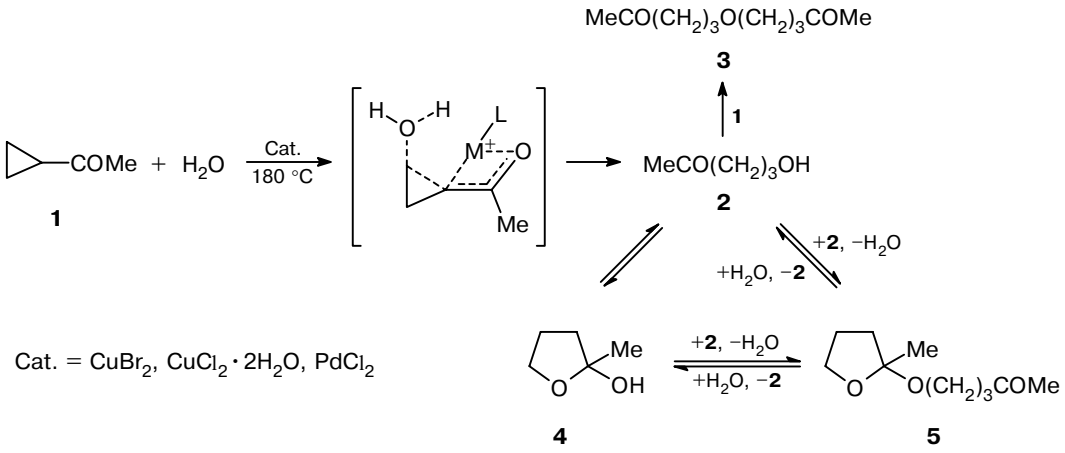
Results and Discussion

Copper and palladium salts ($CuBr_2$, $CuCl_2 \cdot 2H_2O$, and $PdCl_2$) (0.5 mol.%) exhibited the highest catalytic activity and selectivity. The reactions were carried out in an autoclave at 175—180 °C for 8—30 h. Under the above-mentioned conditions, ACP reacts with H_2O with the cleavage of the C(1)—C(2) bond to form 5-hydroxypentan-2-one (**2**) and 6-oxaundecane-2,10-dione (**3**). In the reactions involving $CuBr_2$, $CuCl_2 \cdot 2H_2O$, or $PdCl_2$ as catalysts, compound **3** was obtained in 64, 58, or 40% yields, respectively.

In spite of the drastic conditions (175—180 °C), the reaction of ACP with water proceeded regioselectively. Apparently, the formation of ether **3** involved two stages. In the first stage, the cyclopropane ring underwent hydrolytic scission. In the second stage, the resulting alcohol **2** added analogously at the C(1)—C(2) bond of the next ACP molecule. It should be noted that the reaction mixture contained hydroxy ketone **2** along with compounds of the tetrahydrofuran series, *viz.*, 2-methyltetrahydrofuran-2-ol (**4**) and 2-methyl-2-(4-oxopentyloxy)tetrahydrofuran (**5**), which were formed due to

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 7, pp. 1185—1189, July, 2001.

Scheme 1



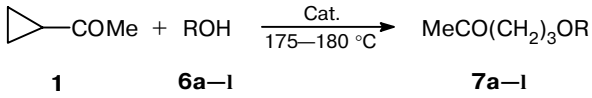
mutual conversions and could not be separated by fractional distillation[10] (Scheme 1). The existence of compounds **2**, **4**, and **5** was confirmed by ^1H and ^{13}C spectroscopy. The total yield of these compounds was ~30%.

The yield of compound **3** could not be increased by increasing the reaction time after complete conversion of ACP due apparently to the existence of the equilibrium between the open and cyclic forms **2**, **4**, and **5** (*cf.* Ref. 10). The ratio between ether **3** and a mixture of compounds **2** + **4** + **5** in the reaction mixture remained virtually unchanged (~2 : 1). However, this ratio depended substantially on the amount of water used in this reaction. The molar ratio **1** : H_2O = 1 : 5 appeared to be optimum. With $CuBr_2$ as a catalyst, the yield of ether **3** was 64%. In the case of a tenfold excess of H_2O, the yield of ether **3** decreased to ~20%. When the **1** : H_2O ratio was reduced to 1 : 2, the reaction proceeded more slowly and the reaction time should be increased to 25 h to obtain ether **3** in satisfactory yield. However, the yield of compound **3** under these conditions was at most 55% with a simultaneous increase in the yields of compounds **4** and **5**.

Taking into account the formation of hydroxy ketone **2** and its possible involvement in the ring opening of the ACP molecule, it was of interest to study the reactions of ACP with alcohols under the action of Cu and Pd salts. The use of monohydric alcohols (**6a—l**) in the reactions with ACP made it possible to prepare a series of 5-alkoxypentanon-2-ones (**7a—l**). The yields of the latter depended on both the nature of the alcohol and the reaction conditions (Scheme 2). Nevertheless, regioselective ring opening with the cleavage of the C(1)—C(2) bond was observed in all cases.

The reactions of ACP with alcohols are efficiently catalyzed by salts and complexes of copper ($CuBr_2$, $CuCl_2 \cdot 2H_2O$, $CuSO_4 \cdot 5H_2O$, or $(CF_3SO_3Cu)_2 \cdot C_6H_6$) and palladium ($PdCl_2$, $K_2[PdCl_4]$, $PdCl_2 \cdot 2PPh_3$, or $Pd_2(DBA)_3 \cdot CHCl_3$). The catalytic activity of copper compounds in a model reaction of ACP with MeOH

Scheme 2



Cat. = $CuBr_2$, $CuCl_2 \cdot 2H_2O$, $PdCl_2$
R = Me (**a**); Et (**b**); Pr (**c**); Pr^i (**d**); Bu (**e**); C_5H_{11} (**f**); $CHEt_2$ (**g**); C_6H_{13} (**h**); $C_{10}H_{21}$ (**i**); $PhCH_2$ (**j**); PhCHMe (**k**); $CH_2CF_2CHF_2$ (**l**)

decreased in the following series (the yield of **7a** is given in parentheses): $CuBr_2$ (99%) > $CuCl_2 \cdot 2H_2O$ (95%) > $CuSO_4 \cdot 5H_2O$ (92%) > $(CF_3SO_3Cu)_2 \cdot C_6H_6$ (89%). For palladiums compounds, the following series was obtained: $PdCl_2$ (98%) > $K_2[PdCl_4]$ (20%) > $PdCl_2 \cdot 2PPh_3$ (13%) > $Pd_2(DBA)_3 \cdot CHCl_3$ (10%). The yields of alkoxypentanones **7** were the highest in the case of lower alcohols (**7a**, 98%) and decreased as the length of the chain and the degree of branching of the alkyl radicals increased (Table 1). The duration of the reaction depends also on the nature of the alcohol and the catalyst. Thus the reaction of ACP with methanol in the presence of $CuBr_2$ as a catalyst proceeded four times more rapidly than that with the use of $PdCl_2$. In the latter case, the reaction should be performed in a 1 : 5 alcohol—water medium because the rate of alcoholysis of ACP in the absence of H_2O decreases sharply.

The studies of the reactions of ACP with alcohols demonstrated that the latter were partially converted into dialkyl ethers under the reaction conditions, their content being increased as the length of the alkyl radical in the alcohol increased. In this connection, we attempted to inhibit their formation by varying solvents and found that the use of diethyl ether (the molar ratio **1** : **6** : Et_2O = 1 : 1 : 3) was actually favorable for the reduction in the portion of dialkyl ethers. It should be noted that an analogous effect was not observed in the case of dibutyl ether, THF, or dioxane.

It is appropriate to use diethyl ether as the solvent in the reactions with alcohols beginning with butanol be-

Table 1. Dependence of the yields of compounds **7a—l** and **9a,b** on the structure of the alcohol

ROH	*t*/h		Reaction product	Yield (%)	
	$CuBr_2$	$PdCl_2$		$CuBr_2$	$PdCl_2$
6a	6	25	**7a**	99	98
6b	6	25	**7b**	77	75
6c	8	25	**7c**	73	65
6d	8	30	**7d**	32	29
6e	8	25	**7e**	75	63
6f	10	25	**7f**	47	45
6g	10	25	**7g**	34	22
6h	10	33	**7h**	76	60
6i	10	40	**7i**	52	43
6j	10	18	**7j**	47	36
6k	8	12	**7k**	6	4
6l	6	10	**7l**	32	31
8a	6	8	**9a**	37	39
8b	6	8	**9b**	32	38

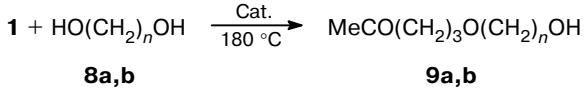
Note. The molar ratio ACP : ROH : H_2O : $CuBr_2$ (or $PdCl_2$) : Et_2O = 1 : 1 : 5 : 0.005 : 3; the temperature was 180 °C.

cause the reactions with MeOH, EtOH, and PrOH afforded the corresponding ethers in yields of no higher than 1—3%. On the contrary, benzyl alcohol gave dibenzyl ether in ~30% yield regardless of the presence or absence of diethyl ether.

The formation of the expected ether **7k** in the reaction of ACP with α-phenylethyl alcohol was accompanied by dehydration as a side reaction giving rise to styrene in 60% yield.

In the presence of copper- or palladium-containing catalysts, ACP reacted with 1,2-ethylene glycol (**8a**) or 1,3-propylene glycol (**8b**) to give 5-(2-hydroxyethoxy)- or 5-(3-hydroxypropoxy)pentan-2-ones (**9a,b**), respectively (Scheme 3). However, the latter were obtained in yields of at most 40% due to the competitive formation of diethylene glycol or dipropylene glycol, respectively.

Scheme 3



Cat. = $CuBr_2$, $CuCl_2 \cdot 2H_2O$, $PdCl_2$
n = 2 (**a**), 3 (**b**)

The optimum temperature for the reactions of ACP with water or alcohols lies in a narrow range of

Table 2. Data from elemental analysis of the compounds synthesized

Compound	B.p./°C (*p*/Torr)	Found / Calculated (%)		Molecular formula
		C	H	
5-Methoxypentan-2-one (**7a**)	91—94 (100)	62.05 62.07	10.36 10.34	$C_6H_{12}O$
5-Ethoxypentan-2-one (**7b**)	82—85 (40)	64.80 64.61	10.75 10.77	$C_7H_{14}O_2$
5-Propoxypentan-2-one (**7c**)	81—84 (8)	66.54 66.67	11.13 11.11	$C_8H_{16}O_2$
5-Isopropoxypentan-2-one (**7d**)	120—123 (10)	66.73 66.67	11.14 11.11	$C_8H_{16}O_2$
5-Butoxypentan-2-one (**7e**)	121—125 (6)	68.62 68.35	11.36 11.39	$C_9H_{18}O_2$
5-Pentyloxypentan-2-one (**7f**)	140—143 (17)	69.98 69.77	11.67 11.62	$C_{10}H_{20}O_2$
5-(Pentan-3-yl)oxypentan-2-one (**7g**)	120—122 (10)	69.63 69.77	11.64 11.62	$C_{10}H_{20}O_2$
5-Hexyloxypentan-2-one (**7h**)	111—114 (2)	70.90 70.97	11.81 11.83	$C_{11}H_{22}O_2$
5-Decyloxypentan-2-one (**7i**)	—	74.23 74.38	12.64 12.40	$C_{15}H_{30}O_2$
5-Benzyloxypentan-2-one (**7j**)	122—124 (3)	75.23 75.00	8.35 8.33	$C_{12}H_{16}O_2$
5-(1-Phenylethoxy)pentan-2-one (**7k**)	158—162 (2)	75.50 75.73	8.72 8.74	$C_{13}H_{18}O_2$
5-(2,2,3,3-Tetrafluoropropoxy)pentan-2-one (**7l**)*	110—114 (30)	44.58 44.44	5.53 5.55	$C_8H_{12}F_4O_2$
5-(2-Hydroxyethoxy)pentan-2-one (**9a**)	—	57.76 57.53	9.57 9.59	$C_7H_{17}O_3$
5-(3-Hydroxypropoxy)pentan-2-one (**9b**)	—	59.82 60.00	9.96 10.00	$C_8H_{16}O_3$

* Found (%): F, 35.05. Calculated (%): F, 35.19.

Table 3. ^{1}H and ^{13}C NMR spectral data for the compounds synthesized ($CDCl_3$)

Compound	δ	
	^{1}H	^{13}C
$MeCO\overset{3}{C}H_2\overset{4}{C}H_2\overset{5}{C}H_2OH$ (**2**)	1.77 (m, 2 H, H(4)); 2.11 (s, 3 H, Me); 2.43 (t, 2 H, H(3)); 3.59 (t, 2 H, H(5)); 3.88 (s, 1 H, OH)	29.9 (Me); 208.8 (C=O); 40.8 (C(3)); 24.6 (C(4)); 60.0 (C(5))
$(\overset{1}{Me}CO\overset{3}{C}H_2\overset{4}{C}H_2\overset{5}{C}H_2)_2O$ (**3**)	1.72 (m, 4 H, H(4)); 2.05 (s, 6 H, Me); 2.41 (t, 4 H, H(3)); 3.29 (t, 4 H, H(5))	29.9 (Me); 208.6 (C=O); 40.4 (C(3)); 23.9 (C(4)); 68.9 (C(5))
$Me\overset{2}{C}(OH)(\overset{3,4}{CH_2})_2\overset{5}{C}H_2$ (**4**)	1.33 (s, 3 H, Me); 1.87 (m, 2 H, H(4)); 2.44 (m, 2 H, H(3)); 3.66—3.86 (m, 2 H, H(5)); 5.10 (s, 1 H, OH)	97.1 (C(2)); 37.1 (C(3)); 26.0 (C(4)); 67.7 (C(5)); 14.9 (Me)
$\overset{1}{Me}\overset{2}{C}O\overset{3}{C}H_2\overset{4}{C}H_2\overset{5}{C}H_2O\overset{6}{C}(Me)(\overset{7,8}{CH_2})_2\overset{9}{C}H_2$ (**5**)	1.36 (s, 3 H, Me); 1.57—1.98 (m, 6 H, H(4,7,8)); 2.08 (s, 3 H, H(1)); 2.35 (t, 2 H, H(3)); 3.36 (t, 2 H, H(5)); 3.80 (m, 2 H, H(9))	29.9 (C(1)); 208.1 (C=O); 40.5 (C(3)); 24.6 (C(4)); 62.3 (C(5)); 107.2 (C(6)); 37.9 (C(7)); 26.2 (C(8)); 67.7 (C(9)); 22.1 (Me)
$\overset{1}{Me}CO\overset{3}{C}H_2\overset{4}{C}H_2\overset{5}{C}H_2OMe$ (**7a**)	1.76 (m, 2 H, H(4)); 2.01 (s, 3 H, Me); 2.45 (t, 2 H, H(3)); 3.30 (t, 2 H, H(5)); 3.21 (s, 3 H, OMe)	29.8 (Me); 208.0 (C=O); 39.1 (C(3)); 23.9 (C(4)); 70.9 (C(5)); 57.4 (OMe)
$\overset{1}{Me}CO\overset{3}{C}H_2\overset{4}{C}H_2\overset{5}{C}H_2O\overset{6}{C}H_2\overset{7}{C}H_3$ (**7b**)	1.14 (t, 3 H, H(7)); 1.78 (t, 2 H, H(4)); 2.11 (s, 3 H, Me); 2.51 (m, 2 H, H(3)); 3.38 (t, 4 H, H(5), H(6))	29.7 (Me); 207.9 (C=O); 40.2 (C(3)); 24.8 (C(4)); 69.0 (C(5)); 66.1 (C(6)); 15.3 (C(7))
$\overset{1}{Me}CO\overset{3}{C}H_2\overset{4}{C}H_2\overset{5}{C}H_2O\overset{6}{C}H_2\overset{7}{C}H_2\overset{8}{C}H_3$ (**7c**)	0.63 (t, 3 H, H(8)); 1.17—1.70 (m, 4 H, H(4), H(7)); 1.90 (s, 3 H, Me); 2.26 (m, 2 H, H(3)); 3.14 (m, 4 H, H(5), H(6))	29.4 (Me); 207.9 (C=O); 39.9 (C(3)); 23.7 (C(4)); 72.1 (C(5)); 69.3 (C(6)); 22.6 (C(7)); 10.2 (C(8))
$\overset{1}{Me}CO\overset{3}{C}H_2\overset{4}{C}H_2\overset{5}{C}H_2O\overset{6}{C}H\overset{7}{Me}_2$ (**7d**)	1.10 (d, 6 H, H(7)); 1.17 (m, 2 H, H(4)); 2.16 (s, 3 H, Me); 2.46 (m, 2 H, H(3)); 3.46 (m, 2 H, H(5)); 3.70 (m, 1 H, H(6))	29.9 (Me); 208.7 (C=O); 40.5 (C(3)); 24.3 (C(4)); 71.3 (C(5)); 66.9 (C(6)); 22.1 (C(7))
$\overset{1}{Me}CO\overset{3}{C}H_2\overset{4}{C}H_2\overset{5}{C}H_2O\overset{6}{C}H_2(\overset{7,8}{CH_2})_2\overset{9}{C}H_3$ (**7e**)	0.90 (t, 3 H, H(9)); 1.16—1.91 (m, 6 H, H(4), H(7), H(8)); 2.15 (s, 3 H, Me); 2.53 (m, 2 H, H(3)); 3.41 (m, 4 H, H(5), H(6))	29.0 (Me); 208.0 (C=O); 40.4 (C(3)); 24.0 (C(4)); 70.6 (C(5)); 66.7 (C(6)); 31.8 (C(7)); 19.4 (C(8)); 13.9 (C(9))
$\overset{1}{Me}CO\overset{3}{C}H_2\overset{4}{C}H_2\overset{5}{C}H_2O\overset{6}{C}H_2(\overset{7-9}{CH_2})_3\overset{10}{C}H_3$ (**7f**)	0.77 (t, 3 H, H(10)); 1.24—1.31 (m, 8 H, H(4), H(7), H(8), H(9)); 2.03 (s, 3 H, Me); 2.47 (m, 2 H, H(3)); 3.28 (m, 4 H, H(5), H(6))	29.4 (Me); 208.4 (C=O); 40.3 (C(3)); 23.9 (C(4)); 70.9 (C(5)); 69.6 (C(6)); 29.8 (C(7)); 28.4 (C(8)); 22.5 (C(9)); 14.0 (C(10))
$\overset{1}{Me}CO\overset{3}{C}H_2\overset{4}{C}H_2\overset{5}{C}H_2O\overset{6}{C}H(\overset{7}{C}H_2\overset{8}{C}H_3)_2$ (**7g**)	0.89 (t, 6 H, H(8)); 1.73 (m, 6 H, H(4), H(7)); 1.96 (s, 3 H, Me); 2.35 (m, 2 H, H(3)); 3.23 (m, 2 H, H(5)); 3.57 (m, 1 H, H(6))	29.7 (Me); 208.2 (C=O); 40.2 (C(3)); 23.8 (C(4)); 69.3 (C(5)); 66.8 (C(6)); 23.7 (C(7)); 14.9 (C(8))
$\overset{1}{Me}CO\overset{3}{C}H_2\overset{4}{C}H_2\overset{5}{C}H_2O\overset{6}{C}H(\overset{7-10}{CH_2})_4\overset{11}{C}H_3$ (**7h**)	0.83 (t, 3 H, H(11)); 1.24—1.77 (m, 10 H, H(4), H(7), H(8) H(9), H(10)); 2.10 (s, 3 H, Me); 2.45 (m, 2 H, H(3)); 3.40 (m, 4 H, H(5), H(6))	29.7 (Me); 208.6 (C=O); 40.4 (C(3)); 24.0 (C(4)); 69.9 (C(5)); 69.7 (C(6)); 31.8 (C(7)); 30.0 (C(8)); 25.2 (C(9)); 22.7 (C(10)); 14.1 (C(11))

(*to be continued*)

Table 3 (*continued*)

Compound	δ	
	^{1}H	^{13}C
$^{1}\quad\ ^{3}\quad\ ^{4}\quad\ ^{5}\quad\ ^{6}\ ^{7-14}\quad\ ^{15}$ $MeCOCH_2CH_2CH_2OCH(CH_2)_8CH_3$ (**7i**)	0.81 (t, 3 H, H(15)); 1.20—1.85 (m, 18 H, H(4), H(7), H(8), H(9), H(10), H(11), H(12), H(13), H(14)); 2.08 (s, 3 H, Me); 2.46 (m, 2 H, H(3)); 3.34 (t, 2 H, H(5), H(6))	29.0 (Me); 208.4 (C=O); 40.4 (C(3)); 24.0 (C(4)); 71.0 (C(5)); 69.7 (C(6)); 32.0 (C(7)); 30.0 (C(8)); 29.9 (C(9)); 29.8 (C10); 29.6 (C(11)); 29.6 (C(12)); 26.2 (C(13)); 22.7 (C(14)); 14.1 (C(15))
$^{3}\quad\ ^{4}\quad\ ^{5}\quad\ ^{6}$ $MeCOCH_2CH_2CH_2OCH_2Ph$ (**7j**)	1.77 (m, 2 H, H(4)); 2.01 (s, 3 H, Me); 2.44 (m, 2 H, H(3)); 3.37 (t, 2 H, H(5)); 4.36 (s, 2 H, H(6)); 7.21 (s, 5 H, Ph)	29.8 (Me); 208.4 (C=O); 40.2 (C(3)); 23.8 (C(4)); 69.2 (C(5)); 72.7 (C(6)); 127.5, 128.3; 138.36 (C_6H_5)
$^{3}\quad\ ^{4}\quad\ ^{5}\quad\ ^{6}\quad\ ^{7}$ $MeCOCH_2CH_2CH_2OCH(Me)Ph$ (**7k**)	1.32 (d, 3 H, H(7)); 1.45 (m, 2 H, H(4)); 2.13 (s, 3 H, Me); 2.44 (m, 2 H, H(3)); 3.29 (t, 2 H, H(5)); 5.17 (q, 1 H, H(6)); 7.31 (m, 5 H, Ph)	29.9 (Me); 208.6 (C=O); 40.0 (C(3)); 24.2 (C(4)); 67.7 (C(5)); 78.4 (C(6)); 126.2, 127.4, 128.4, 144.0 (C_6H_5); 24.1 (C(7))
$^{1}\quad\ ^{3}\quad\ ^{4}\quad\ ^{5}\quad\ ^{6}\quad\ ^{7}\quad\ ^{8}$ $MeCOCH_2CH_2CH_2OCH_2CF_2CF_2H$ (**7l**)	1.82 (m, 2 H, H(4)); 2.02 (s, 3 H, Me); 2.20 (m, 2 H, H(3)); 3.04—3.80 (m, 4 H, H(5), H(6)); 5.00—6.30 (m, 1 H, H(8))	29.0 (Me); 207.7 (C=O); 39.0 (C(3)); 30.0 (C(4)); 71.0 (C(5)); 67.2 (C(6)); 97.2—125.6 (m, C(7), C(8))
$^{3}\quad\ ^{4}\quad\ ^{5}\quad\ ^{6}\quad\ ^{7}$ $MeCOCH_2CH_2CH_2OCH_2CH_2OH$ (**9a**)	1.96 (s, 3 H, Me); 1.65 (m, 2 H, H(4)); 2.35 (m, 2 H, H(3)); 3.00−3.52 (m, 6 H, H(5), H(6), H(7)); 2.85 (s, 1 H, OH)	29.6 (Me); 208.7 (C=O); 39.9 (C(3)); 23.6 (C(4)); 69.8 (C(5)); 69.2 (C(6)); 71.2 (C(7))
$^{3}\quad\ ^{4}\quad\ ^{5}\quad\ ^{6}\quad\ ^{7}\quad\ ^{8}$ $MeCOCH_2CH_2CH_2OCH_2CH_2CH_2OH$ (**9b**)	1.99 (s, 3 H, Me); 1.50—1.80 (m, 4 H, H(4), H(7)); 2.80—3.60 (m, 2 H, H(3)); 3.20—3.62 (m, 6 H, H(5), H(6), H(8)); 2.96 (s, 1 H, OH)	29.8 (Me); 208.7 (C=O); 40.2 (C(3)); 23.7 (C(4)); 69.95 (C(5)); 69.1 (C(6)); 32.1 (C(7)); 60.91 (C(8))

175—180 °C. When the temperature was increased to 190 °C, the reactions afforded higher oligomers as the major products, whereas the reactions sharply slowed down at temperatures below 175 °C.

The compositions and the structures of compounds **3**, **7a—l**, and **9a,b** were established based on the data from elemental analysis (Table 2) and ^{1}H and ^{13}C NMR spectroscopy (Table 3). The spectral characteristics of compounds **2**, **4**, and **5** correspond to those published in the literature.[10]

Thus, we demonstrated the possibility of catalytic regioselective cyclopropane ring opening in acetylcyclopropane under the action of water, monohydric alcohols, or dihydric alcohols in the presence of copper or palladium compounds, which allows the preparation of 6-oxaundeca-2,10-dione, 5-alkoxypentan-2-ones, and 5-(ω-hydroxyalkoxy)pentan-2-ones in good yields.

Experimental

The ^{1}H and ^{13}C NMR spectra were recorded on Tesla BS-567 (100 MHz) and JEOL FX-90Q (22.5 MHz) spectrometers in $CDCl_3$ relative to Me_4Si as the internal standard. The reaction products were analyzed by GLC on a Tsvet-5 chromatograph equipped with a flame ionization detector and a 300×0.3-cm column (Inerton AW-DMCS, SE-30). Preparative separation was carried out on a Carlo Erba instrument equipped with a flame ionization detector and a 600×0.5-cm column (Chromaton N-AW, SE-30) using helium as the carrier gas. Acetylcyclopropane was synthesized according to a procedure reported previously.[11] Alcohols (MeOH, EtOH, PrOH, Pr^{i}OH, BuOH, $C_5H_{11}OH$, Et_2CHOH, $C_6H_{11}OH$, $C_{10}H_{21}OH$, and $PhCH_2OH$) were commercially available compounds (all of reagent grade); $PhCH(Me)OH$ and $CF_2HCF_2CH_2OH$ (both of analytical grade) were purchased from Aldrich. The catalysts $PdCl_2$ and $(CF_3SO_3Cu)_2 \cdot C_6H_6$ (both of reagent grade) were purchased from Aldrich. The complexes $K_2[PdCl_4]$,[12] $PdCl_2 \cdot 2\ PPh_3$,[13] and $Pd_2(DBA)_3 \cdot CHCl_3$ [14] were prepared according to known procedures.

6-Oxaundeca-2,10-dione (3). Acetylcyclopropane (1.35 g, 16 mmol), H_2O (1.40 g, 80 mmol), $CuBr_2$ (0.016 g, 0.07 mmol), and diethyl ether (2.80 g, 38 mmol) were placed in a 17-mL microautoclave and the reaction mixture was heated at 180 °C for 6 h. Then the solvent was distilled off and the residue was fractionated to give a fraction with b.p. 143—146 °C (100 Torr), which corresponded (according to the NMR spectral data) to a mixture of compounds **2**, **4**, and **5**, and a fraction with

b.p 120—122 °C (1.5 Torr). Ether **3** was obtained as a colorless liquid in a yield of 0.96 g (64%). Found (%): C, 64.59; H, 9.80. $C_{10}H_{18}O_3$. Calculated (%): C, 64.50; H 9.76. The ^1H and ^{13}C NMR spectral data for compound **3** are given in Table 3.

Synthesis of 5-alkoxypentan-2-ones (7a—l) (general procedure). Acetylcyclopropane (16 mmol), alcohol (ROH) (16 mmol), H_2O (80 mmol), a catalyst (0.07—0.14 mmol), and a solvent (35—38 mmol) were placed in a 17-mL microautoclave or a glass tube (~20 mL) and the reaction mixture was heated at 175—180 °C from 7 to 50 h depending on the alcohol and the catalyst used. Compounds **7a—h**, **7j**, and **7k** were isolated by vacuum distillation. Compounds **7i**, **7l**, **9a**, and **9b** were isolated by preparative GLC. The boiling points and the data from elemental analysis of the compounds synthesized are given in Table 2. The ^1H and ^{13}C NMR spectral data are listed in Table 3.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 00-15-97312).

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Received September 14, 2000;
in revived form March 2, 2001