ISSN 1070-4272, Russian Journal of Applied Chemistry, 2018, Vol. 91, No. 6, pp. 990−995. © Pleiades Publishing, Ltd., 2018.
Original Russian Text © D.N. Gorbunov, M.V. Nenasheva, N.A. Sinikova, Yu.S. Kardasheva, A.L. Maksimov, E.A. Karakhanov, 2018, published in Zhurnal Prikladnoi Khimii, 2018, Vol. 91, No. 6, pp. 859−865.

ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

Tandem Hydroformylation–Acetalization Using a Water-Soluble Catalytic System: a Promising Procedure for Preparing Valuable Oxygen-Containing Compounds from Olefins and Polyols

**D. N. Gorbunov[a], M. V. Nenasheva[a], N. A. Sinikova[a], Yu. S. Kardasheva[a],
A. L. Maksimov[b], and E. A. Karakhanov[a],***

[a] *Moscow State University, Moscow, 119991 Russia*
[b] *Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Moscow, 119991 Russia*
e-mail: suskab_91@mail.ru

Received May 28, 2018

Abstract—Specific features of the tandem hydroformylation–acetalization of a series of unsaturated compounds and polyols in the presence of a water-soluble catalytic system containing a rhodium catalyst precursor, sodium (triphenylphosphino)trisulfonate, and sulfuric acid were studied. The process parameters (component ratio, temperature, reaction time) were optimized using model substrates. With the suggested catalytic system, the conversion of unsaturated compounds to target products, acetals, reaches 95%, and the catalytic system can be separated from the reaction products and repeatedly used without significant loss of the activity. The acetal preparation procedure is versatile with respect to the raw materials. Batches of acetal mixtures were prepared by the suggested procedure from 1-octene and polyols (ethylene glycol, glycerol, sorbitol).

DOI: 10.1134/S1070427218060174

The mankind’s desire for economical and environmentally friendly consumption of natural resources makes it topical to develop technologies for deep processing of hydrocarbon raw materials and various wastes. Polyols are wastes from the production of sugars and biodiesel. These hydrophilic oxygen-containing wastes do not always find proper application, and on the glycerol market the supply exceeds the demand because of rapid development of the biodiesel production [1, 2]. Therefore, problems of reprocessing polyols become very topical.

One of the ways of reprocessing polyols involves their hydrophobization by reactions with carbonyl compounds to obtain cyclic acetals and ketals. Compounds of these classes can be used as solvents, detergents, emulsifiers, components of cosmetics, and technical additives, e.g., to lubricants and hydraulic oils [3, 4], and also as fragrances [5]. Acetals derived from polyols show promise in agricultural chemistry owing to their ability to considerably reduce the surface tension without foaming. Therefore, their addition to agrochemical formulations, e.g., to those containing herbicides, insecticides, fungicides, or plant growth stimulants, improves the retention of active substances on the surface and their subsequent penetration into plant leaves [6]. It seems promising to use acetals as additives to hydrocarbon fuels for internal combustion engines, namely, to gasolines and diesel fuels. Acetals can be used for increasing the octane number of gasolines [7] or improving the properties of biodiesel (viscosity, oxidation resistance, flash point, etc.), or as antifreezes for biodiesel [8–10]. Addition of acetals to gas oil or diesel fuel decreases the emission of harmful substances, in particular, as solid particles [11]. Addition of 1,3-dioxolanes to lubricating oils and fuels enhances their oxidation resistance, improves the fuel purity, and decreases the friction and fuel consumption [12].

Classical procedures for preparing cyclic acetals consist in performing acetalization on acid catalysts with azeotropic distillation of water [13]. These procedures required the use of expensive aldehydes as raw materials and of high-performance, preferably heterogeneous,

▨ Products of large-tonnage chemistry □ Fine organic synthesis

	Ethylene glycol	Glycerol	Xylitol	Sorbitol	Xylose	Molasses	1,3-Propanediol	Pinacol	Pentaerythritol
Ethylene	□	□	□	□	□	□	▨	▨	▨
Propylene	□	□	□	□	□	□	▨	▨	▨
Linear olefins C_5–C_{14}	□	□	□	□	□	□	▨	▨	▨
Propylene trimers	□	□	□	□	□	□	▨	▨	▨
Butylene dimers	□	□	□	□	□	□	▨	▨	▨
Fischer–Tropsch synthesis products	□	□	□	□	□	□	▨	▨	▨
Styrene	▨	▨	▨	▨	▨	▨	▨	▨	▨
Pinenes	▨	▨	▨	▨	▨	▨	▨	▨	▨
Terpenes	▨	▨	▨	▨	▨	▨	▨	▨	▨
Norbornene	▨	▨	▨	▨	▨	▨	▨	▨	▨
Cycloalkenes	▨	▨	▨	▨	▨	▨	▨	▨	▨
Dienes	▨	▨	▨	▨	▨	▨	▨	▨	▨

Fig. 1. Versatility of the suggested procedure for preparing acetals with respect to the raw material.

catalysts; therefore, they are hardly promising for commercial implementation.

This study deals with the synthesis of cyclic acetals by tandem hydroformylation–acetalization directly from unsaturated raw materials from oil refining processes, without isolation and purification of the intermediate aldehydes. Thus, the study is aimed at expanding the application sphere of the available resources and at developing an efficient procedure for preparing a promising class of oxygen-containing compounds.

RESULTS AND DISCUSSION

Previously our team [14, 15] and other research teams [16–21] examined the possibility of preparing various cyclic acetals by tandem hydroformylation–acetalization under homogeneous conditions in organic solvents. Novel procedures were suggested for preparing acetals from long-chain olefins and polyols of complex structure (xylitol, sorbitol) by hydroformylation–acetalization [14]; some previously unknown compounds were synthesized and characterized. In our study, we used (acetylacetonato)dicarbonylrhodium $Rh(acac)(CO)_2$ as a catalytic precursor for hydroformylation. High catalytic activity of rhodium compounds ensures the possibility of performing the processes at pressures of up to 8.0 MPa, which is considerably lower than the pressures used in cobalt-catalyzed hydroformylation (≥23.0 MPa). However, because of high cost of rhodium, it is topical to search for the ways to stabilize, separate, and repeatedly use rhodium catalysts.

The Poulenc–Ruhrchemie process is one of the most attractive processes for the catalyst separation. It is performed under the conditions of phase-transfer catalysis using a water-soluble phosphine ligand, TPPTS [sodium (triphenylphosphino)trisulfonate] [22].

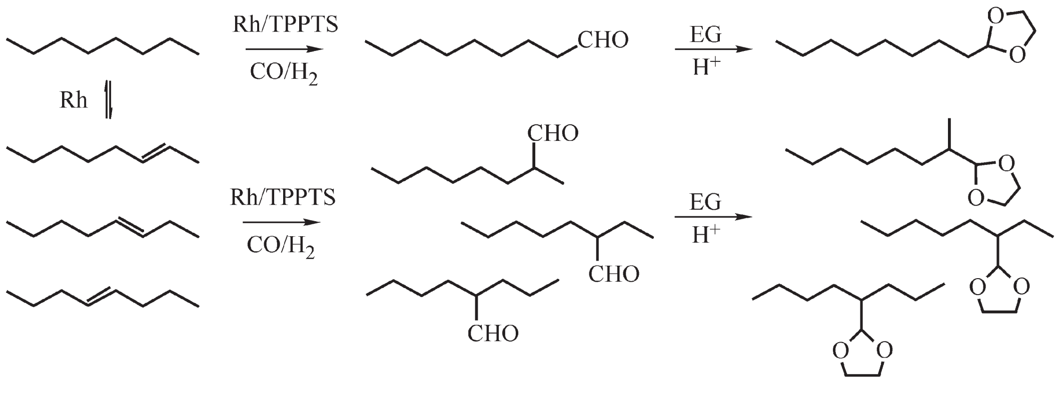


Fig. 2. Scheme of the hydroformylation–acetalization tandem reaction with 1-octene and ethylene glycol as examples.

Table 1. Hydroformylation–acetalization parameters

Parameter[a]	Value
Molar ratio S_1/Rh	1000:1–10000:1
Molar ratio L/Rh	3 : 1–10 : 1
Molar ratio S_2/S_1	1.2 : 1–3 : 1
Weight ratio of aqueous and organic phases	0.2 : 1–1 : 1
Acid content, wt %	0.5–3
Temperature, °C	70–110
CO/H_2 (1 : 1) pressure, MPa	4.0–8.0
Reaction time, h	4–8

[a] L is phosphine ligand TPPTS, S_1 is the unsaturated substrate, and S_2 is the polyol.

In this study, the Poulenc-Ruhrchemie process was taken as a basis for the development of processes for synthesizing cyclic acetals. The possibility of preparing acetals under the phase-transfer conditions is due to different polarity of the catalytic system components and reaction products. The starting polyol, sulfuric acid, and the catalyst occur in the aqueous phase, whereas the formed reaction products are extracted into the organic phase.

Because of the diversity of the starting reactants and versatility of the suggested method, it is possible to prepare a wide range of products, acetals of various structures, both as large-tonnage products and as products of fine chemical synthesis (Fig. 1).

Optimization of conditions of catalytic experiments. Initially we optimized the conditions of the tandem process. The important parameters that require optimization and influence not only the conversion but also the power and resource consumption are the reactant ratio and temperature. The optimum reaction conditions were found using model substrates, 1-octene and ethylene glycol (Fig. 2).

The optimum conditions of catalytic experiments, ensuring high 1-octene conversion (>90%) and high selectivity with respect to acetals (>70%), are given in Table 1.

Our next task was to expand the range of substrates and to scale the synthesis to obtain pilot batches of acetals.

The unsaturated substrates (terminal linear C_6–C_{14} olefins and propylene trimers) and polyols were varied, and the parameters indicated in Table 1 were kept constant. The total yield of the acetals is given in Table 2.

As shown by the examples of hydroformylation–acetalization of 1-octene in the presence of ethylene glycol, glycerol, and sorbitol, recirculation of the catalytic system is possible without significant loss in its activity (Fig. 3).

Thus, we have demonstrated the possibility of preparing ~500-mL batches of acetals for further studies of their consumer properties.

Scaling of the experiment and production of pilot batches of the acetals. The batches were produced in a 1-L high-pressure steel reactor equipped with a power-driven stirrer and a temperature-control device. The olefin was loaded in an amount of 100 mL and more. After the reaction completion, reactor cooling, and

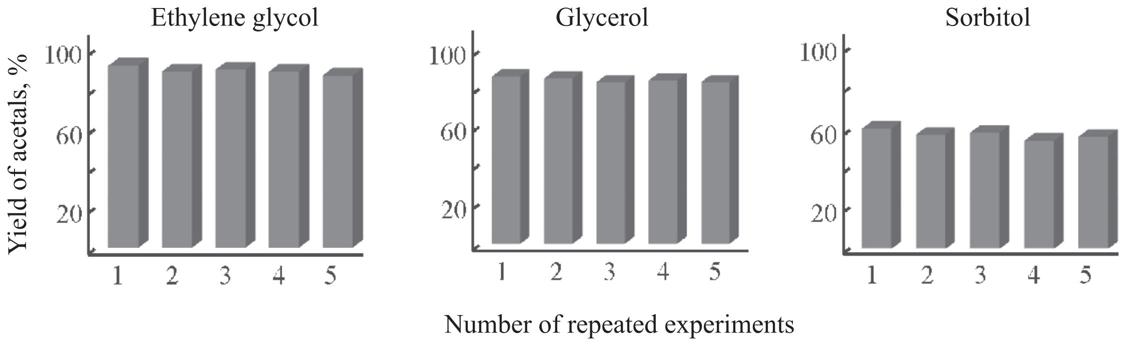


Fig. 3. Recirculation of the catalytic system. Conditions: Rh(acac)$(CO)_2$ (3 mg, 0.011 mmol), TPPTS (34.8 mg, 6 mmol), 1 M aqueous H_2SO_4 (0.6 mL), olefin (7.6 mmol), polyol (10.0 mmol), 80°C, $p(CO/H_2, 1 : 1) = 4.0$ MPa, 5 h.

Table 2. Preparation of acetals from various substrates by hydroformylation–acetalization. Conditions: $Rh(acac)(CO)_2$ (3 mg, 0.011 mmol), TPPTS (34.8 mg, 6 mmol), 1 M aqueous H_2SO_4 solution (0.6 mL), olefin (7.6 mmol), polyol (10.0 mmol), 80°C, $p(CO/H_2, 1:1) = 4.0$ MPa, 5 h

Polyol	Unsaturated substrate					
	C_6	C_8	C_{10}	C_{12}	C_{14}	propylene trimers
	yield of acetals,[a] %					
Ethylene glycol	94	92	92	90	84	42
Glycerol	89	87	85	80	76	
Pentaerythritol	80	79	76	74	70	No tests
Sorbitol	65	60	58	55	54	

[a] The yield of acetals was determined as the product of the unsaturated substrate conversion (%) and the percentage of acetals in the final mixture, determined by GLC.

Table 3. Batches of samples of acetal mixtures

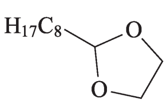
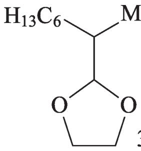
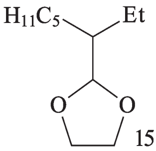
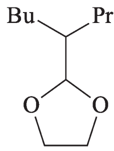
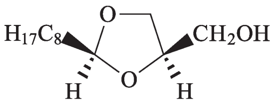
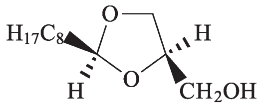
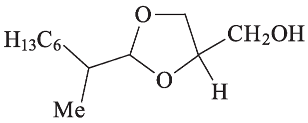
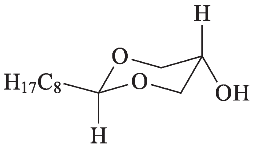
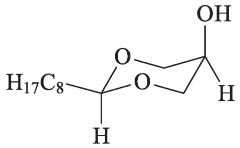
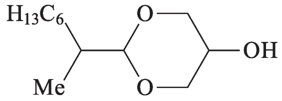
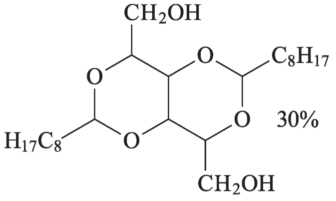
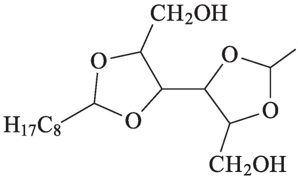
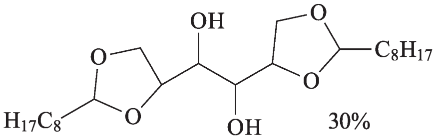
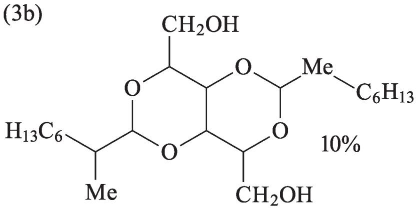
Sample	Substrate	Sample composition and content of components
G1-FA	1-Octene Ethylene glycol	 30% (1a)  30% (1b)  15% (1c)  15% (1d)
G2-FA	1-Octene Glycerol	 (2a) 40%  (2b)  20%  (2c) 40%  (2d)  (2e–h)
G3-FA	1-Octene Sorbitol	 30% (3a)  30% (3b)  30% (3c)  10% (3d)

Table 4. Production of batches of acetal mixtures.[a] Conditions: $Rh(acac)(CO)_2$ (150 mg, 0.58 mmol), TPPTS (2 g, 3.5 mmol), 1 M aqueous H_2SO_4 solution (40 mL), olefin (0.65 mol), polyol (0.8 mol), 80°C, $p(CO/H_2, 1:1) = 6.0$ MPa, 8 h

Substrate	Number of recycles, total synthesis time	Weight of the loaded 1-octene, g	Weight of the acetals obtained, g	Total yield of acetals, %	TOF, h^{-1}
Ethylene glycol	5 recycles, 40 h	350	490	85	197
Glycerol		350	525	75	168
Sorbitol		350	430	60	134

[a] Five repeated experiments on production of acetals for each substrate.

discharge of the gases, we took off the organic phase containing the reaction products (acetals), unchanged olefins, and intermediates (aldehydes). A fresh portion of the polyol was added to the aqueous phase, and after adding a new portion of the olefin in an organic solvent the aqueous phase was reused. The organic phases after a series of repeated syntheses were combined and subjected to fractional vacuum distillation to separate the acetal fraction from the solvent, olefins, and aldehydes. The composition of the acetal fractions was monitored by gas–liquid chromatography and NMR spectroscopy. By the above-described procedure, we prepared acetal mixture samples G1-FA, G2-FA, and G3-FA. Their composition is given in Table 3. The mixtures were not separated into individual components.

To evaluate the processes, we determined the total acetal yields and the turnover frequency (TOF) of the catalytic system (Table 4).

The TOF value obtained appeared to be relatively low. This is caused by the chosen initial olefin/Rh molar ratio and by the long reaction time. Further optimization involves studying the reaction kinetics and determining the reaction time and the substrate/catalyst ratio ensuring the maximal TOF values.

EXPERIMENTAL

1-Hexene, 1-octene, 1-decene, 1-dodecene, ethylene glycol, glycerol, pentaerythritol, xylitol, sorbitol, and TPPTS (Sigma–Aldrich) were used without any pretreatment. Propylene trimers (98% olefins) were placed at our disposal by Tatneftekhiminvest Holding. The solvents were pretreated by standard procedures. (Acetylacetonato)dicarbonylrhodium $Rh(acac)(CO)_2$ was prepared by the known procedure [23].

The ^1H and ^{13}C NMR spectra were recorded on a Varian XL-400 device operating at 400 MHz. Analysis of the mixtures by gas–liquid chromatography was performed with a Hewlett–Packard chromatograph equipped with a flame ionization detector and a 30-m-long capillary column coated with SE-30 under the conditions of programmed heating from 60 to 230°C. The carrier gas was helium. The analysis was performed in the presence of n-nonane as internal reference.

Procedure for preparing acetals under the conditions of phase-transfer catalysis. The reactions were performed in a 50-mL steel autoclave equipped with a magnetic stirrer and a temperature-control device at temperatures of up to 100°C. The autoclave was charged with the solvent (toluene, 1 mL), components of the water-soluble catalytic system [$Rh(acac)(CO)_2$ (3 mg, 0.011 mmol), TPPTS (34.8 mg, 6 mmol)], 1 M aqueous H_2SO_4 (0.6 mL), and the substrates: olefin (7.6 mmol) and polyol (10.0 mmol). The autoclave was purged with syngas, filled with syngas ($CO : H_2 = 1 : 1$) to a pressure of 4.0 MPa, and heated for 5 h at 80°C with continuous stirring. After the reaction completion, the autoclave was cooled to room temperature. The products were analyzed by GLC (with the addition of n-nonane as internal reference, 0.6 mL, 3.8 mmol) and by ^1H and ^{13}C NMR spectroscopy.

Production of pilot batches of acetal mixtures. The reactions were performed in a 1-L steel autoclave equipped with a power-driven stirrer and a temperature-control device operating at temperatures of up to 300°C. The autoclave was charged with the organic solvent (toluene, 30 mL), components of the water-soluble catalytic system [$Rh(acac)(CO)_2$ (150 mg, 0.58 mmol), TPPTS (2 g, 3.5 mmol)], 1 M aqueous H_2SO_4 (40 mL), and the substrates: olefin (0.65 mol) and polyol (0.8 mol). The autoclave was purged with syngas, filled with syngas ($CO : H_2 = 1 : 1$) to a pressure of 6.0 MPa, and heated for 8 h at 80°C with continuous stirring. After the reaction completion, the autoclave was cooled to room temperature, the pressure was relieved, and the organic phase was unloaded. The organic phase composition was determined by GLC and by ^{1}H and ^{13}C NMR. A new portion of the polyol (80% of the previous loading), unsaturated substrate (0.65 mol), and toluene (30 mL) were added to the aqueous phase remaining in the autoclave. The combined organic phases were subjected to fractional vacuum distillation to separate the unchanged olefins, aldehydes, and toluene and obtain a mixture of acetals. Their purity was checked by GLC and by NMR spectroscopy.

CONCLUSIONS

A procedure was suggested for preparing acetals of various compositions and their mixtures by tandem hydroformylation–acetalization using a water-soluble catalytic system. The yield of cyclic acetals is 50–95% depending on the kind of the raw material; i.e., the procedure is versatile. The catalytic water-soluble system can be readily separated from the reaction products; it does not lose the catalytic activity in repeated use. The optimum reaction conditions were determined. Under these conditions, the experiments were performed to produce pilot batches of acetal samples from 1-octene and polyols: ethylene glycol, glycerol, and sorbitol. The performance of the catalytic system, evaluated by TOF, was about 200 h^{-1}, and the time of stable operation of the catalytic system exceeded 40 h.

REFERENCES

1. Ciriminna, R., Pina, C., Rossi, M., and Pagliaro, M., *Eur. J. Lipid Sci. Technol.,* 2014, vol. 116, no. 10, pp. 1432–1439.
2. Gholami, Z., Abdullah, A.Z., and Lee, K.T., *Renew. Sust. Energ. Rev.*, 2014, vol. 39, pp. 327–341.
3. Patent US 4537980 A, Publ. 1979.
4. Patent WO 2009100854 A2, Publ. 2008.
5. Patent EP 1316553 B1, Publ. 2001.
6. Patent EP 2305662 B1, Publ. 2009.
7. Patent RU 2365617, Publ. 2009.
8. Belen Güemez, M., Requies, J., Agirre, I., et al., *Chem. Eng. J.*, 2013, vol. 228, pp. 300–307.
9. Kiss, A., Dimian, A., and Rothenberg, G., *Synth. Catal.,* 2005, vol. 18, pp. 75–82.
10. Silva, P.H.R., Gonçalves, V.L.C., and Mota, C.J.A., *Bioresource Technol*., 2010, vol. 101, pp. 6225–6229.
11. Patent US 6890364 B2, Publ. 2005.
12. Patent US 4906253 A, Publ. 1990.
13. Climent, M.J., Corma, A., and Iborra, S., *Green Chem*., 2014, vol. 16, pp. 516–547.
14. Gorbunov, D.N., Egazaryants, S.V., Kardasheva, Yu.S., et al., *Russ. Chem. Bull*., 2015, vol. 55, no. 4, pp. 943–947.
15. Gorbunov, D.N., Shchukina, T.V., Kardasheva, Yu.S., et al., *Petrol. Chem*., 2016, vol. 56, no. 8, pp. 711–716.
16. Hung-Low, F., Uzcategui, G.C., and Alvarez, J., *React. Kinet. Catal. Lett*., 2006, vol. 88, no. 1, pp. 143–148.
17. Ameri, T., Dennler, G., and Lungenschmied, C., *Energy Environ. Sci*., 2009, vol. 2, no. 4, pp. 347–363.
18. Chapman, C.J. and Frost, C.G., *Synthesis*, 2007, no. 1, pp. 1–21.
19. Alhaffar, M., Suleiman, R., Hussain, S., et al., *React. Kinet. Catal. Lett.,* 2011, vol. 104, no. 2, pp. 323–336.
20. Neubert, L., Paetzold, E., Fischer, C., et al., *Chem. Eng. Technol.,* 2011, vol. 83, no. 3, pp. 322–330.
21. Norinder, J., Rodrigues, C., and Börner, A.*, J. Mol. Catal. A: Chemical*, 2014, vol. 391, pp. 139–143.
22. Cornils, B. and Kuntz, E.G., *J. Organomet. Chem*., 1995, vol. 502, pp. 177–186.
23. Varshavskii, Yu.S. and Cherkasova, T.G., *Zh. Neorg. Khim*., 1967, vol. 1, no. 12, pp. 1709–1711.