ISSN 0965-5441, Petroleum Chemistry, 2008, Vol. 48, No. 3, pp. 206–209. © Pleiades Publishing, Ltd., 2008.
Original Russian Text © Kh.A. Suerbaev, E.G. Chepaikin, G.Zh. Zhaksylykova, K.S. Kanybetov, T.K. Turkbenov, G.M. Abyzbekova, 2008, published in Neftekhimiya, 2008, Vol. 48, No. 3, pp. 208–211.

Hydroxycarbonylation of Isobutylene in the Presence of the Palladium Acetylacetonate–Triphenylphosphine–*p*-Toluenesulfonic Acid Catalyst System

Kh. A. Suerbaev[a], E. G. Chepaikin[b], G. Zh. Zhaksylykova[a], K. S. Kanybetov[a], T. K. Turkbenov[a], and G. M. Abyzbekova[a]

[a] *Al-Farabi Kazakh National University, ul. Al-Farabi 71, Almaty, 050038 Kazakhstan*

[b] *Institute of Structural Macrokinetics and Materials Science, Russian Academy of Sciences, Chernogolovka, 142432 Russia*
e-mail: echep@ism.ac.ru; grig@ism.ac.ru

Received February 16, 2007

Abstract—The reaction of isobutylene hydroxycarbonylation with carbon monoxide and an alcohol (ethanol, l-menthol) in the presence of the palladium acetylacetonate–triphenylphosphine–@p-toluenesulfonic acid catalytic system was investigated. It was shown that the reaction proceeds regioselectively with the formation of linear products (ethyl isovalerate, l-menthyl isovalerate). The optimum conditions for running the process were found, at which the yield of the main products is 67–79%.

DOI: 10.1134/S0965544108030067

Hydroxycarbonylation of isobutylene, a product of oil refining, with carbon monoxide and an alcohol in the presence of homogeneous metal complex catalysts makes it possible to synthesize easily and conveniently in one step isovaleric acid esters, which possess biological activity and are components of pharmaceutical compositions or valuable intermediates for their synthesis. Some isovalerate esters possess a characteristic odor and are used as fragrance compounds in the manufacture of perfumes, cosmetics, and food essences [1].

The menthol ester of isovaleric acid (MIV) is an active principle of validol, a popular medicament [2]. It is synthesized in industry via esterification of isovaleric acid with menthol. The reactant isovaleric acid is obtained via the two-step oxidation of isoamyl alcohol isolated from fusel oils. The presence of the oxidation step, along with the use of feedstock of a plant origin (fusel oils), results in a high content of various undesirable impurities in isovaleric acid. It impairs the quality of MIV and, hence, the final medicine validol. Synthetic *d,l*-menthol contains an admixture of *d,l*-isomenthol (up to 25%) and, therefore, the use of phytogenic menthol (*l*-menthol) is more preferable, as only *l*-menthyl ester of isovaleric acid possesses biological activity [3]. One of the main active ingredients of the medicament corvalol is ethyl α-bromoisovalerate (EBIV) [2]. Commercially, the ester is obtained via a complex four-stage synthesis, in which the key stage is the bromination of isovaleryl chloride [4]. Isobutylene hydromenthoxycarbonylation with the synthesis gas in the presence of $(PPh_3)_2PdCl_2$ with an admixture of free triphenylphosphine was reported [5, 6]. An induction period was observed, which shortened as the ratio H_2/CO increased. There are also patent data that describe the use of a synthesis gas as a source of carbon monoxide [7–9].

Earlier, we developed MIV and EBIV preparation methods that are more economical and environmentally friendly than the current industrial process, with the key steps of the methods being, respectively, the hydromenthoxycarbonylation and hydroethoxycarbonylation of isobutylene with carbon monoxide in the presence of the $PdCl_2(PPh)_2$–PPh_3–TsOH and $PdCl_2$–PPh_3–TsOH (TsOH is *p*-toluenesulfonic acid) catalytic systems [10–12].

In this work, we have investigated the reactions of isobutylene hydromenthoxycarbonylation and hydroethoxycarbonylation in the presence of the halogen-free palladium catalyst system $Pd(Acac)_2$–PPh_3–TsOH with the purpose of the further development of the processes for manufacturing MIV and EBIV. The halogen-free catalytic system is much less corrosive and does not bring halogen in the final commercial product, thus making it possible to abandon testing the pharmaceutical for chlorine.

EXPERIMENTAL

The complex $Pd(Acac)_2$ was obtained according to the known procedure [13.] *p*-Toluenesulfonic acid (chemically pure grade) was recrystallized from 96% ethanol and dried until the composition $TsOH \cdot H_2O$. Triphenylphosphine (chemically pure grade, Chemapol) was recrystallized from an ether–ethanol mixture to a constant melting point. Absolute ethanol, isobutylene of 99.5% purity, carbon monoxide of