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OLEFIN REACTIONS

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This invention relates to the synthesis of organic oxygen and nitrogen compounds and, in particular, to the synthesis of saturated organic oxygen and nitrogen compounds by reaction between organic unsaturated compounds containing olefinic unsaturation, cobalt carbonyl and hydrogen or ammonia.

A wide variety of references have disclosed the reaction of carbon monoxide and hydrogen at high temperatures and high pressures to yield alcohols and hydrocarbons and with ethylene to yield aldehydes, ketones and other oxygenated products. However, there has been a great need for a practical low pressure and low temperature procedure for converting the cheap readily available olefins into desirable saturated organic oxygen and nitrogen compounds.

It is an object of this invention to produce such saturated organic oxygen and nitrogen compounds from organic compounds which contain olefinic double bonds by acting thereon with cobalt carbonyl and hydrogen or ammonia or both.

The present invention involves the discovery that cobalt carbonyls react readily with olefins in the presence of a compound capable of supplying hydrogen, such as hydrogen itself or ammonia or both, to yield saturated organic compounds such as aldehydes, alcohols, amides and amines. The use of cobalt carbonyl affords a number of distinct advantages over the use of carbon monoxide. Cobalt carbonyl is active at low temperatures and does not require the use of additional catalysts. The use of cobalt carbonyl does not necessitate the high pressure equipment necessary for carbon monoxide. Cobalt carbonyl is readily soluble in organic solvents and its low vapor pressure makes it much safer to handle than high pressure carbon monoxide. Cobalt carbonyl appears to function satisfactorily in a number of reactions where carbon monoxide is not entirely satisfactory.

The reaction between the olefinic compound, cobalt carbonyl and hydrogen or ammonia or both is generally conducted at a temperature of about 25° to 250° C. The process may be carried out at ordinary or subatmospheric pressures, but best results are obtained at superatmospheric pressure.

The relative proportions of reactants may be the stoichiometrically required quantities, although other proportions may be employed if desired. In a preferred embodiment, the process of the invention is conducted in the absence of any substantial quantity of carbon monoxide.

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Moreover, one of the important and preferred aspects of the present invention is the use of not merely catalytic quantities of cobalt carbonyl, but quantities sufficient to convert a substantial fraction of the olefin reactant; generally, about 0.1 to 2.0 mols of cobalt carbonyl per mol of olefin is sufficient for this purpose.

In one method of practicing the invention, the olefinic compounds and cobalt carbonyl (preferably $[Co(CO)_4]_2$, although other metallic carbonyls containing cobalt are also effective) are placed in a pressure resistant vessel and hydrogen is injected therein under pressure. Thus, the advantages of the invention are gained by employing a reaction mixture which initially contains cobalt carbonyl, it is not necessary to use catalysts or high-pressure carbon monoxide resistant equipment. After the reaction is completed, the resulting reaction product is separated from the metallic cobalt and the oxygen-containing organic compounds produced by the reaction are separated by any suitable method, such as fractional distillation.

The unsaturated compounds employed as reactants according to the invention include the olefins (monoolefines, diolefines), aryl-substituted olefins, and other substituted olefines such as ethylene, propylenes, butenes, pentenes, hexenes, cyclohexene, styrene, 1-vinylcyclohexene-3, butadiene-1,3, piperylene, diallyl, terpenes, tetramethylethylene, etc.

If desired, an organic solvent may be employed as a reaction medium. When such a medium is used, solvents in which cobalt carbonyl is readily soluble and stable are preferred. Suitable solvents are cyclohexane, benzene, xylene, diethylbenzene, ethylbenzene, etc.

The invention is illustrated further by means of the following examples.

Example 1.—A silver-lined high pressure reaction vessel was flushed with nitrogen and charged with about 28 parts of cobalt carbonyl, 56 parts of isobutylene, 70 parts of cyclohexane as solvent and 285 atmospheres of hydrogen pressure. The reaction mixture was heated several hours at 150° C. before discharging the reaction mixture. A colorless liquid and a black precipitate of cobalt was obtained. Fractionation of the liquid gave a high yield of isoamyl alcohol boiling at 130–131° C. (3,5-dinitrobenzoate derivative M. P. 61–2° C.).

Example 2.—A silver-lined high pressure reactor was flushed with nitrogen and charged with 15 parts of cobalt, 70 parts of cyclohexane, 56 parts of isobutylene and 950 atmospheres of car-

bon monoxide and heated at 135° C. for about 15 hours. The reactor was then cooled in a Dry Ice-methanol mixture and the carbon monoxide gas bled off. Then 38 parts of ammonia and 240 atmospheres of hydrogen was charged into the reactor and the mixture heated to about 185° C. in the absence of any carbon monoxide except for the carbon monoxide which was combined initially in the form of cobalt carbonyl. On working up the reaction mixture about 11 parts of isoamylamine and 5 parts of diisoamylamine were isolated. Other high boiling nitrogen containing products were also obtained.

Example 3.—Following the procedure given in Example 2 but omitting the hydrogen and heating at 225° C. resulted in the formation of isovaleramide M. P. 134° C.

Example 4.—A silver-lined autoclave was charged with about 42 parts of cobalt carbonyl, 70 parts of cyclohexane, 56 parts of isobutylene, and 225 atmospheres of hydrogen. The reaction mixture was heated at 140° C., with agitation for about three hours. After cooling and discharging, the reaction mixture was centrifuged to remove the metallic cobalt. The liquid products were separated by fractional distillation. The isovaleraldehyde was purified by means of the solid sodium bisulfite addition compound. About 20 parts of isovaleraldehyde, 12 parts of isoamyl alcohol and 6 parts of higher boiling oxygen-containing products were obtained.

Example 5.—Repeating Example 4 and heating at 75° C. gave about 8 parts of isovaleraldehyde and 10 parts of higher boiling oxygen containing products.

Example 6.—Repeating Example 4 but omitting the cyclohexane solvent and heating at 50° C. resulted in formation of about 30 parts of oxygen-containing products which consisted principally of isovaleraldehyde.

An experiment was run for comparison, using 5 parts of cobalt catalyst, 56 parts of isobutylene and 300 atmospheres of an equimolar mixture of carbon monoxide and hydrogen and heated at 75 to 88° C. and only about 5 parts of oxygen-containing products were obtained.

Example 7.—An autoclave was charged with 42 parts of cobalt carbonyl, 70 parts of cyclohexane, 20 atmospheres of ethylene and 40 atmospheres of hydrogen. Rapid gas absorption occurred at 35 to 40° C. yielding propionaldehyde.

The products of the invention are useful for various commercial purposes such as solvents and intermediates for other organic syntheses.

As many apparent and widely different embodiments of this invention may be made without departing from the spirit thereof, it is to be understood that it is not limited to the foregoing examples or description except as indicated in the following claims.

I claim:

1. A process for the preparation of oxygen-containing saturated organic compounds which comprises heating a mixture of reactants consisting of an olefinic hydrocarbon, cobalt carbonyl, and hydrogen at a reaction temperature of about 25° to 88° C., under superatmospheric pressure in the absence of any substantial quantity of added carbon monoxide, and separating from the resultant reaction product the oxygen-containing saturated organic compounds produced by the ensuing reaction.

2. A process for the preparation of nitrogen-containing saturated organic compounds which comprises heating a mixture of reactants consisting of an olefinic hydrocarbon, cobalt carbonyl, and ammonia at a reaction temperature of about 25° to 250° C., under superatmospheric pressure in the absence of any substantial quantity of added carbon monoxide, and separating from the resultant reaction product the nitrogen-containing organic compounds produced by the ensuing reaction.

3. A process for the preparation of saturated organic compounds which comprises heating a mixture of reactants consisting of an olefinic hydrocarbon, cobalt carbonyl, and a substance of the class consisting of hydrogen and ammonia at a temperature of about 25° to 250° C., under superatmospheric pressure in the absence of any substantial quantity of carbon monoxide other than the carbon monoxide introduced in the form of cobalt carbonyl, and separating from resultant reaction product the saturated organic compounds produced by the ensuing reaction.

4. The process set forth in claim 1 in which the said olefinic hydrocarbon is isobutylene.

5. The process set forth in claim 2 in which the said olefinic hydrocarbon is isobutylene.

6. The process set forth in claim 1 in which the said olefinic hydrocarbon is ethylene.

7. A process for preparing propionaldehyde which comprises reacting a mixture consisting of cobalt carbonyl, ethylene and hydrogen in an inert organic reaction medium, and separating propionaldehyde from the resultant mixture.

8. A process for preparing propionaldehyde which comprises heating at a temperature within the range of about 25° to 250° C. a mixture of reactants consisting of cobalt carbonyl, ethylene and hydrogen in an inert organic reaction medium and separating propionaldehyde from the resultant mixture.

9. A process for preparing propionaldehyde which comprises heating in an inert organic reaction medium at a temperature within the range of about 25° to 250° C. under superatmospheric pressure a mixture of reactants consisting of cobalt carbonyl, ethylene and hydrogen, the initial molal ratio of cobalt carbonyl to ethylene being about 0.2 to 2.0, and separating propionaldehyde from the resultant mixture.

10. A process for preparing isoamyl alcohol which comprises reacting a mixture consisting of cobalt-carbonyl, isobutylene and hydrogen in an inert reaction medium at a temperature of about 150° C. under superatmospheric pressure, continuing the reaction until a mixture containing metallic cobalt and isoamyl alcohol is produced, and separating isoamyl alcohol from the said reaction mixture.

11. A process for preparing isoamyl amines which comprises reacting a mixture consisting of cobalt carbonyl, isobutylene and ammonia in an inert reaction medium at a temperature of about 185° C. under superatmospheric pressure and thereafter separating isoamyl amine and diisoamyl amine from the resultant mixture.

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