FORMATION OF A CARBON—CARBON BOND IN THE REACTIONS OF OLEFINS WITH IODONIUM YLIDS UNDER LEWIS ACID CATALYSIS CONDITIONS

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We are the first to report the reaction of iodonium ylids [1] with olefins leading to the formation of a new C-C bond.

The reactions of ylid (I) with acyclic alkenes such as 1-hexene, 2-methyl-1-pentene, styrene, and methyl methacrylate proceed in the presence of a Lewis acid such as boron trifluoride etherate and triethyloxonium tetrafluoroboride (1.5-2 eq.) and LiClO₄ (4-5 eq) as co-catalysts at 20°C in ethyl acetate over 1-5 min with the formation of lactones (II) isolated in 60-80% yield after washing of the reaction mixtures with water and chromatography on silica gel.

$$\begin{array}{c} R^{2} \\ C = CH_{2} + Ph - \vec{I} - \overline{C}(CO_{2}CH_{3})_{2} & \xrightarrow{BF_{3} \cdot Et_{2}O, \ LiClO_{4}} \\ R^{1} & (I) & & & & \\ R^{1} = C_{4}H_{3}, \ Ph; \ R^{2} = H; \\ R^{1} = C_{3}H_{7}, \ CO_{2}CH_{3}; \ R^{2} = CH_{3} & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & & \\ &$$

Similar reactions for cyclohexene and 1,5,9-cyclododecatriene lead to the formation of a mixture of unsaturated products. For example, cyclohexene gives a mixture of isomeric 3- and 4-[bis(methoxycarbonyl)]methylcyclohexenes (III) and (IV) in 50-70% yield. Under the same conditions, silyl enol ethers give esters of ketodicarboxylic acids (V) in up to 60% yield. The product composition and structure were confirmed by elemental analysis, PMR and IR spectroscopy, and mass spectrometry.

These reactions are a new type of transformation for iodonium ylids and may serve as a convenient method for the extension of the carbon chain of olefins and ketones.

LITERATURE CITED

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