

Alkylations of Unsaturated Fatty Compounds¹

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The alkylation of alkenes is a reaction of great importance. We have been interested in alkylation reactions of unsaturated fatty compounds such as oleic acid and native oils that are important renewable raw materials, because branched fatty compounds are known to have interesting properties which are useful in lubricant area and in cosmetic formulations. Methods of the direct alkylation of non activated C,C-double bonds with simple primary and secondary alkyl groups are unknown, up to now. Here we report on hydro-alkyl-additions to alkenes using alkyl chloroformates. The reaction of oleic acid with isopropyl chloroformate gave in the presence of ethylaluminium sesquichloride ($\text{Et}_3\text{Al}_2\text{Cl}_3$) after a reaction time of 2 h an approximately 1:1-mixture of the regioisomers 9- and 10-isopropyloctadecanoic acid in a yield of 73%.

Obviously the isopropyl cation that is generated from the isopropyl chloroformate in the presence of $\text{Et}_3\text{Al}_2\text{Cl}_3$ adds to the C,C-double bond of the alkene itself or to a rearranged species. Transfer of hydride from $\text{Et}_3\text{Al}_2\text{Cl}_3$ to the adduct carbenium ion gives the saturated addition product.

The $\text{Et}_3\text{Al}_2\text{Cl}_3$ -induced alkylation with different alkyl chloroformates was applied in addition to ricinoleic acid, 10-undecenoic acid and santalbic acid², to the respective methyl esters and to sunflower oil. In some cases addition of a hydride donor such as triethylsilane was necessary.

¹ U. Biermann, J.O. Metzger, *Angew. Chem. Int. Engl.* **1999**, *38*, 3675.

² U. Biermann, A. Lützen, M.S.F. Lie Ken Jie, J.O. Metzger, *Eur. J. Org. Chem.* **2000**, 3069-3070.