THERMOCATALYTIC REACTION OF ALKYL DIAZOACETATES WITH GASEOUS UNSATURATED HYDROCARBONS

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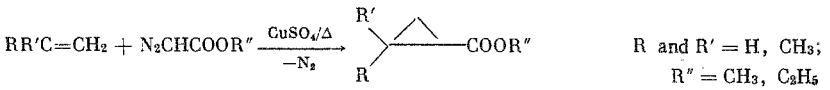
UDC 542.97:547.235.4:547.313-13

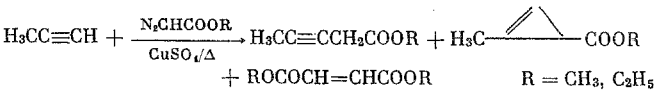
The reaction of alkyl diazoacetates (ADA) with unsaturated compounds is run in the liquid phase at elevated temperatures [1], which excludes the use of gaseous compounds as acceptors of the formed alkoxycarbonylcarbenes. We showed that the thermocatalytic reactions of ADA can be run in the gas phase using gaseous unsaturated hydrocarbons as the acceptors of the formed carbenes. A mixture of a large excess of the unsaturated hydrocarbon and the vapors of the ADA was passed at 130-160°C and a contact time of 3-5 sec through $CuSO_4$ deposited on pumice. The reaction products were worked up in the usual manner. In this way we obtained the ethyl ester of cyclopropanecarboxylic acid [2] in 16% yield from ethylene, the ethyl ester of 2-methylcyclopropanecarboxylic acid [3] in 26.5% yield from propylene, and the ethyl ester of 2,2-dimethylcyclopropanecarboxylic acid [4] in 50% yield from isobutylene.



$$RR'C{=}CH_2 + N_2CHCOOR'' \xrightarrow[-N_2]{CuSO_4/\Delta} \text{(cyclopropane with R, R', COOR'')}$$

R and R′ = H, CH_3; R″ = CH_3, C_2H_5

The products of inserting the alkoxycarbonylcarbenes at the acetylenic C–H bond were formed predominantly from acetylenic hydrocarbons under the same conditions. Thus, from methylacetylene and ethyl diazoacetate we obtained: 1) 13% of the ethyl ester of 2-pentynoic acid, n_D^{20} 1.4400: IR spectrum (ν, cm^{-1}): 1745 (C=O), 2230 (C≡C); NMR spectrum (in CCl_4, δ, ppm): 1.18 t (CH_3 in $COOC_2H_5$), 1.8 t ($CH_3C{\equiv}C$), 3.08 q (CH_2 in $COOC_2H_5$), 4.15 q (CH_2COO); 2) 1-2% of the ethyl ester of 2-methyl-2-cyclopropene-1-carboxylic acid; IR spectrum (ν, cm^{-1}): 1730 (C=O), 1825 (C+C); NMR spectrum (in CCl_4, δ, ppm): 2.00 d (CHCOO), 2.12 d ($CH_3C{=}C$), 6.28 m (C=CH); 3) ethyl esters of maleic, fumaric (total yield 20%), and glycolic acid (6% yield).



$$H_3CC{\equiv}CH + N_2CHCOOR \xrightarrow[CuSO_4/\Delta]{} H_3CC{\equiv}CCH_2COOR + \text{(methylcyclopropene-COOR)} + ROCOCH{=}CHCOOR$$

R = CH_3, C_2H_5

The formation of the esters of cyclopropenecarboxylic acids in the gas phase is unexpected, since, according to [5-6], they undergo complete isomerization to the corresponding alkoxyfurans in similar reactions run in the liquid phase at a $CuSO_4$ concentration $\geq 10^{-2}$ mole/mole of ADA. Alkoxyfurans were not detected by us, which can be associated with the short contact time of the reaction products with the catalyst and their low concentration in the reaction mixture.

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N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 4, p. 957, April, 1974. Original article submitted January 16, 1974.