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A NEW SYNTHESIS OF ETHYL CYCLOPENTADIENE FROM CYCLOPENTADIENE AND ETHYLENE

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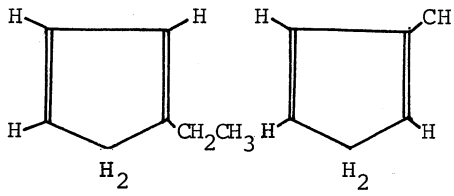
An equimolar mixture of 1-, and 2-ethyl cyclopentadiene was formed in vapor-phase thermal reaction of cyclopentadiene with ethylene.

Recently, with the progress in organic chemistry, many people have devoted themselves to investigating the special nature of cyclopentadiene in liquid-phase reactions[1]. However, its reactivities with various unsaturated compound in vapor-phase reactions remain unclarified even now with a few exceptions[2]. We have investigated vapor-phase thermal reaction of cyclopentadiene with ethylene and observed formation of 1-, and 2-ethyl cyclopentadiene C_7H_{10}, which have so far been synthesized using sodium cyclopentadienide and ethyl halide[3]. This method which we have just developed permits an effective and easy method for the synthesis of these cyclopentadienes.

Vapor-phase thermal reaction of cyclopentadiene with ethylene was carried out using a conventional flow microreactor at 1 atm pressure. Silicon carbide SiC (60-80 mesh) was packed in the reactor for the purpose of heating the reactant mixture. The gaseous effluent from the reactor was analyzed by means of gas chromatography.

First, the reaction product was collected using a trap cooled with Dry Ice - methanol-bath, and then the main product was separated by means of a gas chromatographic column. The analyses showed C:87.59 wt%, H:10.65 wt% (calc. for $(C_7H_{10})_n$, C: 89.28 wt%, H:10.72 wt%); m/e=94(I=76 eV, parent ion), 79(67), 78(45), 66(100) and 65(17). Parent ion corresponds to n=1, and m/e=66 and the difference m/e=15 between m/e=94 and 79 can be attributed to cyclopentadiene ion $C_5H_6^+$ and methyl ion

CH_3^+, respectively. The analyses by IR and by NMR(in CCl_4) also gave the following informations ; $\nu_{C-H}(cm^{-1})$: 3060, 3120 (-CH=CH-), 2960($-CH_3$), 2850($-CH_2-$), $\delta_{C-H}(cm^{-1})$: 1615, 1606(-CH=CH-), 1470, 1435, 1385, 1370($C-CH_3$) and 730, 674(-CH=CH-). δ_{ppm} : 1.16(triplet, $C\bar{H}_3-CH_2$), 2.41(multiplet 1:4:6:4:1, $CH_3-C\bar{H}_2-$), 2.85(multiplet, $=CH-C\bar{H}_2-CH=$), 5.92～6.34(multiplet, 3H unsaturated).



1-ethyl CPD 2-ethyl CPD

By means of the method proposed by K. Alder et al.[3], an equimolar mixture of 1-, and 2-ethyl cyclopentadiene was synthesized, and then it was analyzed with the above methods. The results obtained were in good agreement with those in the case of our product C_7H_{10}. Therefore, it was concluded that C_7H_{10} formed in the thermal reaction of cyclopentadiene with ethylene is an equimolar mixture of these ethyl cyclopentadienes. A little difference in the nature of 1-, and 2-ethyl cyclopentadiene presumably gives the multiplet at δ_{ppm}=2.41 due to the sum of two kinds of the quartet 1:3:3:1.

A typical result based on cyclopentadiene conversion (W/F=74.7 g-hr/g-mol, C_2' : 40 vol%, CPD:10 vol%, N_2:50 vol%) was yield of C_7H_{10} 4.4% (the selectivity 67%) at 530°C, 5.0% (47%) at 550°C, 6.9% (52%) at 570°C, and 7.4% (48%) at 590°C.

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