METATHESIS OF ETHYL 4-PENTENOIC ACID AND ITS COMETATHESIS WITH α-OLEFINS

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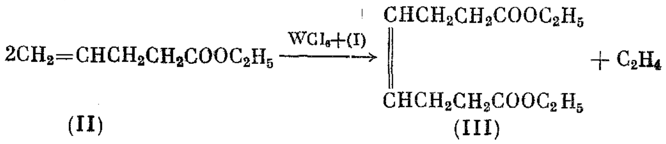
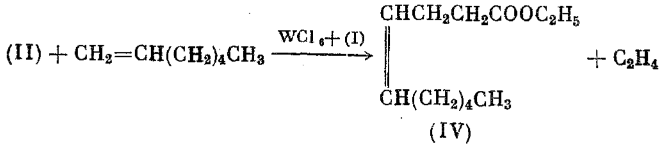
UDC 542.97:546.786'13:547.1'128:
547.395'262:547.313.6

Heterogeneous Re_2O_7 systems promoted by organotin compounds [1] and homogeneous WCl_6–R_4Sn catalysts [2] are the most efficient and widely used catalysts for the reactions of functional derivatives of olefins among the many presently reported catalysts for olefin metathesis.

We have previously reported the use of catalytic systems containing WCl_6 and 1,1,3,3-tetramethyl-1,3-disilacyclobutane (I) in the metathesis of linear and cyclic olefins [3]. In the present work, we have shown that this catalyst is effective for the metathesis of ethyl 4-pentenoic acid (II) and its cometathesis with 1-heptene.



$$\underset{(II)}{2CH_2{=}CHCH_2CH_2COOC_2H_5} \xrightarrow{WCl_6+(I)} \underset{(III)}{\begin{matrix} CHCH_2CH_2COOC_2H_5 \\ \| \\ CHCH_2CH_2COOC_2H_5 \end{matrix}} + C_2H_4 \qquad (1)$$



$$(II) + CH_2{=}CH(CH_2)_4CH_3 \xrightarrow{WCl_6+(I)} \underset{(IV)}{\begin{matrix} CHCH_2CH_2COOC_2H_5 \\ \| \\ CH(CH_2)_4CH_3 \end{matrix}} + C_2H_4 \qquad (2)$$

The yield of the homometathesis product (III) was 45-47% and the selectivity of reaction (1) was 91-93%. The yield of the cometathesis product of (II) with 1-heptene is 40-42% but the selectivity of reaction (2) is only 63-64% due to the formation of the products of the homometathesis of the starting olefins. The yields of 6-dodecene and (III) were 25 and 4%, respectively.

EXPERIMENTAL

All the operations on the preparation of the catalyst, substrates and metathesis reactions were carried out in a dry argon atmosphere. WCl_6 and (I) were used as benzene solutions. The products were analyzed by chromato-mass spectrometry using a KB-2091 spectrometer at 70 eV and a 70-m column packed with SP-2100 and gas-liquid chromatography on a Chrom-5 chromatograph with flame ionization detector and a 3-m column packed with XE-30.

A sample of ethyl 4-pentenoic acid (II) was obtained according to Ritter and Kaniecki [4].

Metathesis of (II). This reaction was carried out by two methods: 1) in an open system consisting of a thermostated reactor equipped with a magnetic stirrer and burette for trapping the gaseous products and 2) in sealed ampuls at 0.001 mm Hg. The reactor or 50-ml ampul was filled with 14 mmoles (2 ml) (II), 0.28 mmole WCl_6 (4 ml benzene solution) and 0.56 mmole (I) (0.56 ml benzene solution). The reaction was carried out at 80-82°C. After 10 h, the reaction was stopped by the addition of 15 ml ethanol. The products were separated by distillation and analyzed by gas-liquid chromatography or chromato-mass spectrometry. Mass spectrum of (III) (intensity, %): 40(32), 55(25), 67(55), 81(48), 108(25), 137(100), 154(29), 182(9), 228(6, M^+).

Cometathesis of (II) with 1-Heptene. The reaction was carried out in a sealed glass ampul at 0.001 mm Hg. The ampul was filled with 7 mmoles (1 ml) (II), 7 mmoles (0.9 ml) 1-heptene, 0.14 mmole WCl_6 (2 ml benzene solution, and 0.14 mmole (I) (0.28 ml benzene solu-

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0568-5230/86/3511-2403$12.50

tion). The products were separated by distillation and analyzed by gas-liquid chromatography and chromato-mass spectrometry. Mass spectrum of (IV), m/z (intensity, %): 40(79), 55(80), 69(80), 88(100), 96(41), 110(80), 152(37), 198 (10, M^+).

CONCLUSIONS

A system containing WCl_6 and 1,1,3,3-tetramethyl-1,3-disilacyclobutane catalyzes the metathesis of ethyl 4-pentenoic acid and its cometathesis with 1-heptene.

LITERATURE CITED

1. A. Ellison, A. K. Coverdale, and P. F. Dearing, J. Mol. Catal., 28, 141 (1985).
2. J. Levisalles and D. Villemin, Tetrahedron, 26, 3181 (1980).
3. N. S. Nametkin, V. M. Vdovin, and N. B. Bespalova, Dokl. Akad. Nauk SSSR, 225, 577 (1975).
4. J. J. Ritter and T. Kaniecki, J. Org. Chem., 27, 622 (1962).

ENTHALPY OF FORMATION OF KETENE, ETHYNOL, AND THEIR ANALOGS IN THE GAS PHASE

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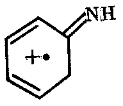
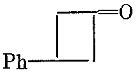
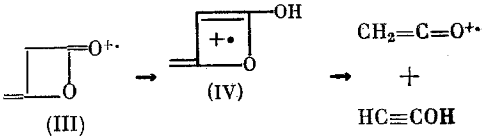
UDC 536.722:547.387:547.362

The reported enthalpies of formation for ketene in the gas phase range from −36.4 to −61.1 kJ/mole [1]. Taking the new value $\Delta H_f{}^0(g)\ (CH_3C{=}O^+) = 627.6$ kJ/mole [2] and the proton affinity $PA(CH_2{=}C{=}O) = 828.4$ kJ/mole [1], we obtain $\Delta H_f{}^0(g) = -74.1$ kJ/mole. Our calculations based on $\Delta H_f{}^0(g)\ (O{=}C{=}C{=}C{=}O) = -97.9$ kJ/mole [3] give $\Delta H_f{}^0\ (CH_2{=}C{=}O) = -91.96$ kJ/mole, while $\Delta H_f{}^0\ (g)\ (CH_2{=}C{=}O) = [\Delta H_f{}^0(O{=}C{=}O) + \Delta H_f{}^0(CH_2{=}C{=}CH_2)]/2 = 101.3$ kJ/mole. In order to determine the enthalpy of formation of ketene, we used a photoionization method which gives the ionization energy (IE) of molecules and appearance potential (AP) of fragment ions [4]. An attempt to obtain $\Delta H_f{}^0(CH_2{=}C{=}O)$ from the fragmentation of acetanilide (IE = 8.20, AP $[M - CH_2{=}C{=}O]^{+\cdot} = 9.74$ eV) was unsuccessful since ion (I) whose enthalpy of formation is unknown was obtained rather than the expected ion, $PhNH_2{}^+$.


(I)


(II)


(III)
(IV)

The values $\Delta H_f{}^0(g)(CH_2{=}C{=}O) = -87.24$ kJ/mole was obtained upon the fragmentation of 3-phenylcyclobutanone (II) with IE + 8.83 and $AP([PhCH{=}CH_2)]^{+\cdot}) = 8.86$ eV. Since the AP is virtually the same as the IE, the thermochemical threshold for the appearance of $[M - CH_2{=}C{=}O]^{+\cdot}$ may lie even lower since $\Delta H_f{}^0(g)\ (ChH_2{=}C{=}O) < -87.24$ kJ/mole, i.e., is significantly lower than the values proposed by Cox [3] (−61.1 kJ/mole) and, especially, by Benson [6] or in the review of Deming [6] (−47.7 kJ/mole).

The fragmentation of diketene (III) (IE = 9.53, AP $[M - 42]^{+\cdot} = 10.98$ eV) gives a very high value for $\Delta H_f{}^0 = +41.6$ kJ/mole for the neutral molecule with mass 42. The molecule may be the ketene isomer, ethynol HC≡COH. Estimation of the IE of HC≡COH give 9.7 eV for IE $(CH_2{=}C{=}O) = 9.61$ eV [7], which is in accord with the scheme for the decomposition of (III) given above. Since the IE of tautomer (IV) should be significantly lower than the IE of (III) (9.53 kJ/mole)(for example, IE = 803 eV [7] for $CH_2{=}CHCH{=}CHOCH_3$), the isomzerization of (III) to (IV) is possible. Thus, we are the first to obtain an experimental value for $\Delta H_f{}^0(g)\ (HC{\equiv}COH) = +41.6$ kJ/mole.

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0568-5230/86/3511-2404$12.50