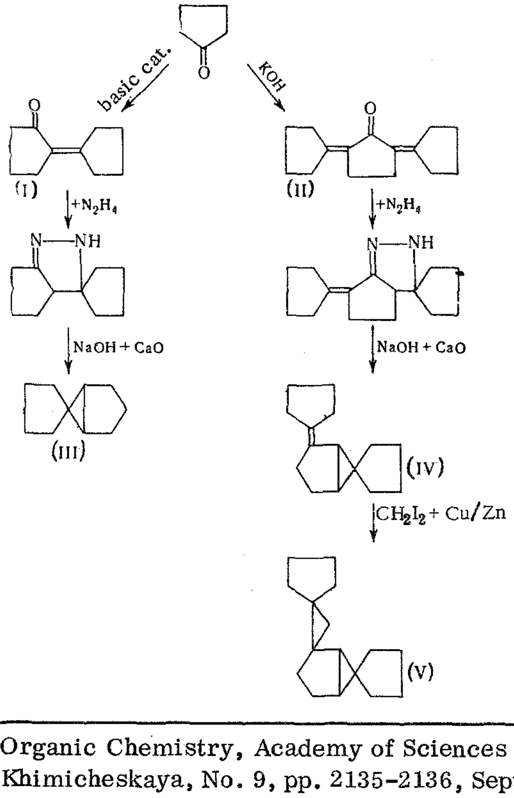
AUTOCONDENSATION OF CYCLOPENTANONE AND THE POLYCYCLIC HYDROCARBONS FROM ITS PRODUCTS

I. E. Dolgii, A. P. Meshcheryakov, and I. B. Shvedova UDC 542.953+547.514.472

The autocondensation of cyclopentanone was accomplished for the first time by Wallach [1], who carried out the reaction with sodium ethoxide in alcohol and obtained 2-cyclopentyldenecyclopentanone (I) and high molecular weight condensation products. Zelinskii and Shuikin [2] condensed cyclopentanone in the presence of anhydrous potassium cyanide (10%, heating for 4 h), and also by passing its vapors over Al_2O_3 at 200°C, obtained (I) in a yield of 41% with insignificant formation of higher products. We condensed cyclopentanone by boiling it in a vacuum of 150-170 mm for 2 h in a Soxhlet apparatus with a basic catalyst in the extraction portion. Here, we obtained 42% of (I), 10-15% of 2,5-dicyclopentylidenecyclopentanone (II), and virtually no high molecular weight products. We obtained (II), which was required for further syntheses, in higher yields by heating a mixture of cyclopentanone, toluene, and KOH in an apparatus fitted with a Dean-Stark water separator [3]. Pyrazolines were prepared from (I) and (II), which were then decomposed to the corresponding hydrocarbons by a double distillation from a mixture of NaOH and freshly calcined CaO. Addition of the latter ties up the water contained in the base and in the pyrazoline, and thus makes it possible to significantly increase complete decomposition of the pyrazoline. In this way, we synthesized bicyclo[3.1.0]hexanespiro-1-cyclopentane (III) and 3-cyclopentylidenebicyclo[3.1.0]hexanespiro-1-cyclopentane (IV). Bicyclo[3.1.0]hexanespiro-1-cyclopentanespiro-2-(cyclopropanespirocyclopentane) (V) was obtained from hydrocarbon (IV) by the Simmons–Smith method in a yield of 62%. Raman spectra were taken of (IV) and (V). In the spectrum of (IV), attention is drawn to the high frequency of the double bond (1692 cm^{-1}). We proposed to obtain the ethyl ester of the corresponding polycyclic carboxylic acid by addition of carboethoxy carbene to the double bond of (IV). Since we had hydrocarbon (IV) in a relatively small amount, the reaction of (IV) with diazoacetic ester was carried out under conditions successfully used for synthesis of tetrakis[(2-carbethoxycyclopropyl)methyl]silane [4]. However, we could not isolate the indicated ester from the reaction mixture.



N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk, Seriya Khimicheskaya, No. 9, pp. 2135-2136, September, 1968. Original article submitted March 6, 1968.

EXPERIMENTAL

2-Cyclopentylidene-1-cyclopentanone (I). In the flask of a Soxhlet apparatus was placed 50 g of cyclopentanone. The extraction portion of the apparatus contained a glass cloth thimble filled with 8 g of basic catalyst. The upper portion of the apparatus (above the reflux condenser) was connected to a vacuum pump. The flask was heated on a bath having a temperature of 125-150°C. Condensation of cyclopentanone was continued for 2 h at a flask temperature of from 86° (166 mm) to 120° (156 mm). The reaction products absorbed by the catalyst were extracted with ether. From the extract and the reaction mixture were isolated 18 g of cyclopentanone and 19 g of (I) in a yield of 42.5% based on cyclopentanone used in the reaction and 66.5% on reacted cyclopentanone: bp 94.5-96.0° (4 mm); d_4^{20} 1.0294; n_D^{20} 1.5216. Found %: C 79.88, 79.70; H 9.23, 9.34. MR 44.47. $C_{10}H_{14}O$. Calculated %: C 79.95; H 9.39. MR 43.55. Literature data [2]: bp 116-118° (10 mm); d_4^{10} 1.0172; n_D^{20} 1.5211. The residue (16.5 g) obtained after separation of cyclopentanone and (I) consisted mainly of (II), bp 180-185° (4 mm); mp 83-84° (alcohol). Literature data [3]: mp 83° (MeOH).

Bicyclo[3.1.0]hexaspiro-1-cyclopentane (III). To 25 g of hydrazine hydrate was added dropwise a solution of 50 g of (I) in 50 ml of alcohol. During this, the temperature rose to 65°. The mixture was heated for 2 h, cooled, and the alcohol and unreacted hydrazine hydrate were distilled. The residue was distilled twice from a mixture of 50 g of NaOH and 30 g of CaO. The distillate was washed with 5% CH_3COOH, dried with KOH, and distilled several times over Na. We obtained 34.5 g of (III) in a yield of 76% [on (I)]; bp 186.5 to 187.5°, solid. t. −60 to −61°; d_4^{20} 0.9150; n_D^{20} 1.4850; viscosity 1.96 centistokes at 20°. Found %: C 87.87, 87.96; H 11.83, 11.84. MR 42.74. $C_{10}H_{16}$. Calculated %: C 88.16; H 11.83. MR 42.40. Literature data [2]: bp 189-190°; d_4^{20} 0.9140; n_D^{20} 1.4855.

3-Cyclopentylidenebicyclo[3.1.0]hexanespiro-1-cyclopentane (IV). To 16 g of hydrazine hydrate was added dropwise a solution of 50 g of (II) in 200 ml of alcohol. The mixture was heated for 20 h at 100° and futher treated as in the synthesis of (III). We obtained 24 g of (IV) in a yield of 51%; bp 123-124° (4 mm); d_4^{20} 0.9583; n_D^{20} 1.5178. Found %: C 88.77, 88.73; H 11.31, 11.30. MR 63.95. $C_{15}H_{22}$. Calculated %: C 89.04 H 10.96. MR 62.96. Raman spectrum ($\Delta\nu$, cm^{-1}): 3128 (1), 3054 (2), 3026 (4), 3005 (4), 2955 (10), 2931 (1); 2908 (1), 2866 (8), 2837 (1), 1692 (10), 1477 (0), 1456 (7), 1438 (2), 1391 (2), 1325 (0), 1299 (0), 1233 (1), 1218 (1), 1170 (1), 1116 (0), 1065 (1), 1039 (2), 1017 (1), 989 (1), 959 (6), 949 (0), 907 (5), 887 (3), 843 (2), 780 (1), 718 (2), 672 (1), 610 (1), 569 (0), 550 (0), 503 (1), 468 (1), 444 (1), 325 (0), 380 (1), 355 (1), 310 (0), 168 (0), 146 (2).

Bicyclo[3.1.0]hexanespiro-1-cyclopentanespiro-3-(cyclopropanespirocyclopentane) (V). To a mixture of 2.31 g of freshly prepared zinc–copper couple, 30 ml of abs. ether, and several crystals of iodine was added dropwise 9.53 g of CH_2I_2. The mixture was boiled for 30 min with stirring, 6 g of (IV) was added dropwise, and heating was continued for an additional 30 h. After cooling, the reaction mass was filtered. The filtrate was washed with 5% HCl and a saturated bicarbonate solution, and dried with $CaCl_2$. We obtained 4 g of hydrocarbon (V) in a yield of 62.4%; bp 105-107° (4.5 mm); d_4^{20} 0.9629; n_D^{20} 1.5081. Found %: C 89.00, 88.94; H 11.30, 11.40. MR 67.01. $C_{16}H_{24}$. Calculated %: C 88.81; H 11.19. MR 66.57. Raman spectrum ($\Delta\nu$, cm^{-1}): 3042 (2), 3007 (5), 2955 (10), 2911 (4), 2860 (10), 2782 (2), 1474 (1), 1447 (10), 1399 (3), 1412 (0), 1289 (1), 1257 (0), 1225 (1), 1175 (0), 1128 (1), 1068 (1), 1034 (3), 1021 (0), 1005 (0), 984 (2), 963 (0), 948 (0), 927 (0), 901 (6), 867 (1), 837 (0), 808 (0), 788 (0), 706 (4), 665 (1), 620 (0), 572 (0), 525 (1), 439 (1), 405 (1), 363 (0), 340 (0), 194 (0), 165 (1), 141 (1).

CONCLUSIONS

1. Conditions for the preparation of cyclopentylidenecyclopentanone by the condensation of cyclopentanone without formation of high molecular weight products were determined.

2. Two earlier unknown polycyclic hydrocarbons were synthesized.

LITERATURE CITED

1. O. Wallach, Ber., 29, 2955 (1896).
2. N. D. Zelinskii and N. I. Shuikin, ZhRFKh, ob-va, 62, 1343 (1930).
3. J. Plesek, Chem. Listy, 50, 246 (1956).
4. I. E. Dolgii and A. P. Meshcheryakov, DAN SSSR, 157, 615 (1964).