

A DRASTIC ACCELERATION OF A DIELS-ALDER REACTION UNDER ADSORPTION CONDITIONS

V. V. Veselovskii, A. V. Lozanova, A. M. Moiseenko,
A. S. Gybin, and V. A. Stim

UDC 541.183:542.91:547.315

The uncatalyzed Diels-Alder reaction of such dienes as butadiene (Ia), isoprene (Ib), 2,3-dimethylbutadiene (Ic), myrcene (Id) or 1,3-cyclohexadiene (Ie) with dienophiles such as methyl vinyl ketone (IIa), acrolein (IIb) or methyl acrylate (IIc) requires heating at 130-160°C for 3-6 h [1].

These reactions were found to proceed even at 20°C when carried out in the absence of solvent upon the deposition of a mixture of the substrates on the surface of a chromatographic adsorbent. Thus, the reaction of (Ib) and (IIa) on Chemapol silica gel (40-100 μ) manufactured in Czechoslovakia (the silica gel was initially roasted at 200°C for 6 h) with (Ib): (IIa) = 1:1 and (Ib) + (IIa):SiO₂ = 1:10 at 20°C is complete in only 30-40 min to give 4-acetyl-1-methylcyclohexene in 70% yield and <3-5% 3-acetyl-1-methylcyclohexene as an impurity. The products of the [4 + 2] cycloaddition of (Ia)-(Ie) with (IIa) and (IIb) were obtained in 70-90% yield under the same conditions (these conditions were not optimized). The Diels-Alder reaction of (IIc) with (Ic) and (Id) requires heating to 80-100°C and proceeds better on fluorisil. The adduct yield in this case is 50-60%.

Adsorption on SiO₂ and/or Al₂O₃ has been shown to produce a drastic acceleration of [2 + 2 + 1] cycloaddition [2] and [3,3]-sigmatropic rearrangement (Carroll reaction) [3]. These results in conjunction with our present data indicate the general nature of the accelerating effect of adsorption on organic reactions differing in mechanism. The activity of the adsorbent surface as a multifunctional catalyst is apparently related both to the specific donor-acceptor interactions of the surface active sites with the polar or readily polarized groups of the substrates and nonspecific effects most likely arising from desolvation of the reagents upon adsorption. The latter factor apparently facilitates approximation of the reagent molecules and fixation of the prereaction complexes of the required geometry due to weak interactions of the molecules deprived of their solvation shell. Limitation of the conformational mobility of the substrates due to adsorption on a surface may also be a factor facilitating many reactions, especially, intramolecular transformations.

LITERATURE CITED

1. A. S. Onishchenko, The Diels-Alder Reaction [in Russian], Izd. Akad. Nauk SSSR, Moscow (1963).
2. S. O. Simonian, V. A. Smit (W. A. Smit), A. S. Gybin, et al., Tetrahedron Lett., 27, 1245 (1986).
3. V. A. Smit, S. I. Pogrebnoi, Yu. B. Kal'yan, and M. Z. Krimer, Izv. Akad. Nauk SSSR, Ser. Khim., 959 (1987).

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. 959, April, 1987. Original article submitted December 26, 1986.