Comparison of these results with previous data [1, 2] shows that [1.1.1]-propellane undergoes completely different transformations in reactions with triorganoboranes than with radical reagents. These findings indicate heterolytic nature for this reaction, which may be described by our previous scheme [4] for the reaction of triorganoboranes with bicyclo-[1.1.0]butane.

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HIGH PRESSURE SYNTHESIS OF 4-AMINO-2-OXO-2H-PYRIDO[1,2-a]PYRIMIDINES FROM 2-AMINOPYRIDINES AND ETHYL CYANOACETATE

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According to Allen et al. [1], the reaction of 2-aminopyridine (Ia) with ethyl cyanoacetate (II) at 180-200°C may be used for the preparation of N-(2-pyridyl)cyanoacetamide (IIIa). The reaction is accompanied by significant tar formation and (IIIa) is obtained in very low yield. We have found, however, that (Ia) and 2-amino-3-methylpyridine (Ib) react with (II) under high pressure at 80-100°C to give corresponding substituted pyrido[1,2-a]pyrimidines (IVa) and (IVb) and not (IIIa) and (IIIb). Upon sublimation, (IVa) and (IVb) isomerize to give (IIIa) and (IIIb) with opening of the pyrimidine ring. On the other hand, in the presence of triethylamine or pyridine, (IIIa) and (IIIb) cyclize upon heating to give (IVa) and (IVb).



A mixture of 0.6 g (Ia), 0.65 g (II), and 1.2 g benzene was heated at 80°C and 14 kbar for 5 h. The reaction mixture was treated with DMF. The solid precipitate was filtered off and dried at 120°C (1 mm) to give 0.41 g (40%) (IVa), mp 160-162°C. Mass spectrum (m/z): 161 (M⁺). PMR spectrum in DMSO-d₆ (δ , ppm): 8.18 m (1H, H⁶), 7.58 m (1H, H⁸), 7.09 m (1H, H⁹), 6.89 m (3H, H⁷, NH₂), 5.50 s (1H, H³). The IR spectrum lacks the vC=N band. Sublimation of (IVa) at 150-180°C (1 mm) gave (IIIa), mp 155-156°C. Mass spectrum (m/z): 161 (M⁺). IR spectrum (ν , cm⁻¹, KBr): 1678 (C=O), 2262 (C=N). PMR spectrum in DMSO-d₆ (δ , ppm): 10.82 s (1H, NH), 8.31 m, 8.00 m, 7.88 m, 7.12 m (4H, Py), 3.98 s (2H, CH₂). Analogously, heating (Ib) and (II) at 100°C and 14 kbar for 5 h gave (IVb) in 65% yield, mp 219-220°C. Sublimation of (IVb) gave (IIIb), mp 216-217°C. The elemental analysis data for the compounds obtained correspond to the calculated values.

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CONCENTRATION FLUCTUATIONS IN THE RADIOLYSIS OF AQUEOUS SOLUTIONS OF PEROXIDASE DERIVED FROM HORSERADISH ROOTS

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In a study of the γ -radiolysis of 1.2-2.4 μ M aqueous solutions of horseradish root peroxidase (HRP) saturated with oxygen and containing 0.1 M HCO₂Na, we discovered self-fluctuating reactions involving the products of the radiolytic transformations of HRP. Spectral changes occur upon the irradiation of this system as a result of reactions with H_2O_2 and 0_2 (HO₂), which are caused by the transformation of HRP to oxygenated forms, termed HRP-(I) and HRP-(II), and a peroxo complex, HRP-(III) [1]. In this case, the dose dependences of the concentrations of these forms have a fluctuating character. For example, the fluctuation period for initial HRP concentration (C_0) 1.6 μ M and dose 9.2 rad/sec is ~18 krad (in the antiphase) and the sum of the concentrations of the products corresponds to C_0 . The effect of the dose (0.8-9.2 rad/sec) and C_0 indicates that the disproportionation of radicals O_2^{-1} (HO_2^{+}) and HRP-(II) play the major role in the mechanism of the fluctuating reaction. After the irradiation, the concentrational fluctuations of HRP-(I) and HRP-(II) continue and are accompanied by the appearance of an HRP, whose concentration also fluctuates. These fluctuations are related to reactions apparently involving H_2O_2 and the enzyme and the disproportionation of HRP-(II). These effects may account for the retention of biological activity of the enzyme under these conditions in doses up to 1 Mrad observed by Metodieva et al. [2].

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