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Chemical and Mutagenic Properties of α -Phosphonooxynitrosamines*

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The chemical and mutagenic properties of the products of solvolysis of α -acetoxynitrosamines in phosphate buffer were investigated. α -Acetoxynitrosamines decomposed in two ways: *O*-acyl fission yielded α -hydroxynitrosamines, which decomposed into aldehydes and alcohols, while *O*-alkyl fission gave a resonance hybrid of α -*N*-nitroso-carbonium and -iminium ions, which was trapped with phosphate and afforded α -phosphonooxynitrosamine. Formation of α -phosphonooxynitrosamines was dependent on the structure of α -acetoxynitrosamines; those with a secondary α -phosphonooxy group, including cyclic nitrosamines, were easily formed, while among those with a primary phosphonooxymethyl group, only those with an alkyl group containing a branched α -carbon as isopropyl, *sec*-butyl and *tert*-butyl were isolated. They were good substrates of alkaline phosphatase and showed a nuclear magnetic resonance spectrum due to the presence of a phosphorus atom. They were decomposed by acid catalysis, and the rate was dependent on the structure. They were directly mutagenic in bacterial tester strains, except for a compound with a *tert*-butyl group. The activity was similar or stronger in *Salmonella typhimurium* TA 1535 and much weaker in *Escherichia coli* WP 2 and WP 2 *hcr*⁻ than those of α -acetoxynitrosamines. Stability in neutral aqueous solution and the strong mutagenicity of α -phosphonooxynitrosamines suggested their possible involvement in metabolic activation as a precursor of α -hydroxynitrosamines, and also in the organotropic carcinogenicity of *N*-nitrosodialkylamines as a transport form.

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