Chemiluminescence involving the phosphorus chemistry. Phospha-1,2-dioxetanes as the most likely high-energy intermediates in autoxidation of phosphonate carbanions

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The phospha-1,2-dioxetanes are the most likely intermediates in autoxidation of the phosphonate carbanions, in which chemiluminescence (CL) should be detected if the suitable substrates are employed, because such the intermediates are the structural analogue of well known chemiluminescent 1,2-dioxetanes. Autoxidation of the phosphonate carbanions derived from several 9-phosphorylacridanes in the aerated aprotic solvents provided CL along with the formation of fluorescent acridones. Detection of the large difference in the CL efficiencies between N-methylacridanes and N-hydroacridanes allows us to apply a CIEEL process as established in the firefly luciferin system. The CL quantum yields as well as the time course of the light emission highly depended on the phosphoryl substituents, which were connected with those found in the Wittig-type olefination reactions. Since the structure of the phosphoryl group is known to affects the rate of the oxaphosphetane ring formation in the Wittig-type reaction, the similar effect observed in the present CL reactions can be linked together, which suggests that the most likely intermediates are the phospha-1,2-dioxetanes. On the other hand, the energy-transfer CL to the externally added fluorescers was also observed in autoxidation of the phosphonate carbanions giving no fluorescent carbonyl products. Consequently, CL involving the phosphorus chemistry is not a peculiar phenomenon for the 9-phosphorylacridanides but a general event for the phosphonate carbanions if the conditions are adjusted.