Molecular structures and preferred conformations of stabilized keto diester phosphonium ylides

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Triphenylphosphonium ylidic keto diesters with a nonylidic ester group, Ph3PC(CO2CH2CH3)COCO 2CH2CH3, 1, and Ph3PC(CO 2CH2CH3)COCH2CO2CH 2CH3, 2, have the keto group syn and the ylidic ester acyl group anti to phosphorus. Conformation of 2 is assigned by X-ray crystallography, while conformations of 1 and 2 are based on 1H and 13C NMR spectroscopy, and comparisons of acyl stretching frequencies with predicted values from HF and DFT methods. Thermolyses of 1 and 2 gave the expected acetylene derivatives in high yield, consistent with the syn keto conformation and in agreement with earlier observations of thermolyses of stabilized phosphonium ylides. Results from the X-ray spectrum of 2 confirm the proposed structure.