DIPHENYL PHOSPHORAZIDATE (DPPA) AS A 1,3-DIPOLE. FORMATION AND DECOMPOSITION OF LABILE 1,2,3-TRIAZOLINE DERIVATIVES

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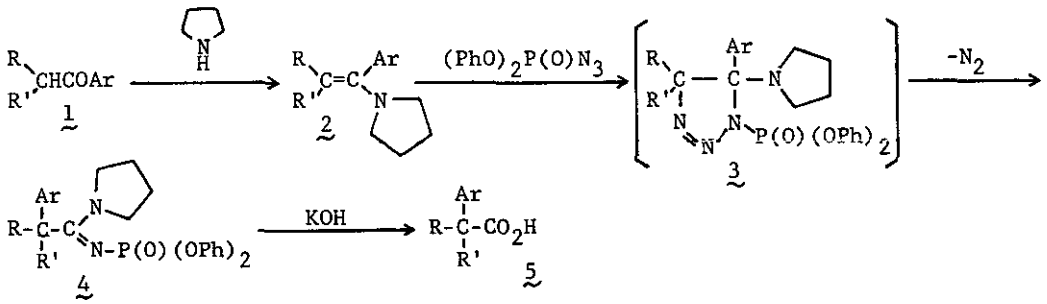
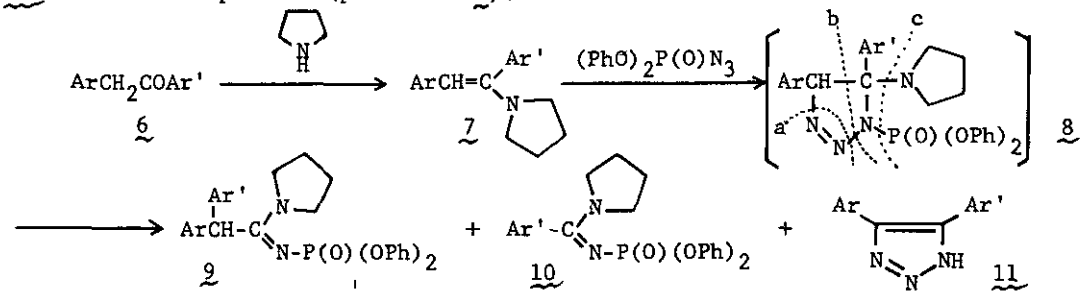
We have already demonstrated[1] a convenient three-step conversion of alkyl aryl ketones 1 to 2-arylalkanoic acids 5. The key step of this conversion is the reaction of diphenyl phosphorazidate (DPPA, $(PhO)_2P(O)N_3$) with the enamines 2, which afforded the amidines 4 by the 1,3-dipolar cycloaddition of DPPA to the enamine double bond, the evolution of nitrogen from the labile intermediate triazoline 3, followed by the 1,2-migration of the aryl groups:



We now prepared the pyrrolidine enamines 7 from diaryl ketones 6 and investigated their reaction with DPPA. The enamine 7a of deoxybenzoin underwent the reaction (path a in 8) similarly to above, giving the amidine 9a mainly. The enamine 7b of benzyl 2-pyridyl ketone afforded the amidine 9b, but another amidine 10b derived by the 1,3-dipolar elimination (path b in 8) also formed considerably. Surprisingly, the reaction of the enamine 7c with DPPA afforded the 1,2,3-triazole 11c as the main product (path c in 8).



a: Ar=Ar'=phenyl b: Ar=phenyl, Ar'=2-pyridyl c: Ar=2-pyridyl, Ar'=phenyl

1) T. Shioiri and N. Kawai, J. Org. Chem., 43, 2936 (1978); N. Kawai, N. Kato, Y. Hamada, and T. Shioiri, Chem. Pharm. Bull., in press.