

1,3-DIPOLAR CYCLOADDITION REACTION
OF DIMETHYL ACETYLENEDICARBOXYLATE WITH HYDRAZONES

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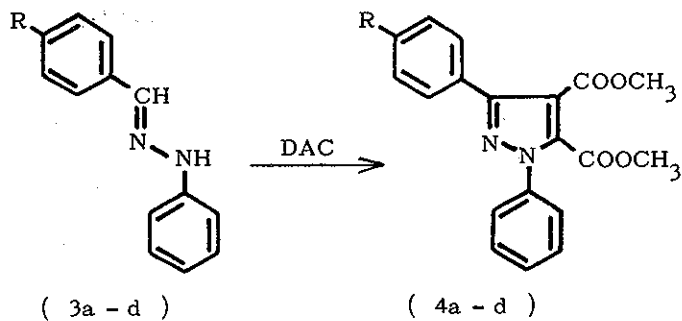
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1,3-Dipolar cycloaddition of aldehyde hydrazones(3) with dimethyl acetylenedicarboxylate(DAC) without solvent gives rise to dimethyl 1,3-diphenylpyrazole-4,5-dicarboxylates(4), and in some cases trimethyl 1-phenylpyrazole-3,4,5-tricarboxylate(5) as a by-product. In the case of *p*-chloro- and *p*-methoxy-benzaldehyde phenylhydrazones, dimethyl 1-phenyl-3-(*p*-substituted-phenyl)-pyrazolines(6c,d) are formed. In dimethylformamide as a solvent, the reaction gives the same product in a similar yield, but when ethanol is used as a solvent, only a small amount of the product is formed.

In the presence of a large excess of DAC, the direct reaction of 2,4 : 3,5-di-*O*-benzylidenealdehydo-D-ribose *p*-nitrophenylhydrazone(8) afforded three products; C-glycosyl nucleoside, 1-*p*-nitrophenyl(1,3 : 2,4-di-*O*-benzylidene-D-ribo-tetrahydroxybutyl)pyrazole-4,5-dicarboxylate(9), 1-*p*-nitrophenylpyrazole-4,5-dicarboxylate(10) and 2-methoxy-3,4,5-tricarbomethoxyfuran(11), the latter is formed on intermolecular thermal reaction of DAC.

A photochemical reaction of phenylhydrazone(3b) and DAC afforded the same pyrazole(4b) and *p*-nitrobenzophenone phenylhydrazone(12) and 1-*p*-nitrobenzoyl-2-phenylhydrazine(13).



	a	b	c	d
R	H	NO ₂	Cl	OCH ₃

