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

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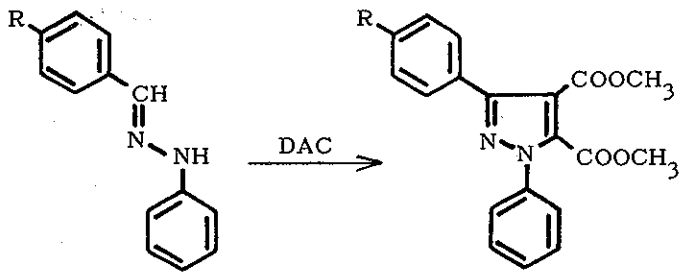
1,3-Dipolar cycloaddition of aldehyde hydrazones(3) with dimethyl acetylenedicarboxylate(DAC) without solvent gives rise to dimethyl 1,3-diphenylpyrazole-4,5-dicarboxylates(4), and in some cases trimethyl 1-phenylpyrazole-3,4,5-tricarboxylate(5) as a by-product. In the case of p-chloro- and p-methoxy-benzaldehyde 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.

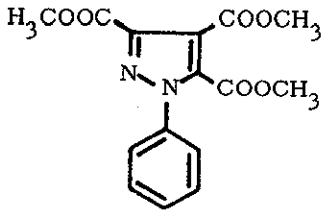
In the presence of a large excess of DAC, the direct reaction of 2,4 : 3,5-di-O-benzylidenealdehydo-D-ribose p-nitrophenylhydrazone(8) afforded three products; C-glycosyl nucleoside, 1-p-nitrophenyl(1,3 : 2,4-di-O-benzylidene-D-ribo-tetrahydroxybutyl)pyrazole-4,5-dicarboxylate(9), 1-p-nitrophenylpyrazole-4,5-dicarboxylate(10)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



(3a - d) (4a - d)

	a	b	c	d
R	H	NO_2	Cl	OCH_3



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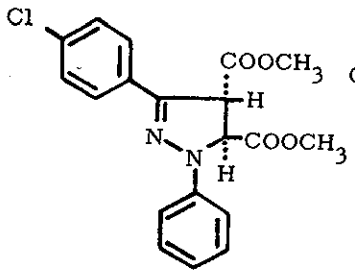

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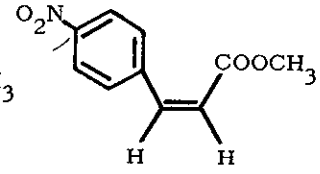

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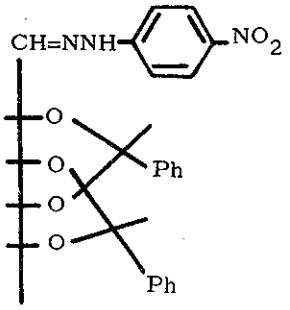

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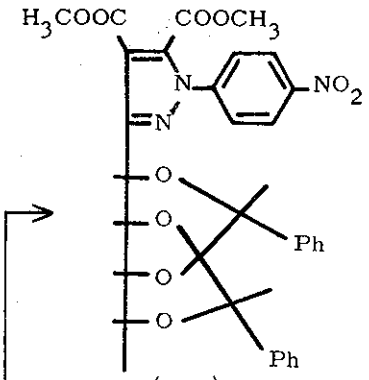

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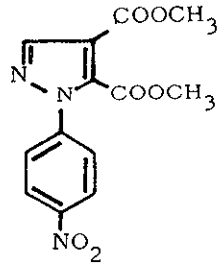

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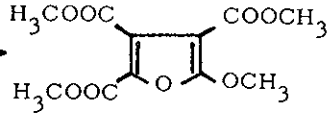

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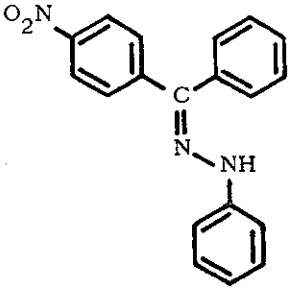

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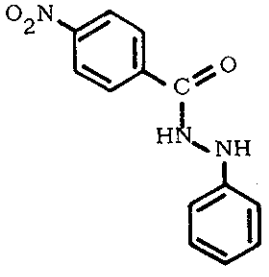

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