Intramolecular Cycloaddition of Olefinic Bonds with 4,6-Dihydroxypyrimidines

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Summary A general method for the addition of functional groups to unactivated olefins is described and exemplified.

FORMATION of carbon–carbon bonds from isolated olefins is often desirable in synthetic work. Cycloadditions have been used for this purpose but, although examples of 1,3-dipolar addition to isolated double bonds are relatively common, cycloadditions of the [2+4] type are rare.[1] We report an intramolecular cycloaddition process which effects the formation of two new carbon–carbon bonds.

The method involves cycloaddition to a heterocyclic system such that the primary adduct contains protected

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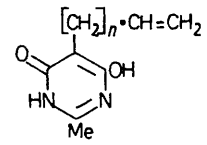
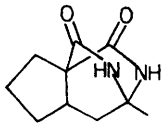


(1) $n = 3$
(4) $n = 4$



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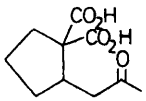

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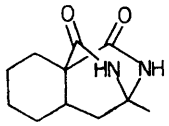

(5)

functional groups. Since 4,6-dihydroxypyrimidines have been shown to undergo cycloaddition, albeit with an electron-deficient substrate,[2] the compound (**1**) was selected for study. This material was prepared by the base-catalysed condensation of acetamidine with diethyl pent-4-enyl malonate. Previous work on the 4,6-dihydroxypyrimidines showed that they exist mainly in the mono-oxo form indicated.[3]

Heating the pyrimidine (**1**) at 200° for 5 h in dimethylformamide gave an almost quantitative yield of the cycloadduct (**2**), ν_{max} ($CHCl_3$) 3400, 1710, and 1675 cm^{-1}.

Acid hydrolysis of the adduct released the keto-acid (**3**), m.p. 124—126° in high yield. The reaction appears to be general, the homologue (**4**) producing the cycloadduct (**5**).‡

The above scheme results in the introduction of two functional groups into an isolated olefin as well as concomitant cyclisation.

We thank the S.R.C. and Allen and Hanburys Research Ltd. for a C.A.S.E. studentship (to R.A.W.).

(*Received, 23rd April* 1975; *Com.* 469.)

‡ All new compounds gave satisfactory analytical and spectral data.

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[2] P. J. Machin, A. E. A. Porter, and P. G. Sammes, *J.C.S. Perkin I*, 1973, 404.
[3] G. M. Kheifets, N. V. Khromov-Borisov, A. I. Koltsov, and M. V. Volkenstein, *Tetrahedron*, 1967, **23**, 1197.