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REACTION OF ENEHYDRAZINES WITH ACETYLENECARBOXYLIC ESTERS [1]

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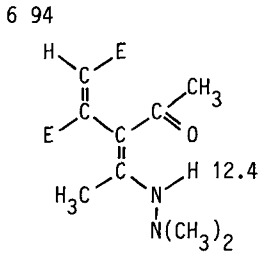
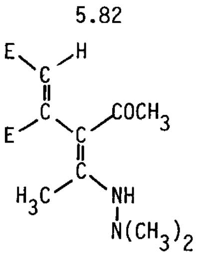
Abstract Eight products from reactions of acetylacetone-, methyl acetoacetate- and methyl formylacetate dimethylhydrazones with dimethyl acetylenedicarboxylate and methyl propiolate have been characterized by the usual spectroscopic methods and, partly, structure analyses.

Recent interest in the electrophilic substitution of enehydrazines[2] prompts us to report on own results with the title reactions.

Acetylacetone dimethylhydrazone[3] reacts with dimethyl acetylenedicarboxylate in ethanol to give a 5 1-mixture of the stereoisomeric compounds **1a** and **1b** from which the (2,3-E)-isomer **1a** can be crystallized (diisopropylether), mp 67°C. A solution of pure **1a** in deuterochloroform equilibrates back to the above mixture. The configurations of **1a** and **1b** and the hydrogen bridge were tentatively assigned by the nmr data indicated at the formulae. Additionally, the constitution of **1a** has been confirmed by a structure analysis.



1a



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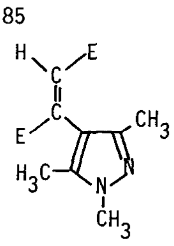
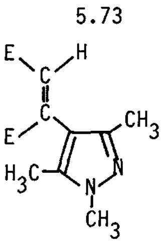


2a



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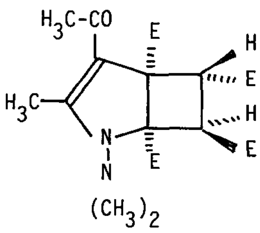

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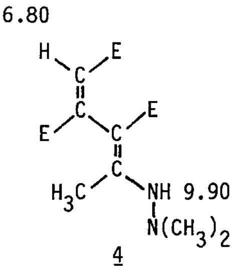

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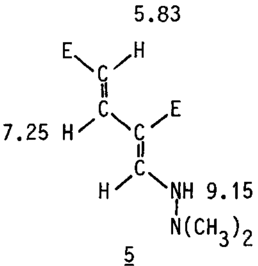


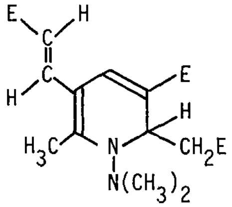
5

E = CO_2CH_3

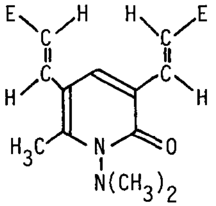
Compounds **1a** and **1b** react with monomethylhydrazine in THF to give the stereoisomeric pyrazoles **2a**,**b** (bp 95 and 125°C/0.1 mm Hg) in moderate yield. By-products in the formation of **1a**,**b** are the cyclobuta[1,2-d]pyrroline **3** the structure of which has been elucidated by an X-ray analysis and a stereoisomer of **3**, probably the other 4,5-trans-isomer.

From methyl acetoacetate dimethylhydrazone[4] in THF only the crystalline **4**, mp 76-78°C could be obtained (with dimethyl acetylenedicarboxylate). Methyl propiolate with dimethylhydrazine in ether gave both the known methyl formylacetate dimethylhydrazone[5] and its reaction product with a second molecule of methyl propiolate, **5**, mp 45-46°C. The E-configuration of **4** was deduced from the similar chemical shift of H-2 to that of **1a**, **5**, however, exhibits a nice coupling constant $J_{2,3}$ = 16.5 cps.

A complex pattern results from the reaction of acetylacetone dimethylhydrazone with methyl propiolate in ethanol. Only cyclic products with a relation of propiolate to hydrazone larger than 1 could be isolated, most of them having lost a CH_3CO-group in the sense of a ketone cleavage, e.g. **6** and **7**. The structure of **6** was confirmed by an X-ray analysis. Only traces of the acetyl containing pyridone **8** could be detected by nmr.



6



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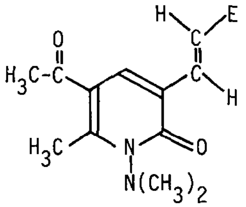

8

E = CO_2CH_3

The N,N-bond may also be cleaved during the reaction with methyl propiolate leading to a number of pyridines and a pyrrole in trace amounts.

A more detailed discussion of the reactions presented here and of the structure analyses will be given in the full paper.

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