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THE ADDITION-CYCLIZATION OF VINYLDIAZOMETHANE

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IT is well known that diazomethane adds to some unsaturated linkages smoothly in mild conditions to lead to pyrazole derivatives without loss of nitrogen.¹ In this case, the addition takes place on 1,3-dipolar positions.

The authors have investigated the addition reactions of vinyldiazomethane with some unsaturated compounds. It is already known that this vinyldiazomethane self-cyclizes into pyrazole² after the manner of 1,5-dipolar cycloaddition. But the addition of this compound upon other unsaturated compounds is not yet known.

Recently, another example of 1,5-dipolar addition was presented where θ -quinone diazide was observed to add with diphenylketene to form 1, l_1 ,5-oxadiazepine, the yield of which was reported to be excellent.³ In these circumstances, vinyldiazomethane is expected to react either on 1,3positions or on 1,5-positions.

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The authors observed that vinyldiazomethane, prepared via allylamine,⁴ corresponding urethane and nitrosourethane,² added very readily with unsaturated linkages having one or more electron-withdrawing substituents. In this article, the authors describe only the results with dimethyl maleate and dimethyl fumarate where 1,3-addition occured exclusively.

The reaction of dimethyl maleate with ether solution of vinyldiazomethane in the dark at room temperature took only a few minutes, till the wine-red colour of vinyldiazomethane and infrared absorption (2080 cm⁻¹) of diazo group disappeared completely without liberation of nitrogen. The product solidified on distillation off the unsaturated starting materials. After recrystallisations, an ester of heterocyclic carboxylic acid I was obtained in 35% yield (crude, based on N-nitrosourethane⁵), m.p. 56°. I was identified as 3-vinyl-h,5-dimethoxycarbonyl-3,h-dihydropyrazole. (Found : C, 51.21 : H, 5.79 : N, 13.37 : Calc. : C, 50.94 : H, 5.70 : N, 13.20), 1000 and 945 cm⁻¹(vinyl), ca. 3300 cm⁻¹(N-H), 1560 cm⁻¹(C=N).

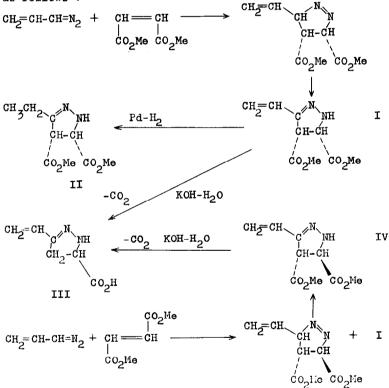
I was hydrogenated to the 3-ethylderivative II, on absorbing 1.06 mole of H_2 in the presence of Pd catalyst. Comparison of the nmr spectra of I with that of II showed the conversion of vinyl group to ethyl group. 7 3.9-5.8 (vinyl H) of I disappeared and 7 9.1 (triplet) and 78.4 (quartet) appeared in II.

Ester I gave a decarboxylic derivative III, n.p. 183° (Found : C, 50.98 : H, 6.01 : N, 19.60 : Calc. : C, 51.42 H, 5.75 : N, 19.99) on hydrolysis with boiling aqueous methanol-NaOH and on subsequent acidification.

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Addition of dimethyl fumarate with vinyldiazomethane gave similarly I and 3-vinyl- l_1 ,5-dimethoxycarbonyl-3,4dihydropyrazole IV, which was a stereoisomer of I, m.p. 123° (Found : C, 50.84 : H, 5.84 : N, 13.53 : Calc. : C, 50.94 : H, 5.70 : N, 13.20) (total yield 30% ⁵). IV was similarly decarboxylated during the hydrolysis to lead to the same carboxylic acid as III, m.p. 183° (mixed with III, 183°)

From these results, the reaction scheme can be pictured as follows :



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Where the initial addition took place with retention of the configuration of the olefin in the case of maleate, which gave cis-dicarboxylate while, in the case of fumarate, ...is-(I) and trans-dicarboxylates (IV) were obtained.

The intermediary formed 3-vinyl-4,5-dicarboxylic acids were rather unstable to liberate carbon dioxide readily by interaction of the 4-carboxyl group with basic nitrogen. This seems to be the unusually strong 1,3-interaction, although there are some examples of the decarboxylation of 3- and/or 5-(di)carboxylic acids⁶, where the carboxyl group interacts with the adjacent nitrogen.

The structure of III was confirmed through conversion to the known pyrazole-1, 3-dicarboxylic acid.

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- 5. Since vinyldiazomethane was unstable, it was not isolated but was determined by esterification of benzoic or p-nitrobenzoic acid. The yield amounted to ca. 25%.² The facts suggests that the yield of I must be excellent based on vinyldiazomethane.
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