

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 vinyl diazomethane with some unsaturated compounds. It is already known that this vinyl diazomethane 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 ϕ -quinone diazide was observed to add with diphenylketene to form 1,1,5-oxadiazepine, the yield of which was reported to be excellent.³ In these circumstances, vinyl diazomethane is expected to react either on 1,3-positions or on 1,5-positions.

The authors observed that vinyl diazomethane, 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 occurred exclusively.

The reaction of dimethyl maleate with ether solution of vinyl diazomethane in the dark at room temperature took only a few minutes. till the wine-red colour of vinyl diazomethane 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-4,5-dimethoxycarbonyl-3,4-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-ethyl derivative 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. τ 3.9-5.8 (vinyl H) of I disappeared and τ 9.1 (triplet) and τ 8.4 (quartet) appeared in II.

Ester I gave a decarboxylic derivative III, m.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.

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, cis-(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 vinyl diazomethane 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 vinyl diazomethane.
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