# Cycloadditions to Methyl 3,3-Dimethyl-3*H*-pyrazole-5-carboxylate

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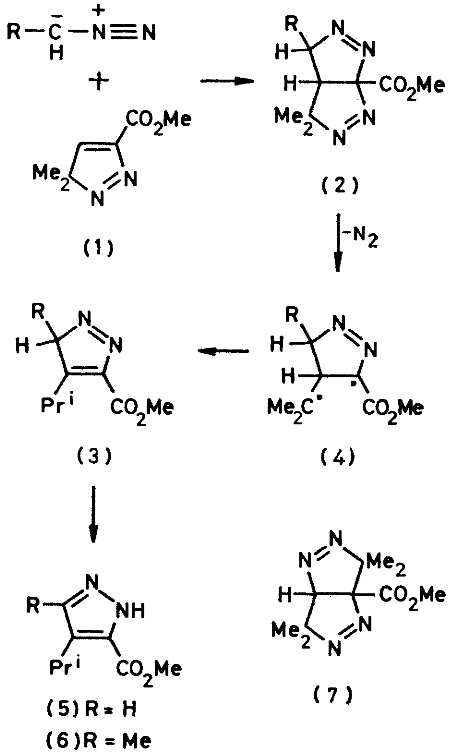
*Summary* Cycloadditions of diazoalkanes, 1-diethylaminopropyne, and diphenylketen to the title compound and the dimerization of the latter are reported.

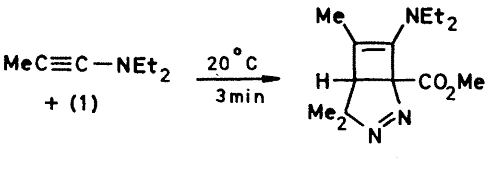
The investigation of 3*H*-pyrazoles has dealt mainly with photochemical nitrogen elimination[1] and the thermal van Alphen–Hüttel rearrangement to aromatic pyrazoles.[2] 3*H*-Pyrazoles are prepared by 1,3-dipolar cycloadditions of disubstituted diazomethanes to activated alkynes, *e.g.*, (**1**) from 2-diazopropane and methyl propiolate.[3] More effective for the preparation of larger quantities is the addition of methyl diazoacetate to *N*-isobutenylpyrrolidine and subsequent amine elimination.[4] Some Diels–Alder reactions of 3*H*-pyrazoles as dienophiles have recently been described.[5]



(1) (2) (3) (4) (5) R = H (6) R = Me (7)

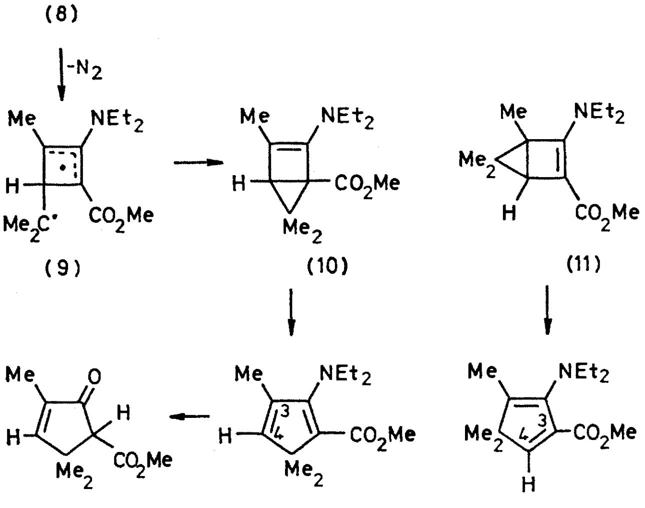
The reaction of (**1**) with diazomethane in dichloromethane at 0 °C was accompanied by nitrogen elimination and yielded 86% of the pyrazole (**5**) and 11% of its *N*-methyl derivative† which were characterised spectroscopically and by degradation of (**5**) to 4-isopropylpyrazole (s at $\tau$ 2·53 for 3-H and 5-H). The probable reason for the $N_2$ loss from the tetrahydropyrazolo[3,4-*c*]pyrazole (**2**; R = H) is the stabilization of the trimethylene intermediate (**4**) by the diaza-allyl system, ester group, and *gem*-dimethyl groups; no product of $N_2$ loss from the upper ring of (**2**) was observed. The preferential formation of $\alpha\beta$-unsaturated esters from pyrazoline-3-carboxylic esters has been described.[6]

That (**1**) combined with diazoethane at 0 °C to give 81% of (**6**), reveals a surprising selectivity in the nitrogen loss from (**2**; R = Me). The stable tetrahydropyrazolo[3,4-*d*]pyrazole (**7**) was reported[7] as the product from the reaction of methyl propiolate and 2 mol. of 2-diazopropane *via* (**1**); the reversal of the usual direction of diazoalkane cycloadditions to $\alpha\beta$-unsaturated esters by bulky $\beta$-substituents (*e.g.*, in $\beta$-t-butylacrylic ester) is a known phenomenon.[8] Extrusion of $N_2$ from (**7**) takes place at $>$80 °C; no diaza-allyl resonance stabilizes the trimethylene intermediate here.



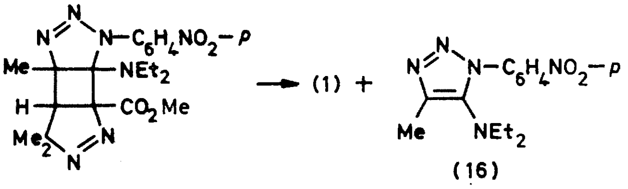
(8)

Diethylaminopropyne converted (**1**) quantitatively into the cyclobutene (**8**). I.r. absorptions at 1743 and 1674 cm$^{-1}$ show the presence of the unconjugated ester and the enamine group, whereas $\lambda_{max}$ 350 nm (log $\epsilon$ 2·45) points to a *cis* azo group and the $^{13}$C n.m.r. spectrum rules out the alternative structure of a Diels–Alder adduct. Thermolysis at 120 °C provided the cyclopentadiene derivatives (**13**) and (**14**) in a 6 : 1 ratio. The strong i.r. band at 1665 cm$^{-1}$ is consistent with the enamine-$\beta$-carboxylic ester system in (**13**). Hydrolysis of (**13**) furnished the keto–enol tautomeric cyclopentenone derivative (**12**).



(8) (9) (10) (11) (12) (13) (14)

Conceivably, the allyl stabilized (**9**) undergoes the two diradical combinations and the bicyclopentenes (**10**) and (**11**) suffer the orbital symmetry-forbidden ring opening which is known for the parent compound.[9]



(15) (16)

The enamine group of (**8**) is expected to add *p*-nitrophenylazide. Surprisingly, the ynamine adduct (**16**) (92%; $CDCl_3$, 25 °C) was formed and (**1**) regenerated. The adduct (**8**) does not dissociate into (**1**) + diethylaminopropyne as its inertness towards pyrrolidine testifies; (**1**) adds amines at the CC double bond with great ease. Thus, the

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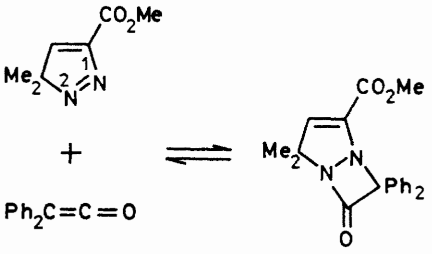
† Satisfactory C, H, and N analyses were obtained for all new compounds.

reaction must take an additive course *via* (**15**) which does not become observable in the n.m.r. spectrum.



(**17**)

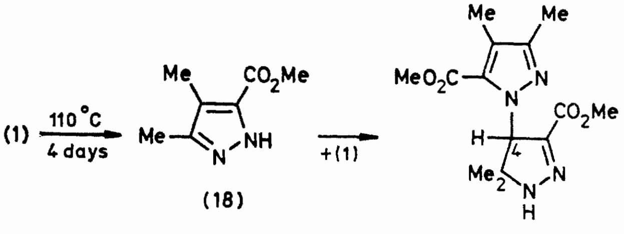
$$\Delta H = -13{\cdot}3 \pm 1\ \text{kcal mol}^{-1}$$

$$\Delta S = -34 \pm 3\ \text{cal K}^{-1}\text{mol}^{-1}$$

$$(1\ \text{cal} = 4{\cdot}184\ \text{J})$$

The 3*H*-pyrazole (**1**) produced with diphenylketen at 20 °C the yellow crystalline bicyclic diazetidinone (**17**); i.r. (KBr): 1772 cm$^{-1}$ (C=O). The vinyl-H at $\tau$ 3·93 suggests that the unsaturated ester system of (**1**) is retained in (**17**). The propensity of *cis* azo-compounds to add ketens is known.[10] The higher nucleophilicity of N-2 in (**1**) and the shielding of the ester methyl ($\tau$ 6·60) in (**17**) by phenyl are arguments for the addition direction.

The n.m.r. spectrum of (**17**) indicates a highly mobile equilibrium with the reactants. A 0·13 M chlorobenzene solution contains 97% of (**17**) at −8 °C, 50% at 70 °C, and 19% at 100 °C. Measurements of the equilibrium constant, based on the ester singlets for (**1**) and (**17**), over a range of 134 °C afforded the thermodynamic parameters shown for the association process.



(**18**) (**19**)

In refluxing toluene (**1**) furnished a crystalline dimer in 90% yield whose spectral properties are consistent with (**19**). In the n.m.r. spectrum the *gem*-dimethyl groups give rise to two singlets at $\tau$ 8·59 and 9·13 and the two aromatic methyl groups to two singlets at $\tau$ 7·85 and 7·89. Obviously, the slow sigmatropic rearrangement (**1**) → (**18**)[4] is followed by the nucleophilic addition to a second molecule of (**1**) as confirmed by a separate experiment at 25 °C. A great variety of amines and enamines add to the electrophilic CC double bond of (**1**).[11]

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