Photochemical Generation of a Vinylketen from 5-Acetyl-3,3-dimethyl-3*H*-pyrazole and the Identification of the End Product as 7-Acetyl-3,5,5,9,9-pentamethyl-1,6-diazabicyclo[4,3,0]nona-3,7-dien-2-one by *X*-Ray Crystallographic Analysis

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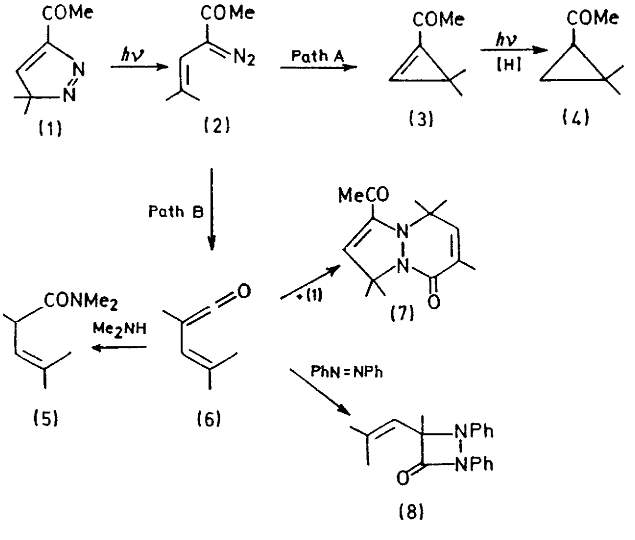
Summary The direct photolysis ($\lambda > 290$ nm) of 5-acetyl-3,3-dimethyl-3*H*-pyrazole (**1**) in ether gives 2-acetyl-1,1-dimethylcyclopropane (**4**; 5%) and 7-acetyl-3,5,5,9,9-pentamethyl-1,6-diazabicyclo[4,3,0]nona-3,7-dien-2-one (**7**; 46%), the structure of which has been determined by *X*-ray crystallography; the latter compound is formed *via* a vinylketen (**6**), which can be trapped with dimethylamine as the amide (**5**) and with azobenzene as the [2 + 2] adduct (**8**).

Upon u.v. irradiation, 3*H*-pyrazoles readily photoisomerise to diazoalkenes. Normally, the diazoalkene then photolyses rapidly to give a cyclopropene *via* a vinylcarbene.[1] However, if an α-acyloxy-substituent is present (as in the diazoalkenes derived from 5-acyloxy-3*H*-pyrazoles), reaction takes a different course, giving allenes and 1,3-dienes *via* vinyl cations.[2] To illustrate the effect of a different type of substituent, we report here the photolysis of 5-acetyl-3,3-dimethyl-3*H*-pyrazole (**1**), in which the intermediate (**2**), an α-diazoketone, undergoes competing carbenoid decomposition to a cyclopropene (path A) and Wolff rearrangement to a vinylketen (path B).

Photolysis of the 3*H*-pyrazole (**1**) in ether (deoxygenated 0·5—1% solutions, 25 °C, medium-pressure mercury-arc lamp, Pyrex filter) gave the known[3] 2-acetyl-1,1-dimethylcyclopropane [(**4**) 4·6%] and traces (*ca.* 3% total) of several other volatile products, together with a pale yellow solid (46%), m.p. 138—138·5°, λ_{max} 312·5 nm (ϵ 1880), which analysed for $C_{14}H_{20}N_2O_2$. It is probable that the acetylcyclopropane (**4**) arose by photoreduction[4] of the corresponding cyclopropene (**3**), since a highly unstable compound having the appropriate mass spectrum (*m/e* 110; fragment ions at *m/e* 95, 67, and 43) was detected by the combined g.l.c.–m.s. technique early in the photolysis and shown to be the precursor of (**4**). Thus, the photolysis of (**1**) follows path A, at least to a limited extent.



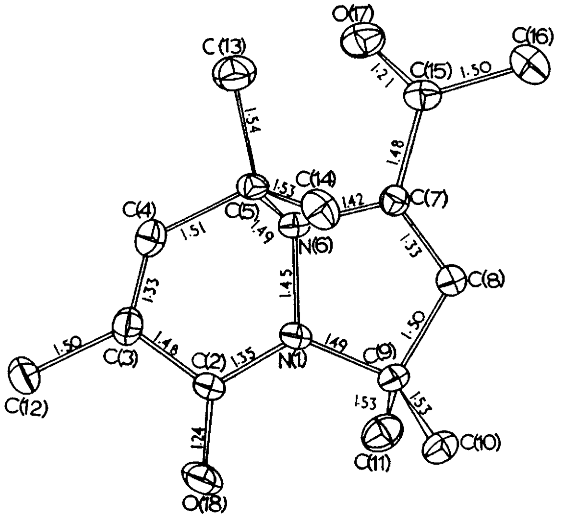


Figure. *Molecular conformation observed in the crystal structure of* (**7**) *as viewed down the* y *axis.*

The spectra of the yellow solid indicated the presence of MeCO and $CMe_2{\cdot}CH{=}CMe{\cdot}CO$, but were otherwise inconclusive. However, *X*-ray crystallographic analysis showed that the compound had the structure (**7**).

Crystal data: 7-acetyl-3,5,5,9,9-pentamethyl-1,6-diazabicyclo[4,3,0]nona-3,7-dien-2-one (**7**), $C_{14}H_{20}N_2O_2$; *M* 248·16; pale yellow orthorhombic plates grown from hexane; $a = 14{\cdot}76$, $b = 10{\cdot}68$, $c = 17{\cdot}38$ Å; $D_m = 1{\cdot}214(1)$ g cm^{-3} (flotation), $Z = 8$, $D_c = 1{\cdot}210$ g cm^{-3}; space group *Pbca* (D_{2h}^{15}, No. 61); Cu-K_α radiation. Intensity data for 2012 independent reflections were collected with a four-circle, computer-controlled Hilger–Watts diffractometer.

The structure was solved by means of a symbolic addition program[5] and refined by block-diagonal least-squares procedures assuming anisotropic thermal motion. All hydrogen atoms were located in a difference map. The final $R = 0{\cdot}088$. The Figure shows one molecule viewed down the *y* axis, with anisotropic thermal ellipsoids and bond lengths. The five-membered ring is nearly planar and the six-membered ring definitely non-planar with C(5) above the plane of the drawing. The amide nitrogen N(1) is coplanar with C(2), C(9), and N(6); the amine nitrogen N(6) is pyramidal and forms a distorted tetrahedron with C(5), C(7), and N(1).†

The structure (**7**) supports path B, in that (**7**) is most simply regarded as a Diels–Alder adduct of the vinylketen (**6**) (the "diene" component) to the N=N bond of the starting material. The observed orientation is that expected on steric grounds.

Confirmation that the keten (**6**) is generated in the photolysis was provided by (*i*) the isolation of the amide (**5**) and the diazetidinone (**8**) when the 3*H*-pyrazole was irradiated in the presence of, respectively, dimethylamine and azobenzene,‡ and (*ii*) the appearance of i.r. absorption at 2080 and 2060 cm^{-1} (diazoketone and keten, respectively) when (**1**) was irradiated in a KCl disc.

It remains to be determined whether, as seems probable,[6] the competition between paths A and B is sensitive to the spin state of the excited diazoalkene (**2**).

Since compound (**1**) and similar 5-acyl-3*H*-pyrazoles are readily prepared by the addition of 2-diazopropane[7] to $\alpha\beta$-acetylenic ketones,[8] path B offers a potentially convenient source of vinylketens, the general chemistry of which has hitherto been little studied.[9]

Grants from the Royal Society for the financial support of T.J.B. and from the S.R.C. for the diffractometer are acknowledged.

(*Received*, 13*th December* 1972; *Com.* 2084.)

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† The relevant angles are: N(6)–N(1)–C(2), 118·5; N(6)–N(1)–C(9), 113·2; C(2)–N(1)–C(9), 127·5° for the amide nitrogen, and N(1)–N(6)–C(5), 109·7; N(1)–N(6)–C(7), 102·4°; C(5)–N(6)–C(7), 119·0° for the amine nitrogen.

‡ In both trapping experiments, the formation of (**7**) was largely suppressed. The dimethylamine reaction also gave 3-acetyl-5,5-dimethyl-4-dimethylamino-2-pyrazoline, which was shown in an independent experiment to be formed rapidly at room temperature from (**1**) and dimethylamine by a non-photochemical process. The best yields of the amide (**5**) *vis-a-vis* the dimethylamino-2-pyrazoline were obtained upon irradiation at −78 °C.

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