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FLASH VACUUM PYROLYSIS OF 1-PROPYNOYLPYRAZOLES: A NEW PRECURSOR OF TRICARBON MONOXIDE

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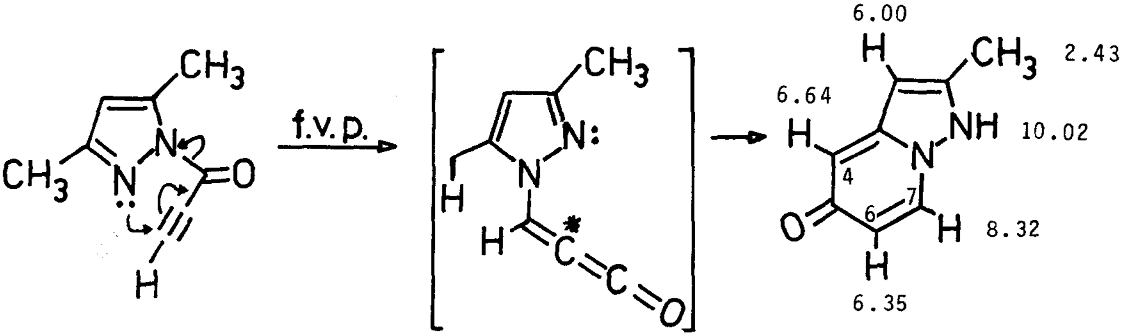
Summary: Pyrolysis of 3,5-dimethyl-1-propynoylpyrazole (1) at 640°C/0.1 torr gives 2-methyl-1*H*-pyrazolo[2,3-a]pyridin-5-one (3) with inversion of the propynoyl chain. 1-Ethynylpyrazole and tricarbon monoxide have been identified in pyrolysates formed at 700-1000°C/0.01-0.1 torr from the parent 1-propynoylpyrazole (4).

In an extension of recent work on the pyrolysis of N-alkenoyl pyrazoles[1], we have recently prepared a number of N-alkynoylpyrazoles and related compounds and examined their behaviour on flash vacuum pyrolysis. In this communication we describe the behaviour of two N-propynoylpyrazoles.

The 3,5-dimethyl compound (1), m.p. 86-86.5°C[2], was readily prepared from propynoic acid and 3,5-dimethylpyrazole with dicyclohexylcarbodiimide in dichloromethane. On pyrolysis at 640°C/0.1 torr through a 30x2.5 cm i.d. silica tube it gave the pyrazolo[2,3-a]pyridin-5-one (3), m.p. 188-189°C as a pale yellow crystalline deposit (52% yield) in the exit tube. A small amount of a pungent oil which showed spectroscopic properties (I.R., M.S., N.M.R.) consistent with the structure 1-ethynyl-3,5-dimethylpyrazole collected in a cold trap at -196°C. The structure of the crystalline product (3) followed from consideration of ^{13}C and ^{1}H-NMR spectra and of n.O.e. experiments which will be fully described elsewhere. The elements of the propynoyl chain in (3) are inverted with respect to their connectivity in the starting material (1). To explain this we propose the involvement of a pyrazolylmethyleneketene intermediate (2) formed from (1) as shown (arrows). After a rotation, intermediate (2) can undergo a [1,8]H shift terminating in the carbon atom marked with an asterisk in (2), followed by cyclization[3] leading ultimately to (3).



1 2 3

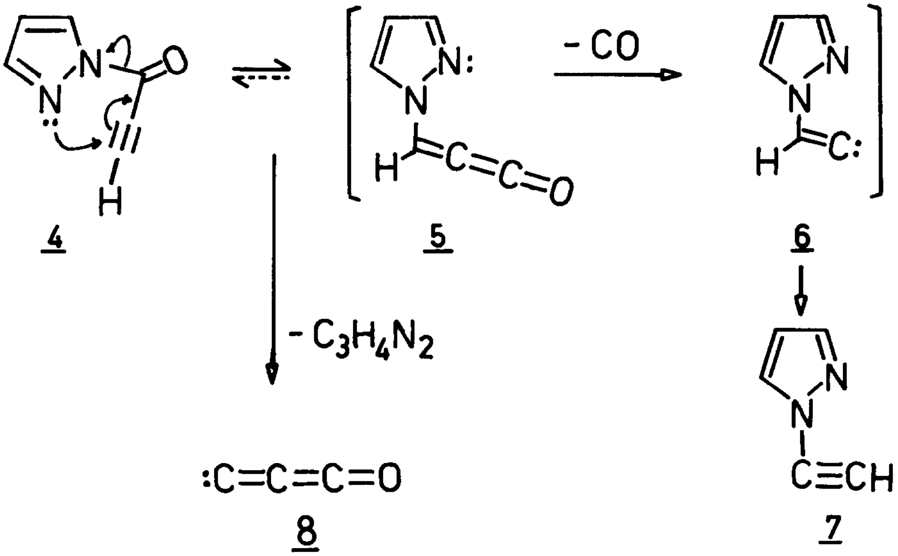
^{1}H n.m.r. (δ , DMSO-d_6)

$J_{6,7}$ = 7.5 Hz $J_{4,6}$ = 2.5 Hz

The parent 1-propynoylpyrazole (4), m.p. 89-91°C (dec.) was similarly prepared and characterized[2] [^{1}H-NMR: δ (300 MHz, $CDCl_3$) 3.57 (s, CH); 6.54 (dd, 2.97, 1.5 Hz, H4); 7.86 (br s, H3); 8.28 (d, 2.97 Hz, H5)]. Pyrolysis of readily volatile (4) at 700-900°C/0.1 torr was not encouraging from the preparative point of view. Extensive blackening of the tube occurred, and the exit glassware became coated with a tenacious reddish-black film. A small amount of dark unpleasant-smelling oil (15-20% of weight of starting material) collected in a cold trap at -196°C. Extraction of this oil with pentane and distillation (100°C bath/20 torr) gave a colourless liquid shown by G.C.-M.S. to contain a single major component[4] [M.S.: m/z 92 (100%. Found, 92.038±0.001. $C_5H_4N_2$ requires 92.037), 68(14), 65(33), 64(13), 52(19)] which we formulate as 1-ethynylpyrazole (7) on the basis of the following spectra of the liquid: I.R.: 3300 and 2170 cm^{-1} (H-C≡C-N). ^{1}H-NMR: δ (300 MHz, $CDCl_3$) 3.14 (s, ≡CH); 6.33 (apparent t, J 2.2 Hz, H4); 7.65 (d, J 1.6 Hz, H3); 7.71 (d, J 2.6 Hz, H5).

The operation of a second mode of thermal fragmentation leading to tricarbon monoxide (8) was revealed by passing the pyrolysate formed from (4) at 800-1000°C/0.01 torr directly into the absorption cell of a microwave spectrometer. The presence of tricarbon monoxide was detected by observation of the J = 7-6 microwave absorption at 67351.31(4) MHz, which showed a Stark shift pattern identical with that of C_3O obtained from the pyrolysis of fumaroyl dichloride.[5,6] The signal intensity was, however, only about 20% of that found with the same apparatus for the generation of C_3O from fumaroyl dichloride. The deposition of a reddish-black film on exit glassware appears characteristic of systems which generate C_3O. The pyrolysis oven and microwave spectrometer were similar to those described previously.[6]

We propose that 1-ethynylpyrazole (7) is formed from (4) by initial N1 to N2 migration of the propynoyl chain with inversion to give (5). In the absence of the 5-methyl group of (2) this is followed by decarbonylation to the carbene (6)[7] and hydrogen migration[7] to form 1-ethynylpyrazole.



We consider it likely that C_3O is formed by a high-temperature α-elimination of pyrazole from (5), but other 3-, 5-, and 6-centred processes can be envisaged starting from (4).

Tricarbon monoxide has previously been generated in the gas phase by the pyrolysis of 5,5'-bis(2,2-dimethyl-4,6-dioxo-1,3-dioxanylidene) (di-isopropylidene ethylenetetracarboxylate)[5] and of fumaroyl dichloride[6], and by a d.c. glow discharge in carbon suboxide.[8] The present work suggests that other propynoyl compounds X-C≡C-CO-Y, where X-Y is a stable fragment, may serve as pyrolytic precursors of C_3O.

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REFERENCES AND NOTES

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4. 1-Ethynylpyrazole (7) had retention time 3.80 min at 100°C on a bonded-phase polyethyleneglycol capillary column; benzonitrile, a trace impurity, had r.t. 6.74 min. The liquid contained ≥90-95% of (7) and no other product was evident in a routine 90 MHz NMR spectrum.
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