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FORMATION AND REACTION OF α-KETO NITRIMINE

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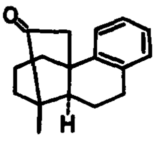
We should like to record here the formation and characteristic reaction of a hitherto undescribed system α-keto nitrimine.

As reported in an earlier paper (1), treatment of a ketone 1 with isoamyl nitrite and five equiv. of potassium tert-butoxide in tert-butanol affords an α-isonitrosoketone 2 in good yield. However, in some runs, where a larger amount of base was employed, two undesired substances were obtained as major products. The one, $C_{17}H_{19}O_2N$, m.p. 235.5-237°, was characterized as a nitrile carboxylic acid 3 on the basis of spectroscopic evidence (ν_{max}^{nujol} 3300-2800 (CO_2H), 2240 (CN) and 1695 cm^{-1} (CO_2H); $\tau_{TMS}^{CDCl_3}$ 8.6 (3H, S)). The other product, $C_{17}H_{18}O_3N_2$, m.p. 145-146°, forms yellow crystals (λ_{max}^{alc} 271 mμ, log ε 3.41; 283 mμ, log ε 3.42; 408 mμ, log ε 1.80) and exhibits an n m r spectrum quite similar to that of 2. The i r spectrum shows absorption bands at 1753 (C = O), 1630 (C = N), 1580 (NO_2) and 1307 cm^{-1} (NO_2) and thus indicates the presence of a nitrimino group (2). Based on these data an α-keto nitrimine structure 4 was assigned to the yellow substance. Since the isonitrosation reaction of ketones is frequently used in synthesis, it is likely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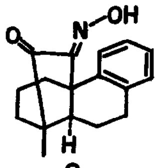
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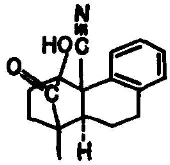
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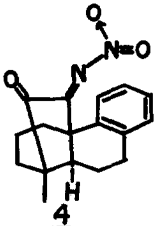
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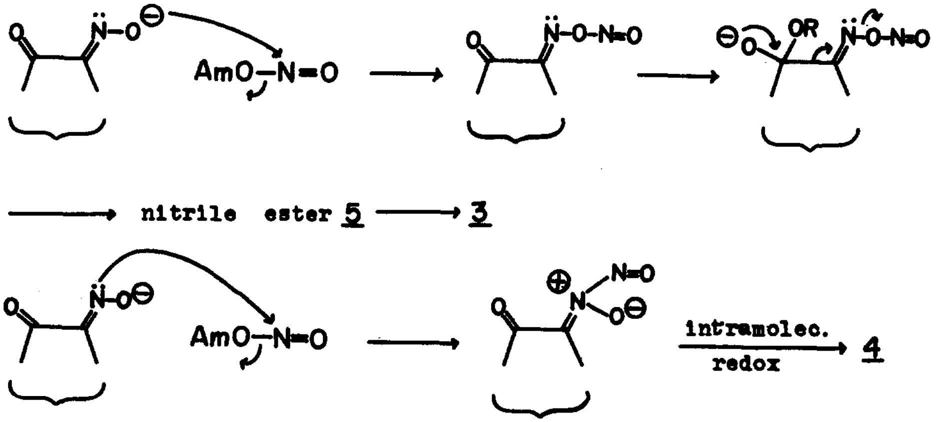
that α-keto nitrimine will be and even might have been encountered in some synthetic studies.*

The structure of the nitrimine 4 suggests that it was formed through the isonitrosoketone 2 as an intermediate. In fact, treatment of 2 with isoamyl nitrite and eight equiv. of tert-butoxide in tert-butanol furnished 3 and 4 in about 20 and 35 % yield respectively. Since the nitrile carboxylic acid 3 was not formed by the action of base alone upon either isonitrosoketone 2 or nitrimine 4, both the products must have arisen from the reaction between 2 and nitrite ester under alkaline conditions. The following mechanism, in which the anion of the isonitrosoketone acts as an ambident species (3), may be postulated.



Intermediary formation of the nitrile ester 5 is supported by the strong absorption band at 1740 cm^{-1} of the crude product. The ready intramolecular redox reaction of nitrosoimine oxide has been already suggested by Freeman (2).

The α-keto nitrimine 4 can be conveniently prepared, without concomitant formation of

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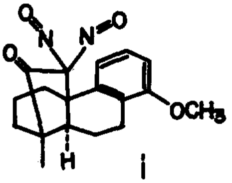
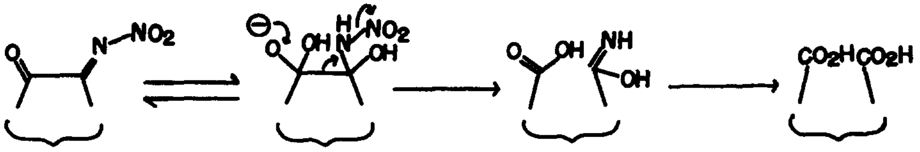
* A structure i has been tentatively assigned to an isonitrosation product of 14-methoxy derivative of 1 (R. B. Turner et al., J. Am. Chem. Soc., in press). Comparison of the reported spectral data of i with those given above suggests that it has rather an α-keto nitrimine structure. We express our thanks to Professor Turner for sending us the preprint of his paper.



i

ester and acid, by treating 2 with aq. sodium nitrite and aq. H_2SO_4 in ether (63 % yield). This provides supporting evidence for the structure 4, since nitrimines have been isolated, in favorable cases, by the action of nitrous acid upon oximes (4).

Nitrimines are generally unstable to acids and bases, giving rise to parent ketones (5). However, 4 is quite stable to acids: on treatment with boiling 3 N aq. HCl-EtOH (1 : 1) for 2 hrs as well as with conc. H_2SO_4 at room temperature the starting material was recovered unchanged. On the contrary 4 is unstable to alkali: hydrolysis with aq. KOH in EtOH-benzene at 0° affords a dicarboxylic acid 6, m.p. 218-219° (ν_{max}^{nujol} 2800-3300 (CO_2H) and 1700 cm^{-1}(CO_2H)) in 70 % yield, rather than an α-diketone. This characteristic reaction proceeds probably in



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the above fashion. In fact ammonia is simultaneously formed in this reaction. The acid 6 is not formed through the nitrile carboxylic acid 3, since the latter compound is stable to alkali and is recovered under the above conditions.

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