Journal of Labelled Compounds and Radiopharmaceuticals—Vol. XXXIII, No. 2

NOTE

Preparation of ^{15}N-^{13}C-Fulminic Acid

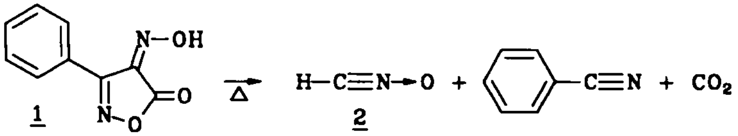
Rolf Wilmes and Manfred Winnewisser

Physikalisch-Chemisches Institut, Justus-Liebig-Universität Gießen
Heinrich-Buff-Ring 58, W-6300 Gießen, Germany

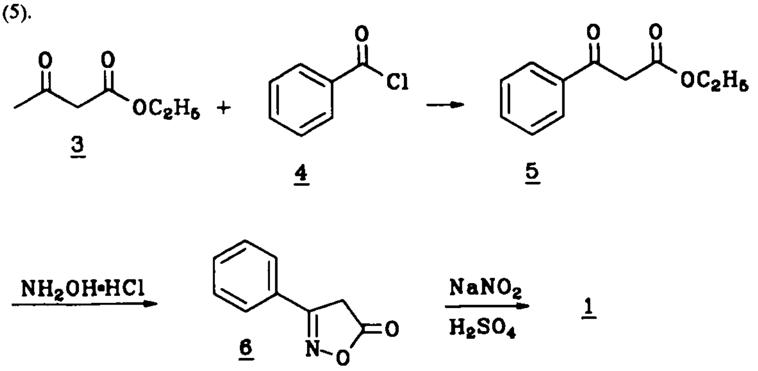
Keywords: 2-^{13}C-ethyl benzoylacetate; 3-phenyl-4-^{13}C-isoxazol-5-(4H)-one; ^{15}N-^{13}C-fulminic acid

Summary: The precursor for the title compound was prepared in a three-step synthesis. The ^{13}C-label was incorporated in the first step employing 2-^{13}C-ethyl acetate and the ^{15}N-label in the last step, using ^{15}N-sodium nitrite. Upon pyrolysis the precursor forms three fragments, one of them being the title compound.

Unlabelled fulminic acid 2 has been prepared in our laboratory following Wentrup's procedure (1) and its rotational and rovibrational spectrum has been investigated (2). Compound 2 forms upon pyrolysis of the precursor 1 at 450°C, together with benzonitrile and CO_2.



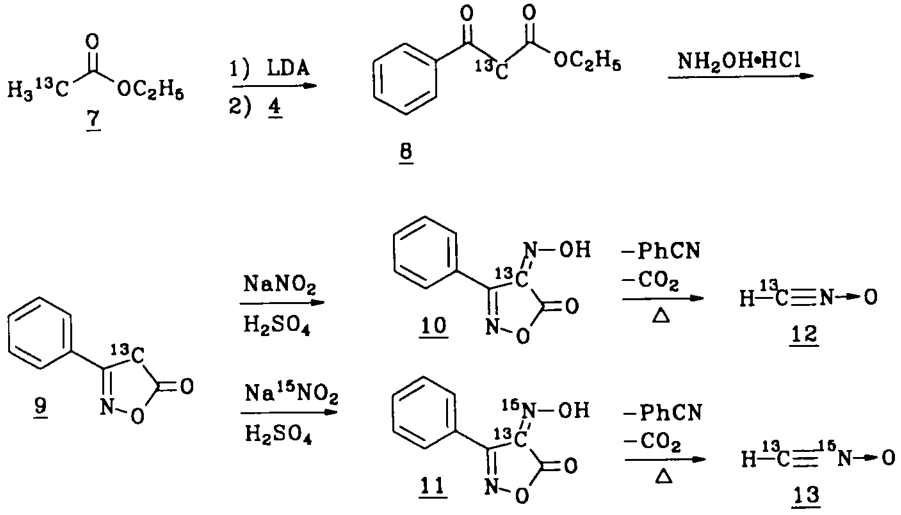
Precursor 1 is made in a three-step synthesis. In the first step the base-catalyzed reaction of acetoacetic acid ethyl ester 3 and benzoyl chloride 4 leads to ethyl benzoylacetate 5 (3), which is converted by treatment with hydroxylamine hydrochloride to the isoxazolone 6 (4). The latter upon treatment with sodium nitrite forms the precursor 1 (5).



0362-4803/93/020157-03$06.50

Received 1 October, 1992
Revised 15 October, 1992

In order to obtain ^{13}C-labelled fulminic acid 12 it was necessary to modify the reaction scheme in the first step. Köhler (6) succeeded in preparing 2-^{13}C-ethyl benzoylacetate 8 by ester-condensation of 2-^{13}C-ethyl acetate 7 and ethyl benzoate with sodium ethanolate in absolute toluene. Compound 8 is obtained, however, in much better yields when ester 7 is deprotonated with lithium diisopropylamide (LDA) and the resulting anion reacted with benzoyl chloride 4. In analogy with the above reaction scheme compound 8 is converted to the isoxazolone 9 and the latter leads to either precursor 10 or precursor 11 (when Na^{15}NO$_2$ is employed). Precursor 10 upon pyrolysis provides ^{13}C-fulminic acid 12 (7), while precursor 11 leads to ^{15}N-^{13}C-fulminic acid 13.



Experimental Section

2-^{13}C-ethyl benzoylacetate 8: A solution of 5.757 g (56.9 mmol) absolute diisopropylamine (DIPA) in 30 ml absolute THF under Ar-atmosphere was cooled to − 78 °C, then 37.9 ml of a 1.5 molar solution of n-butyl lithium in hexane (56.9 mmol) was added to it during 5 min. After stirring for an additional 15 min. a solution of 2.304 g (25.86 mmol) 2-^{13}C-ethyl acetate 7 in 8 ml absolute THF was added to the above freshly prepared LDA-solution during 10 min. and then stirred for another 30 min. To this solution of the enolate of ester 7 was now added 3.30 ml (28.5 mmol) benzoylchloride 4 dropwise with a syringe and the reaction mixture was slowly warmed up from − 78 °C to 20 °C overnight. The low-boiling compounds were evaporated, the residue taken up with 300 ml ether and washed twice with 150 ml 1*N* HCl and once with 150 ml water, then dried with MgSO$_4$. Removal of the ether left 5.106 g yellow liquid raw material which was purified by column chromatography (300 g silica gel, pentane/ether 1:1) yielding 4.430 g (88.7%) of an orange-yellow liquid which contains the product 8. The ^{1}H-NMR-spectrum of this product shows that the ß-keto-ester 8 is present in the form of the enolized tautomer in appr. 20 %.

3-phenyl-4-^{13}C-isoxazol-5-(4H)-one 9: 4.495 g (23.26 mmol) ester 8 and 1.616 g (23.26 mmol) hydroxylamine hydrochloride were taken up in 5 ml water while stirring and then 20 ml ethanol added until all the components were dissolved. The solution was heated until it started to boil and then placed under a hood to cool. A white precipitate formed while the solvent partly evaporated overnight. The precipitate was filtered by suction, washed with ethanol/water 1:1, then with water and finally dried under high vacuum leaving 2.929 g (77.7%) isoxazolone 9, a faintly beige coloured solid with a melting point of 149 °C.

3-phenyl-4-(^{15}N-oximino)-4-^{13}C-isoxazol-5-(4H)-one 11: 2.929 g (18.06 mmol) isoxazolone 9 and 1.517 g (21.67 mmol) $Na^{15}NO_2$ were dissolved in 22 ml 1*N* NaOH. This solution was added within 10 min. to 80 ml 2*N* H_2SO_4 at 0 °C and stirred for another 15 min. The precipitate was filtered by suction, washed with ice water and dried under high vacuum yielding 2.854 g (82.2%) of a yellow solid (decomposes at 166 °C).
Precursor 10 was prepared in the same way using unlabelled $NaNO_2$.

^{15}N-^{13}C-fulminic acid 13: The pyrolysis of precursor 11 was carried out at 450 °C following the procedure described for the synthesis of ^{13}C-fulminic acid 12 (7).

Acknowledgement: This work was supported in part from funds of the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

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