Tetrahedron Letters No. 16, pp 1393 - 1394, 1977. Pergamon Press. Printed in Great Britain.

THE REACTION OF DIETHYL 2-METHYL-3-OXOSUCCINATE WITH BENZAMIDRAZONES. ISOLATION OF ISOMERIC *as*-TRIAZINONES[1]

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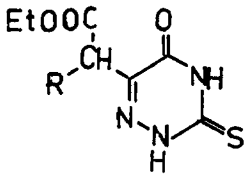
(Received in UK 18 January 1977; accepted for publication 7 March 1977)

CONDENSATION of diethyl 2-alkyl-3-oxosuccinates with thiosemicarbazide in the presence of bases furnishes the tetrahydro-*as*-triazines **1**[3,4] and the corresponding free acids.[4] In contrast, condensation of these succinates with aminoguanidine yields two types of products, *viz*. dihydro-*as*-triazines **2**[3,4] and 3-pyrazolecarboxylic esters **3a**.[4]

We interacted diethyl 2-methyl-3-oxosuccinate with a series of benzamidrazones (1:1 molar ratio, solvent *i*-PrOH, prolonged standing at r.t., followed eventually by short refluxing) and obtained, after fractional crystallization or chromatographic work up (Kieselgel 40, Merck; benzene-EtOAc mixtures) of the resulting mixture, in all cases two isomeric compounds **A** and **B** which, according to the microanalytical data,[5] were formed by elimination of one molec-



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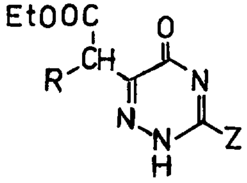

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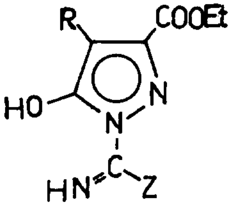

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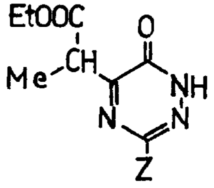

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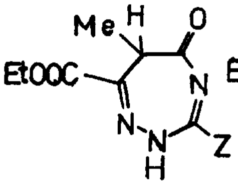
a: Z = NH_2

b: R = Me, Z = *p*-YC_6H_4



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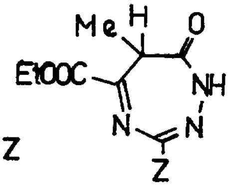

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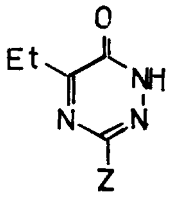

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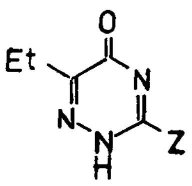

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4 - **6**: Z = *p*-YC_6H_4

ule, each, of EtOH and water. The IR spectra of the lower melting isomers **A** (yield 10-27%) exhibited two bands at about 1745 and 1670 cm^{-1}, those of the higher melting isomers **B** (yield 14-30%) two at about 1745 and 1610 cm^{-1}. The NMR spectra (DMSO-d_6) of both isomers exhibited 3H doublets around δ 1.4 and 1H quadruplets around 4.0 ppm. The type **3b** structures are thereby ruled out for both isomers. The choice between the remaining structures **2b** and **4**-**6** was made possible by alkaline hydrolysis and decarboxylation of the compounds **A** and **B** to yield the isomeric compounds **C** and **D** whose IR spectra exhibited bands at about 1660 and 1610 cm^{-1}, respectively, and whose NMR spectra (DMSO-d_6) displayed typical *C*-ethyl signal patterns (**C**: 3H triplets around 1.15 and 2H quadruplets around 2.9; **D**: 3H triplets around 1.15 and 2H quadruplets around 2.6). On the basis of these results structures **7** and **8** may be assigned to compounds **C** and **D**, respectively, whence structures **4** and **2b** follow for the compounds **A** and **B**, respectively. Further proof for the latter structures comes from the mass spectra[6] of the chloro derivatives which both have M-101 peaks; elimination of Me-$\dot{\mathrm{C}}$H-COOEt radicals is possible only from **4** and **2b**.

This is the first time that isomeric *as*-triazinones have been isolated from the reaction of amidrazones and α-keto acids or their esters, *cf.* Ref's 7-9.

Melting points of the compounds **4**, **2b**, **7** and **8**

Y	**4** = **A**	**2b** = **B**	**7** = **C**	**8** = **D**
H	138-9° (benzene, CCl_4)	217-8° (*i*-PrOH)	180-1° (EtOH)	185° ($MeNO_2$)
Cl	176-7° (EtOH)	206° (EtOAc)	193-4° (EtOH)	285-6° (DMF)
MeO	167-8° (EtOH)	192-3° (dioxane)	204-5° (EtOH)	248-50° (dioxane)

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