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NEW CYCLIC AMINIMIDES CONTAINING PYRAZOLONE SKELETON

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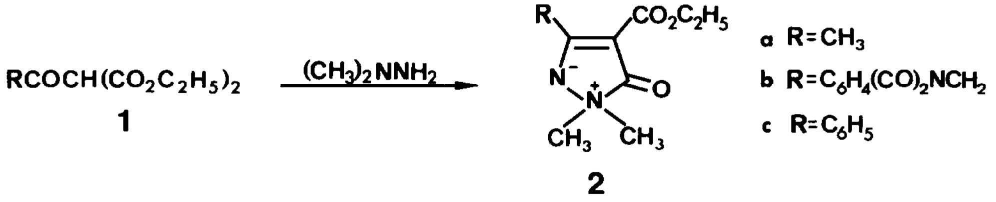
Summary — The synthetic route to 1,1-dimethylpyrazolin-5-on-1,2-aminimides (2), is described, involving the cyclization of diethyl acylmalonates (1) with 1,1-dimethylhydrazine.

Two cyclic aminimides containing the pyrazolone skeleton are possible. Unlike aminimides of the pyrazolin-3-one type,[1] whose general chemistry is well documented, pyrazolin-5-one derivatives are as yet uncharacterized.[2] We now describe a short and highly efficient synthesis of new aminimides 2. Our procedure essentially consists of cyclization of diethyl acylmalonates 1[3] with 1,1-dimethylhydrazine in the presence of an acid catalyst.



A mixture of 1 (0.03 mol) and 1,1-dimethylhydrazine (2 g, 0.033 mol) in glacial acetic acid (20 ml) was heated at 80° under nitrogen. The reaction was completed within 4 h. The solvent was distilled off *in vacuo*, and the residue was crystallized from an appropriate solvent to give 2 as colourless prisms. Additional amounts of 2 were obtained from the mother liquors by chromatography over silica gel (benzene); the overall yields, analytical and spectral data for individual compounds 2a-c are summarized in the Table. Additional evidence for the structure 2 was provided by the following reactions. The ring-opening and decarboxylation was effected by treatment of 2a with bases, affording acetone dimethylhydrazone. The hydrogenation over Raney nickel, however, gave (±)-β-aminobutyric acid. The presence of a carbonyl function attached to the quaternary nitrogen atom was inferred from the displacement of the carbonyl band ($1760 \rightarrow 1820$ cm^{-1}) in the infrared spectrum of 2a hydrochloride.[4] Since this structural type is so unexpected from previously known chemistry, we felt that the structure had to be more rigorously established. The structure of 2a was unambiguosly confirmed by a single-crystal X-ray analysis.[5]

Table. 3-Alkyl(aryl)-4-ethoxycarbonyl-1,1-dimethyl-3-pyrazolin-5-on-1,2-aminimides (2).

2[a]	Yield %	Recrystn Solvent	m.p.[b] °C	Rf[c]	M+[d] m/e	IR[e] cm^{-1}	^{1}H NMR($CDCl_3$), δ [R]	[NMe_2]	[CO_2Et]
a[f]	95	EtOH/ hexane	102-3	0.22	198	1760 1550	2.36(s)	3.00(s)	4.24(q),1.32(t,J=7)
b	55	MeOH	224-5	0.38	343	1770 1540	7.82(m),5.11(s)	2.88(s)	4.28(q),1.34(t,J=7)
c	95	CH_2Cl_2/ hexane	137-8	0.30	260	1760 1520	7.50(m)	3.08(s)	4.16(q),1.22(t,J=7)

a) Satisfactory analytical data (±0.3% for C, H, and N) were obtained for all compounds. *b)* M.ps. are uncorrected. *c)* TLC: Silica gel HF (Merck), benzene-acetone (7:3). *d)* Varian MAT CH-7, 70 eV, 100 μA. *e)* KBr, νC=O and νC=C (ring); 1655-1675/cm (ester C=O). The carbonyl band in salts of 2 is shifted to 1820/cm. The remainig parts of the spectra do not differ much. *e)* The UV spectrum of 2a in ethanol: 236(ε 15900), 274 (ε 5750) nm, showed no marked change on acidification (HCl).

The facile ring closure observed in reactions of 1 with 1,1-dimethylhydrazine is remarkable since structural alterations can utterly change the type of reaction. There was no evidence for the formation of analogous cyclic products in the case of acylacetates. Attempted ring closure with 1 and 1-methyl-1-phenylhydrazine also failed. Although an explanation of the cyclic aminimide formation is not yet available, several factors which depend upon the extent of enolization in ketonic component,[6] as well as on the electron-withdrawing properties of substituents in *unsym*-hydrazine, may be involved. Studies on the mechanism of reaction are currently in progress in our laboratory.[7]

REFERENCES AND NOTES

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2. Carbonyl stabilized aminimides of type •$R_2N \rightarrow$N-CO• are well characterized ylidic compounds: R. L. Hinman and M. C. Flores, *J. Org. Chem.* 24, 660 (1959); W. S. Wadsworth, Jr., *ibid.* 31, 1704 (1966); A. F. Cameron, N. J. Hair, D. G. Morris, and D. M. Hawley, *Chem. Commun.* 215 (1971). The stability is largely effected by the electron delocalisation from anionic moities towards the carbonyl group and by the electron-withdrawing properties of the quaternary nitrogen atom: S. Tsuchiya and M. Seno, *J. Org. Chem.* 44, 2850 (1979). The arrangement •N$\leftarrow NR_2CO$• is so far unknown.
3. H. Lund and A. Voigt, *Org. Syntheses*, Coll. Vol. 2, 594 (1943); J. A. Price and D. S. Tarbell, *ibid.* 4, 285 (1963); N. Bregant, A. Nuri, and M. Štromar, *Croat Chem Acta* 47, 595 (1975).
4. We are indebted to the referee for this helpful suggestion.
5. Comparison of relevant bond lengths in 2a reveals that there is no significant charge delocalisation on the carbonyl oxygen atom (C=O, 119 pm). However, it is clear from the short C-N (131 pm) and lengthened CO-N (157 pm) bond lengths that the negative charge, formally located on the ylidic nitrogen atom, has delocalised towards the C=C (142 pm). The detailed molecular structure will be reported elsewhere.
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7. The support of the Croatian Republic Research Fund is gratefully acknowledged.

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