CORRIGENDUM: In the May issue an unrevised Scheme 1 was used in error. The correct structure is shown below

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SHORT PAPER

Synthesis of 3*c*,4*r*,5*t*-1,2-dimethyl-3,5-diaryl pyrazolidine-4-carboxylic acid *via* intermolecular [3⁺+2] cycloaddition†

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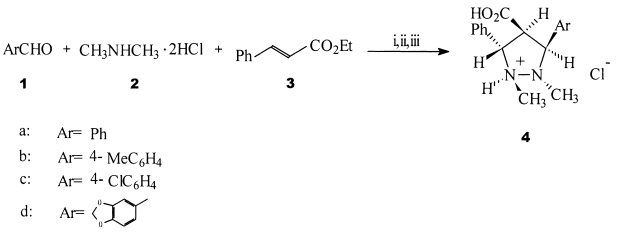
1,2-Dimethyl-3,5-diarylpyrazolidine-4-carboxylic acid derivatives **4a–d** were synthesised stereo-selectively *via* intermolecular [3⁺+2] cycloaddition of aldehydes **1a–d** and 1,2-dimethylhydrazine dihydrochloride (**2**) with ethyl *trans*-cinnamate (**3**), stereochemistries of which were assigned by ^{1}H-NOESY spectroscopy, and relative configurations confirmed by X-ray diffraction of one of them (**4a**).

Some pyrazolidines and their derivatives exhibit a broad range of biological activities or industrially useful chemical properties.[1–5] But the methods for the preparation of functional group substituted pyrazolidines have been reported rarely.[6] Banuelos *et al*.[7] have reported the preparation of functionalised pyrazolidines by the reduction of N-alkylpyrazolium salts with complex metal hydrides.[7] But some of these processes also afforded 3-pyrazolines, particularly when there was an ethoxycarbonyl group at C-4. 1,3-Dipolar cycloaddition is another valuable method for the construction of functionalized pyrazolidines.[8–10] Alternatively, [3⁺+2] cycloaddition[11–13] was proposed as a cycloaddition of cationic dipole with dipolarophile about 20 years ago, where cycloadducts were prepared conveniently under milder conditions by acid-catalysed reaction of hydrazone with dipolarophile and the deprotonation of the products. In our search for novel biologically active lead compounds, we managed to synthesise the compounds **4a–d** *via* [3⁺+2] cycloadditions of cationic dipoles [ArCH=N⁺(Me)NHMe] formed *in situ* by aldehydes **1a–d** and 1,2-dimethylhydrazine dihydrochloride (**2**) with ethyl *trans*-cinnamate (**3**) as dipolarophile, followed by hydrolysis of the adducts and hydrochlorination which made the compounds more stable in the air. (Scheme 1)

Reagents and conditions: (i), ethylene glycol, 140°C, 10h; (ii), NaOH/H_2O/EtOH, r.t, 0.5h. (iii), HOAc/H_2O, then HCl/Et_2O.



Scheme 1

The cycloadducts of the reaction isolated in this paper were 3*c*,4*r*,5*t*-1,2-dimethyl-3,5-diarylpyrazolidine-4-carboxylic acid hydrochlorides. Other isomers of cycloadducts were not detected in the NMR spectra of the reaction mixtures. So it can be seen that the cycloaddition in this paper is highly stereoselective. The structures of the products **4a–d** were established based on the elemental analyses, IR, MS, ^{1}H-NMR and ^{1}H-NOESY spectra, and the relative configurations were confirmed by X-ray diffraction of one of them (**4a**).

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† This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

As the coupling constant between 3-H and 4-H is almost identical to that between 4-H and 5-H , a triplet for 4-H therefore appeared in the ^{1}H-NMR spectra for **4a–d**. In their NOESY spectra, the only strong NOE effect between 3-H and 4-H showed the 3,4-*cis* configuration. The 4,5-*trans* configurations of the products were proved by the absence of significant NOE effect between 4-H and 5-H in their NOESY spectra. Huisgen and Weinberger[14] pointed out that 1,3-dipolar cycloaddition was a stereospecific, concerted cycloaddition, and the configuration of the reactants must be retained in that process. Our observations are consistent with their inference.

The relative configurations were also confirmed by X-ray diffraction of one of them (**4a**)**.** From Fig.1, the conformation of the pyrazolidine ring is near to an envelope with N1 out of the mean plane defined by atoms N2, C3, C4 and C5. The two phenyl rings and the pyrazolidine ring are not coplanar, the angle between the two phenyl rings being 26.66°. The carboxylic group is in *cis* and *trans* positions with respect to the 3-phenyl and 5-phenyl groups, respectively. Furthermore, the 1,5-*trans* relationship of 1-CH_3 and 5-Ph can also be observed from Fig.1, which accords with the demand of molecular lowest energy conformation.

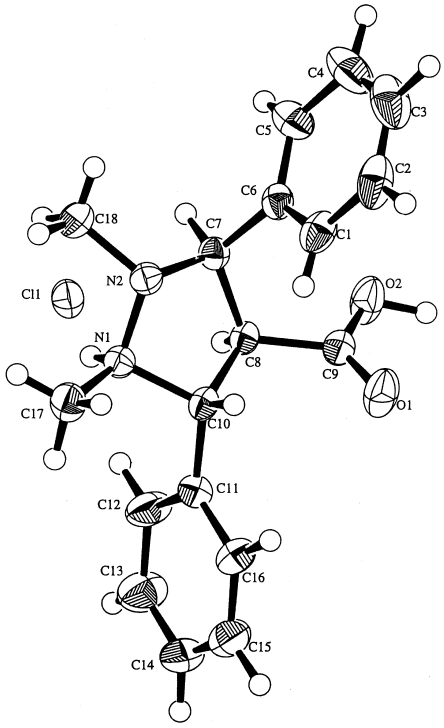

Fig. 1 X-Ray crystal structure of compound 4a.