

## Synthesis and Thermolysis of Highly Halogenated $\Delta^1$ -Pyrazolines

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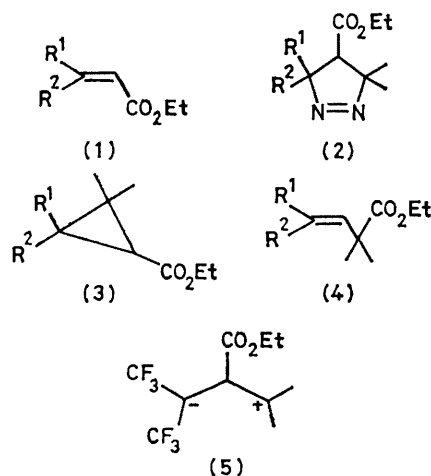
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**Summary** The pyrolysis of highly halogenated  $\Delta^1$ -pyrazolines gives, in addition to cyclopropanes, rearranged olefins.

ESTERS of 3-substituted-2,2-dimethylcyclopropane carboxylic acids are becoming increasingly important as extremely active insecticides.<sup>1</sup> We wished to obtain such acids containing highly halogenated 3-alkyl substituents since these have not previously been reported.

Our approach was based on the substituted acrylic esters (1)<sup>2</sup> readily available, as mixtures of *E* + *Z* isomers where possible, by the reaction of the appropriately substituted ketone with the stable ethoxycarbonylmethylenetriphenylphosphorane<sup>3</sup> in toluene. The acrylates (1) obtained could be titrated with a solution of the red 2-diazopropane<sup>4</sup> in ether to give quantitative yields of the  $\Delta^1$ -pyrazolines (2). The regioselectivity of the cycloaddition was confirmed by n.m.r. spectrometry to be as shown, the proton  $\alpha$  to the ethoxycarbonyl group giving a singlet between  $\delta$  2.7 and 3.1.

Pyrolysis of the neat  $\Delta^1$ -pyrazolines (2) at *ca.* 140 °C for up to 60 min. gave, in addition to the required cyclopropane esters (3), the interesting rearranged products (4). The structures of the two products were confirmed, for example where  $R^1 = R^2 = CF_3$ , by separation of their free acids by the fractional crystallisation of their morpholine salts.



The <sup>1</sup>H n.m.r. spectrum of the acid corresponding to (3),  $R^1 = R^2 = CF_3$ , m.p. 65–66 °C) has singlets at  $\delta$  1.52 (3H), 1.60 (3H), and 2.44 (1H) and that of (4, acid;  $R^1 = R^2 = CF_3$ , m.p. 110–111 °C) has singlets at 1.54 (6H) and 6.88br. (1H) p.p.m. <sup>19</sup>F N.m.r. and mass spectra and elemental analyses were also in accordance with the structures as given.

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The proportion of the two products of the pyrolysis varied according to the total electronegativity of the groups in the 3-position (see the Table) and within each of the two

series studied (with and without Cl) the amount of re-arranged product increased with increasing electronegativity. The cyclopropane esters (3) were shown to be stable under the conditions of the pyrolysis.

These observations could be explained by participation of an intermediate with ionic character, such as (5). A relatively small number of 1,2-carboxy shifts to electron deficient carbon have been described in the literature; these have been mainly confined to dienone-phenol re-arrangements.<sup>5</sup>

TABLE<sup>a</sup>

| R <sup>1</sup>     | R <sup>2</sup>                 | % of<br>(3) | % of<br>(4) |
|--------------------|--------------------------------|-------------|-------------|
| CF <sub>3</sub>    | CH <sub>3</sub> <sup>b</sup>   | 100         | 0           |
| CF <sub>3</sub>    | Ph <sup>b</sup>                | 94          | 6           |
| CF <sub>2</sub> H  | CF <sub>2</sub> H              | 75          | 25          |
| CF <sub>3</sub>    | CF <sub>2</sub> H <sup>b</sup> | 55          | 45          |
| CF <sub>3</sub>    | CF <sub>3</sub>                | 44          | 56          |
| CF <sub>2</sub> Cl | CF <sub>2</sub> H <sup>b</sup> | 38          | 62          |
| CF <sub>2</sub> Cl | CF <sub>2</sub> Cl             | 36          | 64          |
| CF <sub>2</sub> Cl | CF <sub>3</sub> <sup>b</sup>   | 31          | 69          |

<sup>a</sup> All products gave satisfactory elemental analysis.

<sup>b</sup> Mixtures of *E* and *Z* isomers.

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<sup>1</sup> 'Synthetic Pyrethroids,' ed. M. Elliott, Am. Chem. Soc. Symposia Series No. 42, 1977.

<sup>2</sup> For R<sup>1</sup> = R<sup>2</sup> = CF<sub>3</sub>. See for example Y. M. Saunier, R. Danion-Bougot, D. Danion and R. Carriè, *Tetrahedron*, 1976, **32**, 1995.

<sup>3</sup> O. Isler, H. Gutmann, M. Montavon, R. Ruegg, G. Ryser, and P. Zeller, *Helv. Chim. Acta*, 1957, **139**, 1242.

<sup>4</sup> P. Bladon, D. R. Rae, and A. D. Tait, *J. Chem. Soc., Perkin Trans. 1*, 1974, 1468.

<sup>5</sup> R. M. Acheson, *Acc. Chem. Res.*, 1971, **4**, 177.