Synthesis and Thermolysis of Highly Halogenated Δ^1-Pyrazolines

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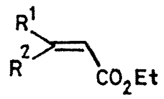
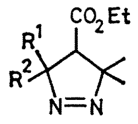
Summary The pyrolysis of highly halogenated Δ^1-pyrazolines gives, in addition to cyclopropanes, rearranged olefins.

Esters of 3-substituted-2,2-dimethylcyclopropane carboxylic acids are becoming increasingly important as extremely active insecticides.[1] 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**)[2] readily available, as mixtures of $E + Z$ isomers where possible, by the reaction of the appropriately substituted ketone with the stable ethoxycarbonylmethylenetriphenylphosphorane[3] in toluene. The acrylates (**1**) obtained could be titrated with a solution of the red 2-diazopropane[4] in ether to give quantitative yields of the Δ^1-pyrazolines (**2**). The regiospecificity of the cycloaddition was confirmed by n.m.r. spectrometry to be as shown, the proton α to the ethoxycarbonyl group giving a singlet between δ 2·7 and 3·1.

Pyrolysis of the neat Δ^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.


(1)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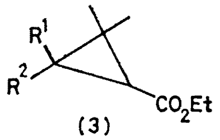
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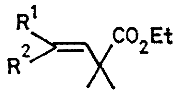
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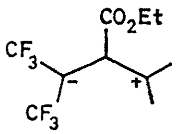
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The ^{1}H n.m.r. spectrum of the acid corresponding to (**3**, $R^1 = R^2 = CF_3$, m.p. 65—66 °C) has singlets at δ 1·52 (3H), 1·60 (3H), and 2·44 (1H) and that of (**4**, acid; $R^1 = R^2 = CF_3$, m.p. 110—111 °C) has singlets at 1·54 (6H) and 6·88br. (1H) p.p.m. ^{19}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 rearranged product increased with increasing electronegativity. The cyclopropane esters (**3**) were shown to be stable under the conditions of the pyrolysis.

TABLE[a]

R^1	R^2	% of (**3**)	% of (**4**)
CF_3	CH_3[b]	100	0
CF_3	Ph[b]	94	6
CF_2H	CF_2H	75	25
CF_3	CF_2H[b]	55	45
CF_3	CF_3	44	56
CF_2Cl	CF_2H[b]	38	62
CF_2Cl	CF_2Cl	36	64
CF_2Cl	CF_3[b]	31	69

[a] All products gave satisfactory elemental analysis.
[b] Mixtures of *E* and *Z* isomers.

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 rearrangements.[5]

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[1] 'Synthetic Pyrethroids,' ed. M. Elliott, Am. Chem. Soc. Symposia Series No. 42, 1977.
[2] For $R^1 = R^2 = CF_3$. See for example Y. M. Saunier, R. Danion-Bougot, D. Danion and R. Carriè, *Tetrahedron*, 1976, **32**, 1995.
[3] O. Isler, H. Gutmann, M. Montavon, R. Ruegg, G. Ryser, and P. Zeller, *Helv. Chim. Acta*, 1957, **139**, 1242.
[4] P. Bladon, D. R. Rae, and A. D. Tait, *J. Chem. Soc., Perkin Trans.* 1, 1974, 1468.
[5] R. M. Acheson, *Acc. Chem. Res.*, 1971, **4**, 177.