# Reactions of Unsaturated Tetra- and Tri-esters with Hydrazine Hydrate and Semicarbazide Hydrochloride

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Various 4,5-disubstituted pyrazolidin-3-ones (IIc—f) have been isolated as intermediates in the reaction between 3-substituted tetraethyl propene-1,1,3,3-tetracarboxylates (I) and hydrazine hydrate. No such intermediates were obtained in the reaction between 3-substituted triethyl propene-1,1,3-tricarboxylates (VI) and with hydrazine hydrate, which gave ethyl 5-oxo-$\Delta^2$-pyrazoline-4-carboxylate (III) and the appropriate saturated esters (VII). Semicarbazide hydrochloride reacted similarly with the various esters to give the same final products as with hydrazine hydrate.

EXTENSIVE work in the field of pyrazolidin-3-ones has been carried out because of their use as photographic developers.[1] 4,5-Disubstituted derivatives have now been isolated by us in the reactions between some 3-substituted tetraethyl propene-1,1,3,3-tetracarboxylates (Ia—g) and hydrazine hydrate; the products were cleaved to form ethyl 5-oxo-$\Delta^2$-pyrazoline-4-carboxylate (III) together with substituted malonic esters (IV) (Scheme). The structure of the intermediates (IIc—f) was inferred from the elemental analysis (Table 1) and i.r. and n.m.r. spectra (see Experimental section).

Regarding structure (III), which can be depicted in many tautomeric forms (IIIa—d), the favoured form could be deduced from the i.r. and the n.m.r. spectra. The i.r. spectrum (Nujol) showed bands at 3150 (NH, sharp), 2400—2800 (strongly bonded OH), 1700 (bonded C=O, broadened by shoulders at 1690 and 1720), 1600 (C=C), and 1550 cm$^{-1}$ (C=N conjugated). The n.m.r. spectrum showed signals at $\tau$ ($Me_2SO$) 8·68 (t, $CH_3$), 5·7 (q, $CH_2$), 2·12 (s, CH=C), and 0·44 (2H, exchangeable NH and OH). Accordingly, the tautomeric forms (IIIc) and (IIId) are favoured over the rest, although the n.m.r. values would also agree with form (IIIb). A

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[1] J. D. Kendall, B.P. 650,911/1951; J. D. Kendall and G. F. Duffin, U.S.P. 2,704,762/1955; G. A. Reynolds, U.S.P. 2,688,548/1954.

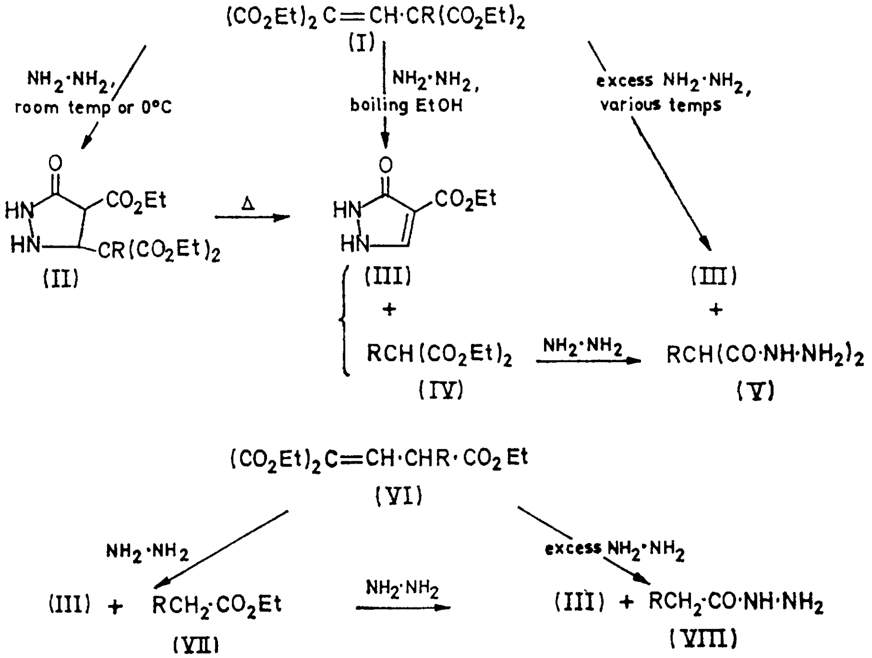
similar conclusion was previously reached by Refn[2] from the i.r. spectrum of 4-phenyl-5-pyrazolone in the solid state. The results of Katritzky,[3] based on u.v. spectroscopy and basicity measurements, for 3-methyl-5-pyrazolone showed that the stability of the forms for the solid state was in the order b > d ≫ c > a.

When various triethyl propene-1,1,3-tricarboxylates (VIa—d) were treated with hydrazine hydrate, compound (III) was obtained along with the appropriate saturated ester (VII) (Scheme). In this case no intermediate compounds could be obtained under various experimental conditions.

Semicarbazide hydrochloride also reacted with esters (I) or (VI) in boiling ethanol to give compound (III), biurea, and esters (IV) or (VII). This could be explained in terms of initial formation of hydrazine:

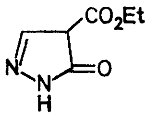
$$2(NH_2\cdot NH\cdot CO\cdot NH_2)\xrightarrow[\text{EtOH}]{\text{Boiling}} NH_2\cdot NH_2 + NH_2\cdot CO\cdot NH\cdot NH\cdot CO\cdot NH_2$$

a—d]

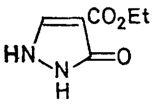


a; R = H. b; R = Me. c; R = Et. d; R = PhCH$_2$. e; R = $p$-MeC$_6$H$_4$·CH$_2$. f; R = $p$-ClC$_6$H$_4$·CH$_2$. g; R = $p$-EtC$_6$H$_4$·CH$_2$

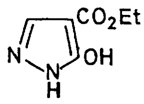
SCHEME



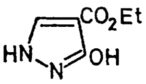
(IIIa)



(IIIb)



(IIIc)



(IIId)

TABLE 1

4,5-Disubstituted pyrazolidin-3-ones

| Compound (II) * | M.p. (°C) | Formula | Found (%) C | Found (%) H | Found (%) N | Calc. (%) C | Calc. (%) H | Calc. (%) N |
|---|---|---|---|---|---|---|---|---|
| c | 105 | $C_{15}H_{24}N_2O_5$ | 52·5 | 6·85 | 8·3 | 52·3 | 6·85 | 8·15 |
| d | 133 | $C_{19}H_{24}N_2O_5$ | 59·0 | 6·4 | 7·0 | 59·1 | 6·15 | 6·9 |
| e | 108 | $C_{20}H_{26}N_2O_5$ | 60·2 | 6·65 | 6·9 | 60·0 | 6·7 | 6·7 |
| f * | 148 | $C_{19}H_{23}N_2O_5Cl$ | 40·8 | 5·5 | 7·0 | 40·55 | 5·7 | 7·0 |

* Found: Cl, 8·1. Calc. 8·05%.

EXPERIMENTAL

Unless otherwise stated, i.r. spectra were measured with a Unicam SP 200 instrument for solutions in chloroform, and $^1H$ n.m.r. spectra with a Varian A-60 instrument for solutions in carbon tetrachloride containing tetramethylsilane as internal standard. Compounds were analysed at the Max Planck Institute, Ruhr, West Germany. M.p.s were determined with a Kofler hot-stage apparatus.

*Reactions between 3-Substituted Tetraethyl Propene-*1,1,3,3-*tetracarboxylates* (Ia—g) *and Hydrazine Hydrate*.—To a

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[2] S. Refn, *Spectrochim. Acta*, 1961, **17**, 40.

[3] A. R. Katritzky, F. W. Maine, and S. Golding, *Tetrahedron*, 1965, **21**, 1693.

solution of the tetraester[4] in ethanol, hydrazine hydrate (98%) (1 mol. equiv.) was added; the mixture was heated under reflux for 4 h. The solution was concentrated under vacuum, cooled, and filtered and the solid obtained was washed with ether to give *ethyl* 5-*oxo*-$\Delta^2$-*pyrazoline*-4-*carboxylate* (III) (*ca.* 95%) as crystals, m.p. 180—181° (from ethanol) (Found: C, 46·2; H, 5·5; N, 17·7. $C_6H_8N_2O_3$ requires C, 46·15; H, 5·3; N, 17·85%). The filtrate and ether washings were concentrated to give the oily malonate ester (IVa—g) as shown from its i.r. spectrum and by conversion into the acid hydrazide (Va—g).

TABLE 2

Malonohydrazides

| Compound (V) * | M.p. (°C) | Formula | Found (%) C | Found (%) H | Found (%) N | Calc. (%) C | Calc. (%) H | Calc. (%) N |
|---|---|---|---|---|---|---|---|---|
| a | 142 | $C_3H_8N_4O_2$ | 28·15 | 6·3 | 42·75 | 28·3 | 6·15 | 42·7 |
| b | 176 | $C_4H_{10}N_4O_2$ | 32·7 | 7·0 | 38·5 | 32·9 | 6·85 | 38·35 |
| c | 162 | $C_5H_{12}N_4O_2$ | 37·65 | 7·65 | 34·9 | 37·95 | 7·6 | 35·1 |
| d | 158 | $C_{10}H_{14}N_4O_2$ | 54·2 | 6·55 | 25·35 | 54·45 | 6·6 | 25·2 |
| e | 153 | $C_{11}H_{16}N_4O_2$ | 55·9 | 6·55 | 23·6 | 55·9 | 6·8 | 23·75 |
| f | 203 | $C_{10}H_{13}N_4O_2$ | 43·6 | 4·85 | 20·85 | 43·45 | 5·0 | 21·0 |
| g | 161 | $C_{12}H_{18}N_4O_2$ | 57·83 | 7·4 | 22·55 | 57·7 | 7·2 | 22·4 |

* Recrystallised from ethanol.

When the reactions were repeated at room temperature or at 0°, the intermediate 4,5-disubstituted pyrazolidin-3-ones (IIc—f) were isolated. Compound (IId) showed $\nu_{max.}$ ($CHCl_3$) 1700, 1720, and 1740 (C=O of amide and ester), and 3300 and 3500 (NH) cm$^{-1}$ (similar assignments are reported[5] for 1-phenylpyrazolidin-3-one); $\tau$ ($CDCl_3$) 8·7 (t, ester Me), 6·46—5·72 (m, ester $CH_2$ and 2-H), 5·0br (HN·N·CO, exchangeable), 2·64 (m, 5H, aromatic), and 1·7br (NH·CO·N, exchangeable). When compounds (IIc—f) were heated just above their m.p.s they were cleaved to give the pyrazoline (III) and the malonate ester (IV). However, when excess of hydrazine hydrate was used, the malonohydrazides (V) (Table 2) were obtained in *ca.* 85% yield.

*Reactions between* 3-*Substituted Triethyl Propene*-1,1,3-*tricarboxylates* (VIa—d) *and Hydrazine Hydrate.*—The ester (VI)[4] and hydrazine hydrate were treated under the same experimental conditions. In all cases, ethyl 5-oxo-$\Delta^2$-pyrazoline-4-carboxylate (III) and monoesters (VIIa—d) were separated and identified.

*Reactions between Semicarbazide Hydrochloride and Esters* (Ia—g) *or* (VIa—d).—The ester was boiled for 6 h with semicarbazide hydrochloride. Cooling and filtration gave biurea, m.p. 245°. The mother liquor was concentrated and filtered to give ethyl 5-oxo-$\Delta^2$-pyrazoline-4-carboxylate (III). Extraction of the filtrate with ether gave the monoester (VII) or the malonate (IV). When such reactions were repeated with excess of semicarbazide hydrochloride, the corresponding acid hydrazides (V) and (VIII) were isolated instead of the esters (VII) and (IV).

[1/1600 *Received, 2nd September,* 1971]

[4] F. B. Thole and J. F. Thorpe, *J. Chem. Soc.*, 1911, **99**, 2187.

[5] K. Kurosaki, *Nippon Kagaku Zasshi*, 1958, **79**, 1339 (*Chem. Abs.*, 1959, **53**, 6764b).