CLXXIV.—*The Influence of Groups and Associated Rings on the Stability of Certain Heterocyclic Systems. Part III. The Substituted Paraconic Acids.*

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THE stability of five- and six-membered heterocyclic systems containing nitrogen having been examined (this vol., pp. 600 1252), a study has been made of five-membered rings containing oxygen. For this purpose the substituted paraconic acids were suitable. Three disubstituted acids had already been prepared by Birch, Gough, and Kon (J., 1921, **119**, 1320), and two others (methylethyl and *cyclo*pentane compounds) were obtained from the corresponding ketones by their method. The monosubstituted paraconic acids were prepared by Fittig's well-known method.

As paraconic acid and its monoalkyl derivatives can be neutralised at the ordinary temperature without fission of the lactone ring, which is only attacked by hot alkali (Fittig, *Ber.*, 1890, **23**, 91), it was possible in the present investigation to use two equivalents of alkali, one to neutralise the acid and the other to effect the opening of the ring; the first process, being instantaneous, had no undesirable effect on the hydrolysis. At 25° the velocity of hydrolysis was conveniently rapid in the solution prepared by adding 10 c.c. of $N/10$-sodium hydroxide to 90 c.c. of an $N/180$-solution of a paraconic acid.

The results of the hydrolyses given in Table I again show strikingly the influence of substituents on the stability of a heterocyclic system. The introduction of a methyl group causes, as was also observed in the two previous investigations, an increase in the stability. The influence of two ethyl groups is, however, greater than that of the *cyclo*pentane or *cyclo*hexane group.

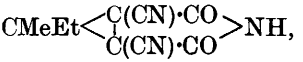
TABLE I.

Substituents.	$k \times 10^5$.	Substituents.	$k \times 10^5$.
H, H	1630	Me, Et	164
Me, H	763	Et, Et	74·5
Et, H	652	*cyclo*Pentane	119
Me, Me	270	*cyclo*Hexane	107

EXPERIMENTAL.

Paraconic acid was prepared by decomposing itabromopyrotartaric acid by water (*Annalen*, 1882, **216**, 77; in the preparation of itabromopyrotartaric acid by the addition of hydrobromic acid to itaconic acid it was found convenient to heat the mixture at

100° for 3 hours) and purified by means of the silver salt. The acid was very hygroscopic; m. p. 57° (Found: C, 45·8; H, 5·0. Calc.: C, 46·15; H, 4·6%). Methylparaconic acid (Fittig, *Ber.*, 1890, **23**, 91) was slightly hygroscopic; m. p. 84·5° (Found: C, 49·8; H, 5·8. Calc.: C, 50·0; H, 5·55%). Ethylparaconic acid (Fittig, *loc. cit.*) had m. p. 85° (Found: C, 53·0; H, 6·6. Calc.: C, 53·2; H, 6·3%). Dimethylparaconic acid (terebic acid) (Birch, Gough, and Kon, *loc. cit.*) crystallised from water in scales, m. p. 174° (Found: C, 53·4; H, 6·4. Calc.: C, 53·1; H, 6·4%). Diethylparaconic acid (Birch and Thorpe, J., 1922, **121**, 1825) had m. p. 105° (Found: C, 57·85; H, 7·4. Calc.: C, 58·05; H, 7·5%). *cyclo*Hexane*spiro*paraconic acid (Birch, Gough, and Kon, *loc. cit.*) had m. p. 184—185° (Found: C, 60·3; H, 7·4. Calc.: C, 60·6; H, 7·1%).

Methylethylparaconic Acid.—This acid was prepared by a method similar to that employed in preparing the dimethyl compound (above). Details are not given, as they differed only in minor points from those recorded by Birch, Gough, and Kon. The *imide*,  $\mathrm{CMeEt}\Big<\begin{array}{l}\mathrm{C(CN)\cdot CO}\\ \mathrm{C(CN)\cdot CO}\end{array}\Big>\mathrm{NH}$, was crystallised from alcohol; m. p. 225—227° (Found: N, 20·4. $C_{10}H_9O_2N_3$ requires N, 20·7%). 2 : 3-*Dicyano*-1-*methyl*-1-*ethyl*cyclo*propane*-2-*carboxylamide* crystallised from benzene in needles, m. p. 127—128° (Found: N, 23·4. $C_9H_{11}ON_3$ requires N, 23·7%). The *γ-lactone* of *β-hydroxy-β-ethylbutane-γδδ-tricarboxylic acid* crystallised from water on the addition of hydrochloric acid, m. p. 157—158° (efferv.) (Found: C, 49·7; H, 5·6. $C_9H_{12}O_6$ requires C, 50·0; H, 5·55%). *Methylethylparaconic acid* crystallised from hot water in needles, m. p. 131—132° (Found: C, 55·45; H, 6·7. $C_8H_{12}O_4$ requires C, 55·8; H, 7·0%. Found for the *silver* salt: Ag, 38·4. $C_8H_{11}O_4Ag$ requires Ag, 38·7%).

cyclo*Pentane*spiro*paraconic Acid.*—The preparation was similar to that of the *cyclo*hexane analogue (above). The bridged *imide* was crystallised from alcohol; m. p. 202—203° (Found: N, 20·3. $C_{11}H_9O_2N_3$ requires N, 20·9%). cyclo*Pentane*spiro-2 : 3-*dicyano*-cyclo*propane*-2-*carboxylamide* was crystallised from dilute alcohol; m. p. 126° (Found: N, 21·8. $C_{10}H_{11}ON_3$ requires N, 22·2%). The *γ-lactone* of 1-*hydroxy*cyclo*pentylethane*-αββ-*tricarboxylic acid* slowly crystallised from a small quantity of water after the addition of hydrochloric acid; m. p. 175—177° (efferv.). cyclo*Pentane*-spiro*paraconic acid* was prepared by heating the tribasic acid at 200° for 2 hours until the evolution of carbon dioxide ceased; it crystallised from water in needles, m. p. 127° (Found: C, 58·3; H, 6·4. $C_9H_{12}O_4$ requires C, 58·7; H, 6·5%. Found for the *silver* salt: Ag, 37·4. $C_9H_{11}O_4Ag$ requires Ag, 37·1%).

Details of the hydrolyses are recorded in Table II. $a = 5$ in all cases. (For the meaning of the letters, see preceding paper.)

TABLE II.

	Paraconic acid.		Methylparaconic acid.		Ethylparaconic acid.		Dimethylparaconic acid.	
t.	$a-x$.	$k \times 10^5$.	$a-x$.	$k \times 10^5$.	$a-x$.	$k \times 10^5$.	$a-x$.	$k \times 10^5$.
0	3·1	—	4·7	—	4·2	—	5·0	—
5	2·8	1430	3·7*	(878)	3·3	(857)	4·4	272
10	1·75	1850	2·8	788	2·75	743	3·9	266
15	1·35	1800	2·3	780	2·35	704	3·55	272
20	1·15	1670	2·0	750	2·2	606	3·2	271
25	1·0	1600	1·8	761	1·9	629	3·0	266
30	0·9	1510	1·55	772	1·65†	601	2·8	252
35	0·8	1560	1·35	730	1·5‡	630	2·5	285
	Mean	1630	Mean	763	Mean	652	Mean	270

	Methylethylparaconic acid.		Diethylparaconic acid.		*cyclo*Pentane-*spiro*paraconic acid.		*cyclo*Hexane-*spiro*paraconic acid.	
t.	$a-x$.	$k \times 10^5$.	$a-x$.	$k \times 10^5$.	$a-x$.	$k \times 10^5$.	$a-x$.	$k \times 10^5$.
0	4·8	—	5·0	—	4·95	—	5·2	—
5	4·6	174	4·9	(41)	4·6	(174)	4·95	(202)
10	4·3	162	4·7	64	4·45	124	4·5	111
15	4·05	155	4·5	74	4·2	127	4·35	100
20	3·8	163	4·35	75	4·0	125	4·1	102
25	3·55	171	4·2	76	3·9	113	3·9	112
30	3·3	163	4·05	78	3·7	117	3·75	111
35	3·15	168	3·95	76	3·6	111	3·6	155
40	—	—	3·8	79	—	—	—	—
	Mean	164	Mean	74·5	Mean	119	Mean	107

*, †, ‡ values for 4, 31, and 37 minutes, respectively.

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