CLXXIII.—*The Influence of Groups and Associated Rings on the Stability of Certain Heterocyclic Systems. Part II. The Substituted Succinimides.*

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In Part I (this vol., p. 600) evidence was brought forward of the well-marked influence of substituents in modifying the stabilities of substituted glutarimides. The present work deals with the velocity of hydrolysis of the substituted succinimides, containing a five-membered ring. Table I, giving the velocity coefficients for these compounds calculated for a bimolecular reaction, clearly shows the close general agreement of the experimental results with the requirements of the modified strain theory. There are, however, several other points of interest in the investigation. For example, the methyl group is found to produce an abnormal increase in the stability of the ring. This abnormality, although present in the glutarimide series, was masked by the unusually high value of the velocity coefficient for glutarimide itself. The anomalous behaviour of methyl in comparison with other alkyl groups is well known, particularly its influence on the dissociation constants of various series of acids (compare *Rec. trav. chim.*, 1912, **31**, 86; J., 1925, **127**, 342). A second point of interest is that the velocity coefficient for the first member of the series of succinimides is very nearly the same as the coefficients for the last two members. It seems as if the limit of stability of this system is reached in succinimide, or as if the *cyclo*pentane and the *cyclo*hexane rings are behaving like strainless systems, contributing little towards increasing the strain in the imide ring.

TABLE I.

Substituents.	$k \times 10^6$.
H,H	232
Me,H	141
Et,H	512
Me,Me	308
Me,Et	288
Et,Et	247
*cyclo*Pentane	235
*cyclo*Hexane	226

TABLE II.

Substance.	$k \times 10^6$.
Phthalimide	8,700
Homophthalimide	12,600
trans-Hexahydrophthalimide	26,500
trans-Hexahydrohomophthalimide	4,980
trans-*cyclo*Pentane-1-carboxy-2-acetimide	6,460

The study of a number of associated ring systems in which the hetero-ring is attached to the carbocyclic ring by two carbon atoms is not without interest. The velocity coefficients are in Table II. The associated systems seem to be less stable than the corresponding *spiro*-systems. This is a logical consequence of the strain theory if it is assumed that during the formation of the ring from the open chain the approximation of the ends of the chain (brought about by the influence of the substituents) may go beyond the requirement of closest spatial proximity; in other words, that the ends of the chain may overlap. In such a case the molecular strain would tend to increase rather than diminish as the effect of the substituent on the individual carbon atom becomes greater. It is also evident that the order of stability in passing from the five- to the six-membered ring may be reversed by this overlapping, making hexahydrohomophthalimide more stable than the lower homologue. In phthalimide and its homologue, however, the internally compensated (either by conjugation or by the mobility of the bonds) benzene nucleus prevents any rigid or permanent alteration in the extracyclic bonds, and the order of stability is the same as in the unsubstituted succinimide and glutarimide.

EXPERIMENTAL.

Preparation of the Imides.—All the imides were prepared by the method described in Part I (*loc. cit.*). Their structures were confirmed by regenerating the parent acids by hydrolysis with alkali.

Succinimide, m. p. 126° (Found: N, 14·4. Calc.: N, 14·1%). Methylsuccinimide, m. p. 66° (Found: N, 12·1. Calc.: N, 12·4%). Ethylsuccinimide, m. p. 77° (Found: N, 11·3. Calc.: N, 11·0%). *as*-Dimethylsuccinimide crystallised from hot water in scales, m. p. 106° (Found: N, 11·1. Calc.: N, 11·0%).

as-*Methylethylsuccinimide* was redistilled and then crystallised from acetone–ether; m. p. 64—65° (Found: N, 9·5. $C_7H_{11}O_2N$ requires N, 9·9%).

as-*Diethylsuccinimide.*—The acid was prepared by a slight modification of Higson and Thorpe's method (J., 1906, **89**, 1456) suggested by Dr. S. B. Dutt (private communication). A mixture of ethyl α-cyano-ββ-diethylacrylate (36 g.) (Birch and Kon, J., 1923, **123**, 2440), alcohol (400 c.c.), and potassium cyanide (15 g. in 30 c.c. of water) was kept for 2 weeks. The alcohol was then distilled off and the solution acidified. The heavy oil thus obtained could not be distilled in a vacuum without decomposition; so it was hydrolysed by boiling it with concentrated hydrochloric acid (5 vols.) for 10 hours under reflux. The material extracted from the cooled solution by ether was itself extracted with sodium carbonate solution, which was then filtered, acidified, saturated with ammonium sulphate, and repeatedly extracted with ether. The oily residue obtained on evaporation of the dried extracts soon solidified; it was then crystallised from dilute hydrochloric acid and again from benzene–petrol, the yield of the acid, m. p. 108°, being 20%. The *imide* crystallised from hot water in needles, m. p. 85—86° (Found: N, 9·5. $C_8H_{13}O_2N$ requires N, 9·0%).

cyclo*Pentane*spiro*succinimide* crystallised from water in plates, m. p. 124° (Found: N, 8·8. $C_8H_{11}O_2N$ requires N, 9·1%).

cyclo*Hexane*spiro*succinimide.*—The imide crystallised from hot water has m. p. 145° (Found: N, 8·25. $C_9H_{13}O_2N$ requires N, 8·3%).

Phthalimide, m. p. 229°. The velocity coefficient obtained by Miolati, *viz.*, 0·087, was utilised.

trans-*Hexahydrophthalimide.*—Hexahydrophthalic acids (*cis*- and *trans*-), prepared by Baeyer's method (*Annalen*, 1890, **258**, 145; 1892, **269**, 145), gave the same imide on distillation of the dry ammonium salts. This is regarded as the trans-*imide*, as it gives the *trans*-

acid on hydrolysis. It crystallised from hot water in large, glistening scales, m. p. 163—164° (Found: N, 9·4. $C_8H_{11}O_2N$ requires N, 9·2%).

Homophthalimide.—The acid, m. p. 173—174°, was prepared by reducing phthalonic acid with hydriodic acid and red phosphorus (*Ber.*, 1898, **31**, 369). The *imide* crystallised from hot water in scales, m. p. 75° (Found: N, 8·2. $C_9H_7O_2N$ requires N, 8·7%).

trans-*Hexahydrohomophthalimide.*—The acid (1-carboxy*cyclo*hexane-2-acetic acid) was prepared by Dutt's method (unpublished work), by condensing ethyl sodiocyanoacetate with ethyl Δ^1-tetrahydrobenzoate, and hydrolysing the resulting cyano-ester (b. p. 216°/20 mm.) by boiling it with concentrated hydrochloric acid (5 vols.) for 18 hours. (If the heating is less prolonged, a difficultly separable mixture of *cis*- and *trans*-acids is obtained.) The *trans*-acid thus formed (also described by Windaus, *Ber.*, 1923, **56**, 90) melted at 158° (Found: C, 58·1; H, 7·3. Calc.: C, 58·0; H, 7·6%). The *imide* crystallised from hot water in scales, m. p. 185° (Found: N, 8·0. $C_9H_{13}O_2N$ requires N, 8·4%).

trans-cyclo*Pentane*-1-*carboxy*-2-*acetimide* was prepared by a method similar to the previous one. *Ethyl* Δ^1-cyclo*pentenecarboxylate* was prepared by treating ethyl *cyclo*pentan-1-ol-1-carboxylate with phosphorus pentachloride and heating the product with diethylaniline (1·2 mols.) for 3 hours at 200°; it boiled at 92°/25 mm. and the yield was about 50% (Found: C, 68·3; H, 8·5. $C_8H_{12}O_2$ requires C, 68·5; H, 8·5%). The unsaturated ester (1 mol.) was treated with ethyl cyanoacetate (1 mol.) in presence of sodium ethoxide (1 mol.) dissolved in alcohol, and the mixture was heated on the steam-bath for 6 hours. The addition *compound* (yield 35%), which boiled at 185—186°/17 mm. (Found: C, 61·3; H, 7·4. $C_{13}H_{19}O_4N$ requires C, 61·6; H, 7·5%), was boiled with concentrated hydrochloric acid for 18 hours. The organic *acid* was extracted with ether and recrystallised thrice from dilute hydrochloric acid and then from benzene–petrol (b. p. 60—80°). It melted at 158°, was presumably the *trans*-acid, and behaved similarly to the *cyclo*hexane analogue (Found: C, 55·4; H, 7·1. $C_8H_{12}O_4$ requires C, 55·8; H, 7·0%). The *imide* crystallised from petrol–ether in scales, m. p. 184—185° (Found: N, 9·4. $C_8H_{11}O_2N$ requires N, 9·15%).

Hydrolysis of the Imides.—*N*/190-Solutions of the imides were hydrolysed in the manner described in Part I (*loc. cit.*, p. 602). The results are in Table III, the letters having the same significance as before. Where $a = 10$, *N*/200-acid was used in the titrations; where $a = 5$, *N*/100-acid was used. For small velocity coefficients, titrations were made at intervals of 10 minutes.

TABLE III.

Succinimide ($a = 10$).

t.	$a-x$.	$k \times 10^6$.
0	10·0	—
5	9·9	(202)
10	9·75	256
20	9·55	232
30	9·35	234
40	9·15	232
50	9·0	202
60	8·75	235
70	8·6	232
	Mean	232

(Miolati's value, 238)

Methylsuccinimide ($a = 10$).

t.	$a-x$.	$k \times 10^6$.
0	10·0	—
10	9·85	152
20	9·75	128
30	9·6	139
40	9·5	132
50	9·4	127
60	9·15	153
70	9·0	157
80	8·8	(174)
100	8·5	(176)
	Mean	141

(Miolati's value, 135)

Ethylsuccinimide ($a = 5$).

t.	$a-x$.	$k \times 10^6$.
0	4·85	—
5	4·8	(833)
10	4·75	526
15	4·6	550
20	4·55	494
25	4·45	494
30	4·35	498
	Mean	512

as-Dimethylsuccinimide ($a = 5$).

t.	$a-x$.	$k \times 10^6$.
0	5·2 ?	—
5	5·0 ?	—
10	4·9	(204)
15	4·8	277
20	4·7	319
25	4·65	301
35	4·5	317
40	4·425	322
	Mean	308

as-Methylethylsuccinimide ($a = 10$).

t.	$a-x$.	$k \times 10^6$.
0	10·0	—
10	9·7	309
20	9·45	264
30	9·25	270
40	8·95	307
50	8·75	285
60	8·5	293
	Mean	288

as-Diethylsuccinimide ($a = 10$).

t.	$a-x$.	$k \times 10^6$.
0	10·0	—
5	9·8	(409)
10	9·75	256
20	9·5	263
30	9·35	231
40	9·1	247
50	8·9	247
60	8·7	241
	Mean	247

*cyclo*Pentane*spiro*-succinimide ($a = 5$).

t.	$a-x$.	$k \times 10^6$.
0	—	—
5	4·95	(202)
10	4·85	(307)
15	4·80	263
20	4·775	233
25	4·725	232
35	4·6	248
	Mean	235

*cyclo*Hexane*spiro*-succinimide ($a = 5$).

t.	$a-x$.	$k \times 10^6$.
0	5·0	—
5	4·95	(202)
10	4·85	(307)
15	4·80	263
20	4·75	232
25	4·725	217
35	4·65	215
46	4·55	—
	Mean	226

trans-Hexahydrophthalimide ($a = 5$).

t.	$a-x$.	$k \times 10^6$.
0	4·5	Excess.
5	2·1	26,600
10	1·35	27,000
15	1·0	26,600
20	0·75	28,300
25	0·65	26,000
30	0·60	24,400
	Mean	26,500

Homophthalimide ($a = 5$).

t.	$a-x$.	$k \times 10^6$.
0	3·7	—
5	2·8	(15,700)
10	2·25	12,700
15	1·75	12,300
20	1·4	12,800
25	1·15	12,700
30	1·05	12,500
35	0·90	13,000
	Mean	12,600

trans-Hexahydrohomophthalimide ($a = 5$).

t.	$a-x$.	$k \times 10^6$.
0	4·75	—
5	4·05	4690
10	3·5	4300
15	3·05	4260
20	2·4	5410
25	2·15	5300
32	1·8	5500
39	1·4	5400
	Mean	4980

trans-*cyclo*-Pentane-1-carboxy-2-acetimide ($a = 5$).

t.	$a-x$.	$k \times 10^6$.
0	4·3	—
5	3·8	6310
10	3·1	6130
15	2·5	6160
20	2·15	6130
25	1·8	7100
30	1·6	7080
35	1·4	6320
	Mean	6460

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