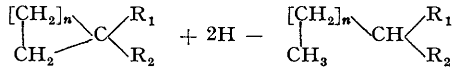
364. *Physical Properties and Chemical Constitution. Part XVIII. Three-membered and Four-membered Carbon Rings.*

By George H. Jeffery and Arthur I. Vogel.

New measurements have been made of the refractivities at 20° and the parachors of a number of *cyclo*propane and *cyclo*butane compounds, largely esters of *cyclo*propane- and *cyclo*-butane-carboxylic and -1 : 1-dicarboxylic acids. The contributions of the three- and four-membered carbon rings have been computed from the relationship :

Ring constant = 

The necessary physical data for H and the reference compounds are given in the earlier papers of this series. The results are :

	P.	R_C.	R_D.	R_F.	$R_{G'}$.	$Mn_D^{20°}$.
Three-carbon ring	12·3	0·592	0·614	0·656	0·646	−4·72
Four-carbon ring	10·0	0·303	0·317	0·332	0·322	−4·67

The new constants differ appreciably from those previously accepted.

The early attempts to determine the contribution to the refractivity of the three- and four-membered carbon rings cannot now be regarded as satisfactory for the following reasons : (1) The selection of compounds included many containing dicyclic structures. (2) The calculations were based upon erroneous values for the CH_2 constants (compare Vogel, Part IX, *J.*, 1946, 133). The most comprehensive data are due to Ostling (*J.*, 1912, **101**, 468), whose R_D values for the *cyclo*propane and *cyclo*butane rings were 0·71 and 0·48, respectively (for a detailed review, see Eisenlohr, " Spektrochemie organischer Verbindungen, Molekularrefraktion und -dispersion ", Ferdinand Enke, 1912, 89—91, 134—141). The parachor contribution of the three-membered ring is based upon data on 9 compounds of very varied type which include ethylene oxide and epichlorohydrin and upon a CH_2 value of 39·0 (compare Vogel, Part IX, who found 40·0) ; the extreme values were 12·9 and 20·2 and the mean was 16·7 (Sugden and Wilkins, *J.*, 1927, 240). The constant of the four-membered ring was computed from the results upon ethyl 1-cyano*cyclo*butane-1-carboxylate, ethyl *cyclo*butane-1 : 1-dicarboxylate, and ethyl *cyclo*butanecarboxylate and was given as 11·6 (Sugden and Wilkins, *J.*, 1927, 141).

We have determined the parachors and refractivities of 10 simple *cyclo*propane compounds (largely esters of *cyclo*propane-carboxylic and 1 : 1-dicarboxylic acids) and have computed the contributions of the three-carbon ring from the relationship given above (n = 1). The necessary experimental data were taken from earlier papers of this series (2H from Part IX, alkyl n-butyrates and alkyl ethylmalonates from Part XIII, this vol., p. 624 ; the data for n-butyric acid are given in Part XX, *ibid.*, p. 1814). The results are summarised in Table I ; the experimental data for dimethyl *cyclo*propane-1 : 1-dicarboxylate were taken from Part I (*J.*, 1934, 340). The slight (and often negative) difference between R_F and $R_{G'}$ is noteworthy ; it is hoped to repeat

Table I.

Values for the three-carbon ring from cyclo*propane compounds.*

	P.	R_C.	R_D.	R_F.	$R_{G'}$.	Mn_D^{20}.
*cyclo*Propanecarboxylic acid..................	14·0	0·59	0·61	0·65	0·66	−4·44
*cyclo*Propyl methyl ketone	13·3	0·69	0·72	0·78	0·78	−5·00
Me *cyclo*propanecarboxylate..................	13·4	0·59	0·61	0·65	0·64	−4·78
Et *cyclo*propanecarboxylate	12·6	0·54	0·60	0·60	0·60	−4·67
Pr^n *cyclo*propanecarboxylate..................	12·4	0·61	0·62	0·66	0·66	−4·59
Bu^n *cyclo*propanecarboxylate	12·0	0·61	0·63	0·67	0·66	−4·81
Am^n *cyclo*propanecarboxylate	11·3	0·49	0·52	0·56	0·55	−4·85
Me_2 *cyclo*propane-1 : 1-dicarboxylate	12·3	0·63	0·63	0·68	0·65	−4·46
Et_2 *cyclo*propane-1 : 1-dicarboxylate	11·2	0·58	0·59	0·65	0·61	−4·91
Pr^n_2 *cyclo*propane-1 : 1-dicarboxylate	10·5	0·45 *	0·44 *	0·51 *	0·48 *	−4·73
Mean (excluding *)	12·3	0·592	0·614	0·656	0·646	−4·72
Mean	12·3	0·578	0·597	0·641	0·629	−4·73

the measurements for n_F and $n_{G'}$ with the new Hilger–Chance refractometer to establish whether the differences are due to experimental error in the measurement of the faint G′ line or whether these are characteristic of *cyclo*propane compounds. It will be noted that two values of the mean constants are given in the table; the first set of figures, which excludes the apparently low results for di-*n*-propyl *cyclo*propane-1 : 1-dicarboxylate, is considered to be more trustworthy.

The contributions of the four-membered carbon ring have been similarly calculated from new measurements upon esters of *cyclo*butane-carboxylic and -1 : 1-dicarboxylic acids and upon the first acid itself; the reference data for alkyl *n*-valerates and *n*-propylmalonates are given in Part XIII and for *n*-valeric acid in Part XX (*locc. cit.*). Precision measurements with the Hilger–Chance refractometer must decide whether the apparently anomalous values for $R_{G'}$ are real or are due to experimental error. The results are collected in Table II.

TABLE II.

Values for the four-carbon ring from cyclo*butane compounds.*

	P.	R_C.	R_D.	R_F.	$R_{G'}$.	$Mn_D^{20°}$.
*cyclo*Butanecarboxylic acid	11·1	0·36	0·37	0·38	0·37	−4·40
Me *cyclo*butanecarboxylate	10·0	0·31	0·33	0·33	0·32	−4·63
Et *cyclo*butanecarboxylate	10·2	0·29	0·31	0·32	0·32	−4·68
Pr^n *cyclo*butanecarboxylate	10·0	0·32	0·35	0·34	0·35	−4·78
Bu^n *cyclo*butanecarboxylate	10·3	0·36	0·36	0·38	0·38	−4·72
Am^n *cyclo*butanecarboxylate	9·9	0·26	0·29	0·29	0·28	−4·63
Me_2 *cyclo*butane-1 : 1-dicarboxylate	10·2	0·32	0·34	0·37	0·34	−4·48
Et_2 *cyclo*butane-1 : 1-dicarboxylate	9·5	0·26	0·26	0·29	0·28	−4·83
Pr^n_2 *cyclo*butane-1 : 1-dicarboxylate	9·7	0·31	0·31	0·35	0·34	−4·82
Bu^n_2 *cyclo*butane-1 : 1-dicarboxylate	9·2	0·24	0·25	0·27	0·24	−4·71
Mean	10·0	0·303	0·317	0·332	0·322	−4·67

EXPERIMENTAL.

Physical Measurements.—Full details applying to this and the subsequent papers of this series are given in Part VII (*J.*, 1943, 18). Surface tensions were measured by the method of capillary rise, and only the values for *H* (= *h* − 0·24 mm.) are given. The constants for the various apparatus are: *A* 1·8725, *B* 2·3449, *C* 2·3740, *D* 2·4696, *E* 2·3290, *F* 2·3282. Unless otherwise stated, all b. p.s are corrected. Measurements of the refractive indices were made at 20° ± 0·05° on a Zeiss Pulfrich refractometer; with some compounds the G′ line was so faint that setting of the crosswires was less accurate than for the *C* and *F* lines.

Previous Work.—The larger proportion of the measurements described in this and succeeding papers of this series are new. The constants deduced will in all cases be based upon the measurements from this laboratory. In order to economise space, no reference will be made (save in exceptional circumstances) to previous work since this can be found in I.C.T., Landolt–Börnstein "Tabellen", or the original literature.

Preparation of Pure Compounds.—cyclo*Propyl methyl ketone.* The Eastman–Kodak product was dried ($CaSO_4$) and distilled through a Widmer column in an all-glass apparatus. A middle fraction, b. p. 111°/757 mm. (semicarbazone, m. p. 117°), was used for the physical measurements.

cyclo*Propanecarboxylic acid.* Decomposition of *cyclo*propane-1 : 1-dicarboxylic acid, m. p. 136—137°, by heating at 160° until evolution of carbon dioxide ceased yielded crude *cyclo*propanecarboxylic acid, b. p. 185—195°. The physical properties of the liquid were anomalous owing to the presence of a considerable quantity of γ-butyrolactone (Perkin, *J.*, 1885, **47**, 815; Bone and Perkin, *J.*, 1895, **67**, 117); a middle fraction, b. p. 188°, had $d_{4°}^{20°}$ 1·1148, $n_D^{20°}$ 1·4395. Upon dissolving the crude acid in dilute sodium carbonate solution, extracting with ether to remove the butyrolactone, acidifying with dilute sulphuric acid at 0°, and extracting with ether, fairly pure *cyclo*propanecarboxylic acid, b. p. 184—185°, was obtained in poor yield: this had $d_{4°}^{20°}$ 1·0891, $n_D^{20°}$ 1·4376 (Bruylants, *Bull. Soc. chim. Belg.*, 1929, **38**, 133, gives $d_{4°}^{20°}$ 1·0885, $n_D^{20°}$ 1·43901 for the acid presumably prepared by hydrolysis of *cyclo*propyl cyanide).

The most convenient method for the preparation of the pure acid in quantity was the oxidation of the readily available *cyclo*propyl methyl ketone (compare *Org. Synth.*, 1944, **24**, 36). In a 3-l. three-necked flask, equipped with a dropping funnel, mechanical stirrer, and thermometer, was placed a solution of 165 g. of sodium hydroxide in 1400 ml. of water, cooled to 0—2°, and 240 g. of A.R. bromine were added with stirring at such a rate that the temperature did not rise above 10°. The sodium hypobromite solution was cooled to 0°; redistilled *cyclo*propyl methyl ketone, b. p. 110·5—111·5°/757 mm., was added with stirring so that the temperature did not rise above 10°. The ice-bath was then removed, and the stirring continued for a further 2 hours. The mixture was steam-distilled to remove the bromoform (105—115 g.; a little solid carbon tetrabromide may separate in the condenser). The liquid was cooled in ice, acidified to Congo-red with concentrated hydrochloric acid, a little sodium hydrogen sulphite added to remove the very pale yellow colour, and the acid isolated by saturation with salt and extraction with ether (4 × 300 ml.). Removal of the solvent and distillation under reduced pressure yielded 36 g. of pure *cyclo*propanecarboxylic acid, b. p. 97°/27 mm., m. p. 17—17·5°. Slight decomposition occurs upon distillation at atmospheric pressure: b. p. 179—180°, m. p. 15·5—16·5°.

Methyl cyclo*propanecarboxylate.* An all-glass apparatus, provided with a reflux condenser and dropping funnel, was charged with 100 g. of redistilled thionyl chloride and 52 g. of pure *cyclo*propanecarboxylic acid were slowly added. The mixture was refluxed for 30 minutes and then distilled through an all-glass Dufton column; 53 g. of the acid chloride, b. p. 119—119·5°/763 mm., were collected.

10·5 G. of pure anhydrous methyl alcohol were placed in an all-glass apparatus (50 ml. round-bottomed flask fitted with an adapter carrying a condenser and a dropping funnel equipped with guard tubes), cooled in ice, and 33 g. of the acid chloride added during 30 minutes. The mixture was kept at room temperature for 5 hours, poured into water, the ester separated, washed successively with saturated sodium hydrogen carbonate solution and water, dried ($CaSO_4$), and distilled. The yield of ester, b. p. 117·5°/761 mm., was 11 g.

Ethyl cyclo*propanecarboxylate.* 10·1 G. of absolute ethyl alcohol and 22 g. of the acid chloride, after standing at room temperature for 90 minutes, gave 13 g. of the ester, b. p. 133°/763 mm.

n-*Propyl* cyclo*propanecarboxylate.* 13·2 G. of absolute *n*-propyl alcohol and 22 g. of the acid chloride, after standing at room temperature for 5 hours, afforded 13 g. of the *ester*, b. p. 155°/766 mm. (Found : C, 65·8; H, 9·2. $C_7H_{12}O_2$ requires C, 65·6; H, 9·4%).

n-*Butyl* cyclo*propanecarboxylate.* 11·8 G. of pure *n*-butyl alcohol and 16 g. of the acid chloride gave, after standing for 1 hour at room temperature, 19 g. of the *ester*, b. p. 175°/759 mm. (Found : C, 67·5; H, 9·7. $C_8H_{14}O_2$ requires C, 67·6; H, 9·9%).

n-*Amyl* cyclo*propanecarboxylate.* 13·2 G. of Boots synthetic *n*-amyl alcohol and 15 g. of the acid chloride gave, after standing for 1 hour at room temperature, 13 g. of the ester, b. p. 193°/753 mm. Redistillation yielded the pure *ester*, b. p. 87°/17 mm. (Found : C, 69·1; H, 10·1. $C_9H_{16}O_2$ requires C, 69·2; H, 10·3%).

cyclo*Propane*-1 : 1-*dicarboxylic acid.* This was prepared by condensation of ethyl sodiomalonate [from sodium, "super-dry" ethyl alcohol (by ethyl phthalate method), and dry ethyl malonate] and dry ethylene dibromide (compare Part I, *J.*, 1934, 337) or preferably from ethyl sodiocyanoacetate and ethylene dibromide (compare Carpenter and Perkin, *J.*, 1899, **75**, 924; Jones and Scott, *J. Amer. Chem. Soc.*, 1922, **44**, 413). The acid is best isolated by continuous ether extraction, and after two recrystallisations from ether–light petroleum (b. p. 60—80°) had m. p. 136—137°.

Diethyl cyclo*propane*-1 : 1-*dicarboxylate.* A mixture of 19·5 g. of the acid, 28 g. of absolute ethyl alcohol, 9 g. of concentrated sulphuric acid, and 55 ml. of sodium-dried A.R. benzene was refluxed for 20 hours and then poured into excess of water. The benzene layer was separated, the aqueous phase was extracted once with ether, and the combined benzene and ether extracts washed successively with water, saturated sodium hydrogen carbonate solution, and water, dried ($MgSO_4$), the solvents removed at atmospheric pressure, and the residue distilled under reduced pressure. The yield of diethyl ester, b. p. 114°/22 mm., was 16 g.

Di-n-*propyl* cyclo*propane*-1 : 1-*dicarboxylate.* A similar preparation, but with 42 g. of absolute *n*-propyl alcohol, gave 17 g. of *di*-n-*propyl* cyclo*propane*-1 : 1-*dicarboxylate*, b. p. 124°/12 mm. (Found : C, 61·5; H, 8·7. $C_{11}H_{18}O_4$ requires C, 61·7; H, 8·5%).

cyclo*Butane*-1 : 1-*dicarboxylic acid.* The yield of acid obtained by condensation of 212 g. of trimethylene dibromide with ethyl sodiomalonate (from 46 g. of sodium, 800 ml. of absolute ethyl alcohol, and 160 g. of ethyl malonate) according to the procedure of *Org. Synth.*, 1943, **23**, 16 (compare Perkin, *J.*, 1887, **51**, 1) can be increased from 30—34 g. to 50—51 g. by the use of perfectly dry materials, *i.e.*, trimethylene dibromide and ethyl malonate dried over anhydrous calcium sulphate, and absolute ethyl alcohol dried by the ethyl phthalate method. The resulting *cyclo*butane-1 : 1-dicarboxylic acid has m. p. 158° unaffected by recrystallisation.

Dimethyl cyclo*butane*-1 : 1-*dicarboxylate.* A mixture of 21·6 g. of the acid, 20 g. of absolute methyl alcohol, 9 g. of concentrated sulphuric acid, and 50 ml. of sodium-dried A.R. benzene was refluxed for 22 hours and yielded, when worked up as detailed for diethyl *cyclo*propane-1 : 1-dicarboxylate, 17 g. of ester, b. p. 87°/8 mm.

Diethyl cyclo*butane*-1 : 1-*dicarboxylate.* This ester was similarly prepared from 28 g. of absolute ethyl alcohol; yield 16 g., b. p. 101·5°/11 mm.

Di-n-*propyl* cyclo*butane*-1 : 1-*dicarboxylate.* In like manner, but from 42 g. of absolute *n*-propyl alcohol and with 34 hours' refluxing, 23 g. of this *ester*, b. p. 129°/13 mm. (Found : C, 63·3; H, 8·8. $C_{12}H_{20}O_4$ requires C, 63·1; H, 8·8%), were obtained.

Di-n-*butyl* cyclo*butane*-1 : 1-*dicarboxylate.* A mixture of 14·4 g. of the acid, 28·2 g. of pure *n*-butyl alcohol, 6 g, of concentrated sulphuric acid, and 40 ml. of dry benzene was refluxed for 22 hours and gave 16 g. of the *ester*, b. p. 146°/11 mm. (Found : C, 65·7; H, 9·3. $C_{14}H_{24}O_4$ requires C, 65·6; H, 9·4%).

cyclo*Butanecarboxylic acid.* The 1 : 1-dicarboxylic acid, m. p. 158°, was decomposed by heating above the m. p. (*Org. Synth.*, 1943, **23**, 17) and gave an 88% yield of the pure acid, b. p. 195·5°/765 mm. (compare *op. cit.*, which gives b. p. 191·5—193·5°/740 mm.).

Methyl cyclo*butanecarboxylate.* The reaction between 100 g. of redistilled thionyl chloride and 65 g. of pure *cyclo*butanecarboxylic acid yielded, as for the *cyclo*propane compound, 62 g. of the acid chloride, b. p. 136—137°/762 mm.

The preparation of all the esters from this acid chloride was conducted as detailed for methyl *cyclo*propanecarboxylate; after the addition of the acid chloride to the appropriate alcohol cooled to 0°, the mixture was kept at room temperature for 60—90 minutes before being poured into water, etc. Thus 38 g. of the acid chloride and 15 g. of absolute methyl alcohol afforded 30 g. of methyl *cyclo*butanec arboxylate, b. p. 134·5°/764 mm.

Ethyl cyclo*butanecarboxylate.* From 18 g. of the acid chloride and 8·0 g. of absolute ethyl alcohol, the yield of ester, b. p. 152°/762 mm., was 13 g.

n-*Propyl* cyclo*butanecarboxylate.* From 22·5 g. of the acid chloride and 13·0 g. of pure *n*-propyl alcohol, the yield of *ester*, b. p. 172°/765 mm., was 23 g. (Found : C, 67·5; H, 9·9. $C_8H_{14}O_2$ requires C, 67·6; H, 9·9%).

n-*Butyl* cyclo*butanecarboxylate.* From 20·1 g. of acid chloride and 13·8 g. of absolute *n*-butyl alcohol, the yield of *ester*, b. p. 98°/32 mm., was 22 g. (Found : C, 69·2; H, 10·2. $C_9H_{16}O_2$ requires C, 69·2; H, 10·3%).

n-*Amyl* cyclo*butanecarboxylate.* From 22·0 g. of the acid chloride and 19·4 g. of Boots synthetic *n*-amyl alcohol, the yield of *ester*, b. p. 105°/20 mm., was 22 g. (Found : C, 70·5; H, 10·8. $C_{10}H_{18}O_2$ requires C, 70·6; H, 10·7%).

The results of the physical measurements upon the freshly distilled compounds are collected below. The numbering of compounds in Clarendon type follows from Part XVII (this vol., p. 683). Reference to compounds, the preparation of which is described in preceding or succeeding papers of this series, will be abbreviated to, *e.g.*, XVII, **418**.

419. cyclo*Propyl methyl ketone.* B. p. 111°/757 mm.; *M* 84·11; n_C 1·42243, n_D 1·42496, n_F 1·43116, $n_{G'}$ 1·43555; R_C 23·78, R_D 23·91, R_F 24·22, $R_{G'}$ 24·43; $Mn_D^{20°}$ 119·86. Densities determined: $d_{4°}^{20°}$ 0·8994, $d_{4°}^{40·0°}$ 0·8803, $d_{4°}^{63·7°}$ 0·8575, $d_{4°}^{87·7°}$ 0·8332. Apparatus *E*.

(These headings apply to all subsequent tables in this paper.)

t.	*H*.	$d^{t°}$.	γ.	*P*.	*t*.	*H*.	$d_{4°}^{t°}$.	γ.	*P*.
17·9°	14·67	0·9014	30·80	219·8	60·9°	12·77	0·8602	25·58	219·9
21·3	14·54	0·8981	30·41	219·9	87·1	11·67	0·8338	22·66	220·1
40·9	13·67	0·8794	28·00	220·0				Mean	219·9

420. cyclo*Propanecarboxylic acid.* B. p. 97°/27 mm., m. p. 17·5°; *M* 86·09; n_C 1·43562, n_D 1·43832, n_F 1·44448, $n_{G'}$ 1·44922; R_C 20·65, R_D 20·77, R_F 21·02, $R_{G'}$ 21·21; $Mn_D^{20°}$ 123·82. Densities determined: $d_{4°}^{20°}$ 1·0889, $d_{4°}^{40·0°}$ 1·0707, $d_{4°}^{60·2°}$ 1·0514, $d_{4°}^{86·5°}$ 1·0262. Apparatus *E*.

22·4°	13·55	1·0867	34·29	191·7	60·9°	12·31	1·0508	30·13	191·9
40·1	12·95	1·0706	32·29	191·7	85·9	11·56	1·0267	27·64	192·3
								Mean	191·9

421. *Methyl* cyclo*propanecarboxylate.* B. p. 117·5°/763 mm.; *M* 100·11; n_C 1·41637, n_D 1·41866, n_F 1·42424, $n_{G'}$ 1·42825; R_C 25·21, R_D 25·34, R_F 25·63, $R_{G'}$ 25·84; $Mn_D^{20°}$ 142·03. Densities determined: $d_{4°}^{20°}$ 0·9972, $d_{4°}^{40·3°}$ 0·9759, $d_{4°}^{63·6°}$ 0·9508, $d_{4°}^{86·5°}$ 0·9272. Apparatus *E*.

20·0°	13·26	0·9972	30·80	236·5	61·5°	11·54	0·9530	25·61	236·3
23·1	13·18	0·9940	30·51	236·7	86·2	10·52	0·9275	22·72	236·0
40·9	12·37	0·9753	28·10	236·3				Mean	236·4

422. *Ethyl* cyclo*propanecarboxylate.* B. p. 133°/763 mm.; *M* 114·14; n_C 1·41789, n_D 1·42076, n_F 1·42573, $n_{G'}$ 1·42979; R_C 29·84, R_D 30·02 R_F 30·33, $R_{G'}$ 30·58; $Mn_D^{20°}$ 162·17. Densities determined: $d_{4°}^{20°}$ 0·9638, $d_{4°}^{40·0°}$ 0·9434, $d_{4°}^{63·4°}$ 0·9196, $d_{4°}^{86·2°}$ 0·8949. Apparatus *E*.

20·9°	12·94	0·9629	29·02	275·1	61·1°	11·28	0·9219	24·22	274·7
41·3	12·15	0·9421	26·66	275·3	85·9	10·36	0·8952	21·60	274·9
								Mean	275·0

423. n-*Propyl* cyclo*propanecarboxylate.* B. p. 155°/766 mm.; *M* 128·27; n_C 1·42216, n_D 1·42446, n_F 1·43011, $n_{G'}$ 1·43395; R_C 34·54, R_D 34·70, R_F 35·10, $R_{G'}$ 35·38; $Mn_D^{20°}$ 182·72. Densities determined: $d_{4°}^{20°}$ 0·9441, $d_{4°}^{41·0°}$ 0·9240, $d_{4°}^{62·8°}$ 0·9029, $d_{4°}^{87·3°}$ 0·8794. Apparatus *E*.

19·8°	13·21	0·9443	29·05	315·4	61·2°	11·58	0·9044	24·39	315·2
22·7	13·08	0·9415	28·68	315·2	85·7	10·68	0·8809	21·91	315·0
40·7	12·34	0·9243	26·56	315·1				Mean	315·2

424. n-*Butyl* cyclo*propanecarboxylate.* B. p. 175°/759 mm.; *M* 142·19; n_C 1·42620, n_D 1·42847, n_F 1·43404, $n_{G'}$ 1·43813; R_C 39·17, R_D 39·36, R_F 39·80, $R_{G'}$ 40·12; $Mn_D^{20°}$ 203·12. Densities determined: $d_{4°}^{20°}$ 0·9304, $d_{4°}^{40·0°}$ 0·9136, $d_{4°}^{61·5°}$ 0·8944, $d_{4°}^{85·6°}$ 0·8714. Apparatus *E*.

25·8°	13·16	0·9254	28·36	354·6	62·2°	11·82	0·8936	24·60	354·4
40·7	12·58	0·9130	26·75	354·2	85·7	10·96	0·8713	22·24	354·4
								Mean	354·4

425. n-*Amyl* cyclo*propanecarboxylate.* B. p. 193°/753 mm. followed by 87°/17 mm.; *M* 156·22; n_C 1·42976, n_F 1·43219, n_F 1·43765, $n_{G'}$ 1·44174; R_C 43·74, R_D 43·96, R_F 44·45, $R_{G'}$ 44·80; $Mn_D^{20°}$ 223·74. Densities determined: $d_{4°}^{20°}$ 0·9221, $d_{4°}^{41·5°}$ 0·9034, $d_{4°}^{60·4°}$ 0·8870, $d_{4°}^{85·9°}$ 0·8639. Apparatus *E*.

15·6°	13·73	0·9259	29·61	393·6	61·5°	11·99	0·8861	24·74	393·2
40·5	12·84	0·9043	27·04	393·9	86·7	11·14	0·8623	22·37	394·0
								Mean	393·7

426. *Diethyl* cyclo*propane*-1 : 1-*dicarboxylate.* B. p. 114°/22 mm.; *M* 186·20; n_C 1·43078, n_D 1·43310, n_F 1·43881, $n_{G'}$ 1·44264; R_C 45·38, R_D 45·60, R_F 46·12, $R_{G'}$ 46·47; $Mn_D^{20°}$ 266·84. Densities determined: $d_{4°}^{20°}$ 1·0615, $d_{4°}^{40·0°}$ 1·0419, $d_{4°}^{60·5°}$ 1·0217, $d_{4°}^{85·3°}$ 0·9962. Apparatus *E*.

16·2°	12·99	1·0653	32·23	416·5	60·3°	11·50	1·0219	27·37	416·8
19·9	12·88	1·0616	31·85	416·7	86·2	10·71	0·9953	24·83	417·6
41·3	12·10	1·0406	29·33	416·4				Mean	416·8

427. *Di*-n-*propyl* cyclo*propane*-1 : 1-*dicarboxylate.* p. 124°/12 mm.; *M* 214·25; n_C 1·43520, n_D 1·43751, n_F 1·44321, $n_{G'}$ 1·44711; R_C 54·57, R_D 54·82, R_F 55·44, $R_{G'}$ 55·87; $Mn_D^{20°}$ 307·98. Densities determined: $d_{4°}^{20°}$ 1·0249, $d_{4°}^{40·5°}$ 1·0052, $d_{4°}^{60·5°}$ 0·9864, $d_{4°}^{86·7°}$ 0·9622. Apparatus *E*.

18·7°	13·16	1·0262	31·45	494·4	61·5°	11·64	0·9854	26·71	494·3
40·4	12·28	1·0053	28·75	493·5	86·8	10·85	0·9621	24·31	494·5
								Mean	494·2

428. *Dimethyl* cyclo*butane*-1 : 1-*dicarboxylate*.* B. p. 87°/8 mm.; *M* 172·18; n_C 1·43920, n_D 1·44154, n_F 1·44079, $n_{G'}$ 1·45100; R_C 40·52, R_D 40·70, R_F 41·15, $R_{G'}$ 41·46; $Mn_D^{20°}$ 248·20. Densities determined: $d_{4°}^{20°}$ 1·1182, $d_{4°}^{40·2°}$ 1·0981, $d_{4°}^{60·3°}$ 1·0786, $d_{4°}^{91·9°}$ 1·0464. Apparatus E.

t.	*H*.	$d_{4°}^{t°}$.	γ.	*P*.	*t*.	*H*.	$d_{4°}^{t°}$.	γ.	*P*.
20·4°	13·49	1·1178	35·12	375·0	60·8°	12·12	1·0781	30·43	375·1
40·1	12·76	1·09882	32·62	374·7	85·0	11·30	1·0532	27·72	375·1
								Mean	375·0

429. *Diethyl* cyclo*butane*-1 : 1-*dicarboxylate*. B. p. 101·5°/11 mm.; *M* 200·23; n_C 1·43364, n_D 1·43590, n_F 1·44140, $n_{G'}$ 1·44539; R_C 49·78, R_D 50·01, R_F 50·56, $R_{G'}$ 50·96; $Mn_D^{20°}$ 287·51. Densities determined: $d_{4°}^{20°}$ 1·0466, $d_{4°}^{40·2°}$ 1·0271, $d_{4°}^{60·8°}$ 1·0075, $d_{4°}^{86·0°}$ 0·9831. Apparatus *E*.

13·4°	13·14	1·0530	32·22	453·1	60·1°	11·59	1·0082	27·21	453·6
18·9	12·98	1·0477	31·67	453·4	87·1	10·72	0·9820	24·52	453·7
40·2	12·33	1·0271	29·49	454·3				Mean	453·6

430. *Di*-n-*propyl* cyclo*butane*-1 : 1-*dicarboxylate*. B. p. 129°/13 mm.; *M* 228·28; n_C 1·43689, n_D 1·43913, n_F 1·44467, $n_{G'}$ 1·44875; R_C 59·07, R_D 59·33, R_F 59·99, $R_{G'}$ 60·47; $Mn_D^{20°}$ 328·52. Densities determined: $d_{4°}^{20°}$ 1·0122, $d_{4°}^{40·9°}$ 0·9937, $d_{4°}^{60·0°}$ 0·9767, $d_{4°}^{86·7°}$ 0·9527. Apparatus *E*.

25·1°	12·89	1·0077	30·22	531·3	61·3°	11·73	0·9755	26·65	531·7
40·4	12·38	0·9941	28·66	531·3	86·4	10·95	0·9530	24·30	531·9
								Mean	531·6

431. *Di*-n-*butyl* cyclo*butane*-1 : 1-*dicarboxylate*. B. p. 146°/11 mm.; *M* 256·33; n_C 1·43976, n_D 1·44205, n_F 1·44765, $n_{G'}$ 1·45163; R_C 68·18, R_D 68·49, R_F 69·24, $R_{G'}$ 69·76; $Mn_D^{20°}$ 369·65. Densities determined: $d_{4°}^{20°}$ 0·9905, $d_{4°}^{40·6°}$ 0·9724, $d_{4°}^{59·7°}$ 0·9566, $d_{4°}^{85·9°}$ 0·9905. Apparatus *E*.

23·9°	13·03	0·9871	29·96	607·5	61·1°	11·83	0·9544	26·20	608·3
40·7	12·57	0·9723	28·46	608·9	86·2	11·15	0·9344	24·26	609·1
								Mean	608·5

432. cyclo*Butanecarboxylic acid*. B. p. 195·5°/772 mm.; *M* 100·11; n_C 1·44115, n_D 1·44355, n_F 1·44932, $n_{G'}$ 1·45337; R_C 25·02, R_D 25·14, R_F 25·42, $R_{G'}$ 25·62; $Mn_D^{20°}$ 144·52. Densities determined: $d_{4°}^{20°}$ 1·0570, $d_{4°}^{40·0°}$ 1·0399, $d_{4°}^{60·5°}$ 1·0217. $d_{4°}^{85·3°}$ 0·9997. Apparatus *A*.

22·8°	16·93	1·0546	33·43	228·3	60·2°	15·47	1·0220	29·60	228·5
28·5	16·66	1·0496	32·74	228·2	86·9	14·34	0·9983	26·81	228·2
40·3	16·12	1·0396	31·38	227·8				Mean	228·2

433. *Methyl* cyclo*butanecarboxylate*. B. p. 134·5°/754 mm.; *M* 114·14; n_C 1·42354, n_D 1·42596, n_F 1·43111, $n_{G'}$ 1·43505; R_C 29·56, R_D 29·71, R_F 30·02, $R_{G'}$ 30·26; $Mn_D^{20°}$ 162·76. Densities determined: $d_{4°}^{20°}$ 0·9844, $d_{4°}^{39·8°}$ 0·9645, $d_{4°}^{61·5}$ 0·9429, $d_{4°}^{86·9°}$ 0·9161. Apparatus *E*.

19·3°	13·54	0·9851	31·06	273·6	61·9°	11·74	0·9425	25·77	272·9
42·3	12·43	0·9620	27·85	272·6	86·8	10·76	0·9162	22·96	272·7
								Mean	273·0

434. *Ethyl* cyclo*butanecarboxylate*. B. p. 152°/762 mm.; *M* 128·17; n_C 1·42353, n_D 1·42581, n_F 1·43103, $n_{G'}$ 1·43498; R_C 34·24, R_D 34·41, R_F 34·78, $R_{G'}$ 35·06; $Mn_D^{20°}$ 192·74. Densities determined: $d_{4°}^{20°}$ 0·9540, $d_{4°}^{40·2°}$ 0·9346, $d_{4°}^{60·7°}$ 0·9143, $d_{4°}^{86·3°}$ 0·8895. Apparatus *E*.

15·1°	13·46	0·9589	30·06	313·0	61·7°	11·52	0·9133	24·50	312·2
20·9	13·22	0·9531	29·35	313·0	89·1	10·45	0·8863	21·57	311·7
40·7	12·30	0·9341	26·76	312·1				Mean	312·4

435. n-*Propyl* cyclo*butanecarboxylate*. B. p. 172°/765 mm.; *M* 142·19; n_C 1·42680, n_D 1·42912, n_F 1·43430, $n_{G'}$ 1·43835; R_C 38·86, R_D 39·06, R_F 39·46, $R_{G'}$ 39·79; $Mn_D^{20°}$ 203·20. Densities determined: $d_{4°}^{20°}$ 0·9389, $d_{4°}^{42·5°}$ 0·9181, $d_{4°}^{61·3°}$ 0·9007, $d_{4°}^{86·5°}$ 0·8766. Apparatus *E*.

17·2°	13·43	0·9415	29·45	351·8	63·2°	11·74	0·8980	24·55	352·5
41·4	12·59	0·9191	26·95	352·5	87·6	10·85	0·8758	22·13	352·1
								Mean	352·2

436. n-*Butyl* cyclo*butanecarboxylate*. B. p. 98°/32 mm.; *M* 156·22; n_C 1·43052, n_D 1·43274, n_F 1·43809, $n_{G'}$ 1·44200; R_C 43·46, R_D 43·66, R_F 44·13, $R_{G'}$ 44·48; $Mn_D^{20°}$ 223·82. Desnities determined: $d_{4°}^{20°}$ 0·9294, $d_{4}^{42·7°}$ 0·9093, $d_{4°}^{62·3°}$ 0·8924, $d_{4°}^{85·2°}$ 0·8732. Apparatus *E*.

15·4°	13·74	0·9334	29·87	391·3	61·9°	12·10	0·8928	25·16	391·9
18·3	13·61	0·9309	29·51	391·1	86·3	11·30	0·8722	22·95	392·0
41·6	12·82	0·9101	27·17	391·9				Mean	391·6

* The results for this new preparation supersede those in Part I, *J.*, 1934, 340.

437. n-*Amyl* cyclo*butanecarboxylate.* B. p. 105°/20 mm.; M 170·24; n_C 1·43362, n_D 1·43600, n_F 1·44131, $n_{G'}$ 1·44533; R_C 48·06, R_D 48·30, R_F 48·80, $R_{G'}$ 49·19; $Mn_D^{20°}$ 244·46. Densities determined: $d_{4°}^{20°}$ 0·9217, $d_{4°}^{41·6°}$ 0·9031, $d_{4°}^{61·3°}$ 0·8863, $d_{4°}^{85·7°}$ 0·8652. Apparatus *E*.

t.	*H*.	$d_{4°}^{t°}$.	γ.	*P*.	*t*.	*H*.	$d_{4°}^{t°}$.	γ.	*P*.
16·1°	13·85	0·9251	29·84	430·1	61·7°	12·24	0·8860	25·26	430·7
41·3	12·91	0·9034	27·16	430·2	86·8	11·43	0·8643	23·01	431·4
								Mean	430·6

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