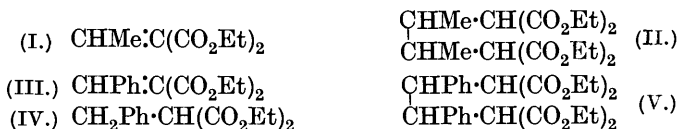CCLXII.—*Syntheses of Cyclic Compounds. Part III. The Reduction of Some Unsaturated Cyano-esters by Moist Aluminium Amalgam. A New Synthesis of Mono-substituted Malonic Acids and of βββ'β'- Tetramethyladipic Acid. Further Evidence for the Multiplanar Configuration of the cycloHeptane Ring.*
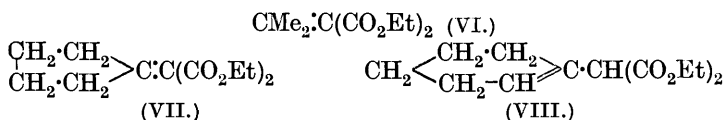
By ISRAEL VOGEL.

IN previous communications (J., 1927, 1985; this vol., p. 1013) it has been shown that whereas ethyl ethylidenemalonate (I) on reduction with moist aluminium amalgam yields almost exclusively the bimolecular compound (II), ethyl benzylidenemalonate (III) yields a mixture of the unimolecular compound (IV) and the bimolecular compound (V) in the proportion of approximately 2 to 1, a result which is obviously due to the presence of the phenyl group (compare Haerdi and Thorpe, J., 1925, **127**, 1237). It was clearly

desirable to study the corresponding *gem*-dimethyl, *cyclo*pentane, and *cyclo*hexane compounds in order to obtain some further inform-

(I.) $CHMe\overset{..}{:}C(CO_2Et)_2$

$\begin{array}{l}CHMe\cdot CH(CO_2Et)_2 \\ CHMe\cdot CH(CO_2Et)_2\end{array}$ (II.)

(III.) $CHPh\overset{..}{:}C(CO_2Et)_2$

$\begin{array}{l}CHPh\cdot CH(CO_2Et)_2 \\ CHPh\cdot CH(CO_2Et)_2\end{array}$ (V.)
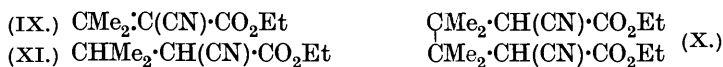
(IV.) $CH_2Ph\cdot CH(CO_2Et)_2$

ation as to the effect of substituents. The *gem*-dimethyl compound, ethyl *iso*propylidenemalonate (VI), had already been prepared in poor yield by Meyenberg (*Ber.*, 1895, **28**, 785), but although an improved method for its preparation has been developed, this compound was not considered suitable for investigation, since it could not be completely freed from ethyl malonate by simple means.

$$CMe_2\overset{..}{:}C(CO_2Et)_2 \quad (VI.)$$

$\begin{array}{l}CH_2\cdot CH_2 \\ CH_2\cdot CH_2\end{array}\!\!>\!\!C\overset{..}{:}C(CO_2Et)_2$

(VII.)

$CH_2\!\!<\!\!\begin{array}{l}CH_2\cdot CH_2 \\ CH_2-CH\end{array}\!\!\!>\!\!C\cdot CH(CO_2Et)_2$

(VIII.)

The *cyclo*pentane analogue (VII) is likewise difficult to prepare in a state of purity (Kon and Speight, J., 1926, 2727); and the *cyclo*hexane compound (VIII) normally possesses the βγ-structure (Kon and Speight, *loc. cit.*), rendering it valueless for the work in view. The unsaturated cyano-esters, however, were obtained in good yield and in a state of purity.
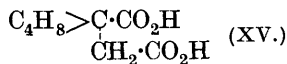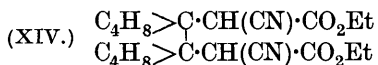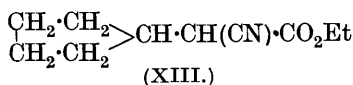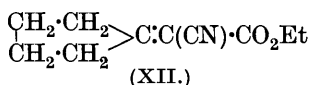
Ethyl *iso*propylidenecyanoacetate (IX) (Komppa, *Ber.*, 1900, **33**, 3530; Scheiber and Meisel, *Ber.*, 1915, **48**, 238; Birch and Kon, J., 1923, **123**, 2443) on reduction with moist aluminium amalgam in ether gave ethyl *r-iso*propylcyanoacetate (XI) (main product)

(IX.) $CMe_2\overset{..}{:}C(CN)\cdot CO_2Et$

(XI.) $CHMe_2\cdot CH(CN)\cdot CO_2Et$

$\begin{array}{l}CMe_2\cdot CH(CN)\cdot CO_2Et \\ CMe_2\cdot CH(CN)\cdot CO_2Et\end{array}$ (X.)

together with the bimolecular compound, *ethyl* αδ-*dicyano*-ββγγ-*tetramethylbutane*-αδ-*dicarboxylate* (X). The constitution of (XI) was established by hydrolysis with alcoholic potash to *iso*propylmalonic acid (Conrad and Bischoff, *Annalen*, 1880, **204**, 144; Stohmann, Kleber, and Langbein, *J. pr. Chem.*, 1889, **40**, 211), and that of (X) by conversion into the crystalline *amide* on treatment with concentrated ammonia and into βββ'β'-tetramethyladipic acid (Farmer and Kracovski, J., 1926, 2318; 1927, 681) by hydrolysis with concentrated hydrochloric acid. Condensation of ethyl *iso*propylidenecyanoacetate with alcoholic potassium cyanide (compare Lapworth and McRae, J., 1922, **121**, 2741) gave a 60% yield of *as*-dimethylsuccinic acid—this appears to be the best method of preparing this compound; Higson and Thorpe's process (J., 1906,
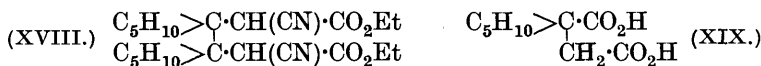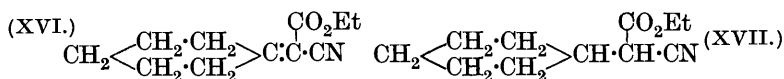
89, 1463) is less convenient and gives a smaller yield (40—45% ; Farmer and Kracovski, *loc. cit.*).

The reduction of ethyl *cyclo*pentylidenecyanoacetate (XII) (Harding and Haworth, J., 1910, **97**, 486) with moist aluminium

$$\begin{matrix} CH_2 \cdot CH_2 \\ CH_2 \cdot CH_2 \end{matrix} \!\!> \!\! C\!:\!C(CN)\cdot CO_2Et \qquad \begin{matrix} CH_2 \cdot CH_2 \\ CH_2 \cdot CH_2 \end{matrix} \!\!> \!\! CH\cdot CH(CN)\cdot CO_2Et$$

$$(XII.) \qquad\qquad (XIII.)$$

$$(XIV.) \quad \begin{matrix} C_4H_8 \!\!>\!\! \dot{C}\cdot CH(CN)\cdot CO_2Et \\ C_4H_8 \!\!>\!\! \dot{C}\cdot CH(CN)\cdot CO_2Et \end{matrix} \qquad \begin{matrix} C_4H_8 \!\!>\!\! \dot{C}\cdot CO_2H \\ CH_2\cdot CO_2H \end{matrix} \quad (XV.)$$

amalgam gave *ethyl* r-*cyclopentylcyanoacetate* (XIII) (which on hydrolysis with alcoholic potassium hydroxide yielded *cyclopentyl-malonic acid*) and a small quantity of a high-boiling bimolecular compound (XIV). Condensation of (XII) with alcoholic potassium cyanide gave a good yield of 1-carboxy*cyclo*pentane-1-acetic acid (XV), a compound first prepared in small quantity by Norris and Thorpe (J., 1921, **119**, 1208) by the oxidation of *cyclo*pentane-*spirocyclo*hexane-3 : 5-dione. The *anhydride* of this substituted succinic acid is only relatively slowly affected by water, concentrated hydrochloric acid, and by alkalis in the cold but is converted into the acid on boiling for a short time.
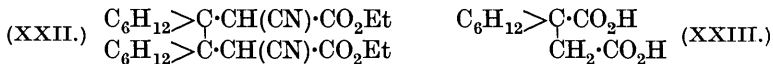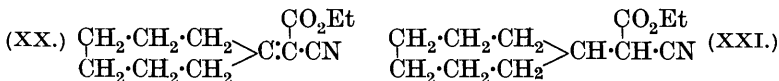
In a similar manner the main product of the reduction of ethyl *cyclo*hexylidenecyanoacetate (Harding, Haworth, and Perkin, J., 1908, **93**, 1943) (XVI) with moist aluminium amalgam was *ethyl* r-*cyclohexylcyanoacetate* (XVII), characterised by conversion into *cyclo*hexylmalonic acid on hydrolysis with alcoholic potassium hydroxide; a small quantity of the dicyano-ester (XVIII) was also produced. 1-Carboxy*cyclo*hexane-1-acetic acid is obtained in good

$$(XVI.) \quad CH_2 \!\!<\!\! \begin{matrix} CH_2\cdot CH_2 \\ CH_2\cdot CH_2 \end{matrix} \!\!>\!\! C\!:\!\overset{\displaystyle CO_2Et}{\underset{\displaystyle}{C}}\!\cdot CN \quad CH_2 \!\!<\!\! \begin{matrix} CH_2\cdot CH_2 \\ CH_2\cdot CH_2 \end{matrix} \!\!>\!\! CH\cdot \overset{\displaystyle CO_2Et}{\underset{\displaystyle}{C}}\!H\cdot CN \;(XVII.)$$

$$(XVIII.) \quad \begin{matrix} C_5H_{10} \!\!>\!\! \dot{C}\cdot CH(CN)\cdot CO_2Et \\ C_5H_{10} \!\!>\!\! \dot{C}\cdot CH(CN)\cdot CO_2Et \end{matrix} \qquad \begin{matrix} C_5H_{10} \!\!>\!\! \dot{C}\cdot CO_2H \\ CH_2\cdot CO_2H \end{matrix} \;(XIX.)$$

yield by the interaction of the unsaturated cyano-ester (XVI) and alcoholic potassium cyanide (Lapworth and McRae, J., 1922, **121**, 2741 ; compare Norris and Thorpe, J., 1921, **119**, 1209), and its anhydride has the remarkable property of being only slowly affected by water, aqueous sodium carbonate and by hydrochloric acid even on boiling. The anhydrides of these " cyclic " succinic acids appear to be intermediate in chemical properties between ordinary unsub-stituted anhydrides and those of tetraethyl- and tetrapropyl-succinic acids (Walker and Walker, J., 1905, **87**, 961 ; Crichton, J., 1906, **89**, 929), which are derived almost spontaneously from the

acids—an experimental fact in striking agreement with the Thorpe–Ingold theory. It is hoped to make a quantitative study of the ease of fission and of formation of these substituted anhydrides in the near future.

Suberone reacts with ethyl cyanoacetate in the presence of piperidine with the formation of *ethyl* cyclo*heptylidenecyanoacetate* (XX);

(XX.) $\begin{matrix} CH_2 \cdot CH_2 \cdot CH_2 \\ CH_2 \cdot CH_2 \cdot CH_2 \end{matrix} > C : \overset{\text{CO}_2\text{Et}}{\underset{}{C} \cdot CN}$ $\begin{matrix} CH_2 \cdot CH_2 \cdot CH_2 \\ CH_2 \cdot CH_2 \cdot CH_2 \end{matrix} > CH \cdot \overset{\text{CO}_2\text{Et}}{\underset{}{CH} \cdot CN}$ (XXI.)

(XXII.) $\begin{matrix} C_6H_{12} > C \cdot CH(CN) \cdot CO_2Et \\ C_6H_{12} > C \cdot CH(CN) \cdot CO_2Et \end{matrix}$ $\begin{matrix} C_6H_{12} > C \cdot CO_2H \\ CH_2 \cdot CO_2H \end{matrix}$ (XXIII.)

the yield, however, is less than those of the corresponding *gem*-dimethyl, *cyclo*pentane and *cyclo*hexane compounds. Reduction of (XX) with moist aluminium amalgam yielded *ethyl* r-cyclo*heptylcyanoacetate* (XXI) (characterised by the formation of cyclo*heptylmalonic acid* on hydrolysis with alcoholic potash) and the *dicyanoester* (XXII). The bimolecular compound (XXII) is produced in better yield than the corresponding *cyclo*hexane compound; the significance of this fact is discussed later (p. 2015). The condensation of ethyl *cyclo*heptylidenecyanoacetate with alcoholic potassium cyanide resulted in a good yield of 1-carboxy*cyclo*heptane-1-acetic acid (XXIII), a compound first prepared in minute amount by Dickens, Horton, and Thorpe (J., 1924, **125**, 1840) by the interaction of *cyclo*heptanonecyanohydrin and ethyl sodiocyanoacetate and subsequent hydrolysis. The *anhydride* resembles the *cyclo*hexane analogue in properties.

trans-β-Decalone (Hückel, *Annalen*, 1925, **441**, 1) condenses more readily than suberone with ethyl cyanoacetate in the presence of piperidine, yielding *ethyl* trans-*decahydro-β-naphthylidenecyanoacetate* (XXIV), which on reduction with moist aluminium amalgam gave only one r-trans-*decahydro-β-naphthylcyanoacetate* (XXV or XXVI), and only one *decahydro-β-naphthylmalonic acid*

(XXIV.)   (XXV.)   (XXVI.)

X = CH(CN)·CO₂Et
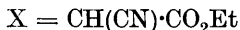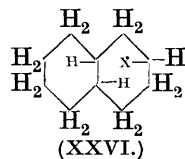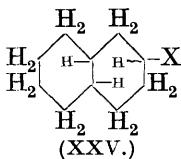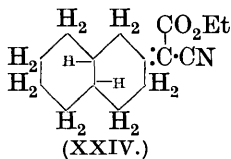
[X = CH(CO₂H)₂] was produced on hydrolysis of the latter with alcoholic potassium hydroxide. A careful search did not reveal the presence of the second theoretically possible saturated cyano-ester or malonic acid (compare Perkin and Sedgwick, J., 1924, **125**,

2437 ; 1925, **127**, 439, who were able to isolate only one octahydro-acridine by the reduction of tetrahydroacridone with sodium amalgam).

The results are in harmony with the complete mechanism of the aluminium amalgam reduction process (this vol., p. 1017). The poor yields of the bimolecular compounds must be attributed to the presence in CR_1R_2:$C(CN)$·CO_2Et of groups R_1R_2 of relatively large molecular volume —" the volume factor "—and also to the presence of the strongly negative cyano- and carbethoxyl groups—" the polar factor "—both of which will tend to render the formation of bimolecular layers difficult. Since the second effect is constant throughout the series, one has here a possible method of determining the configuration of simple rings. The *cyclo*pentane ring is usually regarded as having the relatively strainless uniplanar configuration, and the work of Thorpe and Ingold and their collaborators on *spiro*-compounds (J., 1915—1926), of Thorpe and others on ring-chain tautomerism (J., 1922 *et seq.*), and numerous incidental observations make it extremely probable that the *cyclo*hexane ring is relatively strained and has a uniplanar structure. On this basis, *i.e.*, assuming the uniplanar configurations of these rings, the angle θ (*vide infra*) has been computed by Thorpe and Ingold. It is suggested that the yields of bimolecular products are probably dependent on the tetrahedral angle θ, *i.e.*, on the strain in the ring. If this were so and the *cyclo*heptane ring had a uniplanar configuration, one would anticipate a progressive decrease in the yields of the bimolecular compounds on reduction of the appropriate unsaturated cyano-esters under comparable conditions. If, on the other hand, the strain in the *cyclo*heptane ring is relieved by its having a multiplanar structure, an increased yield of the bimolecular compound would be anticipated in the *cyclo*heptane series. The experimental results are exhibited in Table I and it will be seen that in every case more

TABLE I.

(A) CHR_1R_2·$CH(CN)$·CO_2Et	CR_1R_2·$CH(CN)$·CO_2Et CR_1R_2·$CH(CN)$·CO_2Et (B)		
CR_1R_2:$C(CN)$·CO_2Et.	R_1 $R_2$$>C<$θ.	Yield % (A).	Yield % (B).
R_1R_2 = *gem*-dimethyl	109·5°	63	21
CR_1R_2 = *cyclo*pentane	109·3	79	13
CR_1R_2 = *cyclo*hexane	107·2	84	6
CR_1R_2 = *cyclo*heptane	105·3	72	12

than 80% of the initial material has been accounted for and that there is no doubt that the yield of the bimolecular compound is much greater in the *cyclo*heptane than in the *cyclo*hexane series.

This, then, would appear to provide evidence for the multiplanar configuration of the seven-membered ring, a result in accord with the conclusions reached by other workers (compare Baker and Ingold, J., 1923, **123**, 122; Dickens, Horton, and Thorpe, J., 1924, **125**, 1830; Baker, J., 1925, **127**, 1678; Meerwein, *J. pr. Chem.*, 1922, **104**, 161). Physico-chemical evidence in support of this view is provided by measurements of the parachor (*vide infra*, p. 2018).

A few preliminary experiments, for which no great accuracy is claimed, were made on the effect of substituent groups on the rate of esterification in the succinic acid series. The yields of the diethyl esters under fairly comparable conditions for succinic acid, *as*-dimethylsuccinic acid and 1-carboxy*cyclo*pentane-1-acetic acid were respectively 74%, 65% and 62%; these are in agreement with what would be anticipated from the angles 115·3°, 109·5° and 109·3° calculated on the Thorpe–Ingold theory of valency deflexion. The results of a detailed investigation, comprising all the substituted succinic acids described in this paper, on the rates of hydrolysis and of esterification will form the subject of a future communication.

Various physical constants of some esters have been determined or calculated (see Tables II and III). The refractive indices are for the D line at about 20°; the exact temperatures are given in the experimental section. The surface tensions and densities were determined over a range of temperatures and have been reduced to 20°, a linear variation with temperature being assumed. The parachors $[P]$ (obs.) are computed from the formula $P = \gamma^{\frac{1}{4}} M/d$, where M is the molecular weight, γ is the surface tension, and d is the density at the same temperature. For the calculated values of the parachor, $\Sigma[P]$ (calc.), the structural and the atomic constants of Sugden (J., 1924, **125**, 1187 and subsequent papers) have been employed. The constants for the *cyclo*heptane * and decahydro-β-naphthalene rings have been taken as 3·6 and 12·2 respectively (*vide infra*). It will be seen (Table II) that there is a regular increase in the boiling point, refractive index, and surface tension as the size of the substituent ring is increased. The agreement between the observed and the calculated values of the parachor for the cyclic compounds is satisfactory; ethyl *r-iso*propylcyanoacetate exhibits an anomaly of − 5·0 which is due to the presence of the *gem*-dimethyl group. This negative anomaly in compounds containing *gem*-dimethyl groups has been previously observed by Sugden and Wilkins (J., 1927, 139) for ethyl caronate and by Sugden (this vol., p. 410) for certain phorone derivatives, but no explanation has yet been advanced.

* A provisional value deduced from the parachors of ethyl *cyclo*heptyl-cyanoacetate and suberone.
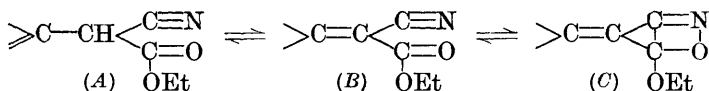
TABLE II.

Cyano-esters $CHR(CN) \cdot CO_2Et$.

	iso-Propyl.	cyclo-Pentyl.	cyclo-Hexyl.	cyclo-Heptyl.	Decahydro-β-naphthyl.
R =					
B. p. (mm.) ...	99°/16	129°/13	145°/14	149°/11	186°/12
n_D	1·4243	1·4536	1·4612	1·4664	1·4802
$d_{4^\circ}^{20^\circ}$	0·9855	1·0246	1·0210	1·0206	1·0301
$[R_L]_D$ (obs.) ...	40·08	47·86	52·39	56·78	68·73
$[R_L]_D$ (calc.)...	39·62	47·65	52·21	56·89	68·54
γ_{20°	31·82	34·77	35·58	36·09	36·33
$[P]$ (obs.)	374·8	430·1	467·6	502·7	594·6
$\Sigma[P]$ (calc.) ...	379·8	431·6	468·7	505·2	596·6

TABLE III.

	(XVI.)	(XX.)	(XXIV.)	(III.)	(IV.)
B. p. (mm.) ...	151°/12	160°/12	196°/14	179·5°/14	163°/14
n_D	1·4974	1·5003	1·5108	1·5380	1·4872
$d_{4^\circ}^{20^\circ}$	1·0558	1·0536	1·0519	1·1037	1·0759
$[R_L]_D$ (obs.) ...	53·57	57·86	70·34	70·25	66·95
$[R_L]_D$ (calc.)...	51·80	56·62	68·08	—	—
γ_{20°	37·89	37·57	37·51	38·68	35·59
$[P]$ (obs.)	454·7	487·7	582·3	561·1	567·7
$\Sigma[P]$ (calc.) ...	457·7	494·2	585·6	559·7	570·7

The exaltations of molecular refractivity of the unsaturated compounds (Table III) are due to the presence of conjugated double bonds. The observed and the calculated values of the parachor agree to within 1% except for ethyl *cyclo*heptylidenecyanoacetate (XX), where the difference is slightly greater. The low values for the unsaturated cyano-esters may be due to the fact that these compounds may exhibit, in addition to ordinary three-carbon tautomerism ($A \rightleftharpoons B$), ring-chain valency tautomerism ($B \rightleftharpoons C$) to a very small degree (compare Ingold and Shoppee, this vol., p. 365; Sugden, *ibid.*, p. 410). No chemical evidence has yet been obtained in support of this suggestion.

$$>C—CH \stackrel{C\equiv N}{\underset{C=O}{}} \rightleftharpoons >C=C \stackrel{C\equiv N}{\underset{C=O}{}} \rightleftharpoons >C=C \stackrel{C=N}{\underset{C-O}{}}$$

$$(A) \quad OEt \qquad (B) \quad OEt \qquad (C) \quad OEt$$

The results for the homologous ketones *cyclo*pentanone (D), *cyclo*-hexanone (E), and *cyclo*heptanone (F) and for *trans*-β-decalone (G), regenerated from their crystalline bisulphite compounds, are in Table IV. The refractive index and the surface tension both increase as the series is ascended. The line headed $\Sigma[P]$ (calc.) comprises the sum of the atomic constants plus the value for one double bond, and $[P]$ (obs.) $— \Sigma[P]$ (calc.) therefore gives the value of the ring constant determined experimentally. The calculated values of the ring constant have been computed from the " degree of unsatur-

TABLE IV.

	D.	E.	F.	G.
B. p. (mm.)	129·5°/761·5	47°/15	71°/19	106°/12
n_D.............................	1·4383	1·4521	1·4635	1·4809
$d_4^{20°}$	0·9486	0·9457	0·9496	0·9787
$[R_L]_D$ (obs.).	23·18	27·89	32·44	44·44
$[R_L]_D$ (calc.)	23·10	27·72	32·34	43·99
$\gamma_{20°}$	33·85	34·51	35·37	36·57
$[P]$ (obs.)	214·2	251·4	288·0	382·4
$\Sigma[P]$ (calc.)	204·0	243·0	282·0	364·8
Ring constant (obs.) ...	10·2	8·4	6·0	17·6
Ring constant (calc.) ...	9·3	7·7	6·6	15·4

ation " (Sugden and Wilkins, J., 1927, 142), and that for decahydro-naphthalene is assumed to be the sum of the values for two *cyclo*hexane rings. The agreement between the observed and the calculated values of the ring constant is noteworthy, but the " constants " vary slightly from substance to substance, being influenced by substitution (compare Sugden and Wilkins, *loc. cit.*). The constants employed in computing $\Sigma[P]$ (calc.) in Tables III and IV are the mean *experimental* values of Sugden (J., 1924, **125**, 1185).

The constant obtained for the *trans*-decahydro-β-naphthalene ring (17·6) is practically twice that found for the *cyclo*hexane ring (8·4); this supports the view that the two rings from which the *trans*-decahydro-β-naphthalene molecule is built up are structurally similar (compare *Ann. Rep.*, 1927, **24**, 99). The ring constants for quinoline (Morgan and Thomssen, *J. Amer. Chem. Soc.*, 1911, **33**, 657; Sugden, J., 1924, **125**, 1187) and naphthalene (Bhatnagar and Singh, *J. Chim. phys.*, 1928, **25**, 21) are respectively 15·0 and 11·7, thus indicating that the structural constant in both cases is that for two six-membered rings.

Almost the only evidence which has been adduced in favour of the multiplanar configuration of large-membered rings (from seven upwards) is that based on the determination of the molecular volume (molecular weight/density) (Ruzicka, Brugger, Pfeiffer, Schinz, and Stoll, *Helv. Chim. Acta*, 1926, **9**, 499). The work of Sugden and his collaborators has shown that much more trustworthy values are obtained by comparing molecular volumes at temperatures at which the substances have the same surface tension, or, in other words, by the measurement of the parachor. Theoretically, it would be expected that the difference in the magnitude of the parachor for CH_2 in large rings would approximate to 39·0, the value for CH_2 in an open-chain system, if the large rings are multiplanar and therefore largely collapsed, so that the effect of an additional CH_2 group would be almost the same as its effect in a similarly crumpled aliphatic chain (compare *Ann. Rep.*, 1926, **23**, 117). No trustworthy surface tension data are available for cyclic hydrocarbons. The

parachors, however, can be readily calculated from the observed values for the cyclic ketones by substituting the value of 2H for :O, both of which are known with some accuracy; the results are under $[P]_1$ in Table V.

TABLE V.

	5-Ring.	6-Ring.	7-Ring.	15-Ring.	16-Ring.
$[P_1]$	205·2	242·4	279·0	—	—
$[P_1]/n$	41·0	40·4	39·7	—	—
$\Sigma[P]$ (calc.)	204·3	241·7	279·6	588·1	626·9
$\Sigma[P]/n$ (calc.)	40·9	40·3	39·9	39·2	39·2

$[P_1]/n$, where n is the number of CH_2 groups in the cyclic hydro-carbon, represents the observed volume occupied by the CH_2 group plus a share of the internal space of the ring. The value for CH_2 in the *cyclo*heptane ring approximates closely to that for CH_2 in an open-chain hydrocarbon and thus gives further support to the view that the seven-membered ring is multiplanar (p. 2015). According to Mohr (*J. pr. Chem.*, 1922, **103**, 316) there are two " strainless " forms of the *cyclo*heptane ring, each of which occupies three planes.
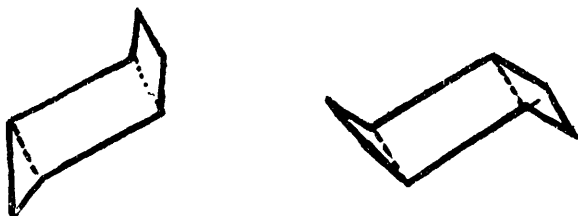
Since, however, the isomerism demanded by these forms has not yet been observed experimentally, it must be assumed that these merely represent phases of the contortions of the molecule.

The parachors of the cyclic hydrocarbons have been computed from the sum of the atomic constants plus the ring constant, the latter being derived from the " degree of unsaturation " (Sugden and Wilkins, J., 1927, 142), and are given in the line $\Sigma[P]$ (calc.); the contribution per CH_2 group is given in the last line of the table. The agreement between experiment and theory for the 5-, 6-, and 7-membered rings is satisfactory and it is hoped to extend the results to larger rings as soon as the necessary materials have been obtained.

The work is being continued and will include a study of the alkylation of the saturated cyano-esters and the optical resolution of the corresponding cyano-acids and their derivatives.

EXPERIMENTAL.

Ethyl iso*Propylidenemalonate* (VI).—Ethyl malonate (100 g.), acetone (54 g., dried over calcium chloride), acetic anhydride (80 g.),

and zinc chloride (23 g.) were heated in a closed vessel at 100° for 36 hours. The products of three such condensations were freed from most of the acetic anhydride and acetic acid by distillation (up to 140°); from the residue, a fraction distilling above 90°/20 mm. was collected, the distillation being stopped when the pressure had risen to 50 mm. On refractionation, ethyl malonate (40 g.) distilled at 90—110°/20 mm. and ethyl *iso*propylidenemalonate (195 g.) at 110—128°/20 mm. For use in syntheses, the latter was redistilled and the middle fraction collected.

Attempts to synthesise norpinic acid by the condensation of ethyl *iso*propylidenemalonate with ethyl sodiocyanoacetate, followed by treatment with methylene iodide and subsequent hydrolysis, under a large variety of conditions were all unsuccessful owing to the tendency of the initial Michael addition product to lose ethyl malonate.

gem-*Dimethyl Series.*

Ethyl α-*Cyano*-ββ-*dimethylacrylate* (IX).—A mixture of 200 g. of dry acetone and 200 g. of ethyl cyanoacetate was treated with 2 g. of piperidine. The deep yellow solution obtained was kept for 60 hours, refluxed for 4 hours, and again kept for 60 hours. Ether was then added and the solution was washed with dilute hydrochloric acid and with water, dried with anhydrous sodium sulphate, and distilled. The pure compound distilled at 114—116°/14 mm. (mainly at 115°/14 mm.) and, unless precautions were taken, solidified in the condenser. Yield, 147 g. or 54%. It had m. p. 33° after being spread on a porous tile (Komppa, *loc. cit.*, gives m. p. 28°; Birch and Kon, *loc. cit.*, p. 2447, give b. p. 117—127°/20 mm. and state that it " solidifies when cooled in ice.").

Reduction with Moist Aluminium Amalgam in Ether. Preparation of Ethyl r-iso*Propylcyanoacetate* (XI) *and of Ethyl* αδ-*Dicyano*-ββγγ-*tetramethylbutane*-αδ-*dicarboxylate* (X).—The ester (50 g.) was reduced with 75 g. of moist aluminium amalgam (J., 1927, 594), and the product worked up after 7 hours. On distillation, ethyl *iso*propylcyanoacetate (31·5 g.) passed over at 100—101°/15 mm., leaving a high-boiling residue (10·5 g.). The former on refractionation distilled at 99°/16 mm. (Fischer and Flatau, *Ber.*, 1909, **42**, 2983, give b. p. 115—116°/24—25 mm.) and had $n_D^{17\cdot2°}$ 1·4243, $d_4^{17\cdot2°}$ 0·9880, $[R_L]_D$ 40·08 (calc., 39·62) (Found : C, 61·8; H, 8·3. Calc. : C, 61·9; H, 8·4%). The latter, an extremely viscid reddish-brown oil, was treated for 48 hours with a large excess of ammonia (d 0·88); the product, after being washed with dilute hydrochloric acid, was crystallised twice from dilute methyl alcohol, the *monoamide* of (X) separating in small, thin prisms, m. p. 95° (Found : C, 60·5; H, 7·7;

M, in camphor by Rast's method, 275. $C_{14}H_{21}O_3N_3$ requires C, 60·2; H, 7·6%; M, 279).

Hydrolysis of the Ester (X). *Preparation of* ββ'β'-*Tetramethyladipic Acid.*—The high-boiling product was boiled for 5 hours with concentrated hydrochloric acid (10 parts); after 12 hours, ββ'β'-tetramethyladipic acid, accompanied by a very small quantity of carbonaceous matter, separated. The acid crystallised from hot water in colourless thin prisms, m. p. 207° alone or mixed with an authentic specimen (Farmer and Kracovski, J., 1926, 2322). This appears to be the most convenient mode of preparing this acid.

Hydrolysis of the Ester (XI). *Preparation of* iso*Propylmalonic Acid.* —Solutions of the ester (18 g.) in rectified spirit (36 g.) and of potassium hydroxide (31 g.) in water (62 g.) were mixed, refluxed for 14 hours, and evaporated to dryness. An aqueous solution of the residue was shaken with ether to remove any unchanged ester, if present, acidified with dilute sulphuric acid, and extracted five times with ether; from the extract, *iso*propylmalonic acid was obtained as an oil which crystallised completely when left over concentrated sulphuric acid in a vacuum desiccator (yield, 12·6 g. or 75%). The acid crystallised from hot chloroform in prisms containing chloroform of crystallisation which was lost on exposure to air; the opaque white residue had m. p. 87—88° after 24 hours, m. p. 88—89° (decomp.) after 48 hours, and was then unaffected by further exposure to the atmosphere (Found : C, 49·2; H, 6·9; equiv., by titration, 74. Calc. : C, 49·3; H, 6·9%; equiv., 73). Similar behaviour was observed by Romburgh (*Rec. trav. chim.*, 1886, **5**, 238), who found that the acid crystallised from benzene with 2 molecules of benzene of crystallisation which were lost on exposure to the atmosphere; the residue melted at 87°.

Condensation of the Ester (IX) *with Alcoholic Potassium Cyanide. Preparation of* as-*Dimethylsuccinic Acid.*—The pure ester (10 g.) in 50 g. of rectified spirit was treated with a solution of 9·6 g. of 96% potassium cyanide (2 mols.) in 20 g. of water. The mixture, which became warm, was kept for 48 hours, the alcohol was then distilled off, a very large excess of concentrated hydrochloric acid added, and the liquid heated under reflux for 3 hours, cooled, diluted with water, and extracted six times with ether after addition of ammonium sulphate. The *as*-dimethylsuccinic acid obtained from the extract (yield, 6·2 g. or 60%) melted, after crystallisation from concentrated hydrochloric acid, at 141°; m. p. of a mixture with an authentic specimen (Higson and Thorpe, J., 1906, **89**, 1465), 141—142°.

Ethyl as-*dimethylsuccinate* was prepared by heating a mixture of 8·0 g. of the crude acid, 40 g. of absolute alcohol, 40 g. of sodium-dried benzene, and 4 g. of concentrated sulphuric acid under reflux

for $5\frac{1}{2}$ hours and was isolated, after the addition of water, from the benzene layer and an ethereal extract of the aqueous layer. It had b. p. 106—108°/20 mm. (yield, 6·9 g. or 62%). On redistillation, it had b. p. 101°/15 mm., $n_D^{22·7°}$ 1·4209, $d_4^{22·7°}$ 0·9945, $[R_L]_D$ 51·53 (calc., 51·69).

For purposes of comparison, ethyl succinate was prepared from Kahlbaum's succinic acid under similar conditions; the quantities employed were 15·0 g. of succinic acid, 75 g. of absolute alcohol, 75 g. of sodium-dried benzene, and 8 g. of concentrated sulphuric acid. The yield of ester, b. p. 102°/15 mm., at the first distillation was 16·3 g. or 74%. On redistillation, it boiled constantly at 103°/14 mm. and had $n_D^{21·6°}$ 1·4193, $d_4^{21·6°}$ 1·0384, whence $[R_L]_D$ 42·37 (calc., 42·45).

cycloPentane Series.

cycloPentanone was prepared by the catalytic decomposition of adipic acid (G.P., 1911, 256,622; Roger Adams, " Organic Syntheses," 1925, 5, 37), but in view of its volatility in ether vapour the crude cyclopentanone was separated from the small aqueous layer, neutralised with anhydrous potassium carbonate, and distilled; the pure ketone passed over at 130°/755 mm. A further small quantity was obtained from the aqueous layer by extraction with ether.

Ethyl cyclopentylidenecyanoacetate (XII) was prepared by the condensation of equimolecular quantities of cyclopentanone and ethyl cyanoacetate in the presence of piperidine (for conditions, see ethyl cycloheptylidenecyanoacetate). The solid obtained when the product was poured into water contained a considerable quantity of oil (compare Harding and Haworth, J., 1910, 97, 490); this was extracted with ether, washed in the ethereal solution with dilute hydrochloric acid and with water, dried with anhydrous sodium sulphate, and distilled; a mixture of cyclopentanone and ethyl cyanoacetate passed over, followed by the ester (XII) as a viscid colourless oil which crystallised on cooling (yield, 55—60%).

Reduction with Moist Aluminium Amalgam. Preparation of Ethyl r-cyclo*Pentylcyanoacetate* (XIII).—The ester (50 g.) was reduced with 75 g. of aluminium amalgam under the usual conditions : there was a period of induction for 3 to 4 hours and the reaction was complete after 10 hours. On being worked up in the usual manner and distilled, the product gave *ethyl* r-cyclo*pentylcyanoacetate* (XIII), b. p. 130—131°/12 mm. (38·5 g.), and a high-boiling residue (XIV) (6·3 g.). The former on redistillation boiled at 129°/13 mm. and had $n_D^{19·2°}$ 1·4536, $d_4^{19·2°}$ 1·0242, $[R_L]_D$ 47·86 (calc., 47·65) (Found : C, 66·0; H, 8·2. $C_{10}H_{15}O_2N$ requires C, 66·3; H, 8·3%). The high-boiling residue, a very viscid reddish-brown oil, has not yet been

3 x

obtained crystalline. Its bimolecular character was established by a determination of its molecular weight in camphor by Houben's modification of Rast's method (*J. pr. Chem.*, 1923, **105**, 27) (Found : *M*, in camphor, 365. $C_{20}H_{28}O_4N_2$ requires *M*, 360). This and all the other bimolecular cyclic compounds are not readily hydrolysed and appear to have cyclic structures analogous to that of the reduction product of mesityl oxide with moist aluminium amalgam (compare Vogel, J., 1927, 594).

Hydrolysis of the Ester (XIII). *Preparation of* cyclo*Pentyl-malonic Acid.*—The hydrolysis was carried out exactly as described under ethyl *iso*propylcyanoacetate. The quantities employed were 19 g. of ethyl *cyclo*pentylcyanoacetate, 40 g. of rectified spirit, 35 g. of caustic potash in 70 g. of water ; the yield of the crude acid was almost quantitative. It separated from hot chloroform in small, glistening plates, m. p. 165° (decomp.) (Found : C, 55·6 ; H, 6·9 ; equiv., by titration, 86. $C_8H_{12}O_4$ requires C, 55·8 ; H, 7·0% ; equiv., 86).

Condensation of Ethyl cyclo*Pentylidenecyanoacetate with Alcoholic Potassium Cyanide. Preparation of* 1-*Carboxy*cyclo*pentane-1-acetic Acid* (XV).—The condensation was carried out exactly as described for *as*-dimethylsuccinic acid : the quantities employed were 25·0 g. of ester, 125 g. of rectified spirit, 20·5 g. (2 mols.) of 96% potassium cyanide in 45 g. of water ; the yield of crude acid was 19·5 g. or 81%. The acid crystallised from concentrated hydrochloric acid, in which it is much less soluble than the *gem*-dimethyl compound, in small glistening prisms, m. p. 160° (Found : C, 55·8 ; H, 7·0 ; equiv., by titration, 86. Calc. : C, 55·8 ; H, 7·0% ; equiv., 86). The original specimen of Norris and Thorpe (J., 1921, **119**, 1209) was found to melt at 154·5—155·5° : mixed m. p. 155—158°.

The *anhydride* was prepared in 90% yield by heating the crude acid with 4 mols. of acetyl chloride and removing the excess of acetyl chloride in a vacuum over caustic potash. After two distillations it boiled at 135—137°/13 mm. as a fairly viscid, colourless liquid which crystallised when left in contact with light petroleum (b. p. 40—60°) ; m. p. 32° (Found : C, 62·0 ; H, 6·4. $C_8H_{10}O_3$ requires C, 62·3 ; H, 6·6%).

The *anilic acid* was formed when the anhydride and aniline were warmed in benzene solution. After removal of the excess of aniline in dilute hydrochloric acid, and spontaneous evaporation of the benzene layer, the residue was crystallised from dilute methyl alcohol, the anilic acid separating in thin, feathery plates which melted at 169° and decomposed with the evolution of steam at 170° (Found : C, 67·8 ; H, 7·1. $C_{14}H_{17}O_3N$ requires C, 68·0 ; H, 6·9%).

The *ethyl* ester was prepared exactly as described under ethyl

as-dimethylsuccinate : the quantities employed were 7·0 g. of crude acid, 35 g. of absolute alcohol, 35 g. of sodium-dried benzene, and 3·5 g. of concentrated sulphuric acid. The yield of ester at the first distillation was 5·9 g. or 65%. On redistillation, the ester boiled at 129°/13 mm. and had $n_D^{20\cdot2°}$ 1·4477, $d_4^{20\cdot2°}$ 1·0412, $[R_L]_D$ 58·63 (calc., 58·72) (Found : C, 63·0; H, 8·9. $C_{12}H_{20}O_4$ requires C, 63·1; H, 8·9%).

<div align="center">cycloHexane Series.</div>

Ethyl *cyclo*hexylidenecyanoacetate (XVI) was prepared by the condensation of pure *cyclo*hexanone and ethyl cyanoacetate in the presence of piperidine (Harding, Haworth, and Perkin, *loc. cit.*) in *ca.* 60% yield. The pure ester, thrice distilled under reduced pressure, boiled at 151°/12 mm. and had $n_D^{18\cdot0°}$ 1·4974, $d_4^{18\cdot0°}$ 1·0556, $[R_L]_D$ 53·57 (calc., 51·80). Lapworth and McRae give b. p. 160—163°/15 mm. (J., 1922, **121**, 2754); Birch, Kon, and Norris (J., 1923, **123**, 1373) give b. p. 151°/10 mm., $d_4^{19\cdot5°}$ 1·05394, $n_D^{19\cdot5°}$ 1·49670, which give $[R_L]_D$ 53·59 in good agreement with the value determined by the present author : the values $[R_L]_D$ 53·94 (calc., 51·59) given by the latter authors are erroneous.

Reduction with Moist Aluminium Amalgam. Preparation of Ethyl r-*cycloHexylcyanoacetate* (XVII).—The ester (100 g.) was reduced with 150 g. of aluminium amalgam; there was a period of induction of about 3 hours and the reaction was complete after 9 hours. When the product was worked up in the usual manner and distilled, *ethyl* r-*cyclohexylcyanoacetate* (XVII) (85 g.) passed over at 144—146°/14 mm. : the viscid residue was dissolved in methyl alcohol, the solvent evaporated in a vacuum over concentrated sulphuric acid, and traces of impurities removed by repeated extraction with boiling light petroleum (b. p. 40—60°); the product crystallised completely when left in a vacuum over concentrated sulphuric acid for 24 hours (yield, 6 g.). It melted at 87° and was the bimolecular *cyano-ester* (XVIII) (Found : M, in camphor, 396. $C_{22}H_{32}O_4N_2$ requires M, 388). The liquid reduction product on redistillation boiled at 145°/14 mm., and had $n_D^{18\cdot3°}$ 1·4612, $d_4^{18\cdot5°}$ 1·0221, whence $[R_L]_D$ 52·39 (calc., 52·21) (Found : C, 67·5; H, 8·5. $C_{11}H_{17}O_2N$ requires C, 67·8; H, 8·7%).

Hydrolysis of the Ester (XVII). *Preparation of* cyclo*Hexylmalonic Acid.*—The hydrolysis was carried out as described under ethyl *iso*propylcyanoacetate and was considered to be complete after 18 hours. The quantities employed were 20 g. of ethyl *cyclo*hexylcyanoacetate, 40 g. of rectified spirit, and 30 g. of potassium hydroxide in 60 g. of water. The acid, which was obtained in practically quantitative yield, separated from acetone–chloroform in feathery plates, m. p. 178° (decomp.), and its identity with

cyclohexylmalonic acid was established by direct comparison with an authentic specimen, m. p. 176—177° (decomp.), synthesised from bromocyclohexane and ethyl sodiomalonate; mixed m. p. 177—178° (decomp.).

The condensation of ethyl cyclohexylidenecyanoacetate with alcoholic potassium cyanide had previously been carried out by Lapworth and McRae (J., 1922, **121**, 2754) : the quantities here employed were 30 g. of ester, 150 g. of rectified spirit, and 21·1 g. (2 mols.) of 96% potassium cyanide in 45·5 g. of water. Hydrolysis was effected by boiling under reflux with a large excess of concentrated hydrochloric acid for 6 hours : the use of fuming hydrochloric acid (Lapworth and McRae) seems unnecessary. The 1-carboxy-cyclohexane-1-acetic acid (yield, 24·7 g. or 86%) crystallised from concentrated hydrochloric acid in flat prisms, m. p. 134°, but was less soluble than the corresponding gem-dimethyl and cyclopentane compounds. It may also be crystallised from chloroform–light petroleum (b. p. 40—60°). Its constitution was confirmed by a comparison with the original specimen of Norris and Thorpe (J., 1921, **119**, 1206), m. p. 132°, mixed m. p. 133—134°. The anhydride, prepared in 92% yield by the method described for the cyclopentane analogue, crystallised from light petroleum (b. p. 40—60°) in plates, m. p. 56° (Norris and Thorpe, loc. cit., give m. p. 57°). The anilic acid, prepared from the anhydride and aniline in benzene solution, crystallised from dilute methyl alcohol in lustrous, glistening plates, m. p. 181° (decomp.) (Norris and Thorpe, loc. cit., give m. p. 180°).

cycloHeptane Series.

Ethyl cyclo*Heptylidenecyanoacetate* (XX).—Suberone, b. p. 181°/769 mm., was prepared in 35—40% yield by the dry distillation of thorium suberate (Ruzicka, Helv. Chim. Acta, 1926, **9**, 515); and later by the catalytic decomposition of suberic acid, full details of which are given in the following communication.

A mixture of the ketone (44 g.), ethyl cyanoacetate (46 g.), and piperidine (1 g.) was after 48 hours heated on a steam-bath for 4 hours, cooled, and poured into water. The heavy oil produced was isolated by means of ether and, after the usual washing and drying, was distilled; suberone and ethyl cyanoacetate passed over first, and then the *cyano-ester* (XX) at 162—163°/14 mm. (yield, 27·3 g. or 31%). By treating the low fraction with a large excess of saturated aqueous-alcoholic sodium bisulphite solution (Ruzicka and Brugger, Helv. Chim. Acta, 1926, **9**, 339), 18 g. of pure suberone were recovered. On redistillation the ester boiled at 160°/12 mm. and had $n_D^{18·6°}$ 1·5003, $d_4^{18·6°}$ 1·0534, $[R_L]_D$ 57·86 (calc., 56·62) (Found : C, 69·4; H, 8·2. $C_{12}H_{17}O_2N$ requires C, 69·5; H, 8·3%).

Reduction with Moist Aluminium Amalgam. Preparation of Ethyl r-cyclo*Heptylcyanoacetate* (XXI).—17·2 G. of ethyl *cyclo*-heptylidenecyanoacetate were treated with 35 g. of moist aluminium amalgam in ether; there was a period of induction for several hours and the reduction was considered complete after 18 hours. The product was isolated in the usual manner and distilled, *ethyl* r-cyclo-*heptylcyanoacetate* (12·4 g.) passing over at 152—154°/12 mm., mainly at 152°/12 mm. The residue, which solidified to a transparent glassy solid on cooling, was treated several times with boiling light petroleum (b. p. 40—60°) to remove impurities; it crystallised after being left in a vacuum over concentrated sulphuric acid for 48 hours (yield, 2·1 g.). It had m. p. 74° and was the bimolecular compound (XXII) (Found : M, in camphor, 418. $C_{24}H_{36}O_4N_2$ requires M, 416). The liquid reduction product on redistillation boiled at 149°/11 mm. and had $n_D^{19\cdot0°}$ 1·4664, $d_4^{19\cdot7°}$ 1·0209, whence $[R_L]_D$ 56·78 (calc., 56·89) (Found : C, 68·7; H, 9·1. $C_{12}H_{19}O_2N$ requires C, 68·9; H, 9·2%).

Hydrolysis of the Ester (XXI). *Preparation of* cyclo*Heptylmalonic Acid.*—The hydrolysis was effected as described under ethyl *iso*-propylcyanoacetate, the quantities employed being 6·5 g. of ethyl *cyclo*heptylcyanoacetate, 13 g. of rectified spirit, and 7·0 g. (4 mols.) of potassium hydroxide in 14 g. of water. The crude acid was only sparingly soluble in chloroform but crystallised from benzene–acetone in thin plates, m. p. 164·5° (decomp.) (Found : C, 60·0; H, 7·9. $C_{10}H_{16}O_4$ requires C, 60·0; H, 8·0%).

Condensation of Ethyl cyclo*Heptylidenecyanoacetate with Alcoholic Potassium Cyanide. Preparation of* 1-*Carboxy*cycloheptane-1-acetic *Acid* (XXIII).—The reaction was carried out as described for *as*-dimethylsuccinic acid : the quantities employed were 12 g. of the ester (XX), 60 g. of rectified spirit, and 8·1 g. (2 mols.) of 96% potassium cyanide in 18 g. of water (yield of crude acid, 9·9 g. or 86%). 1-Carboxy*cyclo*heptane-1-acetic acid is very sparingly soluble in concentrated hydrochloric acid, probably less so than its *cyclo*pentane analogue; it crystallises from dilute hydrochloric acid in small prisms, m. p. 159° (Found : C, 60·0; H, 8·0; equiv., by titration, 100. Calc. : C, 60·0; H, 8·0%; equiv., 100); Dickens, Horton, and Thorpe (*loc. cit.*) give m. p. 153°. The *anhydride*, m. p. 16°, b. p. 166°/13 mm., obtained in excellent yield by treatment of the crude acid with acetyl chloride, was converted in the usual manner into the *anilic acid*, which separated from dilute methyl alcohol in feathery plates, m. p. 159°, decomp. 160° (Found : C, 69·1; H, 7·6. $C_{16}H_{21}O_3N$ requires C, 69·3; H, 7·7%).

trans-*Decahydro-β-naphthalene Series.*

trans-Decahydro-β-naphthol (*trans*-β-decalol) was obtained from the " Dekahydro-β-naphthol rein " of the Deutsche Hydrierwerke Aktiengesellschaft by spreading the oily sticky solid, which probably consisted of a mixture of the *cis*- and *trans*-isomerides, on large porous plates : the resultant crystalline solid melted at 74° (Hückel, *Annalen*, 1925, **441**, 18, gives m. p. 75° for pure *trans*-β-decalol). The alcohol was dissolved in three times its weight of glacial acetic acid and gradually treated, under reflux, with half its weight of recrystallised chromic acid dissolved in the minimum quantity of water. When the initial vigorous reaction had subsided the whole was warmed on the steam-bath for 30 minutes and steam-distilled. The mixture of *trans*-β-decalone (which is only moderately easily volatile in steam) and acetic acid isolated from the distillate by means of ether (three extractions) was shaken for 1 hour with a large excess of saturated aqueous-alcoholic sodium bisulphite solution (Ruzicka and Brugger, *Helv. Chim. Acta*, 1926, **9**, 339). The bisulphite compound, which separated as a silky crystalline solid, was collected and decomposed with an excess of sodium hydroxide solution, and the *trans*-β-decalone isolated by extraction (twice) with ether. It distilled at 106°/12 mm. as a colourless, somewhat viscid liquid with a characteristic odour and had $d_4^{17.7°}$ 0·9800, $n_D^{17.7°}$ 1·4843, whence $[R_L]_D$ 44·44 (calc., 43·99) (Hückel, *loc. cit.*, gives for *trans*-β-decalone regenerated from the semicarbazone, $d_4^{20°}$ 0·975, $n_D^{19.0°}$ 1·48088). The yield of pure *trans*-β-decalone from 87 g. of *trans*-β-decalol was 48 g.

Ethyl trans-*Decahydro-β-naphthylidenecyanoacetate* (XXIV).—A mixture of 35·0 g. of pure *trans*-β-decalone, 26·5 g. of ethyl cyanoacetate, and 1 g. of piperidine was after 24 hours heated on the steam-bath for 6 hours. Ether was then added and the product was washed with dilute hydrochloric acid and with water and dried with anhydrous sodium sulphate. The residue after evaporation of the ether was fractionated : unchanged *trans*-β-decalone and ethyl cyanoacetate were first collected and the condensation product passed over at 190—205°/15 mm. The last on refractionation distilled at 197°/14 mm. (Found : C, 72·8 ; H, 8·5. $C_{15}H_{21}O_2N$ requires C, 72·8 ; H, 8·6%) and had $d_4^{19.4°}$ 1·0523, $n_D^{19.4°}$ 1·5108, whence $[R_L]_D$ 70·34 (calc., 68·08). Yield, 47 g. or 61%.

Reduction with Moist Aluminium Amalgam. Preparation of Ethyl r-trans-*Decahydro-β-naphthylcyanoacetate* (XXV or XXVI).—35·0 G. of the unsaturated cyano-ester (XXIV) were treated with 70 g. of moist aluminium amalgam in ether : there was a period of induction of at least 8 hours and the reduction was complete after 22 hours. The product was isolated in the usual manner and dis-

tilled and the following fractions were collected : (1) B. p. 184°/ 12 mm.; this had $n_D^{18\cdot9°}$ 1·4811, $d_4^{18\cdot9°}$ 1·0263. (2) A large middle fraction, b. p. 184—186°/12 mm., mainly 186°/12 mm., $n_D^{19\cdot9°}$ 1·4802, $d_4^{9\cdot9°}$ 1·0302, whence $[R_L]_D$ 68·73 (calc., 68·54). (3) A small tail fraction, b. p. 186—187°/12 mm., $n_D^{19\cdot3°}$ 1·4805, $d_4^{19\cdot3°}$ 1·0297. Total yield, 27·5 g. The distillate was obviously homogeneous and on redistillation boiled constantly at 186°/12 mm. (Found : C, 72·4 ; H, 9·2. $C_{15}H_{23}O_2N$ requires C, 72·3 ; H, 9·3%) : no trace of a second isomeride could be detected by distillation. The residue was a very viscid yellow oil which did not crystallise when left for a week over concentrated sulphuric acid in a vacuum ; yield, 2·5 g. (Found : M, in camphor, 488. $C_{30}H_{44}O_4N_2$ requires M, 496).

Hydrolysis with Alcoholic Potassium Hydroxide. Preparation of trans-*Decahydro-β-naphthylmalonic Acid.*—A mixture of 8·3 g. of the ester (b. p. 186°/12 mm.) in 16 g. of rectified spirit and 7·5 g. of potassium hydroxide in 15 g. of water was refluxed for 18 hours and then evaporated to dryness on the steam-bath. The residue was triturated with ether to remove unchanged ester, if any, and acidified with very dilute sulphuric acid, a sticky solid separating. The whole was extracted three times with ether : the ethereal solution, which soon deposited a crystalline acid, m. p. 122° (decomp.), was slightly concentrated, and the separated acid collected : this process was repeated five times until practically all the ether had been evaporated. The acid which separated at each crystallisation melted at 122° (decomp.) and the total yield was nearly quantitative (Found : C, 65·3 ; H, 8·1. $C_{13}H_{20}O_4$ requires C, 65·0 ; H, 8·4%). No isomeric acid was isolated. The acid crystallises from benzene or acetone–chloroform as a microcrystalline powder, m. p. 122° (decomp.).

Determinations of Surface Tension and of Density over a Range of Temperatures. Calculation of the Parachor.

The surface tension was determined by the method of Richards, Speyers, and Carver (*J. Amer. Chem. Soc.*, 1924, **46**, 1196) in an apparatus constructed entirely of Pyrex glass. Two capillary tubes of diameters approximately 0·5 mm. and 2 mm. respectively, of nearly circular cross-section and of uniform bore were joined together to form a ∪-tube, which was provided with a small opening at its lowest point. The ∪-tube was fused in a vertical position to the inside of a thin-walled glass cylinder, and this was fused to a larger tube, which could be surrounded by the vapour of boiling chloroform (*ca.* 61°) or trichloroethylene (*ca.* 86°) ; the exact temperature was indicated by a small standard Anschütz thermometer graduated in fifths of a degree. The difference in capillary rise was

measured by means of a travelling microscope capable of reading directly to 0·02 mm. and by estimation to 0·01 mm. and provided with a 5-inch objective, for the construction of which the author is indebted to Mr. W. J. Colebrooke of the Physics Department of this College; it enabled both meniscuses to be observed simultaneously.

The apparatus was cleaned by being immersed in chromic acid mixture for 6 hours, washed with water, rectified spirit, and pure sodium-dried ether, and dried in the steam-oven. It was standard-ised with conductivity water, prepared in a modified Bourdillon still, in the manner suggested by Richards, Speyers, and Carver (*loc. cit.*).

The measurements of capillary rise for each liquid (about 3 c.c.) were made with the usual precautions. The vertical cross-wire in the eye-piece of the microscope was adjusted parallel to and approxim-ately mid-way between the capillary tubes. At least six readings of each meniscus were taken from several directions, so as to minimise the effect of possible imperfections in the glass, the exact temperature at each adjustment being observed.

The corrections for the meniscus, determined by Poisson's equation $h_1 = h + r/3 - 0·1288\ r^2/h$, where h_1 is the corrected capillary rise, h is the observed capillary rise, and r is the radius of the tube (Richards, Speyers, and Carver, *loc. cit.*), were 0·245 mm. for liquids of the water type ($h = ca.$ 50 mm.) and $-$ 0·234 mm. for most organic liquids ($h = ca.$ 25 mm.). Throughout the present paper, the cor-rected difference in height between the meniscuses in the capillary tubes, H, is obtained from the observed difference, h (expressed in mm.), by subtracting 0·24. The constant of the apparatus, K, was obtained from the equation $\gamma = KHd$, where γ and d are respect-ively the surface tension and the density at the same temperature; the surface tension of water at 20° was taken as 72·80 (Harkins and Brown, *J. Amer. Chem. Soc.*, 1919, **41**, 499), and the temperature coefficient 0·15 dyne cm.$^{-1}$ (degree Cent.)$^{-1}$ (compare Ferguson and Vogel, *Proc. Physical Soc.*, 1926, **38**, 193). The mean of several concordant determinations gave $K = 1·8805$.

The densities were determined with a pyknometer of about 1·5 c.c. capacity, carefully calibrated with conductivity water. The pyknometer was completely surrounded by a closely fitting, double-walled glass vessel, the annular space being filled with a suitable vapour.

In the tables, t is the temperature, h the observed difference in height, expressed in mm., of the liquid in the two arms of the U-tube, H the corrected value, $d_4^{t°}$ the density (in g./c.c.) calculated from the observed densities by assuming a linear variation with temperature, and γ the surface tension, expressed in dynes/cm., computed from

the equation $\gamma = KHd$. The parachor in the last column has been derived from the expression $[P] = \gamma^{\frac{1}{4}} M / d_4^{t^\circ}$, where M is the molecular weight; the density of the vapour has been neglected.

Except where stated otherwise, the liquids were thrice distilled under diminished pressure before use.

Ethyl r-iso*propylcyanoacetate*, $M = 155\cdot10$, b. p. $99^\circ/16$ mm. Densities determined : $d_4^{19\cdot2^\circ}$ $0\cdot9862$, $d_4^{62\cdot4^\circ}$ $0\cdot9481$, $d_4^{86\cdot8^\circ}$ $0\cdot9261$.

t.	h.	H.	$d_4^{t^\circ}$.	γ.	Parachor.
$23\cdot3^\circ$	$17\cdot28$	$17\cdot04$	$0\cdot9826$	$31\cdot49$	$373\cdot9$
$61\cdot8$	$15\cdot71$	$15\cdot47$	$0\cdot9486$	$27\cdot60$	$374\cdot8$
$86\cdot6$	$14\cdot78$	$14\cdot54$	$0\cdot9261$	$25\cdot32$	$375\cdot7$
					Mean $374\cdot8$

Ethyl r-cyclo*pentylcyanoacetate*, $M = 181\cdot13$, b. p. $129^\circ/13$ mm. Densities determined : $d_4^{17\cdot7^\circ}$ $1\cdot0263$, $d_4^{61\cdot6^\circ}$ $0\cdot9936$, $d_4^{86\cdot2^\circ}$ $0\cdot9714$.

t.	h.	H.	$d_4^{t^\circ}$.	γ.	Parachor.
$17\cdot7^\circ$	$18\cdot37$	$18\cdot13$	$1\cdot0263$	$34\cdot99$	$429\cdot2$
$61\cdot2$	$16\cdot77$	$16\cdot53$	$0\cdot9932$	$30\cdot87$	$429\cdot9$
$86\cdot4$	$15\cdot89$	$15\cdot65$	$0\cdot9712$	$28\cdot58$	$431\cdot2$
					Mean $430\cdot1$

Ethyl r-cyclo*hexylcyanoacetate*, $M = 195\cdot13$, b. p. $145^\circ/14$ mm. Densities determined : $d_4^{18\cdot5^\circ}$ $1\cdot0221$, $d_4^{61\cdot2^\circ}$ $0\cdot9901$, $d_4^{86\cdot4^\circ}$ $0\cdot9690$.

t.	h.	H.	$d_4^{t^\circ}$.	γ.	Parachor.
$17\cdot3^\circ$	$18\cdot87$	$18\cdot63$	$1\cdot0229$	$35\cdot84$	$466\cdot8$
$61\cdot8$	$17\cdot22$	$17\cdot98$	$0\cdot9897$	$31\cdot60$	$467\cdot5$
$85\cdot6$	$16\cdot34$	$16\cdot10$	$0\cdot9696$	$29\cdot36$	$468\cdot5$
					Mean $467\cdot6$

Ethyl r-cyclo*heptylcyanoacetate*, $M = 209\cdot15$, b. p. $149^\circ/11$ mm. Densities determined : $d_4^{19\cdot7^\circ}$ $1\cdot0209$, $d_4^{61\cdot8^\circ}$ $0\cdot9898$, $d_4^{86\cdot6^\circ}$ $0\cdot9704$.

t.	h.	H.	$d_4^{t^\circ}$.	γ.	Parachor.
$21\cdot3^\circ$	$19\cdot04$	$18\cdot80$	$1\cdot0197$	$35\cdot96$	$502\cdot3$
$61\cdot8$	$17\cdot46$	$17\cdot22$	$0\cdot9898$	$32\cdot05$	$502\cdot8$
$86\cdot0$	$16\cdot53$	$16\cdot29$	$0\cdot9708$	$29\cdot74$	$503\cdot1$
					Mean $502\cdot7$

Ethyl trans-r-*decahydro-β-naphthylcyanoacetate*, $M = 249\cdot19$, b. p. $186^\circ/14$ mm. Densities determined : $d_4^{19\cdot9^\circ}$ $1\cdot0302$, $d_4^{62\cdot2^\circ}$ $1\cdot0011$, $d_4^{84\cdot8^\circ}$ $0\cdot9861$.

t.	h.	H.	$d_4^{t^\circ}$.	γ.	Parachor.
$20\cdot1^\circ$	$18\cdot99$	$18\cdot75$	$1\cdot0301$	$36\cdot32$	$593\cdot9$
$60\cdot8$	$17\cdot65$	$17\cdot41$	$1\cdot0021$	$32\cdot81$	$595\cdot1$
$84\cdot1$	$16\cdot82$	$16\cdot58$	$0\cdot9866$	$30\cdot76$	$594\cdot8$
					Mean $594\cdot6$

cyclo*Pentanone*, $M = 84\cdot06$. The middle fraction, b. p. $130\cdot5^\circ/$ $765\cdot5$ mm., collected from the distillation of a large quantity of cyclopentanone prepared from adipic acid was added to a large excess of saturated aqueous-alcoholic sodium bisulphite solution, the

3 x 2

bisulphite compound, which slowly separated in thin, silky plates, was removed and treated with an excess of a concentrated sodium carbonate solution, and the ketone was separated by steam-distillation and extraction (twice) with ether. The extracts were dried with anhydrous sodium sulphate and the ether was *slowly* distilled through a long column. The residue, after being twice fractionated under atmospheric pressure, boiled at 129·5°/761·5 mm. The pure ketone had $n_D^{16\cdot0^\circ}$ 1·4383, $d_4^{16\cdot0^\circ}$ 0·9524, whence $[R_L]_D$ 23·18 (calc., 23·10) (Wallach, *Annalen*, 1907, **353**, 331, gives d^{20° 0·948, n_D 1·4366, $[R_L]_D$ 23·19).

Densities determined : $d_4^{16\cdot4^\circ}$ 0·9518, $d_4^{62\cdot8^\circ}$ 0·9099, $d_4^{86\cdot4^\circ}$ 0·8871.

t.	h.	H.	$d_{4^\circ}^{t^\circ}$.	γ.	Parachor.
18·0°	19·31	19·07	0·9504	34·08	213·7
61·6	17·19	16·95	0·9110	29·04	214·2
85·4	16·05	15·81	0·8880	26·40	214·6
					Mean 214·2

cyclo*Hexanone*, $M = 98\cdot08$. Boot's pure *cyclo*hexanone was purified through the bisulphite compound by the method described under *cyclo*pentanone; after being distilled twice under reduced pressure, it boiled at 47°/15 mm. and had $d_4^{16\cdot9^\circ}$ 0·9488, $n_D^{16\cdot9^\circ}$ 1·4521, whence $[R_L]_D$ 27·89 (calc., 27·72) (Wallach, *loc. cit.*, gives d^{21° 0·947, n_D 1·4503, $[R_L]_D$ 27·82).

Densities determined : $d_4^{15\cdot7^\circ}$ 0·9492, $d_4^{61\cdot8^\circ}$ 0·9116, $d_4^{86\cdot0^\circ}$ 0·8902.

t.	h.	H.	$d_{4^\circ}^{t^\circ}$.	γ.	Parachor.
17·3°	19·77	19·53	0·9479	34·81	251·3
61·6	17·64	17·40	0·9118	29·84	251·4
86·4	16·44	16·20	0·8899	27·11	251·5
					Mean 251·4

cyclo*Heptanone*, $M = 112\cdot10$. Suberone, b. p. 181°/769 mm., prepared from thorium suberate was purified through the bisulphite compound. The regenerated ketone had a pleasant odour which was somewhat like that of peppermint and quite different from the " hydrocarbon " odour of the ketone isolated directly from thorium suberate. It boiled at 71°/19 mm. during two distillations under reduced pressure and had $n_D^{15\cdot0^\circ}$ 1·4635, $d_4^{15\cdot0^\circ}$ 0·9526, whence $[R_L]_D$ 32·44 (calc., 32·34) (Wallach, *loc. cit.*, gives d^{21° 0·9500, n_D 1·4604, $[R_L]_D$ 32·32).

Densities determined : $d_4^{18\cdot6^\circ}$ 0·9507, $d_4^{61\cdot7^\circ}$ 0·9160, $d_4^{86\cdot8^\circ}$ 0·8954.

t.	h.	H.	$d_{4^\circ}^{t^\circ}$.	γ.	Parachor.
19·9°	20·05	19·81	0·9497	35·38	287·9
61·6	18·12	17·88	0·9161	30·80	288·3
86·4	16·84	16·60	0·8957	27·96	287·8
					Mean 288·0

trans-β-*Decalone*, $M = 152\cdot13$. The specimen employed was purified through the bisulphite compound and was twice distilled

under diminished pressure. It boiled at 106°/12 mm. and had $d_4^{17.7°}$ 0·9800, $n_D^{17.7°}$ 1·4843, whence $[R_L]_D$ 44·44 (calc., 43·99) (Hückel, *Annalen*, 1925, **441**, 1, gives $d_4^{20°}$ 0·975, $n_D^{19°}$ 1·48088, $[R_L]_D$ 44·34). Densities determined : $d_4^{17.9°}$ 0·9802, $d_4^{62.2°}$ 0·9493, $d_4^{85.3°}$ 0·9331.

t.	h.	H.	$d_4^{t°}$.	γ.	Parachor.
19·3°	20·14	19·90	0·9792	36·64	382·2
61·8	18·39	18·17	0·9496	32·45	382·3
85·1	17·55	17·31	0·9332	30·38	382·7
					Mean 382·4

Ethyl cyclo*hexylidenecyanoacetate*, $M = 193·13$, b. p. 151°/12 mm. Densities determined : $d_4^{18.5°}$ 1·0570, $d_4^{62.1°}$ 1·0211, $d_4^{85.4°}$ 1·0030.

t.	h.	H.	$d_4^{t°}$.	γ.	Parachor.
18·1°	19·37	19·13	1·0573	38·04	453·6
61·8	17·80	17·56	1·0213	33·73	455·6
85·0	16·87	16·63	1·0033	31·38	455·6
					Mean 454·7

Ethyl cyclo*heptylidenecyanoacetate*, $M = 207·14$, b. p. 160°/12 mm. Densities determined : $d_4^{16.3°}$ 1·0564, $d_4^{61.6°}$ 1·0219, $d_4^{85.6°}$ 1·0037.

t.	h.	H.	$d_4^{t°}$.	γ.	Parachor.
18·6°	19·25	19·01	1·0546	37·70	486·7
62·0	17·73	17·49	1·0216	33·60	488·1
85·4	16·86	16·62	1·0039	31·37	488·3
					Mean 487·7

Ethyl trans-*decahydro-β-naphthylidenecyanoacetate*, $M = 247·18$, b. p. 196°/14 mm. Densities determined : $d_4^{19.1°}$ 1·0523, $d_4^{62.3°}$ 1·0239, $d_4^{85.0°}$ 1·0091.

t.	h.	H.	$d_4^{t°}$.	γ.	Parachor.
21·6°	19·15	18·91	1·0508	37·37	581·6
61·8	17·86	17·62	1·0242	33·94	582·5
85·0	17·14	16·90	1·0091	32·07	582·9
					Mean 582·3

Ethyl benzylidenemalonate, $M = 248·13$, b. p. 179·5°/14 mm. Densities determined : $d_4^{18.5°}$ 1·1049 (supercooled liquid), $d_4^{61.4°}$ 1·0708, $d_4^{84.0°}$ 1·0528.

t.	h.	H.	$d_4^{t°}$.	γ.	Parachor.
19·8°	18·88	18·64	1·1039	38·70	560·6
61·2	17·33	17·09	1·0710	34·42	561·2
84·3	16·49	16·25	1·0527	32·17	561·4
					Mean 561·1

Ethyl benzylmalonate, $M = 250·14$, b. p. 163°/14 mm. Densities determined : $d_4^{19.7°}$ 1·0761, $d_4^{61.2°}$ 1·0433, $d_4^{85.0°}$ 1·0231.

t.	h.	H.	$d_4^{t°}$.	γ.	Parachor.
20·5°	17·81	17·57	1·0755	35·54	567·9
61·2	16·24	16·00	1·0433	31·39	567·6
83·5	15·39	15·15	1·0243	29·18	567·6
					Mean 567·7

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