120. *Synthesis of Cyclic Hydrocarbons. Part III.** 1 : 2-*Dialkyl*cyclo*hexanes.*

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A series of 1 : 2-dialkyl*cyclo*hexanes with straight-chain alkyl substituents ranging from ethyl to hexyl has been synthesised.

1-ALKYL-2-METHYL*cyclo*HEXANES, with alkyl groups ranging from methyl to *n*-pentyl, were prepared by Cramer and Signaigo.[1] These compounds had boiling ranges of 1·8—3·3°, which were assumed to result from the presence of *cis-trans*-isomers. 1-Butyl-2-ethyl*cyclo*hexane was prepared by Kharasch and Sternfeld,[2] using mainly Cramer and Signaigo's method.[1] 1 : 2-Diethyl*cyclo*hexane was synthesised by Buck *et al.*[3] In 1949 a series of 1 : 2-dialkyl*cyclo*hexanes was prepared by Dice, Loveless, and Cates,[4] using the route employed by Kharasch and Sternfeld.[2] Some discrepancies are apparent in their paper. Many yields were extremely low, and the compounds boiled over a wide range, yet no explanation was offered. For example, they recorded the boiling point of 1 : 2-dipropyl*cyclo*hexene as 162—167°/748 mm., which is unexpectedly low when compared with the boiling point (180—184°/746 mm.) of 1-ethyl-2-propyl*cyclo*hexene. When these compounds were catalytically reduced to the *cyclo*hexanes, 1 : 2-dipropyl*cyclo*hexane, obtained in 25% yield, boiled at 225—228°/748 mm., whereas 1-ethyl-2-propyl*cyclo*hexane boiled at 190—197°/746 mm. It seemed proper to repeat some of the work during the present study; many of the physical constants recorded in this paper do not agree with those given by Dice *et al.*

1 : 2-Diethyl- and 1-ethyl-2-propyl-*cyclo*hexane were prepared by hydrogenation of the corresponding *o*-dialkylbenzenes (Part I). The other members of the series were prepared from *cyclo*hexanone as shown in the attached scheme. Ethyl 2-oxo*cyclo*hexanecarboxylate (I; R = H) was alkylated. Hydrolysis and decarboxylation of the product gave the 2-alkyl*cyclo*hexanone which, when treated with lithium alkyls, yielded 1 : 2-dialkyl*cyclo*hexanols. Dehydration followed by hydrogenation then gave 1 : 2-dialkyl*cyclo*hexanes, which were dehydrogenated to the corresponding *o*-dialkylbenzenes (Part II).

For the preparation of dialkyl*cyclo*hexanes containing at least one *n*-propyl group an alternative route was employed. 2-Allyl*cyclo*hexanone (II) [5] was hydrogenated in the presence of palladium–strontium carbonate to 2-propyl*cyclo*hexanone (with Raney nickel even at room temperature and atmospheric pressure the carbonyl group was attacked),

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* Parts I and II, preceding papers.

[1] Cramer and Signaigo, *J. Amer. Chem. Soc.*, 1933, **55**, 3326.

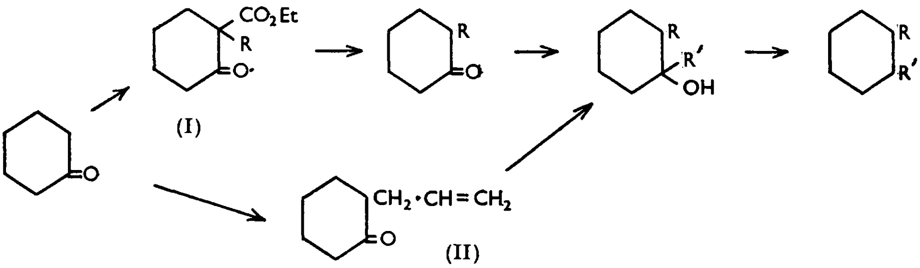
[2] Kharasch and Sternfeld, *ibid.*, 1939, **61**, 2318.

[3] Buck, Elsner, Forbes, Morell, Smith, and Wallsgrove, *J. Inst. Petroleum*, 1948, **34**, 339.

[4] Dice, Loveless, and Cates, *J. Amer. Chem. Soc.*, 1949, **71**, 3546.

[5] Vanderwerf and Lemmerman, *Org. Synth.*, 1949, **28**, 8.

which with propylmagnesium bromide in benzene gave 1 : 2-dipropyl*cyclo*hexanol in 58% yield (Dice *et al.*[4] record 27% from same reaction in ether) and some 2-propyl*cyclo*hexanol. However, the Grignard reaction of 2-allyl*cyclo*hexanone with butylmagnesium bromide in benzene gave 2-allyl-1-butyl*cyclo*hexanol in 80% yield, no reduction of the ketone being observed. Hydrogenation of the double bond proceeded smoothly under the conditions described above. Dehydration of 1 : 2-dipropyl*cyclo*hexanol with iodine and hydrogenation of the product were performed in the manner described by Dice *et al.*[4] Dehydration of 1-butyl-2-propyl*cyclo*hexanol with iodine proceeded less readily than that of the lower homologue, and this method was impracticable with the higher 1 : 2-dialkyl*cyclo*hexanols. It is probable that each 1 : 2-dialkyl*cyclo*hexene obtained in this manner is a mixture of isomers which on hydrogenation give the same *cyclo*hexane (mixture of *cis-trans*-isomers). Hydrogenation in the presence of palladised strontium carbonate yielded an incompletely saturated product. Satisfactory results were obtained by using Raney nickel at 140°/110 atm.



The method of Kharasch and Sternfeld,[2] which was used by Dice *et al.*[4] for the preparation of 2-alkyl*cyclo*hexanones from 2-chloro*cyclo*hexanone, gave low yields. Further, the Grignard reactions of 2-alkyl*cyclo*hexanones give unpredictable yields and not altogether satisfactory products, because of the tendency of the ketone to reduction by the Grignard reagent to the 2-alkyl*cyclo*hexanol. A new approach, giving good yields, was investigated, which is believed to be generally applicable to the preparation of 1 : 2-dialkyl*cyclo*hexanes, although, so far, few compounds have been prepared by it.

The ester (I; R = H) [6] and butyl bromide were added to a solution of sodium methoxide and anhydrous sodium iodide in anhydrous methanol, and the mixture was heated for 12 hr. The butylated product was obtained in a yield of 82%. Attempts to hydrolyse it by relatively mild methods, *e.g.*, with phosphoric acid [7] or potassium hydrogen carbonate in aqueous methanol (1 : 1),[8] failed. The ester underwent hydrolysis and decarboxylation in hot 5% potassium hydroxide solution to 2-butyl*cyclo*hexanone in 62% yield. The latter, with lithium alkyls, gave the dialkyl*cyclo*hexanols in high yields, which decreased with increasing size of the alkyl group : 1 : 2-dibutyl- (95%), 2-butyl-1-pentyl- (89%), and 2-butyl-1-hexyl-*cyclo*hexanol (75%). The *cyclo*hexanols were easily dehydrated indirectly by heating the carbinol first with hydrobromic acid (48%) and then with potassium hydroxide solution. The *cyclo*hexenes, obtained in yields of 85% or more, were hydrogenated at high temperature and pressure.

The physical constants of the 1 : 2-dialkyl*cyclo*hexanes are recorded in the Table.

Infrared Spectra.—Thanks are due to Mr. F. H. L. Hastings for the determination of the spectra and to Dr. F. B. Strauss for their interpretation.

Except for the stretching and bending regions the absorption bands of 1 : 2-dialkyl*cyclo*hexanes are relatively weak and require a cell length of 0·1 mm. Compounds containing CH_2 chains are characterised by a relatively intense absorption near 13·5 μ.

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[6] Snyder, Brooks, and Shapiro, *Org. Synth.*, Coll. Vol. II, 1943 p. 531; Kötz and Michels, *Annalen*, **350**, 204; Tiffeneau, Tehoubar, and Saiaslambert, *Bull. Soc. chim.*, 1947, [5], **14**, 445.

[7] Dehn and Jackson, *J. Amer. Chem. Soc.*, 1933, **55**, 4284.

[8] Lukes, Poos, Beyler, Johns, and Sarett, *ibid.*, 1953, **75**, 1711.

In the present series it can be shown by elimination that ethyl absorbs at 13·42, propyl at 13·64, butyl at 13·79 μ, but the change becomes negligible hereafter. The compounds with two different substituents show the corresponding two separate absorption maxima. All the compounds have two bands in common : at 8·7 and 9·05 μ. These are not contained in the spectra of the corresponding aromatic compounds.

1 : 2-*Dialkyl*cyclo*hexanes*, $C_6H_{10}RR'$.

R	R′	B. p./mm.	n_D^{20}	d_4^{20}
Et	Et	176·5—176·8°/760	1·4473	—
Et	Pr^n	195·5—195·7°/738	1·4497	0·8181
Pr^n	Pr^n	214·7—215·0°/768	1·4510	0·8188
Pr^n	Bu^n	112·1—112·4°/17 237°/760	1·4522	0·8218
Bu^n	Bu^n	120·4—120·5°/15	1·4536	0·8244
Bu^n	n-C_5H_{11}	136·6—136·8°/17	1·4546	0·8251
Bu^n	n-C_6H_{13}	148·9—149·2°/16	1·4560	0·8264

As in the aromatic series differentiation between 1 : 2-dialkyl*cyclo*hexanes becomes increasingly difficult as the molecular weight increases.

Determination of Purity.—We are indebted to Mr. C. S. G. Phillips and Mr. I. W. Scott for the determination of the purities of these compounds by gas-liquid partition chromatography (cf. Part II). The chromatograms were free from extraneous peaks, which indicates a purity of at least 99%, and all, except 1-ethyl-2-*n*-propyl*cyclo*hexane which was prepared by hydrogenation of the corresponding benzene derivative, showed a double peak. This indicates two very closely related compounds (geometrical isomers) present in nearly equal proportions. In the compounds of lower molecular weight, the first peak was slightly lower than the second, whilst in those of higher molecular weight the reverse was found true.

A detailed report on the purity of the hydrocarbons described in this and the two preceding papers, and on their infrared and ultraviolet spectra and other physical properties, will be published elsewhere.

EXPERIMENTAL

1 : 2-*Diethyl*cyclo*hexane*.—*o*-Diethylbenzene (8 g.) in ethanol (15 c.c.) was hydrogenated, with Raney nickel as catalyst, at 200°/110 atm. (initial) during 8 hr. The liquid was diluted with ether and poured into water. The ethereal layer was worked up in the usual way. The product, distilled from sodium, gave 1 : 2-diethyl*cyclo*hexane (6·7 g.).

1-*Ethyl*-2-*propyl*cyclo*hexane*.—*o*-Ethylpropylbenzene (13 g.) was hydrogenated as above. The product (11 g.) was heated under reflux with potassium for 1 hr. and distilled through a Dixon fractionating column (cf. Table) (Found : C, 85·5; H, 14·3. Calc. for $C_{11}H_{22}$: C, 85·6; H, 14·4%).

1 : 2-*Dipropyl*cyclo*hexane*.—2-Allyl*cyclo*hexanone [5] (59 g.; b. p. 82—83°/13 mm.) was reduced with hydrogen under atmospheric pressure, with palladium–strontium carbonate as catalyst, to 2-propyl*cyclo*hexanone (91%), b. p. 79—80°/10 mm. Propylmagnesium bromide [from magnesium (25 g.) and propyl bromide (130 g.)] was prepared in solution in ether (600 c.c.), which was then replaced by dry benzene. To this solution 2-propyl*cyclo*hexanone (93 g.), in benzene (400 c.c.), was added dropwise. The mixture was heated under reflux for 4 hr. and was worked up in the usual manner. The product was distilled under reduced pressure and gave a low-boiling (b. p. 92—110°/14 mm.) and a main fraction of 1 : 2-dipropyl*cyclo*hexanol (58%), m. p. 13·5°, b. p. 111·5—112·5°/14 mm., n_D^{20} 1·4693 (Dice *et al.*[4] record b. p. 70—74°/7 mm., n_D^{25} 1·4641). The low-boiling fraction was dehydrated by heating with hydrobromic acid followed by refluxing with an excess of concentrated potassium hydroxide solution. The unsaturated material was hydrogenated and the product was distilled from sodium. It yielded, on fractional distillation, a product, b. p. 155·2—155·8°/760 mm., n_D^{20} 1·4367 (which agree with the constants of propyl*cyclo*hexane), and then 1 : 2-dipropyl*cyclo*hexane, n_D^{20} 1·4504.

Dehydration of 1 : 2-dipropyl*cyclo*hexanol (61 g.) at 140—160° was catalysed by iodine (0·3 g.). The product was distilled from sodium to give 1 : 2-dipropyl*cyclo*hexene (48 g., 87%),

b. p. 213—214°, n_D^{18} 1·4655 (Found: C, 86·7; H, 13·3. Calc. for $C_{12}H_{22}$: C, 86·7; H, 13·3%) (Dice *et al.*[4] record b. p. 162—167°/748 mm.). The olefin was hydrogenated (cf. 1 : 2-dibutyl*cyclo*hexene), and the 1 : 2-dipropyl*cyclo*hexane (80%) which resulted was heated under reflux with potassium for 1 hr., then fractionally distilled through a Dixon column (Found: C, 85·7; H, 14·4. Calc. for $C_{12}H_{24}$: C, 85·6; H, 14·4%).

*1-Butyl-2-propyl*cyclo*hexane.*—Butylmagnesium bromide [from magnesium (29·2 g.) and butyl bromide (165 g.)] was prepared in ether, which was then replaced by dry benzene (1 l.). 2-Allyl*cyclo*hexanone (132 g., b. p. 82—83°/13 mm.) in benzene (260 c.c.) was added dropwise, and the mixture heated under reflux for 75 min. The usual treatment gave *2-allyl-1-butyl*cyclo*hexanol* (150 g., 80%), b. p. 124—126°/12 mm., $n_D^{16·5}$ 1·4800 (Found: C, 79·5; H, 12·3. $C_{13}H_{24}O$ requires C, 79·5; H, 12·3%). Reduction of this product with hydrogen under atmospheric pressure, with palladium–strontium carbonate catalyst, gave 1-butyl-2-propyl*cyclo*hexanol, b. p. 124—126°/12 mm., n_D^{20} 1·4688, in quantitative yield. The latter (115 g. crude) was dehydrated by iodine (0·35 g.) at 160° (bath) for 20 min. The temperature was then gradually raised until all volatile material had distilled. The partly dehydrated product was dried ($CaCl_2$), iodine (0·2 g.) was added, and the mixture was heated and distilled as before. The olefin was distilled twice under reduced pressure from potassium. 1-Butyl-2-propyl*cyclo*hexene had b. p. 173—174°/145 mm., n_D^{22} 1·4647 (yield 80%). (Dice *et al.*[4] record n_D^{25} 1·4609). The olefin (45 g.) was hydrogenated in ethanol, with Raney nickel, at 140°/110 atm. (initial). When absorption stopped, the temperature was raised to 180° for 2 hr. The mixture was dissolved in ether and poured into water. The ethereal solution was separated and dried ($MgSO_4$), and the ether was evaporated. To the ice-cold residue concentrated sulphuric acid (10 c.c.) was added, and the mixture was stirred vigorously for 1 hr., then poured on ice. The oil was separated, washed, dried ($MgSO_4$), heated with potassium at 200°, and then fractionally distilled through a Dixon column, giving 1-butyl-2-propyl*cyclo*hexane (70%) (Found: C, 85·8; H, 14·3. Calc. for $C_{13}H_{26}$: C, 85·6; H, 14·4%).

1 : *2-Dibutyl*cyclo*hexane.*—To a stirred cold mixture of butyl bromide (415 g.) and ethyl 2-oxo*cyclo*hexanecarboxylate[6] (415 g.) a solution of sodium methoxide (57 g. of sodium) and sodium iodide (67 g.) in anhydrous methanol (470 c.c.) was added dropwise during 45 min. The solution was then allowed to warm to 0°, the liquid solidifying. The mixture liquefied at 60°, and was boiled under reflux for 12 hr. Methanol was distilled off and the residue poured into water. The aqueous layer was extracted with ether, and the extracts were combined with the oily layer and dried ($MgSO_4$). After evaporation the residue was distilled through a 20 cm. Vigreux column, and the crude, colourless ethyl 1-butyl-2-oxo*cyclo*hexanecarboxylate (82%) was used without further purification. The ester (79 g.) was boiled with sodium hydroxide (78 g.) in methanol (780 c.c.) and water (780 c.c.) for 15 hr. To the cold solution concentrated hydrochloric acid (210 c.c.) was slowly added. After the considerable evolution of heat and carbon dioxide had ceased, the mixture was heated to boiling during 1 hr. and was boiled under reflux for another hour. It was cooled and diluted with water (1·5 l.). The aqueous layer was extracted with light petroleum (b. p. 40—60°), and the extracts were combined with the oily layer. The solvent was evaporated from the dried solution, and the residue was distilled through a 40 cm. fractionating column ($\frac{1}{8}''$ gauze rings), to give 2-butyl*cyclo*hexanone, b. p. 93·5—94°/11 mm., n_D^{19} 1·4548 [2 : *4-dinitrophenylhydrazone*, orange crystals (from ethanol), m. p. 110—111° (Found: C, 57·7; H, 6·8. $C_{16}H_{22}O_4N_4$ requires C, 57·5; H, 6·6%)].

A solution of butyl-lithium, prepared from lithium (11·8 g.), butyl bromide (91 g.), and ether (300 c.c.),[9] was cooled in ice–salt, and 2-butyl*cyclo*hexanone (50·3 g.) in ether (70 c.c.) was added dropwise with stirring during 45 min. Oxygen-free nitrogen was passed through the apparatus during the whole operation. When the addition was complete, the solution was stirred at room temperature for 1 hr. and was boiled under reflux for 1 hr. Next morning it was decomposed with ice and ammonium chloride. The ethereal solution was separated and dried ($MgSO_4$), and the ether was evaporated. The residue was distilled, giving 1 : *2-dibutyl*cyclo*hexanol* (95%), b. p. 132—134°/9 mm., n_D^{18} 1·4689 (Found: C, 79·4; H, 13·4. $C_{14}H_{28}O$ requires C, 79·2; H, 13·3%).

The *cyclo*hexanol (65·6 g.) and 48% hydrobromic acid (66 g.) were heated under reflux for 1 hr., then cooled in ice, and a solution of potassium hydroxide (144 g.) in water (96 c.c.) was added. The mixture was heated under reflux for 90 min. The floating oil was separated and

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[9] Gilman, Beel, Brannen, Bullock, Dunn, and Miller, *J. Amer. Chem. Soc.*, 1949, **71**, 1499; Gilman and Esmay, *ibid.*, 1953, **75**, 278.

combined with the ethereal extract of the aqueous layer. The ether was evaporated from the dried solution, and the residue was heated with sodium at 200° for 30 min. and distilled, giving 1 : 2-*dibutyl*cyclo*hexene* (88%), b. p. 114—115°/12 mm., n_{D}^{19} 1·4715 (Found : C, 86·4; H, 13·4. $C_{14}H_{26}$ requires C, 86·5; H, 13·5%). Hydrogenation of the olefin was carried out in ethanol with Raney nickel at 110 atm. (initial), the temperature being allowed to rise slowly to 200°. After treatment with sulphuric acid, the hydrocarbon was heated with potassium and distilled through a Dixon column, giving 1 : 2-*dibutyl*cyclo*hexane* (90%) (Found : C, 85·9; H, 14·4. $C_{14}H_{28}$ requires C, 85·6; H, 14·4%).

1-*Butyl*-2-*pentyl*cyclo*hexane*.—The methods used were similar to those described for the preparation of 1 : 2-dibutyl*cyclo*hexane. 2-*Butyl*-1-*pentyl*cyclo*hexanol* was obtained from 2-butyl*cyclo*hexanone (40 g.) and pentyl-lithium [from lithium (9 g.) and pentyl bromide (67 g.)], b. p. 151—153°/12 mm., n_{D}^{17} 1·4698 (yield 89%) (Found : C, 79·7; H, 13·4. $C_{15}H_{30}O$ requires C, 79·6; H, 13·4%). 1-*Butyl*-2-*pentyl*cyclo*hexene* had b. p. 128—129°/11 mm., n_{D}^{20} 1·4667 (yield 85%) (Found : C, 86·6; H, 13·3. $C_{15}H_{28}$ requires C, 86·5; H, 13·5%). Hydrogenation of the olefin gave 1-*butyl*-2-*pentyl*cyclo*hexane* (85%) (Found : C, 85·8; H, 14·6. $C_{15}H_{30}$ requires C, 85·6; H, 14·4%).

1-*Butyl*-2-*hexyl*cyclo*hexane*.—The methods employed were similar to those described for 1 : 2-dibutyl*cyclo*hexane. 2-*Butyl*-1-*hexyl*cyclo*hexanol*, obtained by reaction of 2-butyl*cyclo*hexanone (50·3 g.) with hexyl-lithium [from lithium (11·8 g.) and hexyl bromide (110 g.)], had b. p. 167—168°/14 mm., n_{D}^{19} 1·4690 (yield 76%) (Found : C, 80·2; H, 13·5. $C_{16}H_{32}O$ requires C, 79·9; H, 13·4%). Since a small amount of *n*-dodecane may have been formed by the reaction of hexyl-lithium with hexyl bromide, the crude *cyclo*hexanol was passed in light petroleum (b. p. 40—60°) through alumina. The column was eluted with light petroleum and then with ether. The pure *cyclo*hexanol was dehydrated, yielding 1-*butyl*-2-*hexyl*cyclo*hexene* (87%), b. p. 144·5—145°/13 mm., n_{D}^{23} 1·4653 (Found : C, 86·5; H, 13·5. $C_{16}H_{30}$ requires C, 86·4; H, 13·6%). The olefin was hydrogenated, and the product was purified as described for 1 : 2-dibutyl*cyclo*hexane, giving 1-*butyl*-2-*hexyl*cyclo*hexane* (84%) (Found : C, 85·9; H, 14·4. $C_{16}H_{32}$ requires C, 85·6; H, 14·4%).

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