119. *Synthesis of Cyclic Hydrocarbons. Part II.* Dehydrogenation of* 1 : 2-*Dialkyl*cyclo*hexanes to* o-*Dialkylbenzenes.*

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Dehydrogenation of 1 : 2-dialkyl*cyclo*hexanes to the corresponding *o*-dialkylbenzenes has been investigated. 1 : 2-Diethyl-, 1 : 2-dipropyl-, 1-butyl-2-propyl-, 1 : 2-dibutyl-, and 1-butyl-2-pentyl-*cyclo*hexane were dehydrogenated by passing the hydrocarbon vapour over platinum or palladium catalysts at 320—350°. 1-Butyl-2-pentyl- and 1-butyl-2-hexyl-*cyclo*hexane were dehydrogenated when boiled in contact with palladised charcoal. The *o*-dialkylbenzenes were purified through the sulphonic acids (calcium salts).

Catalytic dehydrogenation of *cyclo*hexane and methyl*cyclo*hexane was achieved by Zelinski,[1] who also investigated the dehydrogenation of the dimethyl*cyclo*hexanes.[2] However, there is no record of a systematic investigation into the dehydrogenation of di- or poly-alkyl*cyclo*hexanes with alkyl substituents larger than methyl.

In an endeavour to find out the best conditions for the dehydrogenation of 1 : 2-dialkyl*cyclo*hexanes different procedures have now been used, with 1 : 2-diethyl-, 1 : 2-dipropyl-, 1-butyl-2-propyl-, 1 : 2-dibutyl-, 1-butyl-2-pentyl-, and 1-butyl-2-hexyl-*cyclo*hexane.

All the experiments in the vapour phase were performed at 320—350°, the hydrocarbons being carried in a slow current of hydrogen. Two types of catalyst were used: platinised charcoal[3] and palladised asbestos.[4] The former was considerably more effective than the latter, and was used to dehydrogenate 1 : 2-dipropyl*cyclo*hexane- and 1-butyl-2-propyl*cyclo*hexene at 320—330°. The activity of the catalyst, although high at the start, fell rapidly after only a small proportion of the compound had been added, and later more slowly. The partly dehydrogenated material was therefore passed over a number of fresh charges of catalyst. Nevertheless, dehydrogenation was not complete. Raising the temperature above 330° did not appear to increase the efficiency of the dehydrogenation and the product became appreciably more yellow. Even at 320—330° the condensate showed a weak blue fluorescence, which was removed with some difficulty by heating the product with sodium at 200°. Purification by heating with potassium was more efficient, but led to some charring. Potassium was found to be more suitable for the purification of *cyclo*hexanes, which showed no tendency to decompose. Dehydrogenation of 1-butyl-2-propyl*cyclo*hexene required three charges of fresh catalyst for completion. Palladised asbestos was used for further vapour-phase dehydrogenations. Some comparative experiments to establish the most favourable conditions for this reaction were carried out with 1-butyl-2-propyl*cyclo*hexane. The efficiency of the dehydrogenation appears to depend on temperature, on vapour velocity, and on the total quantity of the dialkyl*cyclo*hexane passed over a certain quantity of catalyst (Table 2).

Attempts to dehydrogenate 1 : 2-dipropyl*cyclo*hexane (b. p. 215°) in the liquid phase by heating it under reflux with palladised charcoal failed, presumably because the temperature was too low. The boiling point of 1-butyl-2-hexyl*cyclo*hexane (149°/16 mm.), however, was sufficiently high to permit dehydrogenation, which proceeded smoothly though rather slowly. That the reaction was almost complete was shown by the refractive index of the product, which before purification through the sulphonic acid had n_D^{20} 1·4881, and after purification n_D^{20} 1·4890.

1-Butyl-2-pentyl*cyclo*hexane was also dehydrogenated in the liquid phase. The

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* Part I, preceding paper.

[1] Zelinski, *Ber.*, 1911, **44**, 3121.

[2] *Idem, Ber.*, 1923, **56**, 787; 1935, **68**, 98.

[3] Linstead and Thomas, *J.*, 1940, 1127.

[4] Packendorff and Leder-Packendorff, *Ber.*, 1934, **67**, 1388.

refractive index of the product (n_D^{20} 1·4890) was near to that of the product obtained by vapour-phase dehydrogenation (n_D^{20} 1·4898).

All the dialkylbenzenes thus prepared still contained small amounts of the corresponding *cyclo*hexanes. In order to remove the hydroaromatic impurity, each product, except *o*-butylpentylbenzene, was converted into the sulphonic acid. No attempt was made to determine the configurations of these acids. The calcium salts of the acids were readily soluble in cold water; these solutions were then extracted with ether to remove any hydrocarbon. No difficulties were encountered when this method was applied to the purification of *o*-dipropyl- and *o*-butylpropyl-benzene. The crude *o*-butylpropylbenzene, for example, was found to contain 7% of 1-butyl-2-propyl*cyclo*hexane, which was recovered from the ethereal extract. The method was less satisfactory when applied to *o*-dibutyl- and *o*-butylhexyl-benzene, whose sulphonic acids, and their calcium salts, unlike those derived from *o*-dipropyl- and *o*-propylbutyl-benzene, act as emulsifying agents, probably owing to the length of the aliphatic chains : *e.g.*, the calcium salts readily emulsified mixtures of water and light petroleum. Further, when aqueous solutions of the calcium sulphonates were extracted with ether, the salts, together with a considerable quantity of water, passed into the ethereal layer. Light petroleum was therefore used for the separation of the hydrocarbon impurities, in spite of the tendency to form emulsions.

Vigorous conditions are required for the hydrolysis of the sulphonic acids. For example, butylpropylbenzenesulphonic acid is hydrolysed with great difficulty by the sulphuric acid–superheated steam method used by Melpolder *et al.*[5] for the fractional hydrolysis of the sulphonic acids from mixed di*iso*propylbenzenes, and by Plapinger and Woods [6] in the purification of *m*-dialkylbenzenes. Satisfactory results were obtained when the calcium salts of the sulphonic acids were heated with concentrated hydrochloric acid in sealed tubes at 200°. The acids of the lower members of the series were hydrolysed after four hours; the dibutyl- and the butylhexyl-benzenesulphonic acids required eight hours.

It is believed that the sulphonation of *o*-dialkylbenzenes and the subsequent hydrolysis of the sulphonic acids under the conditions used in this work do not cause structural changes. Even triethylbenzenes, when sulphonated under the more drastic conditions of the Jacobsen rearrangement, reported for tetra- and penta-alkylbenzenes, were recovered unchanged in good yields.[7] Butylpropylbenzenesulphonic acid was hydrolysed by sulphuric acid on steam-distillation, and the calcium salt by hydrochloric acid at 200°. The products recovered from the two hydrolyses had identical refractive indices.

Physical constants are reported in Table 1.

TABLE 1. *Physical constants of* o-*dialkylbenzenes*, *o*-C_6H_4RR'.

R	R′	B. p./mm.	n_D^{20}	d_4^{20}	R	R′	B. p./mm.	n_D^{20}	d_4^{20}
Et	Et	182·9°/755	1·5035	0·8796 *	Pr^n	Bu^n	112·5—112·7°/17	1·4936	0·8662
Et	Pr^n	200·8—201·0°/764	1·4990	0·8732 *	Bu^n	Bu^n	125·3°/15	1·4918	0·8640
Et	Pr^i	192·2—192·3°/752	1·4980	0·8747 *	Bu^n	n-C_5H_{11}	127·3°/10	1·4898	0·8634
Pr^n	Pr^n	99·8—100·0°/21	1·4969	0·8713	Bu^n	n-C_6H_{13}	150·8°/15	1·4890	0·8618

* Cf. Part I.

The following discussion concerning the purity of the *o*-dialkylbenzenes and their spectra includes also the hydrocarbons described in Part 1.

Infrared Spectra.—The authors thank Dr. F. B. Strauss for the interpretation and Mr. F. H. L. Hastings for the determination of the spectra. All spectra were examined, in the rock-salt region only, by means of a Perkin-Elmer double-beam spectrophotometer, with a cell length of 0·10 mm., supplemented by use of a cell length of 0·01 mm. for the more intense absorption bands.

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[5] Melpolder, Woodbridge, and Headington, *J. Amer. Chem. Soc.*, 1948, **70**, 935.

[6] Plapinger and Woods, *ibid.*, 1951, **73**, 5603.

[7] Smith and Guss, *ibid.*, 1940, **62**, 2625, 2631.

o-Dialkylbenzenes show aromatic C–H stretching bands at 3·26 and 3·31 μ, and aliphatic C–H at 3·40 and 3·50 μ; the intensity of the former group decreases in relation to the latter as the proportion of the aliphatic substituent increases.

In the overtone region there is a group of bands between 5 and 6 μ, very nearly identical for all *ortho*-disubstituted benzenes.

A strong double-bond stretching band at 6·24 μ and a weaker band at 6·34 μ are common to all the compounds examined.

In the hydrogen bending region, a conspicuous new band at 7·50 μ appears with the propyl substituent and remains with the higher homologues. The compound containing an *iso*propyl substituent shows complexity of spectrum around 7·25 μ which is a characteristic of this group.

An extremely intense out-of-plane vibration of hydrogen occurs with a maximum between 13·3 and 13·5 μ, characteristic of *ortho*-disubstituted benzenes. A number of characteristic bands are present which distinguish these compounds from one another, but the distinction becomes increasingly difficult as the molecular weight increases.

Ultraviolet Absorption.—All *ortho*-disubstituted benzenes have a maximum at 2650 Å with an extinction coefficient of between 250 and 350. There is always an inflexion near 2720 Å which sometimes appears as a separate maximum with an extinction coefficient of 260.

Determination of Purity.—The purity of the *o*-dialkylbenzenes was kindly determined by Mr. C. S. G. Phillips and Mr. I. W. Scott of the Inorganic Chemistry Laboratory, Oxford, by gas–liquid partition chromatography with the apparatus described by Littlewood, Phillips, and Price.[8] They showed that all the compounds are free from any impurity caused by the presence of isomers or other (dialkyl)benzenes, achieving complete separation of synthetic mixtures of such benzene derivatives: 1% of impurity would have been detected. However, the benzene derivatives prepared by dehydrogenation have not so far been proved free from their corresponding *cyclo*hexanes, as, under the conditions used, their retention volumes are approximately the same. Further investigations, under different conditions, are pending.

EXPERIMENTAL

o-*Diethylbenzene.*—1 : 2-Diethyl*cyclo*hexane (5 g.) was dehydrogenated in the apparatus and with the catalyst described below for the dehydrogenation of 1-butyl-2-propyl*cyclo*hexane. Diethyl*cyclo*hexane was passed over the catalyst at 300—320° at a rate of 6—8 drops per min. The product had n_D^{20} 1·4790. After the product had been passed twice over the same catalyst at 330—350° at a rate of 1—2 drops per min., the refractive index of the condensate, after it had been distilled from sodium, was n_D^{20} 1·5020. No further attempt to purify the product was made as *o*-diethylbenzene was prepared by two other methods (cf. preceding paper).

o-*Ethylpropylbenzene.*—1-Ethyl-2-propyl*cyclo*hexane was dehydrogenated as described for the dehydrogenation of butylpropyl*cyclo*hexane. Only 2 c.c. of the *cyclo*hexane were passed over the palladium catalyst (5 g. of Pd) at a rate of 1 drop per min. The product after distillation from sodium had n_D^{20} 1·4987, in good agreement with the value (n_D^{20} 1·4990) of the product obtained by the method starting from phthalic anhydride (Part 1).

o-*Dipropylbenzene.*—30% Platinised charcoal[3] (1·8 g.) was mixed with purified short-fibre asbestos and a small quantity of glasswool cut into short tufts. The middle 30 cm. of the reaction tube (75 cm. × 1 cm.) were loosely filled with the catalyst, which was held in position by plugs of glasswool. The tube was fixed in a sloping furnace, 50 cm. long. The upper end of the tube was widened to take a gas-inlet tube and the stem of a tap-funnel drawn out to a jet. A thermocouple, encased in a pipe-clay tube, extended approx. 25 cm. into the furnace alongside the reaction tube. The air in the apparatus was displaced by a slow stream of hydrogen which had passed through a bubbler containing paraffin oil, and thence through a tube packed with glasswool. The furnace was heated to 320—330°, the stream of hydrogen then slowed down to one bubble in 3 sec., and 1 : 2-dipropyl*cyclo*hexane (15·5 g.; n_D^{20} 1·4510) added, at the rate of 6 drops per min. The first few drops issuing from the tube had a high refractive index

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[8] Littlewood, Phillips, and Price, *J.*, 1955, 1480.

(n_D^{18} 1·4840), but as more hydrocarbon passed through the tube the refractive index of the product fell continuously, so that the last drops collected had n_D^{18} 1·4715. The reaction tube was filled with fresh catalyst and heated as before. The mixture of 1 : 2-dipropyl*cyclo*hexane and *o*-dipropylbenzene was passed over the catalyst twice at the rate of 3 drops per min., and the product had n_D^{18} 1·4833. It boiled over a considerable range (214·8—216·4°); it was therefore passed over two further charges of fresh catalyst. After distillation from potassium, the product (b. p. 216—217°, n_D^{19} 1·4946) was freed from the unchanged *cyclo*hexane by ether-extraction of calcium dipropylbenzenesulphonate (15·4 g.) [see purification of *o*-propylbutylbenzene (*b*)], and subsequent decomposition of this salt to o-*dipropylbenzene* (6·4 g.) (Found : C, 88·8; H, 11·2. $C_{12}H_{18}$ requires C, 88·8; H, 11·2%).

From the extracts impure 1 : 2-dipropyl*cyclo*hexane (5%, b. p. 97°/20 mm., n_D^{20} 1·4546) was recovered.

The efficiency of the platinised charcoal catalyst used for the dehydrogenation was tested by passing methyl*cyclo*hexane (5 g.) over a fresh charge of this catalyst (1·8 g.) under the same conditions as were used above. After having passed twice over the same catalyst, the liquid had n_D^{20} 1·4970 (toluene, n_D^{20} 1·4969).

o-*Propylbutylbenzene*.—1-Butyl-2-propyl*cyclo*hexene (47 g.) was dehydrogenated in the vapour phase, the method and apparatus described above being used. However, only three charges of fresh catalyst were required to obtain maximum conversion into the benzene. The product (34·7 g.), distilled from potassium, boiled at 110—112°/16 mm. (n_D^{20} 1·4899), and was purified by conversion into the calcium sulphonate.

Dehydrogenation of 1-butyl-2-propyl*cyclo*hexane was performed with 30% palladised asbestos. The catalyst was prepared by a method similar to that of Packendorff and Leder-Packendorff.[4] 15 g. were sufficient to occupy 60 cm., of the reaction tube (115 cm. × 1 cm.), which was fixed in a sloping tube furnace (length 90 cm.). In all other details the apparatus was identical with that described above. Hydrogen was passed through the apparatus and the tube heated to 100°. After 2 hr. the temperature was raised to 150°, after 4 hr. to 330° and kept at 330—350° overnight. The flow of hydrogen was reduced to one bubble in 3 sec., and 1-butyl-2-propyl*cyclo*hexane (10 g.) was passed over the catalyst. The influence of temperature, rate of addition of hydrocarbon, and ratio of substance to catalyst on the dehydrogenation is shown in Table 2. The impure *o*-butylpropylbenzene was heated with potassium at 200° for 20 min. and then distilled; it had b. p. 114—116°/20 mm., n_D^{20} 1·4903.

TABLE 2. *Dehydrogenation of* 1-*butyl*-2-*propyl*cyclo*hexane.*

Wt. taken (g.)	Temp.	Rate of addn. (drops/min.)	Charges of catalyst	n_D^{20} *
10	300°	6	1	1·4720
10	300	4	2	1·4820
10	300	4	3	1·4872
10	330	3	3	1·4913
4	330—350	2	1	1·4810
4	330—350	2	2	1·4912
2	330—350	>1	1	1·4900
2	330—350	>1	2	1·4928

* Pure *o*-butylpropylbenzene has n_D^{20} 1·4936.

Purification of o-*propylbutylbenzene*. (*a*) Through the sulphonic acid. To the hydrocarbon (5 g.), cooled in ice-salt, concentrated sulphuric acid (10 g.) was added with vigorous stirring. The mixture became brown and the two layers emulsified. After 5 min. the ice-bath was removed, and stirring was continued for 3 hr. The liquid was poured on ice. The solution was made alkaline with dilute sodium hydroxide solution and extracted twice with ether. The aqueous alkaline solution was acidified with sulphuric acid and distilled. When the temperature of the liquid reached 140°, superheated steam was passed through the mixture. The distillate was extracted with ether, the ethereal extract dried ($MgSO_4$), and the solvent evaporated. o-*Butylpropylbenzene*, obtained on distillation of the residue, had n_D^{18} 1·4935 (Found : C, 88·3; H, 11·3. $C_{13}H_{20}$ requires C, 88·6; H, 11·4%).

(*b*) Through the calcium sulphonate. From the reaction mixture after sulphonation, carried out as in (*a*), *barium butylpropylbenzenesulphonate* was prepared (Found: C, 48·2; H, 5·7; Ba, 20·9. $C_{26}H_{38}O_6S_2Ba$ requires C, 48·2; H, 5·9; Ba, 21·2%).

Since the barium salt was insufficiently soluble in water (1·5%) and could not be obtained crystalline, the calcium salt was prepared. Oleum (82 g. of acid prepared by mixing 24 c.c. of

20% oleum and 31 c.c. of concentrated sulphuric acid) was added to ice-cold crude *o*-propylbutylbenzene (27·3 g.), and the mixture was stirred at room temperature for 3 hr. The mixture was poured on crushed ice (400 g.), and the solution was exhaustively extracted with ether. The combined ethereal extracts, containing the sulphonic acid and any hydrocarbon, were evaporated, leaving a concentrated aqueous solution of the sulphonic acid, and some hydrocarbon. The yellow liquid was diluted with water (500 c.c.), warmed, and treated with a small excess of calcium carbonate and a sufficient quantity of calcium hydroxide suspension to give a neutral solution. The solution was filtered, cooled, and extracted four times with ether. The aqueous solution was evaporated to dryness, giving pale-brown hygroscopic calcium butylpropylbenzenesulphonate (41 g.). The solvent was evaporated from the ethereal extract, and the residue was distilled, giving impure 1-butyl-2-propyl*cyclo*hexane (1·9 g., 7%; n_D^{20} 1·4537).

Calcium butylpropylbenzenesulphonate (5 g.) was heated in a sealed tube (1·5 × 60 cm.) with concentrated hydrochloric acid (30 c.c.) at 200° for 4 hr., the air in the tube having been displaced by nitrogen. Nine tubes were filled and heated in this manner. The products were combined, and water, sufficient to make 600 c.c. of solution, and some ether were added. The solution was saturated with ammonium chloride, the ethereal layer was removed, and the aqueous solution was extracted four times with ether. The combined ethereal solutions were washed with dilute sodium hydroxide solution, which removed the colour, and dried ($MgSO_4$). After evaporation, the residual liquid was heated with potassium at 200° for 30 min. and fractionally distilled through a Dixon column, to give pure *o*-butylpropylbenzene (19·7 g., 72%) (Found: C, 88·6; H, 11·5%).

o-*Dibutylbenzene*.—1 : 2-Dibutyl*cyclo*hexane (23 g.) was dehydrogenated in the vapour phase over palladised asbestos by the method used for 1-butyl-2-propyl*cyclo*hexane. Four charges of fresh catalyst were required to produce the maximum conversion. The product, which was distilled from sodium, had b. p. 125—126°/16 mm., n_D^{20} 1·4899 (yield 19·7 g., 89%). It was purified through the calcium sulphonate as described below for the purification of *o*-butylhexylbenzene, with similar difficulties. Finally o-*dibutylbenzene* was fractionally distilled through a Dixon column (Found: C, 88·4; H, 11·6. $C_{14}H_{22}$ requires C, 88·3; H, 11·7%).

o-*Butylpentylbenzene*.—1-Butyl-2-pentyl*cyclo*hexane was dehydrogenated over palladised asbestos at 330—350° by the method described above. o-*Butylpentylbenzene* had b. p. 127·3°/10 mm., n_D^{20} 1·4898, d_4^{20} 0·8634 (Found: C, 88·1; H, 11·7. $C_{15}H_{24}$ requires C, 88·2; H, 11·8%). Dehydrogenation of 1-butyl-2-pentyl*cyclo*hexane in the liquid phase, by the method described below for the preparation of *o*-butylhexylbenzene, gave a product which, after distillation from sodium, had n_D^{20} 1·4890.

o-*Butylhexylbenzene*.—1-Butyl-2-hexyl*cyclo*hexane was dehydrogenated in the liquid phase, with palladised charcoal. The catalyst, after preparation by the method of Linstead and Thomas,[8] was heated at 170°/15 mm. for 1 hr. and stored *in vacuo* over phosphoric oxide. The *cyclo*hexane (16·2 g.) and catalyst (1·8 g.) were put in a 100 c.c. long-necked distilling-flask, the side-arm of which was connected to a trap, cooled in solid carbon dioxide–ethanol and connected to a filter-funnel dipping below the surface of water. The air in the apparatus was displaced by nitrogen. The flask was heated gradually to 220—230°, and the stream of nitrogen was stopped. The liquid appeared to boil, although there was little refluxing, and gas was evolved. After 2 hr. the bath temperature was increased to 240—250°, the liquid boiling gently. Liberation of gas had ceased after 26 hr. A slow stream of nitrogen was passed through, and the temperature was raised to 260° for 2 hr. The product was distilled; it had n_D^{20} 1·4880 (yield 15 g., 95%).

The ice-cold hydrocarbon was treated with oleum (37·5 g. of acid prepared by mixing 24 c.c. of 20% oleum and 31 c.c. of concentrated sulphuric acid) and stirred for 2½ hr. At first the oleum solidified, but it melted when the ice-bath was removed. During the last 30 min. of the reaction the flask was warmed to 35°. When cold, the mixture was poured on ice (100 g.). A thick translucent emulsion was formed and did not separate overnight. Water (200 c.c.) and some ether were added. The mixture was shaken, and on standing it rapidly separated into two clear layers. The aqueous layer was extracted four times with ether. The ethereal solutions were combined, and the ether was evaporated. The residual emulsion, containing butylhexylbenzenesulphonic acid and any *cyclo*hexane, was dissolved in water (150 c.c.) and neutralised with excess of calcium carbonate. The suspension was warmed and filtered. The solid was washed with hot water (150 c.c.). The washings were added to the filtrate, which was extracted four times with ether. The ethereal extracts were combined and evaporated, leaving an aqueous solution which was evaporated to dryness, giving a solid residue (21·8 g.) of calcium butylhexylbenzenesulphonate. This was dissolved in water (200 c.c.) and shaken with light petroleum (b. p. 40—60°). A stable emulsion was formed which broke on addition of a little lime-water. Extraction with light petroleum was repeated, and the petroleum layer, which separated slowly, was removed. Some calcium salt, which had separated during the extraction, was added to the aqueous solution, which was evaporated to dryness, giving the calcium salt as a white solid (21 g.). This was decomposed with concentrated hydrochloric acid as described under the purification of *o*-propylbutylbenzene, but with 8 hours' heating. o-*Butylhexylbenzene* (8·8 g., 56%) was fractionally distilled through a Dixon column (Found: C, 88·3; H, 12·0. $C_{16}H_{26}$ requires C, 88·0; H, 12·0%).

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