162. *Syntheses with Isotopic Tracer Elements. Part V.** $[^{14}C_1]$*Benzene.*

By H. S. Turner and R. J. Warne.

A method is described for the preparation of $[^{14}C_1]$benzene from carbon dioxide in 75% yield.

Several syntheses of benzene and its simple derivatives labelled in the nucleus with isotopic carbon have been described. Grosse and Weinhouse (*Science*, 1946, **104**, 402) obtained $[1:3:5\text{-}^{14}C_3]$mesitylene in about 10% yield by condensation of $[2\text{-}^{14}C]$acetone in presence of sulphuric acid. Fields, Leaffer, and Rohan (*ibid.*, 1949, **109**, 35) have announced the preparation of 1-methyl$[1\text{-}^{14}C]$*cyclo*hexanol by the reaction of ethyl [*carboxy*-^{14}C]acetate with pentamethylenebis(magnesium bromide), and its conversion into $[1\text{-}^{14}C]$toluene, $[1\text{-}^{14}C]$benzoic acid, and $[^{14}C_1]$benzene in overall yields of 35—50, 30—40, and 25—40%, respectively. Working details have not yet been published,† but it is perhaps significant

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* Part IV, *J.*, 1951, 1896.

† *Added in proof.* Since the present paper was submitted a more detailed account of this synthesis has appeared (Fields, Leaffer, Rothchild, and Rohan, *J. Amer. Chem. Soc.*, 1952, **74**, 5498). These authors describe the synthesis of toluene, benzoic acid, and benzene on a 63-millimole scale; overall yields from carbon dioxide were 33, 24, and 21% respectively. There was no significant dilution of isotope. It is mentioned that on the scales of 131 and 149 millimoles the yields of benzoic acid were 37 and 25% respectively.

that labelled aromatic compounds made by the process are advertised (Tracerlab Inc., Boston, Mass., U.S.A.; Catalog B) as having a specific activity of 0·01—0·02 millicurie per millimole, whereas barium [^{14}C]carbonate is normally available with specific activities up to 4 mc per millimole. [1 : 3 : 5-$^{14}C_3$]Toluene has been prepared from [α-^{14}C]pyruvic acid by way of dihydromethyltrimesic acid and uvitic acid in 62% yield (Hughes and Reid, *J. Org. Chem.*, 1949, **14**, 516; see also Schepartz and Gurin, *J. Biol. Chem.*, 1949, **180**, 663); the best recorded yield of [α-^{14}C]pyruvic acid from barium carbonate is 40—52% (Calvin and Lemmon, quoted by Calvin *et al.*, "Isotopic Carbon," Chapman and Hall, London, 1949, p. 210). Two syntheses of benzoic acid have been mentioned in a review article. In the first, butadiene and [αβ-$^{14}C_2$]maleic anhydride are condensed to give 1 : 2 : 3 : 6-tetrahydro[1 : 2-$^{14}C_2$]phthalic anhydride, which is dehydrogenated and decarboxylated to give [1 : 2-$^{14}C_2$]benzoic acid [Nystrom, Loo, Mann, and Allen, quoted by Crompton and Woodruff, *Nucleonics*, 1950, **7**, (3), 49; (4), 44]. The synthesis of the maleic anhydride in ~73% yield from barium carbonate on the 10-millimole scale has now been reported in full (Nystrom, Loo, and Leak, *J. Amer. Chem. Soc.*, 1952, **74**, 3434). In the second synthesis 2-methyl-1 : 4-[8-^{14}C]naphthaquinone (Collins, *ibid.*, 1951, **73**, 1038; yield 25% from barium carbonate) is oxidised to [3-^{14}C]phthalic acid, and decarboxylated to [2 : 3-$^{14}C_1$]benzoic acid (Collins, quoted by Crompton and Woodruff, *loc. cit.*). A recent paper has described the preparation of [$^{14}C_1$]benzene *via* [*carboxy*-$^{14}C_2$]pimelic acid and [1-^{14}C]*cyclo*hexanone in 22% yield (Speer, Humphries, and Roberts, *J. Amer. Chem. Soc.*, 1952, **74**, 2443). The maximum overall recovery of isotope in this case is, of course, 50%. Another possible intermediate in this synthesis, [2-^{14}C]*cyclo*hexanone, has been prepared from cyanide, *via cyclo*pentanone cyanohydrin and aminomethyl*cyclo*pentanol, by means of the Tiffeneau reaction in 20—25% yield (Arnold, U.S.A.E.C.U. 575).

With the possible exception of that of Nystrom *et al.*, none of the methods indicated above affords a satisfactory yield of aromatic compound on the relatively small scale (up to 20 millimoles) most suitable for syntheses with ^{14}C. We therefore examined the aluminium halide-catalysed rearrangement of alkyl*cyclo*pentanes to *cyclo*hexanes [Nenitzescu and Cantuniari, *Ber.*, 1933, **66**, 1097 (this paper contains a review of the early literature on the subject); Glasebrook and Lovell, *J. Amer. Chem. Soc.*, 1939, **61**, 1717] which appeared to afford a promising route to labelled benzene and its homologues. Methyl*cyclo*pentane was treated with water-promoted aluminium chloride under approximately the conditions described by Glasebrook and Lovell (*loc. cit.*) except that the reaction was carried out in absence of air in sealed glass tubes. The composition of the mixtures obtained at 77° (surrounded by boiling carbon tetrachloride vapour) though variable, no doubt owing to incomplete equilibration, always contained less methyl*cyclo*pentane than would be expected from Glasebrook and Lovell's results. For example, two parallel isomerisations gave mixtures with 19 and 13 moles % of methyl*cyclo*pentane, these values being based on the concordant results of both refractive index (using Glasebrook and Lovell's n_D^{20}–composition curve) and infra-red absorption measurements. As reported by Glasebrook and Lovell, the composition at equilibrium varies in favour of *cyclo*hexane at lower temperatures; the reaction is slower, and equilibrium is only attained after several weeks at room temperature. The recovery of hydrocarbon was always better than 99%, and no constituents other than methyl*cyclo*pentane and *cyclo*hexane were apparent from the infra-red absorption spectrum.

The *cyclo*hexane in the mixture was dehydrogenated satisfactorily over a platinum–charcoal catalyst as described by Zelinsky (*Ber.*, 1911, **44**, 3121; 1912, **45**, 3678) at ~350°. The platinum–porous pot catalyst described by Berl and Koerber (*Analyt. Chem.*, 1940, **12**, 175, 177) gave excellent results with pure *cyclo*hexane, but even a small concentration of methyl*cyclo*pentane was sufficient markedly to inhibit dehydrogenation. Thus in experiments in which mixtures of *cyclo*hexane and methyl*cyclo*pentane containing approximately 4, 11·5, and 17·5% of the latter were passed over the catalyst at 350°, the extent of dehydrogenation of the *cyclo*hexane was 94, 42, and 20%, respectively. These experiments were carried out by vaporising the mixture in a current of nitrogen as described on p. **794**. Under these conditions the mixture passing over the catalyst becomes progressively richer in *cyclo*hexane during the experiment. Under conditions where the composition of the feed was constant (*i.e.*, when the mixture was added from a dropping-funnel) results were even worse; in the case of the 17·5% mixture (above) the extent of dehydrogenation was only ~1%. There was no permanent effect on the catalyst, and pure *cyclo*hexane was completely dehydrogenated immediately after a run with the mixture.

Benzene was isolated from the hydrogenation mixture, consisting mainly of benzene and methyl*cyclo*pentane, by conversion into the clathrate compound with ammoniacal nickel cyanide solution (Hofmann and Höchtlen, *Ber.*, 1903, **36**, 1149; Evans, Ormrod, Goalby, and Staveley, *J.*, 1950, 3346). Slight modifications were made to the procedure of Evans *et al.*, including use of a greater excess of cyanide solution, and decomposition of the complex by dissolution in strongly alkaline potassium cyanide solution. The recovery of benzene from the mixture was better than 98%. As demonstrated by Evans *et al.*, very pure benzene is obtained by this method. Owing to the very large volume of aqueous solution, it was not possible to recover the methyl*cyclo*pentane left in the liquor. In the ^{14}C run described on p. **794**, this was reduced to 10% of the total by carrying out the isomerisation at room temperature for several weeks. If the isomerisation is to be restricted to a few hours, the loss on methyl*cyclo*pentane may be as high as 20%, and recovery would be desirable. Preliminary experiments have shown that this can be achieved conveniently by sulphonation in a sealed tube, unchanged methyl*cyclo*pentane being readily recovered from the sulphuric acid–benzenesulphonic acid mixture. After isolation by the usual techniques, benzenesulphonic acid may be hydrolysed to benzene in almost quantitative yield by heating it in aqueous solution in a sealed tube at a high temperature.

[^{14}C]Methyl*cyclo*pentane was synthesised from carbon dioxide by the following steps. *cyclo*Pentane[^{14}C]carboxylic acid, prepared in 95% yield by carboxylation of *cyclo*pentylmagnesium chloride, was reduced by lithium aluminium hydride (Nystrom and Brown, *J. Amer. Chem. Soc.*, 1947, **69**, 2548) to *cyclo*pentyl[^{14}C]methanol in 94·5% yield. Dehydration over activated alumina at 320° gave a mixture of olefins which on hydrogenation gave [^{14}C]methyl*cyclo*pentane containing about 34% of [$^{14}C_1$]*cyclo*hexane. This mixture was obtained in ~94% yield from the alcohol. The overall radiochemical yield of benzene from carbon dioxide was 75%; the 25% loss includes the methyl*cyclo*pentane not recovered. The synthesis was carried out on the scale of 60—87 millimoles, but there would be no difficulty in reducing this to about 20 millimoles without changing the techniques adopted. Apart from the use of " chasers " to increase the recovery of isotopic material, no dilution of isotope is involved in the synthesis. Even when " chasers " are used, overall dilution need not exceed ~20%.

A preliminary report of this work has already been published (Turner, *Nature*, 1951, **168**, 73).

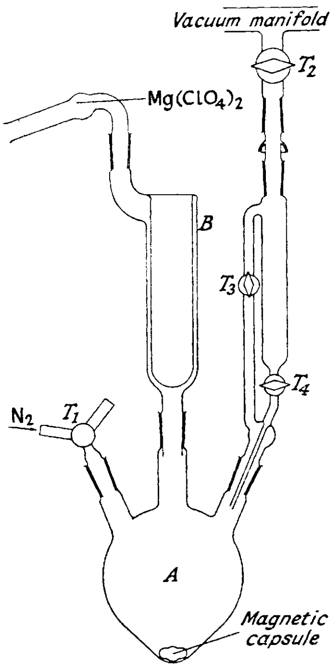
EXPERIMENTAL

General.—The vacuum manifold used in this work was described in Part I (*J.*, 1950, 5167). Samples were converted into carbon dioxide for counting by a modification of the usual microtechnique, based on that of Naughton and Frodyma (*Analyt. Chem.*, 1950, **22**, 711), similar to that described by Anderson, Delabarre, and Bothner-By (*ibid.*, 1952, **24**, 1298). The counting technique has been reported by Audric and Long (Chemical Research Laboratory, Teddington, Scientific Report CRL/AE 51). Enough counts were taken to give a standard error of less than ±1%) The standard deviation of a long series of results on samples of carbon dioxide generated from a standard barium carbonate sample was ±1·2%. Specific activities (s.a.) are quoted in microcuries per millimole (μc/mM) and total activities in millicuries (mc).

cyclo*Pentane*[^{14}C]*carboxylic Acid.*—Carbon dioxide was generated from barium carbonate (0·222 g. of $Ba^{14}CO_3$ of nominal activity 3 mc, plus 17·233 g. of " AnalaR " barium carbonate; 88·5 millimoles total if 100% pure) by addition of 45% perchloric acid, in the apparatus shown in Fig. 1 of Part I (*loc. cit.*), swept in a current of nitrogen into traps β and γ, and there condensed at −196°. It was dried by sublimation between vessels at −80° and −196° in a high vacuum. After removal of an aliquot for radio-assay the residue (87·1 millimoles; 2·42 mc; s.a. 27·8) was stored at −196° until required.

*cyclo*Pentylmagnesium chloride was prepared in the apparatus shown in Fig. 1, T_2 being closed throughout the preparation, from *cyclo*pentyl chloride (12·8 ml., 123 millimoles) and magnesium turnings (3·3 g., 136 millimoles, 10% excess) in anhydrous *n*-butyl ether (85 ml.) under nitrogen. The condenser *B* was charged with solid carbon dioxide, and the reaction mixture was stirred magnetically. When preparation of the Grignard compound was complete, the condenser was removed, and anhydrous *n*-butyl ether (250 ml.) that had previously been out-gassed *in vacuo* and stored under nitrogen was added against a counter-current of nitrogen; *B* was then replaced by an induction stirrer, similar to that described by Calvin *et al.* (*op. cit.*, p. 336), bearing a small link stirrer. T_1 was then closed, T_3 and T_4 were opened, and the apparatus was evacuated by cautiously opening T_2 while the solution was stirred. After a few minutes' pumping at room temperature, the Grignard solution was cooled to −35° and pumping continued until the pressure in the system had fallen to below 10^{-2} mm., and did not increase on isolation of the system from the pumps; T_2 was then closed, and the carbon dioxide allowed to evaporate into the vacuum manifold (vol. with storage bulb, 2700 ml.), giving a pressure of ~60 cm. The solution was stirred vigorously, and T_2 opened. After ~ 3 min. the pressure had fallen to 2 cm.; T_2 was therefore closed, and the carbon dioxide condensed into a system of volume 125 ml. in which on evaporation it gave a pressure of 40 cm. T_2 was again opened; within 5 min. the pressure in the system had fallen to below 10^{-1} mm. The reaction mixture was allowed to warm to −20° and stirred for 45 minutes, after which it was poured on crushed ice (750 g.) containing sodium hydroxide (7 g.) in a 1500-ml. flask, the reaction vessel being rinsed by 2N-sulphuric acid (30 ml.) and *n*-butyl ether (30 ml.). The product was evaporated through an efficient splashhead until the volume was reduced to 150 ml., thereby removing the butyl ether, after which silver sulphate (25 g.) and 10N-sulphuric acid (75 ml.) were added, and the whole was steam-distilled, the distilling flask being heated in an oil-bath. The distillate (500 ml. in all) was collected in the flask of a continuous extractor, saturated with sodium chloride, and extracted with ether for 36 hours, with magnetic stirring. After drying by refluxing over anhydrous calcium sulphate in a Soxhlet apparatus, the ether was evaporated through a 30-cm. Vigreux column, and the residue transferred to a 25-ml. distilling flask with a 14-cm. Vigreux column and a sealed-on condenser. The acid was collected at 112—115°/19 mm. The yield was 9·48 g. (83·2 millimoles; 2·30 mc; s.a. 27·6; radiochemical yield from carbon dioxide, 95%).

FIG. 1.



The same synthesis on the scale of 20 millimoles gave a radiochemical yield of 96%, a small "chaser" of pure *cyclo*pentanecarboxylic acid (~4 millimoles) being used to ensure a high recovery of labelled acid in the distillation. The dry ethereal solution of *cyclo*pentanecarboxylic acid could, of course, be used directly in the next stage.

cyclo*Pentyl*[^{14}C]*methanol*.—Lithium aluminium hydride (5·0 g.; *ca.* 130% excess) was added to anhydrous ether (250 ml.) in a 500-ml. 2-neck flask, fitted with a dropping-funnel and a double-surface water condenser surmounted by a cold-finger condenser (*B* in Fig. 1) containing solid carbon dioxide, through which a slow current of dry nitrogen was passed. The liquid was stirred by means of a large magnetic capsule, and refluxed until the hydride had dissolved, after which the flask was chilled in an ice-bath, and *cyclo*pentane[^{14}C]carboxylic acid (8·52 g., 74·7 millimoles; 2·06 mc) in anhydrous ether (50 ml.) added gradually during 30 min.; the dropping-funnel was rinsed into the flask with a little ether. After 90 min.' stirring at 0°, water (10 ml.) was added cautiously, followed by ice (100 g.) and 10N-sulphuric acid (65 ml.). When the liquid was quite clear the whole was siphoned into a 500-ml. separating funnel, and the lower layer removed and further extracted with ether (5 × 25 ml.). Extractions were carried out by mechanical stirring through the neck of the funnel. The combined ethereal solutions were stirred in this way with saturated potassium carbonate solution (2 × 10 ml.) and dried by transferring them to the flask of a Soxhlet extractor and refluxing over (*a*) anhydrous potassium carbonate and (*b*) anhydrous calcium sulphate. The ether was removed through a 12″-Dufton column, and the residue distilled in the apparatus used for the distillation of the *cyclo*pentanecarboxylic acid. The receiver consisted of a 25-ml. B14 dropping-funnel with a 1-mm. capillary tap. The material appeared to consist only of ether and *cyclo*pentylmethanol, the latter being collected at 159—161°/760 mm. When distillation ceased, and alcohol held up in the column had been driven over by cautious flaming, pure non-isotopic *cyclo*pentylmethanol (1·00 ml., 0·93 g.) was added to the distilling-flask, and the process repeated. The total distillate (7·985 g., 79·85 millimoles; n_D^{20} 1·4572) was thoroughly mixed, and a sample converted into the ***α-naphthylurethane***, m. p. 87·5—88° (Found: C, 75·7; H, 7·0; N, 5·3. $C_{17}H_{19}O_2N$ requires C, 75·8; H, 7·1; N, 5·2%. S.a. 24·6, corresponding to a total activity of 1·96 mc, the alcohol being assumed to be 100% pure. This is equivalent to a radiochemical yield of 95%).

On the scale of $\sim$20 millimoles, a radiochemical yield of 96·5% was obtained. In this case the use of a 4-millimoles " chaser " in the distillation did not significantly increase the recovery of isotope.

Dehydration of cyclo*Pentyl*[^{14}C]*methanol*.—The dropping funnel containing the alcohol (7·81 g., 78·1 millimoles) from the preceding stage was attached, as indicated in Fig. 2*a*, to the top of a vertical Pyrex tube, 80 × 1·3 cm., packed with 50 cm. of 7—10-mesh granulated alumina (Spence's Type N), preceded by a 7·5-cm. preheating section of Pyrex-glass beads. Before use the alumina was heated to 400° for 18 hours in a current of hydrogen. This was replaced by a slow stream of oxygen-free nitrogen, the temperature adjusted to 320°, and the alcohol added dropwise during 1 hour. The last traces of alcohol were carried down by passing the gas stream through the funnel while warming it in a current of hot air. The products of the reaction were collected in two traps, the first cooled to −78°, the second to −196°. Sweeping was continued for $\sim$1¼ hours, after which the traps were attached to a vacuum-manifold, and the contents were distilled into a vessel (see Fig. 2*b*) containing potassium hydroxide pellets ($\sim$5 g.). The stopcock and the joint were lubricated with fluorocarbon grease FCD 759. The vessel and contents were detached from the manifold, warmed to room temperature, and shaken for a few minutes. After re-attachment to the manifold, the flask was cooled to −30° and the hydrocarbon distilled into a weighing trap (Fig. 2*c*). The yield of slightly moist product was 6·06 g. (94·5% from the alcohol). In non-radioactive runs the product had n_D^{20} 1·4350. The treatment with potassium hydroxide described above was found to be the most convenient means for the removal of relatively large amounts of water from these hydrocarbon samples with minimum loss.

FIG. 2.

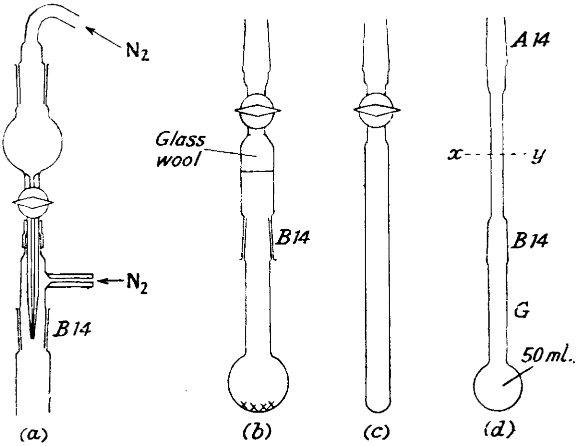
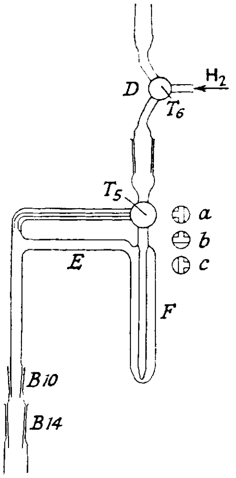


FIG. 3.



Hydrogenation of the Olefin.—The olefin from the previous stage (6·06 g.) was distilled *in vacuo* into the reservoir *F* of the vaporiser unit *E* (Fig. 3) through the 3-way adaptor *D*, the B10 cone being closed by a cap at this stage (T_5, position *a*). While *F* was kept at −78°, hydrogen was admitted into the vaporiser, through T_6, T_5 afterwards being turned to position *b*. The cap was removed, and a current of hydrogen passed in while the apparatus was attached to the B14 socket of an 80 × 1·3 cm. Pyrex tube, packed with 50 cm. of nickel oxide on 8—20-mesh pumice (to give on reduction a 10% nickel content), with a 7·5-cm. preheating section of Pyrex-glass beads. After displacement of the air, the catalyst was reduced in a stream of hydrogen at 400° for about 3 hours, and thereafter kept at 150°. With T_5 in position *c*, the reservoir *F* was heated in a bath at $\sim$50°, and the olefin carried through the catalyst tube in an excess of hydrogen. The leads to the catalyst tube were kept at 90° by means of an Electrothermal heating tape. The product was collected in two traps as used in condensing the olefin (above). The vaporisation required 3½ hours, and the system was swept out for a further 3 hours. The product was distilled into a trap (Fig. 2*b*) containing glass beads and phosphoric oxide (2 g.). After being shaken at room temperature it was distilled into a weighing trap (yield 6·17 g., 94% from the alcohol). In non-radioactive runs this product had n_D^{20} 1·4149, and gave no yellow colour with tetranitromethane in carbon tetrachloride. It was shown by infra-red analysis to be a mixture of *cyclo*hexane and methyl*cyclo*pentane, containing 34 ± 3% of the former. The refractive index corresponds to a *cyclo*hexane content of 30%, a linear relation being assumed between composition and refractive index.

Isomerisation.—The flask *G* (Fig. 2*d*) was charged with glass beads (~10 g.) and carefully dried. After addition of aluminium chloride powder (Hardy and Grant, B.P. 678,563; 0·75 g.), the neck was constricted at *x*—*y*, and the product from the previous stage (6·17 g.) and water (0·03 ml.) were distilled into it *in vacuo*. The flask was sealed at the constriction, and warmed to room temperature, and by warming the neck and cooling the bulb of the flask the water was brought into contact with the aluminium chloride. The isomerisation was then carried out as follows: the flask and contents were (1) heated for 5 hours in refluxing carbon tetrachloride, (2) shaken at ~30° for 2 weeks followed by 4 weeks at ~20°, and (3) kept at 10—15° for 5 weeks. The flask was then cooled to −196°, opened above the joint, and connected to a vacuum manifold through an adaptor packed with glass-wool. The contents were distilled (1) into a trap (Fig. 2*b*) containing moist potassium hydroxide pellets (2 g.) and shaken at room temperature; (2) dried over phosphoric oxide as previously described; and (3) transferred to a weighing trap. The yield was 6·13 g. (93·5% from the alcohol). The material had n_D^{20} 1·4244; on the basis of Glasebrook and Lovell's results (*loc. cit.*) this corresponds to 90% of *cyclo*hexane.

FIG. 4.

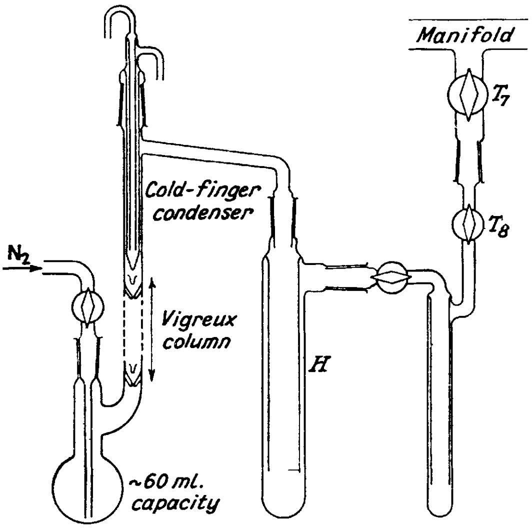
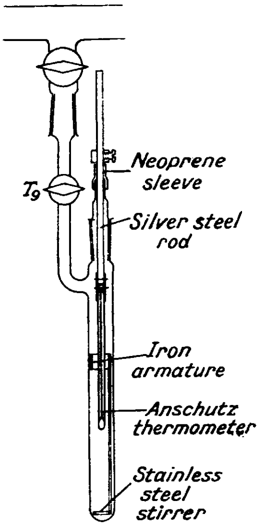


FIG. 5.



Dehydrogenation.—Catalyst. Granular activated charcoal (B.D.H. "For gas analysis," 10—16 mesh) was boiled twice with 5% aqueous nitric acid, washed thoroughly with water, dried at 100°, and finally heated to dull redness *in vacuo*. This charcoal (15·1 g.) was immersed in a solution of $H_2PtCl_6,6H_2O$ (9·0 g.) in water (50 ml.), and the whole evaporated to dryness with stirring. The impregnated charcoal was charged into a 9-mm. bore Pyrex tube carrying a B10 socket and a B14 cone, filling 54 cm. The catalyst was reduced in a current of hydrogen for 12 hours at 135°, and for 4 hours at 380°, after which the hydrogen was replaced by oxygen-free nitrogen (a commercial grade).

Dehydrogenation. The isomerisation mixture (6·10 g.) was distilled into the vaporiser (Fig. 3) as described previously. The contents were kept at −80° while the apparatus was connected to the catalyst tube against a counter-current of nitrogen, and afterwards were volatilised and passed over the catalyst, heated to 360°, in a slow current of nitrogen, the reservoir *F* being immersed in a bath at 65—75°. The dehydrogenated product was collected in two traps, as described for the preparation of the olefin. The volatilisation required 2½ hours; sweeping out was continued for another 4½ hours. After drying over phosphoric oxide 5·49 g. of product were obtained, having n_D^{20} 1·4925.

Formation of the clathrate compound. The dehydrogenation product (5·24 g.) was distilled into a thin-walled soda-glass ampoule and sealed off. Ammoniacal nickel cyanide solution was prepared as described by Evans *et al.* (*loc. cit.*) from 0·25 mole of nickel sulphate, and 450 ml. were charged into a heavy-wall narrow-mouth bottle (a 1-pint milk bottle). The ampoule was carefully placed within the bottle, which was closed by a rubber stopper covered with aluminium foil; vigorous shaking caused the ampoule to break, after which shaking was continued for 16 hours at room temperature. The bottle and contents were chilled to 0° for an hour before the contents were filtered into a sintered crucible (porosity 4), the sinter of which was covered by a disc of filter paper. A few drops of methanol were added towards the end of the filtration to break the foam. The complex was washed with water, methanol, and anhydrous ether, and dried *in vacuo* in a small desiccator ($CaCl_2$). 12·68 G. of dry complex were obtained, 12·58 g. of which were used in the next stage. During the filtration of the complex the filter-flask had been connected to vacuum through three traps, the first and the last at −80°, and the second at −196°. At the end, the contents, mixed with pure benzene (5 ml.) as carrier, were shaken with cyanide solution (450 ml.). The complex (10·8 g.; s.a. 0·31) obtained in this way had a total activity of 16 μc, or about 1% of the total activity in benzene.

[$^{14}C_1$]*Benzene.* The compound (12·58 g.) was transferred to the bulb of the apparatus illustrated in Fig. 4. A solution of " AnalaR " potassium cyanide (13·5 g.) and potassium hydroxide (3·5 g.) in water (35 ml.) was added to the complex, the first trap cooled to −80°, a stream of nitrogen passed through the apparatus, and after displacement of air, the second trap cooled to −196°. The flask was heated in a bath at 90°, and the benzene liberated distilled under partial reflux into the traps during 3½ hours. In order to avoid blockage, the central tubes of these traps were of wide-bore tubing. The distillation flask was detached from the first trap, which was closed by a stopper and evacuated *via* T_7. By closing T_8 and distilling the contents several times between the two traps, at intervals cooling both, and evacuating, entrapped permanent gas was removed. The whole was then distilled through the manifold into another trap (Fig. 2*b*), containing syrupy phosphoric acid (10 ml.), at −196°. When distillation was complete, the liquid-nitrogen cooling bath was replaced by carbon dioxide–methanol, and trap *H* cooled to —196°. The bulk of the ammonia from the decomposition of the complex distilled into *H*, and was thus separated from the benzene and water. After being shaken at room temperature, the benzene (containing some water) was distilled into a similar trap containing powdered potassium hydroxide (5 g.), and then dried over phosphoric oxide. The dry product was distilled into a weighing trap (yield 4·645 g., 81% chemical yield from *cyclo*pentyl[^{14}C]methanol, after allowance for samples removed). For assay of radioactivity, 67·45 mg. of this product were diluted to 8·747 g. with pure benzene, and aliquots were burned and counted, giving a total activity for the 4·645 g. of product of 1·51 mc (s.a. 25·4). With allowance for samples, this represents a 75% recovery of isotope from carbon dioxide.

A freezing-point determination was carried out in the apparatus shown in Fig. 5. The benzene (4·6 g.) was distilled into it *in vacuo*, the thermometer (Anschütz, graduated in 0·2°) being in the position shown; T_9 and the joints were lubricated with fluorocarbon grease FCD 759, and the Neoprene sleeve with a little Silicone high-vacuum grease. With T_9 closed, the benzene was allowed to melt, after which the thermometer was lowered into it, and a freezing-point determination carried out in the usual manner, the stirrer being operated magnetically. A value of 5·4° was obtained. Under the same conditions a sample of 99·99% benzene melted just perceptibly higher (~0·025°). The [$^{14}C_1$]benzene had n_D^{20} 1·5010; the refractive index of the pure benzene was not perceptibly different on the same instrument.

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CHEMICAL RESEARCH LABORATORY, D.S.I.R.,
TEDDINGTON, MIDDLESEX.

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