Summary

1. A series of fifteen β-cyclohexylalkylamines have been prepared by catalytic hydrogenation of the corresponding phenyl analogs.

2. Four of the amines of the series were also prepared by a second method from cyclohexyl intermediates.

3. Pharmacological data for pressor activity, toxicity and central nervous system stimulation are also presented.

Condensation of Saturated Halides with Unsaturated Compounds. IV. Condensation of *t*-Butyl Chloride with Cyclohexene[1]

BY LOUIS SCHMERLING

Previous papers in this series have described the condensation of alkyl halides with olefins[2] and haloölefins[3] in the presence of metal chloride catalysts of the Friedel–Crafts type. Extension of the reaction to a cycloölefin is discussed in the present communication.

Condensation of *t*-butyl chloride with cyclohexene yielded very little, if any, of the product (1-chloro-2-*t*-butylcyclohexane, I) to be expected by the simple addition of the alkyl group and the halogen atom to the doubly-bonded carbon atoms of the cycloölefin. Instead, the principal product was either 1-chloro-1-*t*-butylcyclohexane (II) or 1-chloro-3-*t*-butylcyclohexane (III) depending on the catalyst used. Thus, in the presence of aluminum chloride at −25 to −15°, there was obtained a 72% yield of chloro-*t*-butylcyclohexane, about 85% of which was III, the remainder being II; the principal by-product, chlorocyclohexane, was obtained in 5% yield. On the other hand, with boron fluoride as catalyst at 0°, quite pure II was produced in 23% yield together with a 15% yield of chlorocyclohexane and a 12% yield of 1-*t*-butyl-1-cyclohexene. When bismuth chloride was used at 0° or at room temperature, the chlorobutylcyclohexane (formed in 5 or in 21–25% yield, respectively) was similar to that obtained with aluminum chloride at −25 to −15°.

The composition of the product was also affected by the reaction conditions. At a lower temperature, −32 to −28°, with aluminum chloride, the proportion of III was decreased. On the other hand, by carrying out the bismuth chloride-catalyzed condensation at a higher temperature, namely, 80–97°, virtually pure III was obtained, probably because the tertiary chloride (II) which was formed was dehydrochlorinated to *t*-butylcyclohexene.

The compositions of the various chloro-*t*-butylcyclohexane products were estimated from their refractive indices and their infrared spectra. The refractive index, $n^{20}D$, of substantially pure III is 1.4685; that of II, 1.4778–1.4789.

Simons and Meunier[4] have reported that the reaction of *t*-butyl chloride with cyclohexene in the presence of hydrogen fluoride at 0 to 5° resulted in an 11% yield of 1-chloro-3-*t*-butylcyclohexane (III), an 11.5% yield of cyclohexyl fluoride, and a 65% yield of chlorocyclohexane. The structure of the chloro-*t*-butylcyclohexane was proved by showing that dehydrochlorination of the compound yielded 4-*t*-butyl-1-cyclohexene, indicating that it was either 1-chloro-3-*t*-butylcyclohexane (III) or 1-chloro-4-*t*-butylcyclohexane (IV). The *t*-butylcyclohexanol prepared from the chloride by way of the Grignard reagent yielded a 3,5-dinitrobenzoate which was not the same as the 3,5-dinitrobenzoate of 4-*t*-butylcyclohexanol obtained by hydrogenation of *p-t*-butylphenol. Hence, it was concluded that the chloride was not IV and that by process of elimination, it had to be III. However, this method does not take into consideration the fact that 4-*t*-butylcyclohexanol can exist in two stereoisomeric forms. It is quite possible that hydrogenation of *p-t*-butylphenol would yield one geometric isomer or a mixture of both isomers[5] while oxidation of the Grignard reagent of the chloride IV (which may itself be a *cis*, a *trans* compound, or a mixture) would yield the other isomer or a mixture. Therefore, the isolation of different 3,5-dinitrobenzoate derivatives can hardly be used as structural proof, particularly since 3-*t*-butylcyclohexanol was not synthesized for purposes of comparison.

The proof of structure used in the present investigation is not susceptible to the above objection. The butylcyclohexanol prepared from the chlorobutylcyclohexane was oxidized to the corresponding *t*-butylcyclohexanone which is not subject to *cis–trans* isomerism and which can, therefore, be characterized with certainty. Comparison of the semicarbazone of the unknown with the semicarbazones of authentic 2-, 3- and 4-*t*-butylcyclohexanone established the structure of the chloride as 1-chloro-3-*t*-butylcyclohexane (III).

The identity of the 1-chloro-1-*t*-butylcyclohexane (II) was indicated by the fact that it was re-

(1) Presented before the Division of Organic Chemistry of the American Chemical Society at the Chicago meeting, September, 1946.

(2) L. Schmerling, THIS JOURNAL, **67**, 1152 (1945).

(3) L. Schmerling, *ibid.*, **68**, 1650, 1655 (1946).

(4) J. H. Simons and A. C. Meunier, *ibid.*, **65**, 1269 (1943).

(5) H. E. Ungnade and A. D. McLaren, *ibid.*, **66**, 118 (1944).

versibly dehydrochlorinatable. The other isomers would yield mixtures on dehydrochlorination followed by rehydrochlorination of the resulting *t*-butylcyclohexene. That the compound in question was a tertiary chloride was further indicated by the ease with which it lost hydrogen chloride when attempts were made to convert it to *t*-butylcyclohexanol by reaction with water at room temperature or via the Grignard reagent. The relatively high melting point of the chloride (-10 to $-9°$) also seems to support the tertiary chloride structure.

It is recognized that the above proof of structure is open to the criticism that it is conceivable that 1-chloro-2-*t*-butylcyclohexane (I) might also be reversibly dehydrochlorinated due to steric effects which might prevent the addition of hydrogen chloride to the 1-*t*-butyl-1-cyclohexene in the expected manner to yield the tertiary chloride (II) and might yield the secondary chloride (I) instead. However, since there does not seem to be any precedent for addition of hydrogen chloride contrary to Markownikoff's rule, it is believed that the structure II may be safely assigned to the chlorobutylcyclohexane which is obtained by the reaction of *t*-butyl chloride and cyclohexene in the presence of boron fluoride.
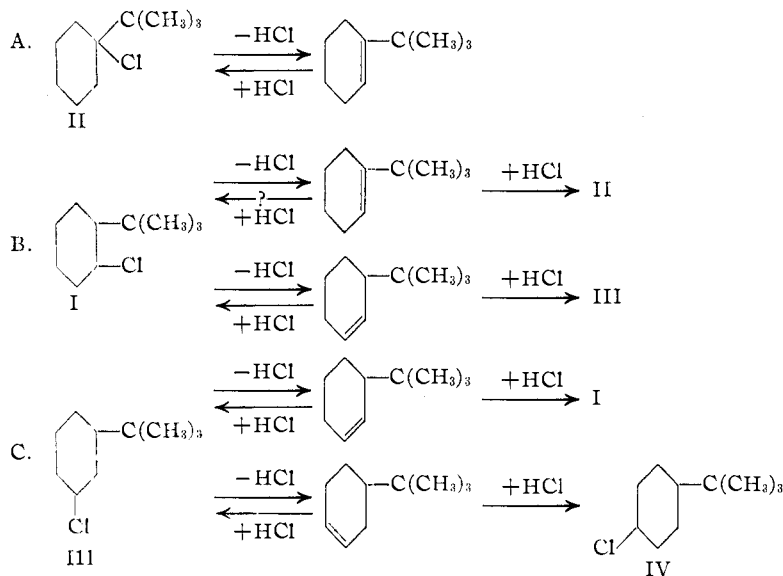
The ease with which the tertiary chloride (II) loses hydrogen chloride affords a method for removing it from mixtures with the secondary chloride III such as are obtained when aluminum chloride or bismuth chloride is used as catalyst. When the mixture of chlorides is heated with water at about 200°, the recovered chloride is quite pure III.

t-Butylcyclohexene was obtained in 10–20% yield as a by-product of the reaction of *t*-butyl chloride with cyclohexene in the presence of boron fluoride or bismuth chloride. The olefin usually

consisted largely of 1-*t*-butyl-1-cyclohexene regardless of which catalyst was used. It was apparently formed by dehydrochlorination of chlorobutylcyclohexane, the hydrogen chloride adding to cyclohexene to produce chlorocyclohexane.

Experimental

Condensation of *t*-Butyl Chloride with Cyclohexene

Aluminum Chloride as Catalyst.—Cyclohexene (170 g., 2.1 moles) was added during one hour to a stirred mixture of 185 g. (2.0 moles) of *t*-butyl chloride, 50 g. of *n*-pentane diluent, and 10 g. of resublimed, powdered aluminum chloride, the reaction temperature being maintained at -25 to $-20°$. The catalyst was slowly converted to a red-brown sludge. Stirring was continued at -20 to $-15°$ for an additional hour after all the cyclohexene had been added. The mixture was then cooled to $-25°$ and the clear yellow upper layer (379 g.) was decanted from the viscous catalyst layer (25 g.), washed with water, dried over potassium carbonate and distilled. There was obtained 11 g. (5% yield) of chlorocyclohexane and 252 g. (72% yield) of chloro-*t*-butylcyclohexane, b. p. 63–66° (3 mm.) and 208–212° (760 mm.)[6]; n^{20}D 1.4690–1.4720; m. p. below $-78°$. From the refractive index data, it may be estimated that the product consisted of about 85% of the secondary chloride III and 15% of the tertiary chloride II.

Anal.[7] Calcd. for $C_{10}H_{19}Cl$: C, 68.72; H, 10.97; Cl, 20.31. Found: C, 68.80; H, 10.86; Cl, 20.47.

In a similar experiment using one-half the above quantities of reactants and catalyst at a lower temperature, -32 to $-28°$, there was obtained 59 g. (34% yield) of chloro-*t*-butylcyclohexane, b. p. 60–62° (2.5 mm.) and 208–211° (760 mm.)[6]; n^{20}D 1.4719–1.4735; $d^{20}{}_4$ 0.9669; *MR* (calcd.), 51.0; *MR* (obs.), 50.7. From the refractive index data, it may be concluded that the chloride consisted of 60% III and 40% II.

Bismuth Chloride as Catalyst. (A) At Room Temperature.—To a mixture of 46 g. (0.5 mole) of *t*-butyl chloride and 26 g. (0.3 mole) of cyclohexene there was added 3.5 g. of bismuth chloride. The catalyst turned pink and then orange within five minutes but a test sample showed that very little material boiling above 80° was present. More catalyst (2 g.) was added and the mixture was set aside for two weeks. The liquid product was then washed, dried and distilled. There was obtained 14 g. (40% yield) of chlorocyclohexane and 11 g. (21% yield) of chloro-*t*-butylcyclohexane, b. p. 71–73° (7 mm.) and 202–206° (760 mm.)[6]; n^{20}D 1.4722; m. p. -50 to $-40°$.

It is estimated from the refractive index that the chlorobutylcyclohexane consisted of about 65% of III and 35% of II.

In another experiment, a mixture of 46 g. (0.5 mole) of *t*-butyl chloride, 42 g. (0.5 mole) of cyclohexene and 10 g. of bismuth chloride were permitted to stand at room temperature for two and one-half months. The products consisted of cyclohexyl chloride (30% yield), *t*-butylcyclohexene (13% yield) and chloro-*t*-butylcyclohexane (25% yield), b. p. 100–103° (19 mm.) and 211–215° (760 mm.)[6]; n^{20}D 1.4703.

(B) At 0°.—A solution of one mole each of *t*-butyl chloride and cyclohexene was cooled to 0° and 10 g. of bis-

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(6) Calculated from boiling point under reduced pressure using nomograph prepared for hydrocarbon boiling point conversions.

(7) Microanalysis by Dr. T. S. Ma, University of Chicago.

muth chloride was added. The mixture was placed in a refrigerator for thirteen days, after which the liquid product was decanted, washed, dried and distilled. There was obtained cyclohexyl chloride, 12% yield; *t*-butylcyclohexene, 14% yield, b. p. 66–70° (20 mm.) and 168–173° (760 mm.),[6] $n^{20}D$ 1.4590; and chloro-*t*-butylcyclohexane, 5% yield, b. p. 99–101° (20 mm.) and 209–212° (760 mm.),[6] $n^{20}D$ 1.4710.

(C) **At Reflux Temperature.**—A mixture of 92 g. (1.0 mole) of *t*-butyl chloride, 92 g. (1.1 moles) of cyclohexene and 5 g. of bismuth chloride was left to stand at room temperature for four days. About 20% by volume of material boiling above 90° was formed. Five grams of fresh catalyst was added and the mixture was heated at 80 to 97° under reflux for five hours. Working up the liquid product in the usual manner gave chlorocyclohexane, 46% yield; *t*-butylcyclohexene, 20% yield, b. p. 62–65° (14 mm.) and 171–174° (760 mm.),[6] $n^{20}D$ 1.4490; and chloro-*t*-butylcyclohexane, 20% yield, b. p. 67–70° (3 mm.) and 213–217° (760 mm.),[6] $n^{20}D$ 1.4690, m. p. below —78°. The chloro-*t*-butylcyclohexane apparently consisted of at least 95% III (sample A, Fig. 1).

Boron Fluoride as Catalyst.—Boron fluoride (10 g.) was bubbled during one-half hour into a stirred solution of 185 g. (2.0 moles) of *t*-butyl chloride and 164 g. (2.0 moles) of cyclohexene in a flask immersed in an ice–water-bath. Stirring was continued at 0–3° for sixteen hours (overnight) after which the liquid product (340 g.) was decanted from the catalyst sludge (19 g.) and was washed, dried and distilled. There was obtained 35 g. (15% yield) of chlorocyclohexane; 33 g. (12% yield) of *t*-butylcyclohexene, b. p. 41–43° (5 mm.), 170–172° (760 mm.),[6] $n^{20}D$ 1.4592; 80 g. (23% yield) of 1-chloro-1-*t*-butylcyclohexane (Sample C, Fig. 1), b. p. 57–58° at 2 mm. and 208–209° (760 mm.),[6] m. p. —10 to —9°; $n^{20}D$ 1.4778–1.4789, d^{20}_4 0.9736, *MR* (calcd.), 51.0; *MR* (obs.), 50.8; higher-boiling product, 65 g.

Anal.[8] Calcd. for $C_{10}H_{19}Cl$: C, 68.72; H, 10.97; Cl, 20.31. Found: C, 69.03; H, 10.94; Cl, 20.29.

The infrared spectra of the various chlorobutylcyclohexane products showed that the compound obtained with boron fluoride was definitely different from those obtained with the aluminum chloride and bismuth chloride catalysts but that minor amounts of it were present in the latter products, which were shown to be quite similar to each other (see Fig. 1 and the discussion below).

Identification of 1-Chloro-3-*t*-butylcyclohexane

Synthesis of *t*-Butylcyclohexanones. (A) **2-*t*-Butylcyclohexanone.**—2-*t*-Butylcyclohexanol was prepared by the hydrogenation of an alcoholic solution of 45 g. of *o*-*t*-butylphenol (obtained through the courtesy of the Dow Chemical Company) in the presence of U. O. P. nickel-kieselguhr catalyst; yield, 33 g. of white rhombs, m. p. 52–53° (filtered from liquid geometric isomer).

Anal.[8] Calcd. for $C_{10}H_{20}O$: C, 76.84; H, 12.91. Found: C, 76.2; H, 12.9.

A solution of 9 g. of the crystalline cyclohexanol in 25 cc. of acetic acid was oxidized by the gradual addition to 10 g. of chromic oxide in 10 cc. of water and 50 cc. of acetic acid, the temperature being maintained at 30–35°. The mixture was allowed to stand at room temperature overnight; 5 cc. of methanol and 50 cc. of water were added and the product was steam-distilled. The distillate was washed to remove formaldehyde and acetic acid, dried and distilled. The 2-*t*-butylcyclohexanone boiled at 62.5° at 4 mm. pressure; $n^{20}D$ 1.4579.

Anal.[7] Calcd. for $C_{10}H_{18}O$: C, 77.85; H, 11.77. Found: C, 77.61; H, 11.08.

It yielded a semicarbazone which crystallized very slowly from the reaction mixture; m. p. 182–183°.

Anal.[8] Calcd. for $C_{11}H_{21}N_3O$: N, 19.9. Found: N, 19.8.

(8) Microanalysis by Mr. C. W. Beazley, Micro-Tech Laboratories, Skokie, Illinois.

(B) **3-*t*-Butylcyclohexanone** was prepared by the reaction of *t*-butylmagnesium chloride with 2-cyclohexen-1-one using the procedure described by Whitmore and Pedlow.[9] It yielded a semicarbazone which crystallized rapidly from the reaction mixture; nacreous flakes (from alcohol), m. p. 205–206° (melting point tube inserted in bath at 200°) or 200–201° (inserted at 180°; rate of rise of bath temperature, 3° per minute).

(C) **4-*t*-Butyl-cyclohexanone.**—4-*t*-Butylcyclohexanol was prepared by the hydrogenation of *p*-*t*-butylphenol; m. p. 77–78°. Vavon and Barbier[10] reported that *cis*- and *trans*-4-*t*-butylcyclohexanol melt at 80–80.5° and 83–83.5°, respectively. Preparation of the 3,5-dinitrobenzoate of the cyclohexanol in the usual manner yielded three crystalline fractions, m. p. 156, 137 and 78–80°.

4-*t*-Butylcyclohexanone was prepared by the oxidation of the cyclohexanol with an acetic acid solution of chromic oxide using the procedure described above for the 2-*t*-butyl isomer; m. p. 49–50°.

Anal.[8] Calcd. for $C_{10}H_{18}O$: C, 77.85; H, 11.77. Found: C, 77.77; H, 11.7.

The semicarbazone of the 4-*t*-butylcyclohexanone precipitated immediately when semicarbazide hydrochloride was added to an aqueous solution of the ketone (*i. e.*, it precipitated even before sodium acetate was added). The semicarbazone melted at 212–213° when inserted in a bath at 205°; if inserted at 180°, it melted at 210–211°.

Anal.[8] Calcd. for $C_{11}H_{21}N_3O$: N, 19.9. Found: N, 19.5.

A mixture of this semicarbazone with that of the 3-*t*-butylcyclohexanone melted at 185–190°.

Conversion of the Chlorobutylcyclohexane to Corresponding Butylcyclohexanone.—The Grignard reagent was prepared from 29 g. (0.17 mole) of the chlorobutylcyclohexane ($n^{20}D$ 1.4711) obtained by the condensation of *t*-butyl chloride and cyclohexene in the presence of aluminum chloride at —25 to —15°. Dry air was then bubbled through the product for three hours and the product was worked up in the usual manner. There was obtained 6 g. (26% yield) of *t*-butylcyclohexene (b. p. 47–47° (7 mm.) and 170–170° (760 mm.)[6]; $n^{20}D$ 1.4533) and 12 g. (45% yield) of *t*-butylcyclohexanol (b. p. 98–100° at 7 mm.; $n^{20}D$ 1.4702–1.4714). The cyclohexanol yielded a 3,5-dinitrobenzoate, m. p. 122–123°.

Oxidation of the cyclohexanol gave an oil, $n^{20}D$ 1.4660, the semicarbazone of which crystallized rapidly from the reaction mixture. The semicarbazone melted at 205–206° if inserted in the bath at 200°; if it was inserted at 180°, the melting point was 200–202°. A mixture of this semicarbazone and that of authentic 3-*t*-butylcyclohexanone also melted at 205–206° (sample inserted at 200°). A mixture with the semicarbazone of 4-*t*-butylcyclohexanone (m. p. 210–211° with insertion at 180°) melted at 189–193° (inserted at 180°).

Dehydrochlorination of the Chloro-*t*-butylcyclohexane. —A mixture of 40 g. of the chlorobutylcyclohexane ($n^{20}D$ 1.4710) obtained in the —25 to —15° aluminum chloride catalyzed reaction, 30 g. of sodium bicarbonate and 100 g. of water was heated at 225° for four hours in a glass liner in an Ipatieff-type rotating autoclave. Fractionation of the washed product yielded 17 g. (54% yield) of butylcyclohexene (b. p. 48–51° (8 mm.) and 169–172° (760 mm.)[6]; $n^{20}D$ 1.4600–1.4608) and 9.5 g. (24%) of chloro-*t*-butylcyclohexane (b. p. 67–68° (3.5 mm.) and 210–211° (760 mm.)[6]; $n^{20}D$ 1.4685) which apparently consisted of pure 1-chloro-2-*t*-butylcyclohexane uncontaminated with the more readily dehydrochlorinatable 1-chloro-1-*t*-butylcyclohexane.

That the butylcyclohexene was largely 1-*t*-butyl-3-cyclohexene was shown by oxidizing 17 g. with dilute potassium permanganate using the procedure of Simons and Meunier.[4] Evaporation of the ether extract of the acidified product yielded an oil which crystallized partially on

(9) F. C. Whitmore and G. W. Pedlow, Jr., THIS JOURNAL, **63**, 758 (1941).

(10) G. Vavon and M. Barbier, *Bull. soc. chim.*, [4] **49**, 578 (1931).

standing for two days. Recrystallization from hot water yielded 6 g. of β-t-butyladipic acid, white needles, m. p. 114°. It is probable that the oil (4 g.) which did not crystallize contained 5-pivalylpentanoic acid, the product of the oxidation of 1-t-butyl-1-cyclohexene (see below).

Identification of 1-Chloro-1-t-butylcyclohexane

Hydrolysis of the Chloro-t-butylcyclohexane.—Nine grams of the chloride (b. p. 57–57° (2 mm.), n^{20}D 1.4785) obtained by the reaction of t-butyl chloride and cyclohexene in the presence of boron fluoride was stirred with 2000 cc. of water at room temperature for twenty hours. The product was extracted with pentane and the extract distilled under reduced pressure. There was obtained 2.5 g. (36% yield) of t-butylcyclohexene, b. p. 65–70° (18 mm.), 170–176° (760 mm.),[6] n^{20}D 1.4638; and 1.5 g. of chlorine-containing product, b. p. 96–99 (18 mm.), 207–212° (760 mm.),[6] n^{20}D 1.4720; and 1.0 g. of residue.

Preparation and Oxidation of the Grignard Reagent.—The Grignard reagent was prepared from 20 g. of the chlorobutylcyclohexane (b. p. 57–58° (2 mm.), n^{20}D 1.4789) using 4 g. of magnesium and 160 cc. of ether. After all of the chloride had been added, the mixture was stirred for ten hours, allowed to stand for eight hours, and then oxygen was passed over the stirred product during two hours. The product was worked up in the usual manner. It consisted of 12 g. (76% yield) of material (principally t-butylcyclohexene), b. p. 49–51° (8 mm.), 169–171° (760 mm.),[6] and 1.5 g. of residue, n^{20}D 1.4780.

Hydrochlorination of t-Butylcyclohexene. (A) That Derived from the Chloro-t-butylcyclohexane.—Eight grams of the butylcyclohexene which was obtained in the above Grignard reaction was dissolved in 20 cc. of n-pentane and the solution was cooled in a trap immersed in a Dry Ice–acetone-bath. Dry hydrogen chloride was bubbled through the solution until it was saturated. The product was washed, dried and distilled. There was obtained 1.5 g. of material, b. p. 50–53° (8 mm.), 170–173° (760 mm.),[6] n^{20}D 1.4480; 3.5 g. b. p. 84–86° (8 mm.), 212–214° (760 mm.),[6] n^{20}D 1.4790, m. p. −14 to −12°, "mixed m. p." with 1-chloro-1-t-butylcyclohexane from the condensation reaction, −11 to −10°; and 1.0 g. residue.

Comparison of the infrared spectrum of the product boiling at 84–86° (8 mm.) showed that it contained at least 90% of material in common with the original chloro-t-butylcyclohexane product obtained by the condensation of t-butyl chloride with cyclohexene in the presence of boron fluoride (Sample D, Fig. 1).

(B) That Obtained as By-product of the Reaction of t-Butyl Chloride with Cyclohexene.—A n-pentane solution of 9.5 g. of the t-butylcyclohexene which was obtained as

Fig. 1.—Infrared absorption spectra of various samples of chloro-t-butylcyclohexane.

a by-product of the reaction of t-butyl chloride with cyclohexene in the presence of boron fluoride was cooled to about −78° and saturated with hydrogen chloride (5 g.). Distillation of the washed product yielded 7 g. (58%) of 1-chloro-1-t-butylcyclohexane, b. p. 81–83° (7 mm.), 212–213° (760 mm.),[6] n^{20}D 1.4785, m. p. −2°; "mixed m. p." with the chlorobutylcyclohexane from the boron fluoride-catalyzed condensation, −8 to −7°.

Oxidation of the By-product t-Butylcyclohexene.—The oxidation of 13 g. of the t-butylcyclohexene which was obtained as a by-product of the reaction of t-butyl chloride with cyclohexene in the presence of boron fluoride was carried out by stirring the material with a mixture of 40 g. of potassium permanganate and 250 cc. of water at 3–6° for twenty hours and then at room temperature for about one hour. Sodium sulfite was added to decompose the excess permanganate and the product was filtered. The filtrate consisted of an aqueous solution and a small amount of insoluble oil. The oil was taken up in ether, the ether was distilled off and the residue (about 2 g.) was placed in the refrigerator. Crystals (m. p. 69–70°) having a musty odor were obtained; they were presumably the glycol, 1,2-dihydroxy-1-t-butylcyclohexane.

Anal. Calcd. for $C_{10}H_{20}O_2$: C, 69.70; H, 11.71. Found: C, 69.91; H, 10.84.

Acidification of the aqueous solution yielded an oil which was extracted with ether. Removal of the ether left an oil (4 g.) which crystallized in part when cooled in the refrigerator. The crystals were separated on a cold filter: m. p. 47°; the melting point of 5-pivalylpentanoic acid has been reported[11] as 45–47°. The crystals yielded a 2,4-dinitrophenylhydrazone, m. p. 158–160° (softens at 145–150°).

Infrared Spectral Analysis (by W. S. Gallaway).—The infrared spectra of samples A, B, C and D were obtained on a large recording Gaertner spectrometer similar to the instrument described by McAlister.[12] The cell used provided a liquid film of 0.09 mm. The particular wave length range of 7.5 to 11 microns was chosen since the differences between the spectra of isomers is usually more pronounced in this interval.

The intensities of the several absorptions found are plotted as bar diagrams in Fig. 1. This type of representation of spectra is extremely useful for qualitative work. It should not, however, be used for quantitative work since the intensities of very strong bands (where $\log I_0/I$ is greater than 1.0) are not reliable and no data are given for the extent of absorption between bands. Further, the breadths of the absorptions are not given, hence it is difficult to ascertain the true intensities of weaker lines close to stronger ones.

A straightforward comparison of the patterns, especially in the neighborhood of 8 microns, shows that samples A and D are definitely different materials, with very little, if any, of A in D while a small amount (about 5%) of D may be present in A. Further, it can be seen that sample B is mainly the same as A with appreciable amounts (about 15%) of D present. Similarly, C is found to be predominantly D with some A present. For these inspections, the better absorptions to show the presence or absence of these two materials are found at 7.90, 8.06, and 10.01 μ for A and 8.00, 8.14, and 8.91 μ for D. The remaining bands are either too weak or lie too close to strong or broad absorptions of the other component. As an example, the bands of A at 7.77 and 8.20 μ and the one of D at 9.05 μ each lie too close to broad lines of the other compound and thus reliable intensity measurements cannot be made but the presence of these absorptions can be observed.

A very careful and detailed study of the original recordings of the spectra shows them to be, in all respects, what one would expect for mixtures of A and D in the proportions given above.

(11) R. C. Fuson and J. W. Robinson, Jr., THIS JOURNAL, **62**, 358 (1940).

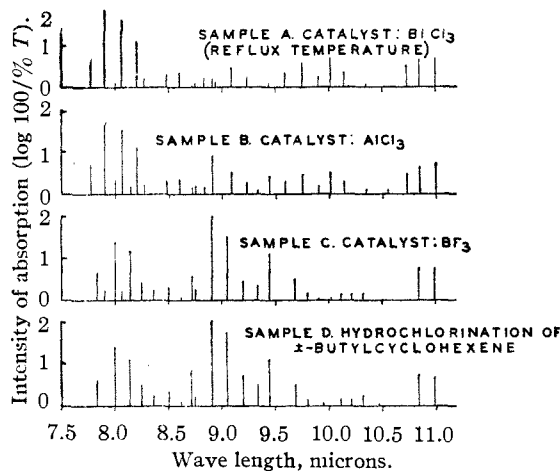(12) E. D. McAlister, G. L. Matheson and W. J. Sweeney, *Rev. Sci. Instruments*, **12**, 314 (1941).

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Summary

1. The condensation of t-butyl chloride with cyclohexene in the presence of aluminum chloride at -25 to $-15°$ results in a 72% yield of chlorobutylcyclohexane, about 85% of which is 1-chloro-3-t-butylcyclohexane, the remainder being 1-chloro-t-butylcyclohexane.

2. The use of bismuth chloride as catalyst at $0°$ and at room temperature results in 5 and 21–25% yields, respectively, of similar mixtures of 1-chloro-3-t-butylcyclohexane with minor amounts of 1-chloro-1-t-butylcyclohexane. At 80–97°, a 20% yield of 1-chloro-3-t-butylcyclohexane of at least 95% purity is obtained.

3. On the other hand, quite pure 1-chloro-1-t-butylcyclohexane (23% yield) is produced when boron fluoride is used at $0°$.

4. t-Butylcyclohexene (usually chiefly 1-t-butyl-1-cyclohexene) and chlorocyclohexane are by-products of the reaction in the presence of boron fluoride or bismuth chloride. The former is presumably produced by dehydrochlorination of the chlorobutylcyclohexane, the hydrogen chloride adding to cyclohexene to yield the chlorocyclohexane.

5. The proofs of structure of the two chlorobutylcyclohexanes are discussed. Incidental to their identification, two new ketones, 2- and 4-t-butylcyclohexanone, were synthesized and characterized by means of the semicarbazone derivatives.

Cross-linkage of Linear Polyesters by Free Radicals

BY W. O. BAKER

Introduction

The chemistry of rubber vulcanization and thermosetting of plastics has been hard to specify because relatively few bonds per unit volume are involved. This is notable in the statistics of chemical gelation.[1,2] The sensitivity of gelation reactions has apparently diverted attention to the fascinating array of organic by-products. This, in turn, has led to explanations of vulcanization as polar, colloidal, interfacial, etc., changes in the polymer, of great mystery and complexity. Such unclear interpretations persist, to some degree, despite excellent demonstrations of the physical effects of a few chemical cross-links.[3] Thus, in a review[4] of the multitude of different theories, it was said: "In the light of our present knowledge, it is probable that every type of vulcanization differs from every other type in the kind and extent of the various changes which together produce the vulcanized state." It is easy to see how the by-products, say, of olefin–sulfur reactions, and the general reactivity of double bonds, could inspire this statement.

Hence, it seemed worth-while to report briefly some observations made several years ago, on thermosetting and vulcanization of pure, linear polymers which contained no olefinic bonds nor complex functional groups. These were linear polyesters, and the reaction studied was with materials (chiefly benzoyl peroxide) which generate free radicals. The reaction mechanism therefore resembled those now so widely recognized in organic chemistry,[5] including that of "curing" agents. Such reactions were later applied to the vulcanization, in the sense of rubber technology, of polyester rubbers ("Paracon").[6,7,8] Likewise they were seemingly used with saturated acrylic esters (Lactoprene).[9]

With these polyesters, the thermosetting of plastics and the vulcanization of typical rubbers can be produced in virtually the same chemical composition. That is, by periodic insertion of methyl (or similar) groups the plastic is converted into a rubber.[7,10] Hence, with negligible change of chemical behavior the two curing processes may be identified with what is almost certainly a mechanism general for high polymers.

Since the details of the decomposition even of benzoyl peroxide itself are still under active study,[11] its effect on the saturated polymers will

(1) Flory, THIS JOURNAL, **63**, 3083, 3091, 3096 (1941); *J. Phys. Chem.*, **46**, 132 (1942).

(2) Stockmayer in "High Polymers," Reinhold Publishing Co., New York, N. Y., 1944.

(3) Flory, *Ind. Eng. Chem.*, **38**, 417 (1946).

(4) Williams, "Chemistry and Technology of Rubber." A. C. S. Monograph No. 74, Reinhold Publishing Co., New York, N. Y., 1937, chap. VI, p. 237.

(5) Waters, *J. Chem. Soc.*, 409 (1946).

(6) Fuller and Biggs, meeting of Division of Rubber Chemistry, American Chemical Society, N. Y., Oct. 5, 1943, to be published.

(7) Biggs and Fuller, *Chem. Eng. News*, **21**, 962 (1943).

(8) Sumner and Myers, Meeting of Division of Rubber Chemistry, New York N. Y., Oct. 5, 1943.

(9) Mast, Rehberg, Dietz and Fisher, *Ind. Eng. Chem.*, **36**, 1022 (1944).

(10) Baker, *Rubber Chem. Tech.*, **18**, 632 (1945).

(11) For example, its decomposition depends on the chemical nature of its environment, as found in various solvents: Wieland, Ploetz and Indest, *Ann.*, **532**, 166 (1937); Wieland and Meyer, *ibid.*, **551**, 249 (1942); McClure, Robertson and Cuthbertson, *Can. J. Research*, **20B**, 103 (1942). Recent important studies include Nozaki and Bartlett, THIS JOURNAL, **68**, 1686 (1946), and Cass, *ibid.*, **68**, 1976 (1946).