

stirring apparatus during addition. Within six minutes addition of 15 ml. had been completed. The thick mixture was then forced onto solid carbon dioxide and water was added. The polymer was isolated and dried in the usual manner. The yield was 3.3 g. or 64% from 5.1 g. of isoprene. The intrinsic viscosity of this polymer was 6.6.

The effect of 17 ml. of the same catalyst was tested with 25 ml. of the same quality isoprene (distilled from the lot described in the previous section) in a bottle polymerization in pentane sufficient to make a volume of 250 ml. The conversion was 63% within one hour and the intrinsic viscosity of the polymer was 6.3.

**Effect of Temperature in Alfin Polymerization (R. L.).**—The 50 and 20% alkoxide sodium isopropoxide/1-butenylsodium (PB<sub>1</sub>) catalysts for these experiments (Fig. 8) were made by addition of 7.65 or 3.05 ml. of isopropyl alcohol, respectively, to amylsodium that had been made from 30.6 ml. of amyl chloride, 11.5 g. of sodium in 270 ml. of pentane. Phillips pure grade 1-butene (60 ml.) was then added at 0° and the mixture allowed to warm slowly to room temperature.

The polymerizations were carried out in each case with 20 ml. of the above catalyst suspension, well shaken before removal of sample, 30 ml. of butadiene and 250 ml. of the hydrocarbon solvent in the high-speed stirring apparatus. Other pertinent conditions are recorded in Fig. 8. The antioxidant used was phenyl-β-naphthylamine.

The sodium 2-butoxide/1-butenylsodium (B<sub>2</sub>B<sub>1</sub>) catalyst was made similarly from 0.5 g. atom of sodium, 0.25 mole of amyl chloride, 0.1 mole of 2-butanol and 60 ml. of 1-butene. The sodium isopropoxide/1-octenylsodium (PO<sub>1</sub>) catalyst was made similarly, except for the use of 200 ml. of freshly distilled 1-octene in place of 1-butene.

**Effect of Solvents and Alkoxide Content (by R. L.).**—The catalysts were prepared by addition of appropriate amounts of alcohol and olefin to amylsodium which had been previously prepared in 80% yield from 0.5 g. atom of sodium and 0.25 mole of amyl chloride. Sixty ml. of 1-butene or its equivalent of other olefins was used. Larger quantities were made in proportion.

The polymerizations were carried out by addition of 30 ml. of butadiene to 20 ml. of the catalyst suspension, stirred in 250 ml. of the solvent in the high-speed stirring apparatus. Other significant data are recorded in Figs. 9, 10 and 11.

**Comparative Formation of Polybutadiene and Polystyrene by Alfin Catalysts (by R. L.).**—The catalysts were

prepared by the method already described. Any variations are described in Table V. The polymerizations were carried out in the high-speed stirring apparatus at 20°. In each experiment 20 ml. of catalyst suspension in 250 ml. of pentane was used with 30 ml. of butadiene or 15 ml. of styrene. The styrene (Eastman Kodak Co. grade) was previously shaken with sodium hydroxide to remove inhibitor, then dried over magnesium sulfate, filtered and distilled at 4 mm. in order to get a middle fraction. After polymerization, the polystyrene was lifted from the pentane and water, squeezed as dry as possible and dried in a vacuum oven at 50°.

**Comparative Yields, Intrinsic Viscosities, Pentane Solubilities of Polymers Produced by Alfin Catalysts (by E. M.).**—The catalysts were prepared as described in the previous sections. The polymerizations were carried out in the high-speed stirring apparatus with 20 ml. of catalyst suspension, 30 ml. of butadiene and 240 ml. of solvent. Data are recorded in Table VI.

### Summary

Di-isopropyl ether reacts with amylsodium to give sodium isopropoxide and allylsodium which form a complex that causes the catalytic polymerization of butadiene and isoprene, rather than the formation of a series of adducts.

Similar agents can be made from sodium alkoxides of methylalkyl carbinols and from metalated olefins. The reagents are called alfin catalysts because a secondary alcohol and an olefin enter into their preparation.

These catalysts are unique because the intrinsic viscosities of the polymers produced therewith are dependent on the components of the catalyst but independent of the monomer-catalyst ratio.

The testing of the catalyst and the general character of the polymerization reactions are described.

A cyclic formula is suggested for the catalyst complex.

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CONTRIBUTION FROM THE INSTITUTE FOR CHEMICAL TECHNOLOGY, COLLEGE OF ENGINEERING, KYOTO IMPERIAL UNIVERSITY, JAPAN]

## Friedel-Crafts Reactions with Organic Dihalides<sup>1</sup>

BY KEIITI SISIDO AND HITOSI NOZAKI

The Friedel-Crafts reaction of 1,3-dichlorobutane and benzene might be expected to yield 1-methylindane, since the latter substance is produced by the action of aluminum chloride upon δ-chlorobutylbenzene<sup>1a</sup>; since the Friedel-Crafts reaction of 1,4-dichlorobutane and benzene<sup>2</sup> as well as that of δ-chlorobutylbenzene<sup>3</sup> both yield tetralin; and, further, since 1,3,3-trimethyl-6-hydroxyindane and 1,1,2-trimethyl-5-hydroxyindane are obtained from the reactions of phenol with diace-

tone alcohol and pinacol, respectively, in the presence of zinc chloride as the condensing agent.<sup>4</sup>

Our experiments show, however, that treatment of 1,3-dichlorobutane with benzene and aluminum chloride does not yield 1-methylindane, but rather a mixture of substances among which we have been able to identify 2,3-diphenylbutane and *s*-butylbenzene. The identity of the 2,3-diphenylbutane was established by a mixed melting point determination of material obtained from the reaction by fractional distillation with an authentic sample of the substance.

In addition to the solid 2,3-diphenylbutane obtained by fractionation of the crude product of

(1) This paper represents a combination of two manuscripts originally entitled "The Organic Reactions with Aluminum Chloride. XIX and XX."

(1a) v. Braun and Neumann, *Ber.*, **50**, 50 (1917).

(2) Yura and Oda, *J. Soc. Chem. Ind., Japan*, **46**, 531 (1943).

(3) v. Braun and Deutsch, *Ber.*, **45**, 1267 (1912).

(4) Niederl, *THIS JOURNAL*, **58**, 657 (1936).

the reaction, there was isolated a liquid fraction whose analysis and properties were in accord with those of *s*-butylbenzene. Oxidation of this oil gave material which on treatment with semicarbazide yielded the semicarbazone of acetophenone, identity being established in a mixed melting point with an authentic sample. The secondary isomer is the only one of the butylbenzenes which can be oxidized to acetophenone. Similar cases of reduction during the Friedel-Crafts reaction have been reported.<sup>1,3,5</sup>

In our experiments higher reaction temperatures favored the production of *s*-butylbenzene; and it is of interest that the production of 2,3-diphenylbutane requires that the 1,3 dihalide be transformed to the 2,3 isomer in the course of reaction. Such isomerizations are well-known.<sup>5</sup>

In view of the anomalous behavior of 1,3-dichlorobutane in the Friedel-Crafts reaction we undertook a study of the reaction of 2,3-dichloro-2,3-dimethylbutane and 3,4-dichloro-3,4-dimethylhexane with benzene in the presence of aluminum chloride. The dihalides were obtained from the corresponding pinacols.

The reaction of 2,3-dichloro-2,3-dimethylbutane and benzene was carried out in the usual way and the product was subjected to fractional distillation. Two fractions were obtained, one of b.p. 65–69° at 16 mm. and one of b.p. 180–190° at 8 mm., both liquid. The higher boiling fraction could not be crystallized and in view of the low yield in which it was obtained, we have abandoned further investigation into its nature. Chromic acid oxidation of the lower boiling fraction yielded  $\alpha,\alpha$ -dimethylhomophthalic acid, benzoic acid and a trace of phthalic acid, the latter presumably being due to farther oxidation of the homophthalic acid derivative. The isolation of  $\alpha,\alpha$ -dimethylhomophthalic acid indicated that the fraction in question contained 1,1,2-trimethylindane.<sup>6</sup> The presence of benzoic acid among the oxidation products may have indicated the presence of a monophenylalkane in the fraction. The analysis and physical constants for the fraction are in accord with the hypothesis that it was a mixture of the indane derivative and a hexylbenzene.

The Friedel-Crafts reaction of 3,4-dichloro-3,4-dimethylhexane with benzene afforded almost exclusively a condensation product composed of one mole each of the reactants as an oil,  $C_{14}H_{20}$ , of b.p. 100–110° at 11 mm. Dehydrogenation of the oil with selenium yielded a liquid mixture from which 1,2,3,4-tetramethylnaphthalene<sup>7</sup> was isolated and oxidation of the oily fraction yielded a mixture of acids from which phthalic acid slowly separated. The results of the dehydrogenation and oxidation experiments are considered to indicate the presence of 1,2,3,4-tetramethyltetralin in the oil fraction in question.

(5) Nenitzescu, *Angew. Chem.*, **52**, 231 (1939).

(6) Price, Davidson and Bogert, *J. Org. Chem.*, **2**, 540 (1938).

(7) Hewett, *J. Chem. Soc.*, 298 (1940).

Dehydrogenation of a fraction boiling at 165–180° at 11 mm. afforded a crystalline hydrocarbon whose picrate melted at 190–193°, but the material was obtained in such small amount that its further investigation was not possible.

In view of the course of the reaction of 1,3-dichlorobutane with benzene in the presence of aluminum chloride, leading, as pointed out above, to 2,3-diphenylbutane, it is of interest that the analogous formation of 2,3-dimethyl-2,3-diphenylbutane and 3,4-dimethyl-3,4-diphenylhexane did not occur during the Friedel-Crafts reactions of the corresponding dihalides with benzene, but rather that isomerization of the dihalides with consequent cycli-alkylation took place. Thus, in the latter reactions an unusual shift of the halide atoms from tertiary to primary or secondary carbon atoms occurred.

### Experimental<sup>8</sup>

**1,3-Dichlorobutane.**—The former<sup>9</sup> preparation using a sealed tube was abandoned. To a solution of 176 g. of butanediol-1,3 and 473 g. of dimethylaniline cooled in ice water was added with stirring 465 g. of thionyl chloride during six hours. The reaction mixture was heated at 85–90° for an additional forty-five minutes. The product was diluted with 2 liters of water, taken up in ether, and washed in turn with dilute hydrochloric acid, water, sodium carbonate solution and finally, with water. After drying over calcium chloride, the ether extract was distilled and at 131–133° colorless liquid came over which was 1,3-dichlorobutane; yield 109 g. (44%),  $d_{20}^{20}$ , 1.1191.

**The Condensation of 1,3-Dichlorobutane and Benzene at Higher Temperature.**—To a suspension of 27 g. of aluminum chloride in 156 g. of benzene heated at 40–45° was added with stirring 51 g. of 1,3-dichlorobutane during about one hour. The temperature was raised gradually. After one hour it reached 85°, and the refluxing was continued for additional two hours. The product was poured on to ice water acidified with hydrochloric acid and treated as usual. The solvent was removed and the residue was distilled. Following fractions were obtained.

TABLE I

Fraction	B. p., °C.	Pressure, mm.	Yield g.	Appearances
I	97–150	758	22	Colorless liquid
II	170–200	758	13	Colorless liquid
III	200–220	758	7	Colorless liquid
IV	120–140	9	5	Yellow oil. Deposited
V	140–160	9	4.5	crystals
VI	160–200	9	5	Red viscous oil
VII	Residue			

***s*-Butylbenzene.**—Fractions I, II and III were combined and redistilled under reduced pressure. Colorless oil which distilled at 60–65.5° at 17 mm., weighed 15 g.: b. p. 173–174° at 758 mm. (Siwoloboff's method);  $d_{20}^{20}$ , 0.8600;  $n_D^{20}$  1.4895; molecular refraction calcd. 44.78, observed 45.1. These data are very close to those of *s*-butylbenzene, and differ apparently from those of other isomers of butylbenzenes.

*Anal.* Calcd. for  $C_{10}H_{14}$ : C, 89.49; H, 10.51. Found: C, 89.13; H, 10.24.

To a solution of 5.0 g. of the hydrocarbon in glacial acetic acid was added 10 g. of chromic anhydride dissolved in dilute sulfuric acid, and the mixture was stirred at 40–50° for five hours, allowed to stand overnight and poured into water. The product was extracted with ether and

(8) Microanalyses by Miss Yasuko Meizyo of this Laboratory.

(9) Fargher and Perkin, *J. Chem. Soc.*, 105, 1356 (1914).

this ether solution was extracted with sodium hydroxide solution. After working up in the usual way, the sodium hydroxide solution gave 0.8 g. of benzoic acid which was identified by a mixed melting point with a known sample. Neither phthalic acid nor  $\alpha$ -methylhomophthalic acid could be detected. The ether layer was dried, filtered and treated with 2 g. of semicarbazide hydrochloride, 2 g. of sodium acetate, 12 cc. of water and 20 cc. of alcohol. After this mixture was evaporated to a small volume and allowed to stand, it gave crystals, m. p. 195-196°. A mixed melting point of this solid with a known sample of acetophenone semicarbazone showed no depression. Among the isomers of butylbenzenes only the secondary one gives acetophenone on oxidation.

These properties indicate that the hydrocarbon  $C_{10}H_{14}$  was *s*-butylbenzene and that the fractions did not contain tetralin nor 1-methylindane.

**2,3-Diphenylbutane.**—The crystals obtained from fractions IV, V and the distillation residue of crude *s*-butylbenzene melted always at 122-124°. The total yield of this solid reached 0.6 g. After recrystallization from alcohol, the product melted at 126-127°; when mixed with an authentic sample of *ms*-2,3-diphenylbutane synthesized from  $\alpha$ -chloroethylbenzene and metallic sodium the melting point showed no depression.

*Anal.* Calcd. for  $C_{16}H_{18}$ : C, 91.42; H, 8.57. Found: C, 91.04; H, 8.42.

Since the mother liquor of the crystals solidified completely upon cooling in an ice-salt mixture, it was thought to consist of *dl*-2,3-diphenylbutane (m. p. 9°) and to contain no 1,3-diphenyl compound (m. p. below -20°).

**The Condensation of 1,3-Dichlorobutane and Benzene at Lower Temperature.**—To a mixture of 312 g. of benzene and 53 g. of aluminum chloride at 0° was added dropwise with stirring 102 g. of 1,3-dichlorobutane during one hour, the reaction temperature being maintained at 0-5°. After an additional six and a half hours of stirring at the same temperature, the mixture was poured over crushed ice. The organic layer was separated and distilled. At 67-72° and 23 mm., 10.0 g. of colorless oil came over. This oil was *s*-butylbenzene, since it gave acetophenone and benzoic acid upon oxidation. From the higher boiling fractions there were obtained 12.5 g. of crystals which proved to be *ms*-2,3-diphenylbutane. The mother liquor of this solid weighed 30 g.

**2,3-Dichloro-2,3-dimethylbutane and 3,4-Dichloro-3,4-dimethylhexane.**—These dichlorides were prepared by the method of Kondakow<sup>10</sup> from hydrogen chloride and pinacols obtained by the reduction of acetone and methyl ethyl ketone, respectively. The pinacolic reductions were carried out according to the procedure of the "Organic Syntheses"<sup>11</sup> as well as that of MacAllum and Whitby.<sup>12</sup> Here we have observed that magnesium foil described in the "Organic Syntheses" can be successfully substituted for "electron metal" shavings.

2,3-Dichloro-2,3-dimethylbutane formed prisms melt at 160°, and 3,4-dichloro-3,4-dimethylhexane<sup>13</sup> a colorless oil boiling at 102-110° and 38 mm.

*Anal.* Calcd. for  $C_8H_{16}Cl_2$ : C, 52.47; H, 8.81. Found: C, 52.52; H, 8.87.

**The Condensation of Benzene with 2,3-Dichloro-2,3-dimethylbutane.**—To a solution of 22 g. of the dichloroalkane and 68 g. of benzene cooled in an ice-salt mixture was added with stirring 12 g. of aluminum chloride in small

TABLE II

Fraction	B. p., °C.	Pressure, mm.	Yield, g.	Appearances
I	65-90	16	4.4	Colorless liquid
II	90-96	16	5.1	Colorless liquid
III	150-190	8	3.7	Yellow viscous oil
IV	190-230	8	1.8	Red viscous oil

(10) Kondakow, *J. prakt. Chem.*, [2] **62**, 169 (1900).

(11) "Organic Syntheses," Coll. Vol. I, 1932.

(12) MacAllum and Whitby, *C. A.*, **22**, 2080 (1928).(13) Frumina, *Chem. Zentr.*, **81**, I, 1001 (1910).

portions. The mixture was stirred for one hour at -10° and for an additional six hours at -5°. After standing overnight at 0-10°, the product was poured onto iced water acidified with hydrochloric acid. The organic layer was separated and distilled giving several fractions.

**1,1,2-Trimethylindane and Hexylbenzene.**—Fractions I and II were combined and the mixture was redistilled under ordinary pressure. At 193-205° came over colorless liquid which was a mixture of 1,1,2-trimethylindane and a hexylbenzene;  $n_D^{20}$  1.5110,  $d_4^{20}$  0.8950.

*Anal.* Calcd. for  $C_{12}H_{18}$ : C, 88.82; H, 11.18. Calcd. for  $C_{12}H_{16}$ : C, 89.94; H, 10.06. Found: C, 89.94; H, 10.71.

Attempted sulfonation of this oily substance according to the method of Bogert and Davidson<sup>6</sup> failed to give crystals of 1,1,2-trimethylindanesulfonic acid.

**Oxidation.**—To a mixture of 2.0 g. of the condensate above mentioned and 12 g. of glacial acetic acid was added dropwise a solution of 6.5 g. of chromic anhydride in 26 g. of acetic acid and 25 cc. of concentrated sulfuric acid. After stirring for eight hours at 15-20°, a solution of 2.5 g. of chromic anhydride and 8.2 g. of acetic acid was added. The mixture was stirred at 80° for an additional six and a half hours, diluted with water and extracted with ether. The ether extract was shaken with dilute sodium hydroxide solution. The aqueous layer was separated, acidified with hydrochloric acid and extracted with ether. After distilling off the solvent, there remained a colorless oil which solidified gradually. Although it was impossible to obtain acidic crystals having a sharp melting point by recrystallizations of this oxidation product, pure crystals of  $\alpha,\alpha$ -dimethylhomophthalic acid anhydride melting at 81-82° were isolated when the free acid was heated at 120° for two minutes and the dehydrated product was recrystallized from alcohol.

*Anal.* Calcd. for  $C_{11}H_{10}O_2$ : C, 69.47; H, 5.30. Found: C, 69.72; H, 5.80.

From the mother liquor of the anhydride there was obtained benzoic acid which was identified by a mixed melting point.

*Anal.* Calcd. for  $C_7H_6O_2$ : C, 68.84; H, 4.95. Found: C, 68.43; H, 5.11.

No phthalic acid was isolated from the oxidation product, but a qualitative test with phenol<sup>14</sup> demonstrated its presence. It is to be added that  $\alpha,\alpha$ -dimethylhomophthalic acid is negative toward this color-reaction.

**The Condensation of Benzene with 3,4-Dichloro-3,4-dimethylhexane.**—To a mixture of 102 g. of benzene and 11 g. of aluminum chloride maintained at 20-25° was added dropwise with stirring 24 g. of 3,4-dichloro-3,4-dimethylhexane during three hours. The temperature was raised to 35° after one hour and kept at 35-40° for an additional three hours. The product was poured over crushed ice and the benzene layer was separated and subjected to fractional distillation. Following fractions were obtained.

TABLE III

Fraction	B. p., °C.	Pressure, mm.	Yield, g.	Appearance
I	-95	11	0.5	Colorless liquid
II	100-110	11	8.4	Colorless liquid
III	110-155	11	0.9	Colorless liquid
IV	165-180	11	1.6	Colorless viscous
V	185-200	11	1.0	oil

Further experiments under the same conditions gave analogous results.

**1,2,3,4-Tetramethyltetralin Contaminated with Indane Derivative.**—Fraction II yielded analytical figures which agreed with  $C_{14}H_{20}$ .

*Anal.* Calcd. for  $C_{14}H_{20}$ : C, 89.29; H, 10.71. Found: C, 89.70; H, 10.72.

A mixture of 5.0 g. of this fraction, 34 g. of potassium

(14) Breithut and Apfelbaum, *Ind. Eng. Chem.*, **17**, 534 (1925).

permanganate and 1020 cc. of water was stirred and refluxed for seven hours. The product was filtered. The concentrated filtrate was acidified with hydrochloric acid and extracted with ether. The ether extract was dried and evaporated. The oily residue deposited crystals melting at 175–177° on standing several days. Sublimation of the crystals gave colorless needles melting at 131°, which did not depress the melting point of a known sample of phthalic acid anhydride.

*Anal.* Calcd. for  $C_8H_4O_3$ : C, 64.86; H, 2.72. Found: C, 65.09; H, 3.01.

No other crystalline acid was obtained from the mother liquors of phthalic acid.

**1,2,3,4-Tetramethylnaphthalene.**—A mixture of 8.4 g. of fraction II and 8.0 g. of selenium was heated on a metal-bath at 280–340° for seventeen hours. The product was extracted with ether. After removing the solvent from this extract, the residue was distilled under reduced pressure. At 105–120° (bath temperature) and 8 mm. came over yellow oil which did not solidify on standing. To a hot solution of this oily substance in alcohol was added picric acid. Upon cooling a crude picrate separated as red needles which weighed about 1 g. It was decomposed with aqueous ammonia and the product was extracted with ether. The ether solution was washed with water, dried and distilled to remove the solvent. Recrystallization of the residue from alcohol yielded colorless plates melting at 106°, which was 1,2,3,4-tetramethylnaphthalene.

*Anal.* Calcd. for  $C_{14}H_{16}$ : C, 91.25; H, 8.75. Found: C, 90.91; H, 8.79.

The picrate of the hydrocarbon melted at 181°.

The mother liquors of the crude picrate were dissolved in ether. This solution was washed with aqueous ammonia and water, dried and evaporated. The residual oil weighed 3.5 g. Since this product was suspected to be the indane derivative which had remained unchanged in the dehydrogenation, it was subjected to oxidation in order to ascertain its structure. To an emulsion of 3.5 g. of this oil in 200 cc. of 25% sulfuric acid was added a solution of 30 g. of chromic anhydride in 40 cc. of water, and the mixture was stirred and refluxed for twenty hours. The product was diluted with 1300 cc. of water and extracted with ether. The ether extract was shaken with sodium hydroxide solution. After working up in the usual way, the sodium hydroxide layer gave an oily product which could not be solidified in spite of several trials. It was observed that a part of this product was now insoluble in dilute sodium hydroxide solution. But when the emulsion was warmed on a water-bath a clear solution was obtained. These facts may show that the oxidation product contains a mixture of an acid, probably  $\alpha$ -methyl- $\alpha$ -ethylhomophthalic acid, and its anhydride. Attempted isolation of the homophthalic acid derivative was unsuccessful.

**Dehydrogenation of Fraction IV.**—The analytical figures of fraction IV agreed with  $C_{22}H_{34}$ .

*Anal.* Calcd. for  $C_{22}H_{34}$ : C, 88.52; H, 11.48. Found: C, 88.95; H, 11.29.

A mixture of 3.8 g. of the oily substance and 4.1 g. of selenium was heated at 310–360° for thirteen and a half hours. The product was extracted with ether and the ether extract was distilled *in vacuo* after removing the

solvent. Recrystallization of the distillate from chlorobenzene gave yellowish crystals whose melting point was not sharp. The picrate of the dehydrogenation product formed dark violet needles melting at 190–193°. When the picrate was decomposed with aqueous ammonia, the resulting hydrocarbon melted at about 142–180°.

*Anal.* Calcd. for  $C_{22}H_{30}$ : C, 89.73; H, 10.27. Found: C, 89.47; H, 10.62.

If the fraction IV is a di-cycli-alkylated product of benzene, 1,2,3,4,5,6,7,8-octamethylnaphthalene may be expected in the dehydrogenation. The melting points of this compound and its picrate were given by Backer, Strating and Huisman<sup>15</sup> as 299–300° and 223°, respectively.

Thus, the dehydrogenation product is apparently a mixture. The detailed studies about its nature will be carried out at a following opportunity.

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### Summary

1. 1,3-Dichlorobutane was condensed with benzene in the presence of aluminum chloride. There resulted a mixture of *s*-butylbenzene and 2,3-diphenylbutane.

2. An excellent yield of 2,3-diphenylbutane was obtained when the reaction was carried out at low temperature, proving that the molecular rearrangement occurs even in the cold.

3. The Friedel-Crafts reaction between benzene and 2,3-dichloro-2,3-dimethylbutane afforded 1,1,2-trimethylindane as well as a hexylbenzene.

4. The condensation of benzene and 3,4-dichloro-3,4-dimethylhexane gave 1,2,3,4-tetramethyltetralin besides, presumably, indane derivatives. This reaction affords a new route to 1,2,3,4-tetramethylnaphthalene.

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(15) Backer, Strating and Huisman, *Rec. trav. chim.*, **55**, 761 (1939).