yielding 3.84 g. of a dark sirup. This was reacetylated with acetic anhydride (35 ml.) containing a drop of sulfuric acid. Isolation of the product in the usual way gave a gummy, semicrystalline mass. This was crystallized from 2-propanol to produce 1.98 g. of tetraacetyl-β-D-glucopyranosylbenzene, m. p. 155–156°, mixed m. p. with a known sample 155–156°. The mother liquors from these crystals yielded 1.66 g. of a dark amber sirup on evaporation. The residual sirups in the remaining Runs of Table I were processed similarly, yielding approximately proportional amounts of α-D-glucopyranosylbenzene.

Tetraacetyl-α-D-glucopyranosylbenzene.—α-D-Glucopyranosylbenzene (256 mg.) was acetylated with acetic anhydride (10 ml.) and pyridine (5 ml.) at 25° for two days. Processing in the usual manner gave 377 mg. (87%) of clear sirup which crystallized spontaneously. Recrystallization from 2-propanol (2 ml.) gave 148 mg. of product, m. p. 68.5–69.5°. Two further recrystallizations gave the pure substance, m. p. 70–71°, $[\alpha]^{23}\mathrm{D}$ 95.1° (*c*, 4.43; chloroform).

Anal. Calcd. for $C_{20}H_{24}O_9$: C, 58.70; H, 5.92; CH_3CO, 42.15. Found: C, 58.89, 58.90; H, 5.91, 6.02; CH_3CO, 42.28.

Tetramethyl-α-D-glucopyranosylbenzene.—One gram of α-D-glucopyranosylbenzene was methylated with methyl sulfate (5 ml.) and 30% aqueous sodium hydroxide (14 ml.) according to the procedure of Haworth.[6] There was isolated a sirup, $[\alpha]^{23}\mathrm{D}$ 36.5° (*c*, 2.216, chloroform). This was further methylated with methyl iodide (10 ml.) and silver oxide (4.8 g.) according to the method of Purdie and Irvine.[7] There resulted 0.85 g. of a colorless sirup. This was distilled *in vacuo* to yield two fractions, $[\alpha]^{24}\mathrm{D}$ 74.7° and 47.2°, suggesting incomplete methylation. The combined fractions were accordingly treated again with methyl iodide and silver oxide. The sirup obtained was distilled (bath temperature 150°, 0.05 mm.) to give 0.44 g. of a colorless, mobile sirup, $[\alpha]^{24}\mathrm{D}$ 93.2° (*c*, 3.37, chloroform).

Anal. Calcd. for $C_{16}H_{24}O_5$: C, 64.90; H, 8.15; OCH_3, 41.88. Found: C, 64.64, 64.66; H, 8.18, 8.20; OCH_3, 41.82.

Tetramethyl-β-D-glucopyranosylbenzene.—Tetraacetyl-β-glucopyranosylbenzene (10 g.) was dissolved in methanol (200 ml.) and potassium (0.1 g.) added. After one day the solvent was distilled, and the residue treated with methyl sulfate (50 ml.) and 30% aqueous sodium hydroxide (140 ml.) as before. The product was 6.32 g. of clear, viscous sirup. After drying *in vacuo* over phosphoric anhydride it was remethylated by Purdie and Irvine's procedure to give 5.62 g. of sirup. On standing in a vacuum desiccator this material underwent partial crystallization. The crystalline paste was thinned with absolute ether (3 ml.) and the product filtered and washed with small portions of petroleum ether. The 0.67 g. of solid obtained had m. p. 97–102°. This was recrystallized once from petroleum ether and four times from water to give trimethyl-β-D-glucopyranosylbenzene hydrate, m. p. 106–107°, $[\alpha]^{24}\mathrm{D}$ 36.3° (*c*, 2.757, chloroform).

Anal. (of dehydrated substance) Calcd. for $C_{15}H_{22}O_5$: C, 63.90; H, 7.86. Found: C, 64.14, 63.95; H, 7.85, 7.90. Water of hydration: Calcd. 6.0. Found, 7.4.

The ethereal filtrate from these crystals was evaporated at reduced pressure to give a clear sirup, $[\alpha]^{24}\mathrm{D}$ 34.5°. This was remethylated again with methyl iodide and silver oxide to yield 4.28 g. of sirup. No further crystalline material was obtained on seeding, so the sirup was distilled. The distillation occurred at 118–120° (0.1 mm.) and 2.86 g. of tetramethyl-β-D-glucopyranosylbenzene was obtained, $[\alpha]^{18}\mathrm{D}$ 18.0° (*c*, 5.002, chloroform).

Anal. Calcd. for $C_{16}H_{24}O_5$: C, 64.90; H, 8.15; OCH_3, 41.88. Found: C, 65.00, 64.60; H, 8.30, 8.15; OCH_3, 40.53, 40.40.

Summary

The dextrorotatory sirup obtained as a by-product with tetraacetyl-β-D-glucopyranosylbenzene by the action of phenylmagnesium bromide on tetraacetyl-α-D-glucopyranosyl bromide has been deacetylated to yield α-D-glucopyranosylbenzene. The acetate and methyl ether derivatives of this compound are described, along with tetramethyl-β-D-glucopyranosylbenzene. The application of Hudson's rules of isorotation to the anomeric compounds in this series is discussed.

STANFORD, CALIFORNIA RECEIVED JANUARY 27, 1950

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[6] Haworth, *J. Chem. Soc.*, **107**, 8 (1915).

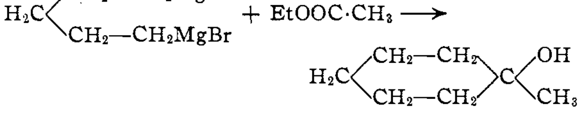
[7] Purdie and Irvine, *ibid.*, **83**, 1021 (1903).

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY, SCOALA POLITEHNICA]

The Synthesis of Cyclic Alcohols and Olefins by the Interaction of Dimagnesium Halides and Esters

BY COSTIN D. NENITZESCU AND ILEANA NECSOIU

Grignard and Vignon[1] have shown that the dimagnesium derivative of 1,5-dibromopentane reacts with ethyl acetate to give 1-methylcyclohexanol



This type of reaction has received but little attention up to the present, and therefore we have studied the possiblity of its generalization, especially as, today, dibromo derivatives are easily accessible.

Besides 1,5-dibromopentane, we have studied 1,4-dibromobutane, and made use of esters of saturated monobasic acids, aromatic acids, halogen acids, saturated dibasic acids and 1,2-unsaturated acids. The last three kinds of esters are of special interest, since the corresponding alcohols and/or olefins cannot be prepared by the usual method of treating organomagnesium derivatives with cyclic ketones.

The experimental results are summarized in the tables.

In general the yields exceed 50%, and reach 65% in the case of the esters of saturated acids. Cyclization is preferred over the reaction in which each of the active groups of the dimagnesium

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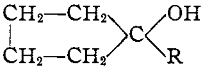
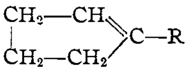
[1] V. Grignard and G. Vignon, *Compt. rend.*, **144**, 1358 (1907).

TABLE I

TERTIARY ALCOHOLS AND OLEFINS OBTAINED FROM 1,4-BUTANEDIMAGNESIUM DIBROMIDE AND VARIOUS ESTERS



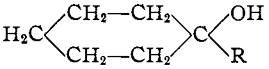
Reactant, ethyl ester	R	Method	Yield, %	B. p., °C.	Mm.	n^{20}_D	d^{20}_4	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
Butyrate	$CH_3CH_2CH_2—$	..	65	170–172	760	1.4504	0.902	^{a}	...	...	...
Palmitate	$CH_3(CH_2)_{14}—$	..	50	180 (M. p. 32)	5	....	....	81.08	81.31	13.62	13.62
Benzoate	$C_6H_5—$	..	66	135–136	12	1.5473	....	81.48	81.18	8.71	8.74
Hydrocinnamate	$C_6H_5CH_2CH_2—$	..	50	146–147	10	1.5319	....	^{b}	...	...	...
2-Chloropropionate	$ClCH_2CH_2—$	..	41	90	12	1.4496	1.061^{c}	56.55	56.37	8.82	8.84^{a}
Succinate	$—CH_2—CH_2—$	..	67	(M. p. 135)	...	....	....	72.73	72.39	11.20	11.40
Olefin	R										
Succinate	$—CH_2—CH_2—$	A^{e}	62	85	3	1.5500	0.987^{b,f}	88.89	88.67	11.19	11.52
Crotonate	$CH_3CH=CH—$	B	30	60–70	12	1.4860	.832^{g,h}	88.89	88.67	11.20	11.12
Cinnamate	$C_6H_5CH=CH—$	B	50	138 (M. p. 52)	5	....	....^{i}	91.71	91.54	8.30	8.36
Sorbate	$CH_3(CH=CH)_2—$	B	33	60	3	....	....^{j}	89.49	89.05	10.52	10.34



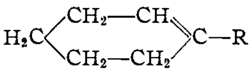
[a] Prepared by another method by G. Chavanne and F. Becker, *Bull. soc. chim. Belg.*, **36**, 591 (1927); *Chem. Centr.* **99**, I, 1169 (1928). [b] Prepared by another method by G. I. Denissenko, *Ber.*, **69**, 2183 (1936). [c] Calcd.: mol. refr., 38.73; Cl, 23.88. Found: mol. refr., 38.81; Cl, 23.55. [e] Obtained from the corresponding alcohol by distillation with *p*-toluenesulfonic acid (Method A), or by direct decompn. of the Grignard compound (Method B). [f] Calcd.: mol. refr., 52.30. Found: mol. refr., 52.28. [g] Calcd.: mol. refr., 36.02. Found: mol. refr., 37.26; exalt., 1.24. [h] Compd. with maleic anhydride, m. p. 159°. [i] Compd. with maleic anhydride, m. p., 178°. *Anal.* Calcd.: C, 76.09; H, 6.01. Found: C, 75.87; H, 6.08. [j] Rapidly autoxidized in the air.

TABLE II

TERTIARY ALCOHOLS AND OLEFINS OBTAINED FROM 1,5-PENTANE DIMAGNESIUM DIBROMIDE WITH VARIOUS ESTERS



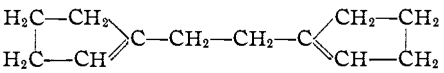
Reactant, ethyl ester	R	Method	Yield, %	B. p., °C.	Mm.	M. p., °C.	n^{20}_D	d^{20}_4	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
Butyrate	$CH_3CH_2CH_2—$	..	41	179–181	760	...	1.4634	0.933	^{a}	...	...	...
Benzoate	$C_6H_5—$	..	51	142–145	12	60	....	...	^{a}	...	...	...
Hydrocinnamate	$C_6H_5CH_2CH_2—$	..	20^{b}	141–142	4	56	....	...	^{c,d}	...	...	...
Succinate	$—CH_2—CH_2—$	..	40	135–137	3	129	....	...	^{e}	...	...	...
Cinnamate	$C_6H_5CH=CH—$	..	30	150	3	...	1.5491	...	83.12	82.96	8.99	9.27
Olefin	R											
Hydrocinnamate	$C_6H_5CH_2CH_2—$	A	70	116–117	4	...	1.5343	...	^{c}	...	...	...
Crotonate	$CH_3CH=CH—$	B	44	56	3	...	....	^{f,g}	88.45	88.18	11.56	11.67
Sorbate	$CH_3(CH=CH)_2—$	B	33	105	5	...	1.5040^{f}	...	89.13	88.75	10.88	11.04



[a] Prepared by another method by F. Signaigo and P. Cramer, THIS JOURNAL, **55**, 3326 (1933). [b] Yields, besides the alcohol, also, the corresponding olefin in 28% yield. [c] Prepared by another method by M. T. Bogert, *Science*, **77**, 289 (1933). [d] J. W. Cook and C. L. Hewitt, *J. Chem. Soc.*, 1089 (1933). [e] Prepared by another method by P. S. Pinkney, G. A. Nesty, C. S. Marvell and D. E. Pearson, THIS JOURNAL, **59**, 2666 (1937). [f] Rapidly autoxidized in contact with air. [g] Compound with maleic anhydride, m. p. 225°. *Anal.* Calcd.: C, 70.88; H, 7.33. Found: C, 70.97; H, 7.38.

derivative reacts independently with a molecule of ester.

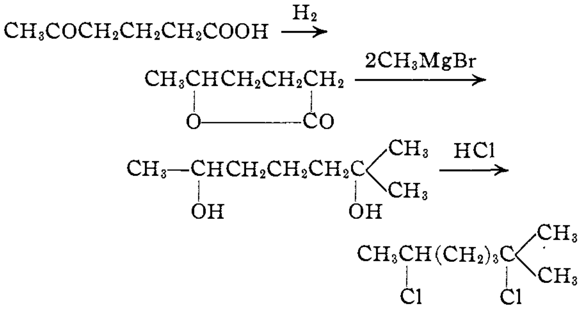
With regard to the different types of esters used, the following was found: (1) ethyl β-chloropropionate and 1,4-butanedimagnesium dibromide yielded the expected chloroethylcyclopentanol. Thus, the halogen atom in the ester molecule does not influence the course of the reaction. (2) Ethyl succinate reacts normally at both its carbethoxy groups, yielding a dicyclic glycol, which upon dehydration with dilute sulfuric acid gives a diolefin with a double bond in each of the cycles.



This structure follows from the molecular refraction, which did not show any exaltation, as well as from the fact that the compound does not combine with maleic anhydride. (3) Esters of unsaturated 1,2-acids yield tertiary alcohols only if all trace of acid is removed before distillation, otherwise dehydration takes place during the process and a diolefin with conjugated double bonds is produced. Dehydration is quantitative if a trace of *p*-toluenesulfonic acid is added during the distillation. The diolefins obtained by this procedure readily yield compounds with maleic anhydride. (4) Ethyl sorbate reacts normally with the dimagnesium derivative, giving a triene. This triene, as well as the dienes obtained from cinnamic ester readily undergoes autoxidation and polymerization in contact with air to produce colorless, transparent resins, resembling methyl polyacrylate.

Grignard and Vignon[2] have shown that, during the synthesis of tertiary alcohols from organomagnesium compounds and esters, secondary products are formed by the reaction between the resulting tertiary alcohol and the original ester. Therefore, in the experiments described in this paper, an excess of the original ester with respect to the dimagnesium derivative was used and then the crude reaction product was heated with alcoholic potassium hydroxide, to hydrolyze the excess of original ester as well as the ester of the tertiary alcohol. Although this procedure did not improve the yield of tertiary alcohol, it ensures that the tertiary alcohol is not contaminated by esters. The hydrolysis was not used in the case of chloropropionic ester, where the elimination of halogen should be avoided.

For the synthesis of an iononic cycle, 2,6-dichloro-2-methylheptane was prepared



$$CH_3COCH_2CH_2CH_2COOH \xrightarrow{H_2} \underset{O\text{---------}CO}{CH_3CHCH_2CH_2CH_2} \xrightarrow{2CH_3MgBr}$$

$$\underset{OH}{CH_3\text{—}CH}CH_2CH_2\underset{OH}{CH_2C}(CH_3)_2 \xrightarrow{HCl} \underset{Cl}{CH_3CH}(CH_2)_3\underset{Cl}{C}(CH_3)_2$$

It has not been possible to obtain until now a magnesium derivative from this dihalide.

Experimental

Raw Materials.—1,4-Butanediol was prepared by hydrogenation of ethyl succinate with a copper–chromoxide catalyst according to Adams.[3] 1,5-Pentanediol was prepared similarly from ethyl glutarate.

1,5-Pentanediol was also prepared from furfural.[4] Three hundred grams of furfural was hydrogenated in the presence of 15 g. of copper–chromoxide in a one-liter autoclave at initial pressure of 150 atm. and a temperature of 120–130°. The yield was 270 g. of tetrahydrofurfuryl alcohol.

This quantity of alcohol was further reduced by using 15 g. of copper–chromium oxide catalyst, at an initial pressure of 200 atm. and a temperature of 225°. The product was first distilled through a 20-cm. Vigreux distillation column. From 2 kg. of furfural, 450 g. of a fraction boiling at 95–100° (10 mm.) and 700 g. of a fraction, b. p. 110–135°, were obtained. This later fraction was redistilled through a 150-cm. column, discarding the fraction boiling below 130°. The residue was purified by distillation from a Claisen flask; yield 270 g. (13% with respect to the furfural initially used); b. p. 135° at 10 mm.

For the conversion of 1,4-butanediol to its dibromide, the method of Kamm and Marvel[5] results in the formation of large amounts of brown-black resins and a yield of only 40%. An 83% yield of product boiling at 78° (10 mm.) was obtained by a slight modification of procedure, as follows: concentrated sulfuric acid (117 g.) was added slowly, with stirring, to 138 g. of ice-cold hydrobromic acid, and to this cold solution was added dropwise 27 g. of butanediol. The reaction mixture was allowed to stand for twenty-four hours, heated for three hours on the steam-bath and the product separated in a funnel, washed and dried in the usual way; b. p. 78° at 10 mm.; the yield is 54 g. or 83%.

Reaction of Ester with Di-Grignard Reagent.—The procedure described below may be considered as typical: Into a three-necked 1.5-liter flask, provided with a mechanical stirrer (Jean K. P. G.), 0.3 mole of magnesium and 50 cc. of dry ether were introduced and then a mixture of 0.1 mole of dibromo derivative, diluted with 260 cc. of ether, was added dropwise at a rate just sufficient to keep the reaction mixture boiling. The contents of the flask were refluxed for an hour, then cooled with ice and a solution of 0.2 mole of ester in 40 cc. of ether is allowed to flow in, dropwise, the stirring being continued. (In the case of the esters of unsaturated acids, the reaction was carried out in an atmosphere of dry nitrogen.) The flask was allowed to stand overnight and the contents then decomposed with dilute sulfuric acid (or with acetic acid and ice, in the case of the unsaturated acids). After washing with dilute sodium carbonate and evaporating over the steam-bath, 0.5 mole of alcoholic potassium hydroxide (40%) was added and the mixture then boiled for four hours. The alcohol was removed, the residue diluted with water, extracted with ether, the ether evaporated and the residue distilled under reduced pressure.

δ-Caprolactone.—One hundred grams of δ-ketocaproic acid, dissolved in 150 cc. of dry ether, was hydrogenated with 10 g. of Raney nickel at 100 atm. at 50–60°. The calculated amount of hydrogen was absorbed in two days; 50 g. of lactone was obtained.

2-Methyl-2,6-heptandiol.—Forty-five grams of the caprolactone, diluted with a double quantity of absolute ether, was added dropwise to a solution of methylmagnesium bromide, prepared from 24 g. of magnesium. The product was decomposed with diluted acetic acid, the ether layer washed with concentrated sodium carbonate and the glycol distilled at 120° (12 mm.); yield 28 g.

Anal. Calcd. for $C_8H_{18}O_2$: C, 65.71; H, 12.41. Found: C, 65.45; H, 12.34.

2,6-Dichloro-2-methylheptane.—Hydrogen chloride was passed for twenty-four hours into a solution of 5 g. of glycol in 50 cc. of dry ether while the mixture was cooled in an ice-salt-bath. After evaporation of the ether at reduced pressure there remained a semi-solid residue which was distilled under reduced pressure (b. p. 93–95° at 10 mm.). Crystals in the partially solidified distillate were separated by suction, and dried on a porous plate; m. p. 40°.

Anal. Calcd. for $C_8H_{16}Cl_2$: C, 52.46; H, 8.81; Cl, 38.75. Found: C, 52.70; H, 9.16; Cl, 38.89.

Summary

Some 1-substituted derivatives of cyclopentanol and cyclohexanol have been prepared, by the action of Grignard reagents obtained from 1,4-dibromobutane or 1,5-dibromopentane on various esters. Esters of the following types of acids were used: monobasic saturated, unsaturated,

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[2] V. Grignard and G. Vignon, *Compt. rend.*, **132**, 336 (1901); see also G. Stadnikoff, *Ber.*, **57**, 1 (1924).

[3] Adams, *Angew. Chem.*, **54**, 469 (1941).

[4] Schering-Kahlbaum Company, German Patent 555,405; *Chem. Centr.*, **103**, II, 1971 (1932); G. Natta, R. Rigamonti and E. Beati, *Chim. e Ind.*, **23**, 117 (1941); *Chem. Centr.*, **112**, II, 114 (1941).

[5] O. Kamm and C. S. Marvel, "Organic Syntheses," Vol. I, p. 8, 1920.

aromatic, dibasic saturated and β-halogen. The reaction may be considered therefore as general.

The tertiary alcohols thus obtained can be transformed easily by dehydration into the corresponding olefins. In the case of 1,2-unsaturated acids, the tertiary alcohols obtained lose water easily, sometimes even during the preparation procedure, and pass into the respective cyclic olefins.

BUCHAREST, ROUMANIA RECEIVED JUNE 30, 1948[6]

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[6] Publication delayed because of difficulty of communication.

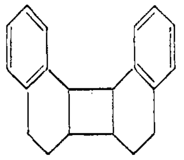
[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY, SCOALA POLITEHNICA]

The Polymerization of 1,2-Dihydronaphthalene and the Dehydrogenating Condensation of 1,2,3,4-Tetrahydronaphthalene

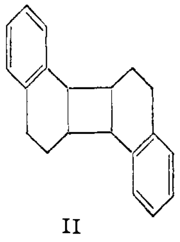
BY COSTIN D. NENITZESCU AND MARGARET AVRAM

By the action of sulfuric acid on 1,2-dihydronaphthalene (dialin), von Braun and Kirschbaum[1] obtained a solid dimeride $C_{20}H_{20}$ (m. p. 93°), which they called bis-dialin, along with a liquid isomeride corresponding to the same empirical formula but probably not of uniform composition. To these hydrocarbons, which possess a saturated character, the structures I or II have been attributed.

These hydrocarbons, dehydrogenated with lead oxide, yield a yellow hydrocarbon $C_{20}H_{12}$ (m. p. 165°) named by the above authors bis-naphthylene. To these, similar formulas have been assigned with all the four cycles being aromatic.



I

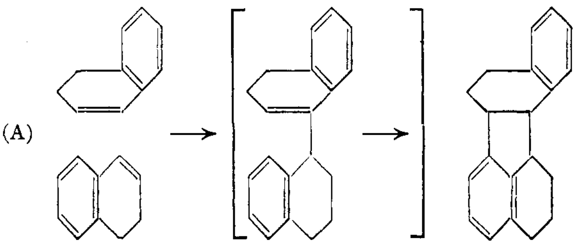


II

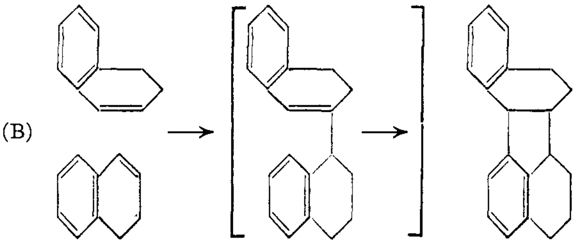
By the action of aluminum chloride on tetralin, at 30–80°, Dansi and Ferri[2] obtained a hydrocarbon $C_{20}H_{20}$ (m. p. 150.5°), which by dehydrogenation with selenium, yields a hydrocarbon, thoroughly aromatic in character, $C_{20}H_{12}$ (m. p. 165°), which yields a picrate of m. p. 195°.

By repeating the experiments of von Braun and Kirschbaum we found that their hydrocarbon $C_{20}H_{12}$ gives a picrate which melts at the same temperature as that indicated by Dansi and Ferri. Thus, it is obvious that the hydrocarbons $C_{20}H_{12}$, obtained by these authors, are identical. We were unable to reproduce the work of Dansi and Ferri, probably because we had no precise knowledge of the conditions under which this work was accomplished. The results which we obtained by treating tetralin with aluminum chloride, under various conditions, coincide exactly with those described by G. Schroeter.[3]

Working Hypothesis.—The structures I and II, with their cyclobutanic cycles, seem improbable; therefore we propose for the dimerization of 1,2-dialin under the influence of sulfuric acid, one of the following two mechanisms.



III



IV

The transformation which the tetralin molecule undergoes through the influence of aluminum chloride, in the reaction of Dansi and Ferri, is a dimerization with elimination of hydrogen.

$$2C_{10}H_{12} \longrightarrow C_{20}H_{20} + 4[H]$$

The expelled hydrogen is used in undefined hydrogenation reactions. The probable course of this reaction is as follows: first, a molecule of tetralin loses two hydrogen atoms, passing into 1,2-dialin. Such formation of an olefin from a saturated hydrocarbon, under the influence of aluminum chloride, has been proved in other instances.[4] The resulting dialin reacts then with tetralin, which is present in great excess, following one of the mechanisms shown.

If these hypotheses are correct, the two isomeric hydrocarbons, $C_{20}H_{20}$ (m. p. 93 and 150.5°), ought to possess the structure III and IV, respectively. The hydrocarbon $C_{20}H_{12}$ with the

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[1] Julius von Braun and G. Kirschbaum, *Ber.*, **54**, 597 (1921).

[2] A. Dansi and G. Ferri, *Gazz. chim. ital.*, **71**, 648 (1941); *Chem. Centr.*, **113**, I, 2525 (1942).

[3] G. Schroeter, *Ber.*, **57**, 1990 (1924).

[4] C. D. Nenitzescu and C. N. Ionescu, *Ann.*, **419**, 189 (1931).