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Chemistry. — “Action of Organo-magnesium Compounds on, and Reduction of Cineol.” By C. F. VAN DUIN, chem. docts. (Communicated by Prof. P. VAN ROMBURGH).

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The first communication in the literature about the action of organo-magnesium compounds on internal oxides is given by BLAISE ¹⁾, who found that on action of RM_gBr on ethylene oxide, both a primary alcohol and the bromic hydrine of glycol are formed. The formation of these two products led him to assume that the organo-magnesium compound is added to part of the oxide according to equation $\text{RM}_g\text{Br} + (\text{CH}_2)_2\text{O} = \text{RCH}_2 - \text{CH}_2\text{OM}_g\text{Br}$ (I) and to another part according to the reaction scheme: $\text{RM}_g\text{Br} + (\text{CH}_2)_2\text{O} = \text{CH}_2\text{Br} - \text{CH}_2\text{OM}_g\text{R}$ (II).

GRIGNARD ²⁾, however, rightly pointed out that according to BLAISE's reaction scheme II the organo-magnesium compound splits up into RM_g and halogen in its addition; a case which had never yet been observed. He then proved that in this first of all an oxonium

compound is formed of the formula $\begin{array}{c} \text{CH}_2 \quad \text{M}_g\text{Br} \\ \diagdown \quad / \\ \text{O} \\ / \quad \diagdown \\ \text{CH}_2 \quad \text{R} \end{array}$, which on heating

passes into $\begin{array}{c} \text{CH}_2\text{OM}_g\text{Br} \\ | \\ \text{CH}_2\text{R} \end{array}$ through an intramolecular conversion. The

appearance of the bromic hydrine of the glycol can then also be explained by action of HBr (formed at the hydrolysis of the M_gBr^2) on oxide that has not reacted and had then split off. The mechanism of the reaction had been made clear by this. HENRY studied the action of organo-magnesium compounds on isobutylene oxide ³⁾, symm. butylene oxide ⁴⁾, and propylene oxide ⁵⁾; the first reacts then as the

¹⁾ BLAISE. C. R. d. l'Acad. des sciences **134**, 551 (1902).

²⁾ GRIGNARD C. R. d. l'Acad. des sciences **136**, 1260 (1903), Bull. Soc. chim. (3) **29**, 944 (1903).

³⁾ HENRY C. R. de l'Acad. des sciences **145**, 21 (1907); cf. *ibid.* **145**, 154 (1907).

⁴⁾ *Ibid.* **145**, 406 (1907).

⁵⁾ *Ibid.* **145**, 453 (1907).

isomeric isobutylaldehyde, the second as methylethylketon, the reaction for propylene oxide proceeding as for ethylene oxide.

Numerous are the investigations with epichloric hydrine; IOSITSCH ¹⁾ got on action of C_2H_5MgBr a chloric amylalcohol, and KLING ²⁾ obtained quantitatively the chloric iodine hydrine with C_2H_5MgI , IOSITSCH ³⁾. repeating his experiments, now got both the chloric bromic hydrine and a chloric amylalcohol. Then FOURNEAU and TIFFENEAU ⁴⁾ found that with aliphatic organo magnesium bromides only the chloric bromic hydrine is formed, while with aromatic organo-magnesium compounds chloric propanoles with the constitution $RCH_2 - C \begin{matrix} H \\ COH \end{matrix} CH_2Cl$ arise for which formerly the formula $CH_2Cl C \begin{matrix} H \\ R \end{matrix} CH_2OH$ had been assumed. ⁵⁾

In conclusion we may mention that FOURNEAU and TIFFENEAU ⁶⁾ drew the conclusion from their study on the action of organo-magnesium compounds on mono substituted and asymmetrically di-substituted ethylene oxides that for the former the general process of reaction is: $RC \begin{matrix} \diagup H \\ \diagdown O \end{matrix} CH_2 + R'MgBr \rightarrow RC \begin{matrix} \diagup H \\ \diagdown OH \end{matrix} CH_2R'$, whereas for the latter a previous isomerisation to the isomeric aldehyde must be assumed.

When we take the general result of the above mentioned researches into consideration, we should expect the primary formation of an addition product on the action of an organo-magnesium compound on cineol; that this is really so on action of CH_3MgI was already shown by GRIGNARD ⁷⁾, who also observed that on heating of this addition product a violent reaction sets in. This reaction, however, consists in more than only in an intra-molecular conversion; the reaction taking place at about 160° is very violent; the temperature rises to about 260° , while during violent gas generation a liquid distills over, which is coloured brown through free iodine. The reaction is not always equally violent; in connection with this the quantity of gas that escapes, and the quantity of liquid that distills

¹⁾ IOSITSCH, Journ. russ. phys. chem. Ges. **34**, 96. (1902).

²⁾ KLING, Bull. Soc. chim. (3), **31**, 14 (1904) C. R. d. l'Acad. des sciences **137**, 756 (1903).

³⁾ IOSITSCH, Journ. russ. phys. chim. Ges. **36**, 6 (1904).

⁴⁾ FOURNEAU and TIFFENEAU, Bull. Soc. chim. (4) **1**, 1227 (1907).

⁵⁾ J. D. RIEDEL, Akt. Ges. D. R. P. 183361; Ch. C. 1907 **1**, 1607.

⁶⁾ FOURNEAU et TIFFENEAU, C. R. d. l'Acad. des sciences **145**, 437 (1907).

⁷⁾ GRIGNARD, Bull. Soc. chim. (3) **29**, 944 (1903).

over, varies. The latter is best obtained by adding 52 grammes of cineol to an etheric suspension of 56 grammes of CH_3MgI , obtained from 8 grammes of Mg and 48 grammes of CH_3I ; the whole mass is heated for a few hours and left for 3 or four days.

Then the ether is distilled off, in which but very little cineol goes over, the residue is heated up to $\pm 160^\circ$ on a sand bath, a very wide exit tube is placed on the flask and the reaction proceeds without further supply of heat. Thus from 30—40 grammes of distillate are obtained and from 4—5 L. of gas. There is, however, always some liquid left behind in the flask; it is obtained by treating the residue further in the usual way; the thus obtained liquid is the same as that which distills over. The latter is first washed with a thiosulphate solution and then fractionated in vacuo, collecting everything together that goes over at 21 mm. to 85° . Then the distillation is stopped, because then the residue begins to decompose with splitting off of iodine. What is distilled over is shaken a few times with a 50% resorcine-solution for the removal of unchanged cineol, which is present in a fairly large quantity; then it is dried on chloric calcium and finally distilled over metallic sodium. Then a liquid is obtained of b.pt. 170° — 178° at 759 mm., consisting of a mixture of hydrocarbons $\text{C}_{10}\text{H}_{16}$. The elementary analysis namely gave: (burned with lead chromate in a closed tube): C = 87, 84%; H = 12.00% (calculated for $\text{C}_{10}\text{H}_{16}$: C = 88.15%, H = 11.85%), the determination of the physical constants of the fractions obtained by repeated fractionation:

fraction b.pt. 170° — 172° , 5,	Sp. Gr. _{16°} = 0.841
	n_{D16° = 1.4679
	Mol. Refr. = 44.99
fraction b.pt. 172° 5— 175° :	Sp Gr ₁₆ = 0.846
	n_{D16° = 1.4706
	Mol.Refr. = 44.94
fraction b.pt. 175° — 178° :	Sp. Gr. _{16°} = 0.853
	n_{D16° = 1.4752
	Mol.Refr. = 44.95

Calculated for $\text{C}_{10}\text{H}_{16}$ 2 F: Mol.Refr. = 45.25.

Besides, the fact that in not a single way a crystalline product could be obtained from any of these fractions points to the presence of a mixture. I tried the preparation of the tetrabromide according to WALLACH¹⁾ in alcohol ether, in sulphuret of carbon, and in

¹⁾ WALLACH, Annalen 227, 280 (1885).

methyl alcohol, of a nitrosochloride, and of a chloric hydrate, but could not obtain a crystalline product anywhere. Nor did oxidation with potassium manganate according to WAGNER¹⁾ lead to a result; the only products that could be identified were acetone and oxalic acid; hence I must rest satisfied with the communication that with generation of methane a mixture of hydrocarbons $C_{10}H_{16}$ is formed.

With C_2H_5MgBr the reaction takes place much less vigorously, and chiefly unchanged cineol distills over; the diminution of the specific gravity, as well as the reduction of an ammoniacal silver oxide solution pointed, however, to the presence of hydrocarbons $C_{10}H_{16}$.

The action of C_6H_5MgBr proceeds quite differently; it is true, here too an addition product is formed, but this remains unchanged on being heated, even up to 200° , so that when treating it we get back the cineol, besides diphenyl. Perhaps that here an intramolecular conversion may be obtained on continued action in the cold, for then crystals separate from the etheric solution of cineol and C_6H_5MgBr , if these crystals are treated separately, a little (3 grammes from 42 Gr. C_6H_5MgBr and 36 Gr. cineol after 3 months' standing) of a liquid that goes over between 80° and 90° at 21 mm., which with phenylisocyanate gave no crystalline urethane. The liquid which was poured off the crystals, yielded nothing but cineol.

With regard to the reduction of internal oxides according to the method of SABATIER and SENDERENS, there exists in the literature only one example, viz. the reduction of cyclohexene oxide to cyclohexanol²⁾, in which the yield was even quantitative. Besides SABATIER³⁾ expressed the opinion that all the ethylene oxides could be hydrated according to his method.

I could not get a reduction for cineol in this way; when at 170° this substance with an excess of hydrogen had been led twice through a tube 40 cm. long, filled with pumice nickel, the sp. gr. had not changed in the least.

These researches, both with cineol and with other oxides, are being continued.

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¹⁾ WAGNER, B. B. 23, 2315 (1896).

²⁾ BRUNEL, Ann. Chim. Phys. (8) 6, 237 (1905).

³⁾ SABATIER, Die Katalyse in der organischen Chemie Leipzig 1915, pag. 80.