Mengel[6] for the production of 2,4-methylated quinolines: *p*-aminoethylbenzene (8 g.) and 6.6 g. of acetylacetone were refluxed for thirty minutes and then, for removal of water formed in the reaction, refluxing was continued for fifteen minutes with the condenser steam-heated. After addition of 115 cc. of concentrated sulfuric acid and heating on a steam cone for twenty minutes, the mixture was poured onto ice. The base was liberated with caustic and extracted with ether. Next, diazotization in dilute hydrochloric acid for removal of *p*-aminoethylbenzene was carried out in the usual way. After removal of non-basic admixtures by ether extraction, the solution was made alkaline with caustic and the liberated base was extracted with ether. The yield of crude 2,4-dimethyl-6-ethylquinoline was 4 g. (33%). The picrate prepared in alcohol solution crystallizes from alcohol in fine needles melting at 190–191°.

Anal. Calcd. for $C_{19}H_{18}O_7N_4$: C, 55.07; H, 4.35; N, 13.53. Found: C, 54.99; H, 4.66; N, 13.56.

The following constants were determined on the base prepared from the picrate: b. p. 299–300° (742 mm.), n^{25}_D 1.5860.

3-Methyl-2,8-diethylquinoline.—This product was synthesized in poor yield from propionaldehyde and *o*-aminoethylbenzene through the Doebner–Miller synthesis as modified by Harz.[7] After the usual process of isolation of quinolines through picrates, the picrate of the new base was recrystallized from alcohol in needles melting at 194–195°. The free base, prepared from picrate recrystallized to constant melting point, has the following constants: m. p. 18.5–19.5°, b. p. 298° (754 mm.), n^{25}_D 1.5778, d^{20}_4 1.0014.

Anal. Calcd. for $C_{20}H_{20}O_7N_4$: C, 56.07; H, 4.71. Found: C, 56.38; H, 4.70.

3-Methyl-2,6-diethylquinoline.—This product was synthesized from propionaldehyde and *p*-aminoethylbenzene through the Doebner–Miller synthesis as modified by Mills, Harris and Lambourne.[8] It was isolated and purified through the picrate. The yield of the new base was 8 g. from 25 g. of *p*-aminoethylbenzene or 19.5%. The picrate was recrystallized from alcohol in needles melting at 152–153°. The base has the following constants: b. p. 313.5° (748 mm.), n^{25}_D 1.5834, d^{20}_4 1.0049.

Anal. Calcd. for $C_{20}H_{20}O_7N_4$: C, 56.07; H, 4.71. Found: C, 56.26; H, 4.83.

Summary

Experimental proof is presented of (1) an increased yield of carboxylic acids by employing step-wise chromic acid oxidation of 8-alkylquinolines and (2) an increase in the velocity of reaction, where chromic acid anhydride is employed, by the addition of potassium acid sulfate.

The direct conversion of *Bz*-ethylquinolines to corresponding *Bz*-quinolyl methyl ketones through oxidation with chromic acid anhydride or dichromate is reported.

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[6] Koenigs and Mengel, *Ber.*, **37**, 1325, 1333 (1904).

[7] Kurt Harz, *ibid.*, **18**, 33, 84 (1885).

[8] Mills, Harris and Lambourne, *J. Chem. Soc.*, **119**, 1300 (1921).

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Grignard Reductions. IX.[1,2,3] Further Studies on the Reduction of Acid Halides

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The discovery by F. L. Greenwood and H. M. Crooks of the quantitative reduction of trimethylacetyl chloride by *t*-butylmagnesium chloride to the corresponding primary alcohol[2] represents a new general reaction.[3]

Mechanism of the Reaction

The following steps are apparently involved in the action with a Grignard reagent R′MgX

$$\begin{tikzcd}
 & \mathrm{RCOR'} \arrow[dr] & \\
\mathrm{RCOCl} \arrow[ur] \arrow[r] & \mathrm{RCHO} \arrow[r] \arrow[d] & \mathrm{RCHOHR'} \\
 & \mathrm{RCH_2OH} &
\end{tikzcd}$$

The change RCOCl′ to RCOR′ has been observed in the preparation of pinacolone from acetyl chloride and *t*-butylmagnesium chloride[4] and on addition of primary Grignard reagents to primary acid chlorides[3a] and of tertiary Grignard reagents to primary, secondary, and tertiary acid chlorides.[2b,3a]

The reduction RCOR′ to RCHOHR′ is possible by means of Grignard reagents. Thus, methyl isopropyl ketone was reduced to the second-

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[1] The material here presented was originally submitted in about a dozen papers which gave full experimental details; received October 7, 1939.

[2] (a) Whitmore, *Rec. trav. chim.*, **57**, 563 (1938); (b) Greenwood, Whitmore and Crooks, THIS JOURNAL, **60**, 2028 (1938).

[3] Whitmore and co-workers, *ibid.*, **60** (1938); (a) Heyd, 2030; (b) Popkin, Whitaker, Matill and Zech, 2458; (c) 2462; (d) Meyer, Pedlow and Popkin, 2788; (e) Whitaker, Matill and Popkin, 2790; (f) Wheeler, 2899.

[4] Whitmore and Badertscher, *ibid.*, **55**, 1559 (1933).

ary alcohol by *t*-butylmagnesium chloride and by *t*-amylmagnesium chloride in 29 and 50% yields. Similarly 2,2-dimethyl-4-ethyl-3-hexanone gave a 38% yield of the secondary alcohol with *t*-butylmagnesium chloride. Methyl neopentyl ketone was reduced by normal Grignard reagents in the following yields[3b]: Et, trace; Pr, 5.5%; Bu, 5.7%; Am, 3.4%. The literature contains much work on similiar reductions of ketones, especially of benzophenone. Kharasch has given an excellent summary.[5]

The production of the secondary alcohol RCHOHR′ from RCOCl apparently does not go through the ketone stage since the yields from the acid chlorides are considerably higher than those from the ketones.

Although it was early surmised that the conversion of RCOCl to the primary alcohol RCH_2OH and the secondary alcohol RCHOHR′ must pass through the aldehyde stage, the aldehyde has been actually isolated in only three cases. Addition of trimethylacetyl chloride and of *t*-butylacetyl chloride to *t*-butylmagnesium chloride gave traces of trimethylacetaldehyde and *t*-butylacetaldehyde, respectively. Apparently most aldehydes react almost completely with the Grignard reagent either by addition or reduction. In the case of methyl-*t*-butylneopentylacetyl chloride with *t*-butylmagnesium chloride and *t*-amylmagnesium chloride, however, the corresponding aldehyde was obtained in about 70% yields. In this case the aldehyde is sufficiently inert toward the Grignard reagent to be isolated. This aldehyde autooxidizes somewhat more slowly than does benzaldehyde.

The conversion of RCHO to RCHOHR′ is a normal and expected process except with highly branched reagents.[5,6] Diethylacetaldehyde with *t*-butylmagnesium chloride and with *t*-amylmagnesium chloride gave yields of secondary alcohols corresponding to those from diethylacetyl chloride and the same reagents. The amount of secondary alcohol obtained from the aldehyde intermediate depends on the relation between the ease of addition and ease of reduction.

The conversion of RCHO to RCH_2OH by the Grignard reagent was observed by Conant and co-workers,[6] who found that trimethylacetaldehyde with *t*-butylmagnesium chloride gave a 65% yield of neopentyl alcohol. No other product was found. *i*-Propylmagnesium bromide gave only 10% of the primary alcohol together with the expected secondary alcohol. Dimethylethylacetaldehyde and *i*-propylmagnesium bromide gave the primary alcohol in 40% yield. Isobutyraldehyde with *t*-butylmagnesium chloride gave a 20% yield of isobutyl alcohol.[2b] Isobutyraldehyde with *t*-amylmagnesium chloride gave an 84% yield of isobutyl alcohol. Isobutyryl chloride with the same reagent gave a 44% yield of isobutyryl isobutyrate calculated on the Grignard reagent. Methyl-*t*-butyl-neopentylacetaldehyde was reduced to the primary alcohol in 90% yield on long treatment with *t*-amylmagnesium chloride. Diethylacetaldehyde with *t*-butylmagnesium chloride and with *t*-amylmagnesium chloride gave yields of primary alcohol corresponding to those obtained from diethylacetyl chloride.

When the Grignard reagent acts as a reducer its oxidation product is an olefin or related product. Thus, the action of *t*-butylmagnesium chloride with trimethylacetyl chloride gave isobutylene in the proportion of two moles for each mole of primary alcohol formed and one mole for each mole of secondary alcohol formed.[2b] This indicates the following changes

$$RCOCl + C_4H_9MgCl \longrightarrow MgCl_2 + RCHO + C_4H_8$$
$$RCHO + C_4H_9MgCl \longrightarrow RCH_2OMgCl + C_4H_8$$

With *t*-amylmagnesium chloride as the reducing agent amylenes are formed. By-products may be formed by the action of the acid chloride with the olefin in presence of the anhydrous magnesium chloride. Thus acetyl chloride and *t*-butylmagnesium chloride gave mesityl oxide as a by-product.[3f] *t*-Amylmagnesium chloride gave some of the corresponding compound 2,3-dimethyl-2-pentene-4-one.

Miscellaneous Factors

An excess of free magnesium has no measurable effect on the yield of reduction products. In spite of this fact, the Grignard solutions used throughout this work were filtered through glass wool by nitrogen pressure.

Acid chlorides and bromides behave essentially the same but acid iodides give troublesome side reactions which have not been completely solved.

The Grignard chlorides, bromides, and iodides give closely similiar results.

In most reactions the acid chloride was added to an excess of the filtered Grignard chloride or

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(5) Kharasch and Weinhouse, *J. Org. Chem.*, **1**, 209 (1936).

(6) Conant and Blatt, THIS JOURNAL, **51**, 1233 (1929); Conant, Webb and Mendum, *ibid.*, **51**, 1246 (1929).

bromide in anhydrous ethyl ether. In certain cases the addition was made in the reverse order, the filtered Grignard solution being added to an excess of the acid chloride in anhydrous ethyl ether. Butyl ether gave similiar results.[3f,7] This reverse addition apparently gave no significant change in the amount of reduction to primary alcohol.[2b,3c,e,7] Of course the product isolated is the ester formed with the excess acid chloride. The reduction to primary alcohol in presence of excess acid chloride is significant. One might have expected the exclusive formation of the ketone. It is true that somewhat larger amounts of ketone are formed by the reverse addition but correspondingly smaller amounts of secondary alcohol are formed.[8] The latter appears as the ester formed by the excess of acid chloride. The yield of ketone apparently can be increased by adding the Grignard solution at lower temperatures.[2b] This is perhaps because the reduction is preferentially slowed down by cooling.

A by-product of the addition of a Grignard reagent to an acid chloride is the ethyl ester of the acid. This is formed by the action of the acid chloride with the solvent ether in presence of anhydrous magnesium chloride.[3e,f] In butyl ether a butyl ester is formed.

The ester of the secondary alcohol sometimes appears in small yields even when the acid chloride is added to the Grignard solution. This is usually due to an insufficient excess of the latter[3a] or to inadequate stirring.

Increase in concentration of the Grignard reagent appears to give a slight increase in the yield of primary alcohol. As much as 50% of isobutyl alcohol has been obtained by the action of isobutraldehyde with *t*-butylmagnesium chloride.[7,9]

In view of all the experience in this Laboratory it follows that the best conditions for studying the reducing action of a Grignard reagent is to add the acid chloride gradually with vigorous stirring to about 3 moles of about 2 molar Grignard solution.

Influence of Structure

Structure of the Acid Chloride.—Increased branching at the alpha carbon increases the reduction to primary alcohol by *t*-butylmagnesium chloride. Five primary acid chlorides, RCH_2COCl, gave 10–20% yields of RCH_2CH_2OH. Individual yields: *n*-butyryl,[2b] 9%; lauroyl, 14%; neopentylacetyl, 13%; *t*-butylacetyl, 5%; and phenylacetyl, 9%. Six secondary acid chlorides, $RR'CHCOCl$, gave 20–60% yields of $RR'CHCH_2OH$: isobutyryl,[2b] 20%; diethylacetyl, 18–30%; ethylbutylacetyl, 30%; methylneopentylacetyl, 17%; dineopentylacetyl, 60%; and diphenylacetyl, 67%. Four tertiary acid chlorides have been studied. With *t*-butylmagnesium chloride the trisubstituted acetyl chlorides containing trimethyl, triethyl, and tributyl gave nearly quantitative yields of R_3CCH_2OH.[2b,7] No other products were found. Methyl-*t*-butylneopentylacetyl chloride[10] with *t*-butylmagnesium chloride gave 63 and 20% of the corresponding aldehyde and primary alcohol, respectively. As shown below the use of *t*-amylmagnesium chloride distinctly increases the reduction of an acid chloride to a primary alcohol.

It should be noted that secondary acid chlorides containing large groups such as neopentyl and phenyl give yields of primary alcohols approaching those obtained from tertiary acid chlorides. It is interesting to recall that dineopentylacetic acid was originally classified as a tertiary acid because of its low esterification rate.[11]

Structure of the Grignard Reagent.—Branching and increase in molecular weight of the Grignard reagent increase the reduction of trimethylacetyl chloride to neopentyl alcohol. As yet no conclusive evidence has been obtained for any reduction by methylmagnesium chloride. Ethylmagnesium chloride gave a 69% yield of ethyl-*t*-butylcarbinol when the acid chloride was added to it.[3d] Presumably the trimethylacetaldehyde first formed adds ethylmagnesium chloride instead of being reduced by it. The Grignard reagents of *n*-propyl, *n*-butyl, *n*-amyl and *i*-amyl gave about 20% yields of neopentyl alcohol and about 70% yields of the secondary alcohols, $RCHOHCMe_3$.[3d] *i*-Propylmagnesium bromide and *i*-butylmagnesium bromide gave 23 and 61% of neopentyl alcohol and 53 and 26% of the secondary alcohols, respectively.[3d] The type reaction of *t*-butylmagnesium bromide and trimethylacetyl chloride gave 94% neopentyl alcohol. *t*-Amylmagnesium chloride shows much stronger reducing action than does *t*-butylmagnesium bromide. With lauroyl chloride the two reagents gave 14 and 55% of lauryl alcohol, re-

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(7) See also present paper.

(8) See Refs. 2b, 3c, d, e, f and 7.

(9) Favorsky, *J. prakt. Chem.*, [2] **88**, 651 (1913).

(10) Whitmore and Laughlin, THIS JOURNAL, **56**, 1128 (1934).

(11) Conant and Wheland, *ibid.*, **55**, 2500 (1933).

spectively. From diethylacetyl chloride the yields of Et_2CHCH_2OH were 20–30 and 75% with the two Grignard reagents. With ethylbutylacetyl chloride they gave 30 and 75% yields of $EtBuCHCH_2OH$. The greater reducing power of *t*-amylmagnesium chloride is also shown in its action with aldehydes. Thus with diethylbutylacetaldehyde it gave the primary alcohol in 67% yield as contrasted with 19% for *t*-butylmagnesium bromide; isobutyraldehyde gave an 84% yield of the primary alcohol against 20% with *t*-butylmagnesium chloride.[6]

t-Amylmagnesium chloride is a valuable reducing agent for special cases. Thus, methyl-*t*-butylneopentylacetaldehyde is slowly reduced by it quantitatively to the corresponding primary alcohol.

The possibility of reducing the salt of a carboxylic acid was considered. Ethylbutylacetic acid, on refluxing for over five hundred hours with three moles of 2 molar *t*-amylmagnesium chloride in ether, gave a quantitative recovery of unchanged acid.

It is significant that neopentylmagnesium chloride has little or no reducing power. With trimethylacetyl chloride it gave an 87% yield of *t*-butylneopentyl ketone and only a trace of neopentyl alcohol. The latter may well have been formed by accidental access of air to the Grignard reagent.

I wish to thank most heartily my students and colleagues in these studies, especially A. H. Popkin, W. A. Mosher, and J. S. Whitaker who have directed many parts of the work and without whose help the present paper would not have been finished.—F. C. W.

Experimental

The products obtained in the present studies were very complex and required careful fractionation through columns of the type used in this Laboratory. These columns were equivalent to 10–15 theoretical plates. Reflux ratios of over 10:1 were used in practically all cases. Dozens of small fractions were taken and studied in each case. Only summaries of these studies are included.

The Grignard reagents were prepared in the usual manner,[4] titrated by the method of Gilman[12] after filtration through glass wool under nitrogen pressure.

Miscellaneous Studies (J. S. W.)

Addition of Diethylacetyl Chloride to *t*-Butylmagnesium Chloride.—All the acid chlorides used in these studies were prepared from the corresponding acids and Eastman practical thionyl chloride. The yields of the products on fractionation were from 85–90%.

To 3.7 moles of 1.85 molal *t*-butylmagnesium chloride 134.5 g. (1 mole) of undiluted diethylacetyl chloride, b. p. 71° (88 mm.), $n^{20}D$ 1.4234, was added during one hour. The vigorous stirring was continued for two more hours. After standing overnight the complex was poured onto ice, the ether decanted, and the solid residue washed with ether. The ethereal solutions were combined, the ether removed, and the oil dried over anhyd. magnesium sulfate. This product was designated as neutral extract. The solid mass from the decomposition was dissolved in cold dil. sulfuric acid and the aqueous layer extracted with ether to give an acid extract. The acid extract was washed with dil. sodium carbonate. The ether was distilled off and the residual oil dried as before.

The two extracts were fractionated separately. Combination of separate fractions gave products in amounts and with b. p. (150 mm.) and $n^{20}D$, respectively, as follows: 2-ethyl-1-butanol, 19.6 g., 103°, 1.4220–1.4230, plus an estimated 2.1 g. in a mixed fraction, total yield of 21.7 g., α-naphthylurethan m. p. and mixed m. p. 63–64°; 2,2-dimethyl-4-ethyl-3-hexanol, 88.3 g. 131–132°, 1.4340–1.4362, d^{20} 0.8339, mol. ref. obsd. 49.29, calcd. 49.90, α-naphthylurethan m. p. and mixed m. p. (with product from diethyl-acetaldehyde and *t*-butylmagnesium chloride) 99–102°; hexamethylethane, 21.7 g. was obtained, m. p. 103°.

Preparation of 2,2-Dimethyl-4-ethyl-3-hexanol.—Diethyl-acetaldehyde, b. p. 114° (730 mm.), 1.4015, was obtained from Carbon and Carbide Chemicals Corp. 95% product. The aldehyde, 25 g. (0.25 mole) dissolved in three volumes of dry ether was added with cooling to 0.31 mole of 1 molar *t*-butylmagnesium chloride during two hours. After standing overnight the complex was worked up as usual. The product on distillation from a modified Claisen flask gave 2-ethyl-1-butanol, 4.8 g. 105° (150 mm.), 1.4272, α-naphthylurethan, m. p. and mixed m. p. 63–64° and 2,2-dimethyl-4-ethyl-3-hexanol, 24 g., 130–132° (150 mm.), 1.4360–1.4370, **α-naphthylurethan,** 101–102°. *Anal.*[13] Calcd. for $C_{21}H_{29}NO_2$: C, 77.01; H, 8.88. Found: C, 77.05; H, 8.92.

Reaction of 2,2-Dimethyl-4-ethyl-3-hexanone with *t*-Butylmagnesium Chloride.—The ketone, 120.5–121° (150 mm.), 1.4240, was prepared in 84% yield from the corresponding secondary alcohol described above by dichromate oxidation. A solution of 0.8 mole of 1.87 molar *t*-butylmagnesium chloride was heated to rapid refluxing and 0.5 mole of the ketone added during fifteen minutes. Refluxing and stirring was continued for an hour. After standing overnight the complex was decomposed to give an acid extract and a neutral extract as above. These extracts were fractionated to give a 38% yield of 2,2-dimethyl-4-ethyl-3-hexanol, α-naphthylurethan, m. p. 101–102°, and a 45% recovery of the ketone. The experiment was repeated at 25°; the starting ketone was

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[12] Gilman, Wilkinson, Fishel and Meyers, THIS JOURNAL, **45**, 150 (1923).

[13] The authors are grateful to Dr. J. R. Adams, Jr., of this Laboratory for the analyses reported with this work.

recovered in 85% yield and no alcohol derivatives could be obtained from the fractions.

Addition of Ethylbutylacetyl Chloride to *t*-Butylmagnesium Chloride.—The addition of 162 g. (1 mole) of ethylbutylacetyl chloride, 93° (43 mm.), 1.4320, with half its volume of dry ether to 4.25 moles of 2.56 molar *t*-butylmagnesium chloride required two hours. Treatment as described above gave a 29.6% yield of 2-ethyl-1-hexanol, 133–134° (150 mm.), 1.4302–8, α-naphthylurethan m. p. and mixed m. p. 58–59°, oxidized by chromic anhydride to ethylbutylacetic acid, anilide m. p. and mixed m. p. 88.5–89.5°, and a 64% yield of 2,2-dimethyl-4-ethyl-3-octanol, 105° (17 mm.), 162° (150 mm.), 1.4420, d^{20} 0.8409, mol. ref. obsd. 58.51, calcd. 59.14, phenylurethan, m. p. 96–97°. *Anal.* Calcd. for $C_{19}H_{31}NO_2$: C, 74.93; H, 10.15. Found: C, 74.93; H, 10.36.

Degradation of 2,2-Dimethyl-4-ethyl-3-octanol.—The alcohol gave an 89% yield of the acetate on treatment with an excess of acetyl chloride; 170° (150 mm.), 1.4310. Pyrolysis of this acetate at 480–500° gave an olefin, 128° (150 mm.), 1.4368, the ozonolysis of which gave trimethylacetaldehyde, 2,4-dinitrophenylhydrazone m. p. and mixed m. p. 210°, and 3-heptanone, semicarbazone m. p. and mixed m. p. 102–103°. The olefin was 2,2-dimethyl-4-ethyl-3-octene thus confirming the structure of the alcohol.

Addition of Ethylbutylacetyl Chloride to *t*-Butylmagnesium Chloride and Magnesious Iodide.[14]—To 6 g. of magnesium in 275 ml. of anhyd. ether was added 32 g. of iodine. When the reaction had subsided the mixture was added to 2.47 moles of *t*-butylmagnesium chloride solution. To this mixture was added 0.75 mole of ethylbutylacetyl chloride, 113.5° (100 mm.), 1.4320, during one hour. The complex was decomposed as described above and the extracts washed with dil. sodium thiosulfate before distilling into 20 fractions. The results were similar to those without the magnesious iodide except that more high boiling material was formed and the yields of primary and secondary alcohols were cut to 19.3 and 42.8%, respectively.

Addition of Trimethylacetyl Chloride to *i*-Butylmagnesium Iodide.—Isobutyl iodide, 61° (100 mm.), 1.4953, was prepared in 50% yield from isobutyl alcohol, red phosphorus, and iodine. The addition of 55.8 g. (0.465 mole) of trimethylacetyl chloride, 48° (100 mm.), 1.4121–1.4125, to 0.98 mole of 1.86 molar *i*-butylmagnesium iodide required one hour. The usual methods gave a 74% recovery of neopentyl alcohol, 98° (726 mm.), 1.3950, phenylurethan m. p. and mixed m. p. 112°.

Addition of Neopentylacetyl Chloride to *t*-Butylmagnesium Chloride.—Neopentylacetic acid, 159° (150 mm.), 1.4215, was prepared in 78% yield by the action of solid carbon dioxide on 3,3-dimethyl-1-butylmagnesium bromide. Thionyl chloride converted this to neopentylacetyl chloride. To 3.3 moles of 2.28 molar *t*-butylmagnesium chloride, 126 g., 0.85 mole, of neopentylacetyl chloride, 94° (100 mm.), 1.4290–1.4298, was added during two hours. The product was worked up in the usual manner to give a 13.5% yield of 4,4-dimethyl-1-pentanol,[15] 160° (728), 1.4185–1.4190, α-naphthylurethan m. p. and mixed m. p. 80–80.5°, and a 67% yield of 2,2,6,6-tetramethyl-3-heptanol, m. p. 58–59°, acetate b. p. 152° (150 mm.), 1.4225, mol. ref. calcd., 63.88, obsd. 63.78; α-naphthylurethan, 92°. (*Anal.* Calcd. for $C_{22}H_{31}NO_2$; C, 77.4; H, 9.1. Found: C, 77.65; H, 9.09); 3,5-dinitrobenzoate 99.5°.

Degradation of 2,2,6,6-Tetramethyl-3-heptanol.—Pyrolysis of the acetate described directly above gave an olefin, 98° (150 mm.), 1.4162, in 72% yield. Ozonolysis showed this olefin to be 2,2,6,6-tetramethyl-3-heptene thus proving the structure of the alcohol.

Addition of *t*-Butylmagnesium Chloride to Butyryl Chloride.—The addition of 1.86 moles of 1.86 molar *t*-butylmagnesium chlorde to 200 g., an excess, of butyryl chloride, 100.5° (733 mm.), 1.4130, in 500 ml. of anhyd. ether was completed in three hours. The product was worked up to give a 21% yield of 2,2-dimethyl-3-hexanone, 138–142° (740 mm.), 1.4097–1.4100, 2,4-dinitrophenylhydrazone m. p. and mixed m. p. 119–120°, 11.6% yield of *n*-butyl butyrate, and a 36.8% yield of 2,2-dimethyl-3-hexyl butyrate which on saponification gave 2,2-dimethyl-3-hexanol, phenylurethan m. p. and mixed m. p. 71°, and butyric acid, anilide m. p. and mixed m. p. 95–96°. All yields are based on the Grignard reagent.

Addition of *t*-Butylmagnesium Chloride to Isobutyryl Chloride.—The addition of 1.86 moles of 1.86 molal *t*-butylmagnesium chloride to 1.86 moles of isobutyryl chloride, 91–92° (738 mm.), in 500 ml. of anhyd. ether during three hours and decomposition and treatment as usual gave a 45% yield of 2,2,4-trimethyl-3-pentyl isobutyrate, 131° (100 mm.), 1.4214–1.4219, which gave 2,2,4-trimethyl-3-pentanol, phenylurethan m. p. and mixed m. p. 86–87°, and isobutyric acid on saponification in alcohol, a 17.7% yield of 2,2,4-trimethyl-3-pentanone,[16] 131–140° (737 mm.), 1.4030–1.4035, oxime m. p. and mixed m. p. 142–143°, and a 19% yield of crude isobutyl isobutyrate, 144–150° (727 mm.), 1.4060–1.4095, yielding isobutyl alcohol, phenylurethan m. p. and mixed m. p. 84–85°, and isobutyric acid on saponification.

Addition of Trimethylacetyl Chloride to Neopentylmagnesium Chloride.—Neopentylmagnesium chloride was prepared in 91% yield by the addition of neopentyl chloride,[17] 84° (740 mm.), 1.4042, to a suspension of magnesium in boiling anhyd. ether. The addition of 67.8 g. (0.56 mole) of trimethylacetyl chloride, 56° (150 mm.), 1.4125, to 1.13 moles of 2.26 molar neopentylmagnesium chloride, at reflux temperature, was not accompanied by the gas evolution common to reduction reactions. Thus, after a day of refluxing it was concluded that the acid chloride had not been reduced and an additional 35 g. was added, bringing the total acid chloride to 0.85 mole or 75% of the amount for ketone formation. After stirring and refluxing for another day the products were isolated as above to give an 87% yield (based on the acid chloride) of 2,2,5,5-tetramethyl-3-hexanone, 108–110° (150 mm.), 1.4160–1.4170, d^{20} 0.8112, mol. ref. obsd. 48.37, calcd. 48.39, no solid derivative was formed although, contrary to a previous report,[18] aluminum isopropoxide gave a 40% yield of 2,2,5,5-tetramethyl-3-hexanol, m. p. and

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[14] Gomberg and Bachmann, THIS JOURNAL, **49**, 236 (1927).

[15] Whitmore and Homeyer, *ibid.*, **55**, 4555 (1933).

[16] Whitmore, Noll and Meunier, *ibid.*, **61**, 683 (1939).

[17] Whitmore and Fleming, *ibid.*, **55**, 4161 (1933).

[18] Whitmore and Heyd, *ibid.*, **60**, 2030 (1938).

mixed m. p. 51.5–52°. A trace of neopentyl alcohol was also found among the Grignard products.

The Reducing Action of *t*-Butylmagnesium Chloride and *t*-Amylmagnesium Chloride on Methyl Isopropyl Ketone (W. A. M., A. R. L.)

The halides used were prepared from the corresponding alcohols and were carefully fractionated: *t*-butyl chloride, b. p. 50–52° (738 mm.), n^{20}D 1.3850; *t*-amyl chloride, 55° (175 mm.), 1.4055–1.4060. Methyl isopropyl ketone was prepared by brominating *t*-amyl alcohol and hydrolyzing the resulting trimethylethylene dibromide thus formed.[19] The ketone used boiled 92–94° (736 mm.), n^{20}D 1.3888.

The Addition of Methyl Isopropyl Ketone to *t*-Butylmagnesium Chloride.—To a solution of 1.52 moles of *t*-butylmagnesium chloride in 750 ml. of ether 129 g. (1.5 moles) of methyl isopropyl ketone in 125 ml. of dry ether was added with stirring and ice-water cooling. A white precipitate formed and gas was liberated. All evolved gas was condensed in a dry-ice and acetone trap. After the ketone had been added the product was gently refluxed for fifteen minutes. The complex was decomposed with a mixture of ice, ammonium chloride and ammonium hydroxide, the ether layer separated and the water layer steam distilled. The combined extracts were dried over anhyd. sodium sulfate and the ether distilled off. The product was divided into a low boiling fraction and a high boiling fraction by distillation through a 15-plate column at 12–18 ml. The low boiling fraction was refractionated at atmospheric pressure and the high boiling fraction at 15 mm. This procedure was to prevent dehydration of any tertiary alcohol present. The products of the reaction were as follows: hexamethylethane, 0.39, 90–100 (736 mm.), solid, m. p. 90–94° (sealed tube); methyl isopropyl ketone, 59.2 g. (46%), 90–100° (736 mm.), 1.3888–1.3903, semicarbazone m. p. and mixed m. p. 113°, 2,4-dinitrophenylhydrazone m. p. and mixed m. p. 122–123°; methyl-*i*-propylcarbinol, 38.7 g. (29%) 110–113° (736), 1.4085–1.4098°, phenylurethan m. p. and mixed m. p. 72°; 2,3,6-trimethyl-3-heptanol-5-one, 23.2 g. (18%) 96–98° (15 mm.), 1.4363, semicarbazone m. p. 116°. The total weight of gas condensed was 85 g., 63.6% isobutane and 34.6% isobutylene, absorbed by 63% sulfuric acid in an Orsat apparatus.

The cuts which would contain any methyl-*i*-propyl-*t*-butylcarbinol were refluxed for five hours with a crystal of iodine. The dried product was fractionated through a 12-plate column to give only material boiling 185–191° (736 mm.), 1.4476, semicarbazone m. p. 108°.

From another reaction of 4.27 moles of *t*-butylmagnesium chloride and 4.25 moles of methyl-*i*-propyl ketone 41 g. of 2,3,6-trimethyl-3-heptanol-5-one, 98° (15 mm.), 1.4363, d^{20} 0.9061, mol. ref. calcd. 49.84, found 49.66, was isolated. *Anal.* Calcd. for $C_{10}H_{20}O_2$: C, 69.70; H, 11.61. Found: C, 69.85; H, 11.84.

The ketol gave a semicarbazone of m. p. 116°. The ketol was dehydrated by refluxing with a small crystal of iodine. The product was washed with thiosulfate soln. and dried over calcium chloride. Fractionation gave 53 g., 77–78° (15 mm.), 187–189° (740 mm.), 1.4487, d^{20} 0.8506, semicarbazone m. p. 108°. This was 2,3,6-trimethyl-3-heptene-5-one, mol. ref. calcd. 47.92, found 48.42. *Anal.* Calcd. for $C_{10}H_{18}O$: C, 77.85; H, 11.77. Found: C, 77.67; H, 11.63.

Ozonolysis of 30 g. of the dehydrated ketol gave methyl *i*-propyl ketone, semicarbazone m. p. and mixed m. p. 112–114°, and a water soluble compound probably isopropyl glyoxal.

The Addition of Methyl Isopropyl Ketone to *t*-Amylmagnesium Chloride.—A solution of 86 g. of methyl *i*-propyl ketone in 100 ml. dry ether was added dropwise to a cooled solution of 1.01 moles of *t*-amylmagnesium chloride during three hours. No gas was evolved. The product was refluxed gently for fifteen minutes and then decomposed and worked up as above except that only one distillation was made. The products were methyl *i*-propyl ketone, 2.4%; methyl-*i*-propylcarbinol, 49%; and 2,3,6-dimethyl-3-hexene-5-one, 35.6%. Redistillation of the fractions boiling above methyl-*i*-propylcarbinol gave only material boiling 180–190° (736) on dehydration.

The ether removed from the above reaction was cooled and 25 ml. of bromine added slowly with stirring to give a permanent color. The ether was distilled off to yield 118 g. of dibromide. This was refluxed with 500 ml. of water for twenty-four hours. The condenser was changed for downward distillation and the ketone formed distilled off directly. The aqueous layer in the distillate was saturated with potassium carbonate, the ketone separated, dried and fractionated to yield 24 g. of methyl *i*-propyl ketone, 90–95° (736 mm.), 1.3888, semicarbazone m. p. and mixed m. p. 113°.

In another experiment the ether was distilled directly from the undecomposed reaction mixture; the ether solution was treated as above and yielded a corresponding amount of methyl *i*-propyl ketone.

The Effect of Initial Concentration of *t*-Butylmagnesium Chloride on its Reaction with Diethylacetyl Chloride (O. N. B.)

The acid chloride, b. p. 72–74° (85 mm.), n^{20}D 1.4238–1.4239, was prepared in 84% yield from thionyl chloride and diethylacetic acid, 190 (740 mm.), 1.4135.

Preparation of *t*-Butylmagnesium Chloride, Run #1.—*t*-Butylmagnesium chloride was prepared in 77% yield in the usual manner. The filtered solution was 2.17 molar; it was divided into three equal parts one of which was concentrated to 3.95 molar and the other diluted to 1.07 molar as determined by titration.

Run #2.—*t*-Butylmagnesium chloride was prepared for another series of reactions; the entire solution was concentrated by warming and evaporating the ether under diminished pressure. The concentrated solution was divided into three equal parts, two of which were diluted with anhyd. ether which had been distilled from Grignard reagent. In each case the concentration of the Grignard solution was determined by titration immediately before use.

Addition of Diethylacetyl Chloride to 1.07 Molar *t*-Butylmagnesium Chloride.—Diethylacetyl chloride, 134.5 g. (1 mole), was added to 2.56 moles of 1.07 *M* *t*-butylmagnesium chloride. The acid chloride was added during ninety minutes. After standing for a day the complex was decomposed with ice and worked up to give a neutral and

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[19] "Organic Syntheses," Vol. XIII, 1933, p. 68.

an acid extract as described above. Fractionation showed the presence of 7 g. hexamethylethane; a 20% yield of 2-ethyl-1-butanol, 94–100° (100 mm.), 1.4228–1.4232, α-naphthylurethan m. p. and mixed m. p. 63–64°; and a 63% yield of 2,2-dimethyl-4-ethyl-3-hexanol, 123–124° (100 mm.), 1.4375–1.4378, α-naphthylurethan m. p. and mixed m. p. 99–100°.

Five other concentrations were used with the results shown in Table I.

TABLE I

ACTION OF *t*-BuMgCl ON 1 MOLE LOTS OF DIETHYLACETYL CHLORIDE

t-BuMgCl Molarity	*t*-BuMgCl Moles	Time of addn., min.	Standing, days	Yields, % 2-Et-1-butanol	Yields, % 2,2-Me$_2$-4-Et-3-hexanol
1.07	2.56	90	1	20	63.3
2.17	2.56	90	10	25.3	60.5
3.95	2.56	65	10	30	43.2
0.98	2.12	75	0.7	18.6	68.6
2.06	2.12	75	.7	24.6	63
3.78	2.12	85	.7	28.7	45

Increase in concentration of the Grignard solution slightly increases the yield of primary alcohol and decreases that of the secondary alcohol. The decrease in combined yield at the highest concentration is perhaps due to the pasty character of the mixture.

Proof of the Structure of 2,2-Dimethyl-4-ethyl-3-hexanol.—The secondary alcohol from the above reaction was converted to the acetate, b. p. 90° (16 mm.), $n^{20}D$ 1.4262–1.4265, d^{20} 0.8718, in 90% yield by treatment with acetyl chloride. Pyrolysis of this ester at 490–520° gave a 70% yield of 2,2-dimethyl-4-ethyl-3-hexene, 99° (200 mm.), 1.4297. This olefin, 0.12 mole, was ozonized to give trimethylacetaldehyde and 3-pentanone. No other products were found from the ozonolysis.

Reduction of Isomeric Dodecanoyl Chlorides by *t*-Butylmagnesium Chloride (C. S. M., Jr., J. S. W.)

Addition of Dineopentylacetyl Chloride to *t*-Butylmagnesium Chloride.—The addition of 152 g. (0.7 mole) of the acid chloride to 2.3 moles of *t*-butylmagnesium chloride in 1.1 of ether required two hours. The product was worked up in the usual manner to give a 60% yield of 2,2-dineopentylethanol, m. p. 44°, b. p. 108° (17 mm.), 3,5-dinitrobenzoate m. p. 101–102°, and a 17% yield of 2,2,6,6-tetramethyl-4-neopentyl-3-heptanol, 97–101° (5 mm.), 1.4530–1.4546, *3,5-dinitrobenzoate*, m. p. 96–97°. *Anal.* Calcd. for $C_{23}H_{36}N_2O_6$: C, 63.3; H, 8.25. Found: C, 63.71; H, 8.30. Oxidation of the primary alcohol with chromic anhydride in acetic acid gave dineopentylacetic acid, m. p. and mixed m. p. 86–88°.

Addition of Lauroyl Chloride to *t*-Butylmagnesium Chloride.—Lauroyl chloride, 0.75 mole, b. p. 140° (15 mm.), $n^{20}D$ 1.4457–1.4459, was added to 2.4 moles of *t*-butylmagnesium chloride in 1 liter of solution during one hour. To the thick and gelatinous solution was added 500 ml. of dry ether and the mixture was warmed to facilitate stirring. Decomposition and fractionation as usual gave a 13.7% yield of lauryl alcohol, 150° (22 mm.), m. p. 24°, α-naphthylurethan m. p. and mixed m. p. 79–80°, and a 67% yield of 2,2-dimethyl-3-tetradecanol, 149° (7 mm.), 1.4477–1.4479, d^{20} 0.8356, mol. ref. calcd. 77.61, found 77.49, mol. wt. calcd. 242, found 240, 3,5-dinitrobenzoate, m. p. 64°; on oxidation it gave 2,2-dimethyl-3-tetradecanone, 155° (20 mm.), 1.4390, *semicarbazone* 79°. *Anal.* Calcd. for $C_{17}H_{37}N_3O$: C, 68.68; H, 11.7. Found: C, 68.89; H, 11.73.

On working up the residue from the distillation, a 10.4% yield of undecyl-*t*-butyl-carbinyl laurate, m. p. 69–70°, was obtained. Saponification gave lauric acid, m. p. and mixed m. p. 45–46°, neutral equivalent 200, and 2,2-dimethyl-3-tetradecanol, 3,5-dinitrobenzoate m. p. and mixed m. p. 63°. No indication of lauric aldehyde was found.

Addition of Methyl-*t*-butyl-neopentylacetyl Chloride to *t*-Butylmagnesium Chloride.—To 3 moles of 2 molar *t*-butylmagnesium chloride, 218 g. (1 mole) of methyl-*t*-butyl-neopentylacetyl chloride, 128° (30 mm.), 1.4648, was added during one hour. The same difficulties in stirring were encountered and overcome as in the lauroyl chloride reaction. Decomposition and fractionation gave 2-methyl-2-*t*-butyl-2-neopentylethanol, 19.7%, mol. wt. calcd. 186, found 185, 113–114° (16 mm.), 1.4610, d^{20} 0.8748; mol. ref. calcd. 59.14, found 58.34; **3,5-dinitrobenzoate,** m. p. 83–84°. *Anal.* Calcd. for $C_{19}H_{28}N_2O_6$: C, 60; H, 7.37. Found: C, 59.99; H, 7.36.

Chromic anhydride oxidized the alcohol to methyl-*t*-butylneopentylacetic acid, m. p. and mixed m. p. 130°.

The main product was a 62.5% yield of methyl-*t*-butylneopentylacetaldehyde, 101–104° (14 mm.), 1.4485–1.4490, **2,4-dinitrophenylhydrazone,** m. p. 153°. *Anal.* Calcd. for $C_{18}H_{28}N_4O_4$: C, 59.4; H, 7.7. Found: C, 59.37; H, 7.89; mol. wt. for $C_{12}H_{24}O$, calcd. 184, found 184.

Oxidation of the aldehyde with chromic anhydride in acetic acid gave methyl-*t*-butylneopentylacetic acid. A few drops left on a watch glass exposed to the air for a day gave the acid, m. p. 128° without further crystallization.

Auto-oxidation of Methyl-*t*-butylneopentylacetaldehyde.—Refractionated aldehyde, 113° (28 mm.), m. p. 23°, 1.4498, on exposure to air readily gave a positive peroxide test with acidified potassium iodide solution. The rate of autoöxidation of this aldehyde was compared with that of freshly distilled benzaldehyde by weighing several samples, leaving them exposed to the air for various time intervals and then titrating with standard alkali using phenolphthalein as the indicator. Titration of the original aldehydes showed the absence of free acid. The results are summarized in Table II. Addition of a small amount of hydroquinone greatly increased the induction period of the reaction.

TABLE II

Benzaldehyde		Me-*t*-Bu-neopentylacetaldehyde	
Hours	% oxidized	Hours	% oxidized
		0.5	3.0
1	26.54	1	5.25
1.58	36.07	2	10.5
4	78.2	5	28.2
8	80.34	8	46.6

The Reducing Action of *t*-Amylmagnesium Chloride, I (W. A. M.)

Addition of Isobutyraldehyde to *t*-Amylmagnesium Chloride.—To a solution of 1.47 moles of *t*-amylmagnesium chloride, 107 g. (1.48 moles) of isobutyraldehyde, 63–64° (730 mm.), 1.3275, was added during two hours. Fractionation of the products of the reaction, after decomposition, gave an 84% yield of isobutyl alcohol, 73–75° (205 mm.), 1.3990–1.4009, phenylurethan m. p. and mixed m. p. 84°.

Addition of *t*-Amylmagnesium Chloride to Isobutyryl Chloride.—The addition of 1.3 moles of *t*-amylmagnesium chloride to 160 g. (1.5 moles) of isobutyryl chloride, 91–92° (730 mm.), 1.4080, in 850 mol. of dry ether required six hours. The reaction, after the usual treatment, gave a 44% yield of isobutyl isobutyrate, 146–150° (731 mm.), 1.4006–1.4048, d^{20} 0.8475. Saponification of the ester gave isobutyl alcohol and isobutyric acid, anilide m. p. and mixed m. p. 105°. The yield of ester was 44% based on the Grignard reagent.

The Reducing Action of *t*-Amylmagnesium Chloride, II

(J. S. W.)

The diethylacetaldehyde, ethylbutylacetic acid, mesityl oxide and cinnamaldehyde used in these reactions were obtained by fractionating the commercial products.

Addition of Diethylacetyl Chloride to *t*-Amylmagnesium Chloride.—The addition of 134.5 g. (1 mole) of the acid chloride, 87° (150 mm.), 1.4232, to 3.15 moles of 1.9 molar *t*-amylmagnesium chloride was completed in one hour. Stirring was continued for an hour and the product was allowed to stand overnight. Decomposition and fractionation in the usual manner gave a 74.5% yield of 2-ethyl-1-butanol, 99–103° (150 mm.), 1.4230–1.4225, α-naphthylurethan m. p. and mixed m. p. 63–64°, a 7.8% yield of 3,3-dimethyl-5-ethyl-4-heptanol, 150–152° (150 mm.), 1.4438–1.4440, mol. wt. calcd. 172, found 170.3, d^{20} 0.8530, m. p. and mixed m. p. of α-naphthoylurethan 85°.

Addition of Ethylbutylacetyl Chloride to *t*-Amylmagnesium Chloride.—As described above, 162.5 g. (1 mole) of the acid chloride, 93° (43 mm.), 1.4320, was treated with 2.56 moles of 1.9 molar *t*-amylmagnesium chloride to give a 74.5% yield of 2-ethyl-1-hexanol, 118° (80 mm.)–82° (20 mm.), 1.4305–1.4315, and a 15.7% yield of 3,3-dimethyl-5-ethyl-4-nonanol, 125–137° (25 mm.), 1.4482–1.4490, d^{20} 0.8512; mol. ref. calcd. 63.76, found 62.99, **phenylurethan**, m. p. 91–92°. *Anal.* Calcd. for $C_{20}H_{33}NO_2$: C, 75.24; H, 10.35. Found: C, 75.45; H, 10.40.

Addition of Diethylacetaldehyde to *t*-Amylmagnesium Chloride.—The aldehyde, 0.4 mole, was added to 0.5 mole of 0.84 molar *t*-amylmagnesium chloride during one hour. The usual procedure gave a 67% yield of 2-ethyl-1-butanol, 101° (145 mm.), 1.4222, and a 21% yield of 3,3-dimethyl-5-ethyl-4-heptanol, 151° (150 mm.), 1.4438–1.4435, d^{20} 0.8496, mol. ref. calcd. 54.52, found 53.8, **phenylurethan**, m. p. 71–72°. *Anal.* Calcd. for $C_{18}H_{29}NO_2$: C, 74.23; H, 9.97. Found: C, 74.15; H, 10.07. M. p. α-naphthylurethan 85°.

Addition of Trimethylacetyl Chloride to *t*-Amylmagnesium Chloride.—The addition of 0.5 mole of the acid chloride to 1.17 moles of 1.46 molar *t*-amylmagnesium chloride was completed in thirty mniutes. The usual treatment gave a 97.5% yield of neopentyl alcohol, m. p. and mixed m. p. of phenylurethan 112°.

Addition of Lauroyl Chloride to *t*-Amylmagnesium Chloride.—To 1.22 moles of 1.43 molar *t*-amylmagnesium chloride 0.5 mole of lauroyl chloride, 140° (15 mm.), 1.4457–1.4459, was added in thirty minutes. The mixture was diluted with 500 ml. of dry ether and heated to facilitate stirring. Decomposition and fractionation gave a 54.8% yield of lauryl alcohol, 153.5° (25 mm.), solid, m. p. 24°, α-naphthylurethan m. p. and mixed m. p. 79–80°, and a 17.7% yield of 3,3-dimethyl-4-pentadecanol, 190° (25 mm.), 1.4525–1.4510, mol. wt. calcd. 256, found 255, d^{20} 0.8437, mol. ref. calcd. 82.25, found 81.95, phenylurethan 150–151°.

Addition of Methyl-*t*-Butylneopentylacetyl Chloride to *t*-Amylmagnesium Chloride.—The addition of 0.435 mole of the acid chloride, 128° (30 mm.), 1.4652, in 200 ml. of anhyd. ether to 1.19 moles of 1.94 molar *t*-amylmagnesium chloride was completed during thirty minutes. After stirring and refluxing for two days the mixture was decomposed and fractionated to give a 78% yield of methyl-*t*-butylneopentylacetaldehyde, 104° (30 mm.), 1.4490–1.4500, m. p. 24°, 2,4-dinitrophenylhydrazone m. p. and mixed m. p. 153°, and a 19% yield of 2-methyl-2-*t*-butyl-2-neopentylethanol, 118–120° (25 mm.), 1.4560–1.4610.

Addition of Methyl-*t*-butylneopentylacetaldehyde to *t*-Amylmagnesium Chloride.—The aldehyde, 36.8 g. (0.2 mole) m. p. 23°, was dissolved in a minimum of dry ether and this solution was added to 0.4 mole of 1.76 molar *t*-amylmagnesium chloride during thirty minutes. The usual treatment gave a 90% yield of 2-methyl-2-*t*-butyl-2-neopentylethanol, 126.5° (28 mm.), 1.4610, 3,5-dinitrobenzoate m. p. and mixed m. p. 83–84°.

Addition of Ethylbutylacetic Acid to *t*-Amylmagnesium Chloride.—To 1 mole of 1.76 molar *t*-amylmagnesium chloride 43.2 g. (0.3 mole) of the acid, 135° (28 mm.), 1.4250, in 100 ml. of dry ether was added. The addition was accompanied with a vigorous reaction that ceased as soon as all of the acid was added. Stirring and heating was continued for over five hundred hours. A 99% yield of the acid was recovered, neutral equivalent 144.

Addition of Cinnamaldehyde to *t*-Amylmagnesium Chloride.—To 0.79 mole of 1.94 molar *t*-amylmagnesium chloride 64 g. (0.485 mole) of cinnamaldehyde, 138° (25 mm.), in 100 ml. of dry ether was added. It was worked up in the usual manner to give a 10% yield of 4,4-dimethyl-3-phenylhexanal, 160–165° (24 mm.), **2,4-dinitrophenylhydrazone** 130–131°. Calcd. for $C_{20}H_{24}N_4O_4$: C, 62.5; H, 6.25. Found: C, 62.8; H, 6.25. No cinnamyl alcohol could be found.

Addition of Mesityl Oxide to *t*-Amylmagnesium Chloride.—To 3.5 moles of 2.03 molar *t*-amylmagnesium chloride 318.5 g. (3.25 moles) of mesityl oxide, 128° (731 mm.), 1.4430, was added during three hours. The addition was accompanied with vigorous refluxing of the solvent ether. The product was worked up in the usual manner. Clean separation of all the products could not be obtained. A mixture of methyl isobutyl ketone and mesityl oxide was identified by the fractional crystallization of the 2,4-dinitrophenylhydrazones. The estimated methyl isobutyl ketone, 2,4-dinitrophenylhydrazone m. p. and mixed m. p. 80–82°, corresponded to a 4% yield; the mesityl oxide, 2,4-dinitrophenylhydrazone m. p. and mixed m. p. 200°, corresponded to 8%. An 8.3% yield of a highly unsaturated compound, 75° (35 mm.), 1.4490, d^{20} 0.7858, mol, ref. calcd. for a C_{11} conjugated diolefin 52.06, found 51.89.

was obtained. Such a compound would have been formed by the dehydration of 2,4,5,5-tetramethyl-2-heptene-4-ol; the presence of water in the early cuts indicated such dehydration. Physical properties indicated the presence of a trace of 4-methyl-3-pentene-2-ol but conclusive evidence was not obtained. A 16.2% yield of 4,4,5,5-tetramethyl-2-heptanone, 118–120° (35 mm.), 1.4620–1.4625, mol. ref. calcd. 53.0, found 52.78, was obtained, m. p. of **2,4-dinitrophenylhydrazone** 114°. *Anal.* Calcd. for $C_{17}H_{26}N_4O_4$: C, 58.27; H, 7.43. Found: C, 58.95; H, 7.47. The parent compound did not add bromine. It was degraded through the bromoform reaction to give 3,3,4,4-tetramethyl-hexanoic acid, m. p. 41–42°, **anilide**, m. p. 153°. *Anal.* Calcd. for $C_{16}H_{28}NO$: C, 77.7; H, 10.11. Found: C, 77.59; H, 10.23.

The Action of *t*-Butylmagnesium Chloride and *t*-Amylmagnesium Chloride on Acetyl Chloride (W. R. W.)

The acetyl chloride, 50° (740 mm.), was obtained from Eastman practical grade by careful distillation from dimethylaniline. Commercial Solvents Corp. di-*n*-butyl ether was dried and purified by distillation.

Preparation of *t*-Butylmagnesium Chloride in Di-*n*-butyl Ether.—Dry di-*n*-butyl ether, 25 ml., and 5 ml. of pure *n*-propyl bromide were added to 4 moles of magnesium turnings in the usual apparatus to initiate the reaction. When the reaction started 1 liter of dry ether containing 5 ml. of *n*-propyl bromide was added. The addition of this relatively large amount of *n*-propyl bromide was necessary to ensure continued reaction. *t*-Butyl chloride, 370 g. (4 moles), in 1700 ml. of the ether was added over a period of twenty-four hours; stirring was continued for eighteen hours. The flask was cooled in a stream of running water at 16–18°. The yield was 73%.

Reaction of *t*-Butylmagnesium Chloride with Acetyl Chloride in Di-*n*-butyl Ether.—To 345 g. (4.4 moles) of acetyl chloride in 500 ml. di-*n*-butyl ether 2.72 moles of the above Grignard reagent in 2860 ml. of solution was added during a period of three hours. The temperature was held at 25–35° by a cold water-bath. About 1 liter of gas was evolved during the reaction. After stirring overnight the complex was decomposed by adding 1 liter of water to the reaction flask with cooling. No additional gas was evolved but about one mole of gas was obtained during the later fractionation. The product was washed thoroughly with sodium bicarbonate solution and worked up in the usual way to give unreacted *t*-butyl chloride, hexamethylethane, a 10% yield of pinacolone, 2,4-dinitrophenylhydrazone m. p. and mixed m. p. 125.3–126°, a 2% yield of *n*-butyl acetate, identified by hydrolysis to give *n*-butyl alcohol, phenylurethan m. p. and mixed m. p. 61.5°, and acetic acid, identified by Duclaux number, a 5% yield of mesityl oxide, and an 11% yield of pinacolyl acetate, identified by hydrolysis to give pinacolyl alcohol, phenylurethan m. p. and mixed m. p. 78° and acetic acid, identified by Duclaux number. The residue containing di-*n*-butyl ether was not investigated. Analysis of the gaseous products by means of an Orsat apparatus indicated 0.356 mole isobutylene, 0.522 mole isobutane, and 0.005 mole carbon monoxide.

Reaction of *t*-Amylmagnesium Chloride and Acetyl Chloride.—This reaction was carried out in diethyl ether in the usual manner. Fractionation of the product gave 4% ethyl acetate, 73–78° (728 mm.), 1.3844–1.3869, 9% methyl *t*-amyl ketone, 128–129° (744 mm.), 1.4083–1.4087, 2,4-dinitrophenylhydrazone m. p. and mixed m. p. 109–110°, 9% 3,4-dimethyl-3-pentene-2-one, 73–83° (56 mm.), 1.4320–1.4393, **semicarbazone**, m. p. 185.5–187.5°.[20,21,22] *Anal.* Calcd. for $C_8H_{15}ON_3$: C, 56.76; H, 8.94. Found: C, 57.13; H, 9.04. No mesityl oxide could be identified.

Possible Effect of Excess Magnesium on the Action of Diethyl-acetyl Halides on *t*-Butylmagnesium Chloride (R. B. W.)

A solution of 7.9 moles of *t*-butylmagnesium chloride in 3800 ml. of ether made as usual was divided into three equal portions. Diethyl-acetyl chloride, 40° (20 mm.), 1.4239, was prepared in 77% yield from Carbide and Carbon Chemicals Corp. diethyl-acetic acid and thionyl chloride.

Addition of Diethyl-acetyl Chloride. a. Free from Suspended Magnesium.—To one portion of the above Grignard solution was added 0.32 mole of anhyd. mercuric chloride to remove any suspended magnesium. After standing one hour, the solution was filtered through glass wool under nitrogen pressure. To this solution was added, during one hour, 110.5 g. (0.824 mole) of diethyl-acetyl chloride. After standing overnight the complex was decomposed and fractionated in the usual manner to give a 33.5% yield of 2-ethyl-1-butanol, 61° (20 mm.), 4225, and a 51.8% yield of 2,2-dimethyl-4-ethyl-3-hexanol, 80° (20 mm.), 1.4375; α-naphthylurethan m. p. and mixed m. p. 100–101°. A check run gave a 32.8 and a 57.8% yield for the primary and secondary alcohols, respectively.

b. Filtered Free from Excess Magnesium.—To a second portion of the Grignard solution was added 2.6 moles of the acid chloride to give a 25.2% yield of the primary alcohol and a 58.9% yield of the secondary alcohol. A second experiment gave yields of 30.5 and 62.2%.

c. Containing Excess Magnesium.—To the third portion of the above Grignard solution all of the excess magnesium, 26.6 g., from the original filtration was added to ensure a large excess of free magnesium. To this suspension was added 1 mole of the acid chloride during one hour. The products contained the primary and secondary alcohols in 29 and 60% yields. A repetition gave 30.5 and 62.2%.

Addition of Diethyl-acetyl Bromide to *t*-Butylmagnesium Chloride.—Diethyl-acetyl bromide, 56° (20 mm.), 1.4513, was prepared in 63% yield by the action of phosphorus tribromide, 173–174° (733 mm.), on Carbon and Carbide Chemicals Corp. diethylacetic acid. The acid bromide, 1.24 moles, was added to 3.03 moles of *t*-butylmagnesium chloride in 1750 ml. of solution. Isolation of the products as before gave 27.7 and 60% of the primary and secondary alcohols, respectively.

Addition of Diethylacetyl Iodide to *t*-Butylmagnesium Chloride.—Dry hydrogen iodide from a mixture of rosin, sand, and iodine[23] was purified by passage over anhyd. calcium chloride and red phosphorus. The gas was

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[20] Krapiwin, *Bull. Soc. Naturalistes Moscou*, **22**, 1 (1908); *Chem. Zentr.*, **81**, I, 1336 (1910).

[21] Stevens, THIS JOURNAL, **56**, 450 (1934).

[22] Nenitzescu and Chicos, *Ber.*, **68B**, 1584 (1935).

[23] Kastle and Bullock, *Am. Chem. J.*, **18**, 105 (1896).

bubbled for thirteen hours through 170 g. of diethylacetyl chloride in the cold. The reaction was considered complete when the exit gas no longer gave a test for hydrogen chloride. Dissolved hydrogen iodide was removed by bubbling in dry nitrogen and free iodine was removed by shaking with mercury.

The above undiluted crude iodide, 277 g., was added to 3.27 moles of *t*-butylmagnesium chloride in 1760 ml. of solution during fifty minutes. The complex was decomposed as usual and the ethereal solution washed with potassium carbonate and dilute sodium thiosulfate. Fractionation gave a 12% yield of 2-ethyl-1-butanol, a 36% yield of 2,2-dimethyl-4-ethyl-3-hexanol; the remainder of the product was a high boiling material, 112–125° (19 mm.), 1.4412–1.4510, which has not as yet been identified.

The Action of *t*-Butylmagnesium Chloride on Methylneopentylacetyl Chloride (L. H. S.)

Methyl-neopentylacetic acid was isolated in about 5% yield from the chromic acid oxidation of the equilibrium mixture of diisobutylenes. The acid chloride boiled at 65° (24 mm.), 1.4300–1.4310.

Reaction of Methyl-neopentylacetyl Chloride with *t*-Butylmagnesium Chloride.—Over a period of four hours 110 g. (0.67 mole) of the acid chloride was added to 2.7 moles of *t*-butylmagnesium chloride. Gas was evolved throughout the addition. Decomposition with ice and hydrochloric acid and fractionation yielded 2,4,4-trimethyl-1-pentanol, 21%, and 2,2,4,6,6-pentamethyl-3-heptanol, 67%. The former, b. p. 78–80° (22 mm.), 1.4278–1.4285, gave a **3,5-dinitrobenzoate,** m. p. 72.5–73.5°. *Anal.* Calcd. for $C_{15}H_{20}O_6N_2$: C, 55.53; H, 6.22. Found: C, 55.74; H, 6.15, and an α-naphthylurethan, m. p. 70°. This compound was synthesized in 67% yield by treatment of the ethyl ester of methylneopentylacetic acid with sodium in toluene and absolute ethanol[24] and also by the addition of formaldehyde to methylneopentylcarbinylmagnesium chloride.[25] Mixed melting points with derivatives from both sources showed no depression. The second product, b. p. 102–106° (22 mm.), 1.4400–1.4416, d^{20} 0.8380, mol. wt. calcd. for $C_{12}H_{25}OH$ 186, found 180.5; mol. ref. calcd. 59.14, found 58.61. **3,5-Dinitrobenzoate.** *Anal.* Calcd., for $C_{19}H_{28}O_6N_2$: C, 59.96; H, 7.42. Found: C, 60.12; H, 7.18. Oxidation of the secondary alcohol with chromic anhydride in acetic acid gave a 51% yield of a neutral oil, 87–90° (16–18 mm.), 1.4288–1.4290, and a 10% yield of methylneopentylacetic acid identified through its anilide, m. p. 117–118°. The neutral oil, presumably 2,2,4,6,6-pentamethyl-3-heptanone, gave no solid derivatives.

Action of Phenylacetyl Chloride and Diphenylacetyl Chloride on *t*-Butylmagnesium Chloride (T. W. C.)

Addition of Phenylacetyl Chloride to *t*-Butylmagnesium Chloride.—The acid chloride, 247 g. (1.6 moles) 99° (19 mm.), 1.5325, was added to 3.14 moles of *t*-butylmagnesium chloride in 2200 ml. of solution during three hours. After standing overnight, the complex was decomposed and the liquid products were fractionated in the usual manner to give a 9.2% yield of phenylethyl alcohol, 116° (20 mm.), 1.5215, α-naphthylurethan m. p. and mixed m. p. 117–118°, and a 14.9% yield of benzyl-*t*-butylcarbinol, 128° (20 mm.), 1.5066, **phenylurethan,** m. p. 84.5–85.5°. *Anal.* Calcd. for $C_{19}H_{23}NO_2$: C, 76.72: H, 7.67. Found: C, 76.69; H, 7.80. Oxidation of benzyl-*t*-butylcarbinol with potassium dichromate in acid solution gave a ketone, 2,4-dinitrophenylhydrazone m. p. 134–135°. The solid material represented a 20% yield of benzyl-*t*-butylcarbinyl phenylacetate. Saponification in alcoholic solution gave phenylacetic acid, m. p. and mixed m. p. 76–77° and benzyl-*t*-butylcarbinol, phenylurethan m. p. and mixed m. p. 84–85°.

Addition of Diphenylacetyl Chloride to *t*-Butylmagnesium Chloride.—The acid chloride was prepared from the acid and thionyl chloride. The addition of the recrystallized product, m. p. 53–54°, 1.3 moles in 1200 ml. dry ether, to 3.4 moles of *t*-butylmagnesium chloride in 1750 ml. of solution required ten hours. Decomposition and fractionation gave a 67.5% yield of 2,2-diphenylethanol, 190–195° (20 mm.), m. p. 62°, benzoate m. p. 90–91°.[26] The residues were not investigated.

Action of *t*-Butylacetyl Chloride on *t*-Butylmagnesium Chloride (O. N. B.)

To 2.87 moles of *t*-butylmagnesium chloride 134.5 g. (1 mole) of *t*-butylacetyl chloride, 51° (44 mm.), 1.4230, in a half volume of dry ether was added during one hour. The decomposition and fractionation were carried out in the usual manner to give a 5% yield of neopentylcarbinol, 82–85° (85 mm.), 1.4140–4150, α-naphthylurethan m. p. and mixed m. p. 80–81°, and a 48.5% yield of *t*-butylneopentylcarbinol, m. p. and mixed m. p. 51–52°.

Formation of Traces of Aldehydes from Trimethylacetyl Chloride and *t*-Butylacetyl Chloride (A. H. P.)

Reaction of Trimethylacetyl Chloride with *t*-Butylmagnesium Chloride.—The addition of 302 g. (2.5 moles) of the acid chloride, 58° (150 mm.), 1.4126, to 7 moles of *t*-butylmagnesium chloride gave approximately the same proportion of neopentyl alcohol and di-*t*-butyl ketone as reported previously.[2] However, a low boiling fraction was also obtained, 50.4 g., 35–85° (719 mm.), which gave the 2,4-dinitrophenylhydrazone of trimethylacetaldehyde, m. p. 208.5–209.5°. On refractionation this cut yielded 2.5 g., about 1%, 73–76° (719 mm.), of trimethylacetaldehyde.[6]

Reaction of *t*-Butylacetyl Chloride with *t*-Butylmagnesium Chloride.—The addition of 135 g. (1 mole) of the acid chloride to 2.1 moles of *t*-butylmagnesium chloride gave, together with the expected products, a fraction, 10 g., 80–106°, 1.3940, which yielded an impure 2,4-dinitrophenylhydrazone m. p. 128–133°. This m. p. was raised to 141–142.5° after six recrystallizations from dil. ethanol. On mixing with a sample of the derivative of *t*-butylacetaldehyde, m. p. 141–142.5°, a m. p. of 145–147° was obtained. Less than 1% of the aldehyde was found.

Reduction of Trialkylacetyl Chlorides (C. E. L.)

Triethylacetic and tributylacetic acids were prepared in 65 and 45% yields, respectively, by the addition of

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(24) Levene and Marker, *J. Biol. Chem.*, **91**, 701 (1931).

(25) "Organic Syntheses," Vol. VI, 1926, p. 22.

(26) Ramart and Amagat, *Ann. chim.*, (X) **8**, 263 (1927).

gaseous carbon dioxide under pressure to triethylmethylmagnesium chloride and tributylmethylmagnesium chloride. The acids were converted to the acid chlorides in 88 and 83% yields by treatment with thionyl chloride.

Addition of Triethylacetyl Chloride to *t*-Butylmagnesium Chloride.—The acid chloride, 101° (65 mm.) 1.4432–1.4439, 144 g. (0.88 mole) was added to 2 moles of *t*-butylmagnesium chloride during four hours. Decomposition and fractionation gave an 89.5% yield of 2,2-dieithyl-1-butanol, 75° (13 mm.), 1.4430, α-naphthylurethan 133–134°. This carbinol was oxidized by acid dichromate to give triethylacetic acid, m. p. and mixed m. p. 38°.

Addition of Tributylacetyl Chloride to *t*-Butylmagnesium Chloride.—The acid chloride, 137–138° (12 mm.), 1.4540–1.4543, 119 g. (0.477 mole) was added to 1.5 moles of *t*-butylmagnesium chloride during two hours. Decomposition of the complex and fractionation of the product gave an 88.5% yield of 2,2-dibutyl-1-hexanol, 114–118° (3 mm.), 1.4532–1.4535, phenylurethan m. p. 77–77°. Acid dichromate oxidation of the alcohol gave tributylacetic acid, m. p. and mixed m. p. 37°.

Summary

1. The general reactions by which a Grignard reagent reduces an acid chloride to an aldehyde and then reacts with the latter to give an ordinary addition reaction or further reduces it to a primary alcohol have been surveyed in relation to (a) mechanism, (b) miscellaneous factors including presence of free magnesium, the halogen present, the concentration of the Grignard solution and the order of adding the reagents, and (e) influence of structure of the acid chloride and of the Grignard reagent.

2. *t*-Butylmagnesium chloride was treated with the following substances with the indicated results. (a) Diethylacetyl chloride gave 2-ethyl-1-butanol, 18–30%, and 2,2-dimethyl-4-ethyl-3-hexanol, 43–68%. Increasing the concentration of *t*-butylmagnesium chloride slightly increased the yield of primary alcohol and decreased that of the secondary alcohol. (b) Diethylacetaldehyde gave the same two alcohols in 19 and 60% yields. The latter alcohol gave 2,2-dimethyl-4-ethyl-3-hexene on dehydration. On oxidation it gave 2,2-dimethyl-4-ethyl-3-hexanone. (c) This ketone was only slowly reduced to the secondary alcohol by *t*-butylmagnesium chloride. (d) Ethylbutylacetyl chloride gave 2-ethyl-1-hexanol, 29% and 2,2-dimethyl-4-ethyl-3-octanol, 64%. (e) The pyrolysis of the acetate of the latter alcohol gave 2,2-dimethyl-4-ethyl-3-octene. (f) The addition of magnesious iodide in reaction (a) cuts the yields to 19 and 43% and increases the high boiling by-products. (g) Neopentylacetyl chloride gave 2,2,6,6-tetramethyl-3-heptanol, 67%. (h) Pyrolysis of the acetate of the latter alcohol gave 2,2,6,6-tetramethyl-3-heptene. (i) Butyryl chloride, on addition of the Grignard solution, gave 2,2-dimethyl-3-hexanone, 21%, the butyrate of 1-butanol, 11%, and of 2,2-dimethyl-3-hexanol, 36%. (j) Isobutyryl chloride, on addition of the Grignard solution, gave 2,2,4-trimethyl-3-pentanone, 17%, the isobutyrate of isobutyl alcohol, 18%, and of 2,2,4-trimethyl-3-pentanol, 45%. (k) Methyl *i*-propyl ketone gave methyl-*i*-propylcarbinol, 29%, the aldol condensation product, 2,3,6-trimethyl-3-heptene-5-one, 18%, and 46% recovered ketone, presumably due to the formation of the chloromagnesium enolate. This is in sharp contrast to the greater reducing action obtained with the *t*-amyl Grignard reagent, *cf.* 3 (a) below. (l) Dineopentylacetyl chloride gave 2,2-dineopentylethanol, 60%, and 2,2,6,6-tetramethyl-4-neopentyl-3-heptanol, 17%. (m) Lauroyl chloride gave lauryl alcohol, 13%, 2,2-dimethyl-3-tetradecanol, 67%, and the laurate of 2,2-dimethyl-3-tetradecanol, 10%. (n) Methyl-*t*-butylneopentylacetyl chloride gave 2,4,4-trimethyl-2-*t*-butyl-1-pentanol, 19%, and, astonishingly, methyl-*t*-butylneopentylacetaldehyde, 62%. (o) Acetyl chloride in di-*n*-butyl gave a trace of trimethylacetaldehyde, pinacolone, 9%, mesityl oxide, 5%, pinacolyl acetate, 11%, and *n*-butyl acetate, 2%. (p) Diethylacetyl iodide gave products like the chloride and bromide but also considerable higher boiling material; *cf.* 2 (a) above. (q) Methylneopentylacetyl chloride gave 2,4,4-trimethyl-1-pentanol, 17%, and 2,2,4,6,6-pentamethyl-3-heptanol, 67%. Oxidation of the latter gave 10% of methylneopentylacetic acid and 51% of a high boiling neutral liquid, probably 2,2,4,6,6-pentamethyl-3-heptanone. (r) Phenylacetyl chloride gave 2-phenylethanol, 9%, and phenyl-*t*-butylcarbinol, 15%, with 20% of its phenylacetic ester. (s) Diphenylacetyl chloride gave 2,2-diphenylethanol, 67%, and some unidentified products. (t) *t*-Butylacetyl chloride gave neopentylcarbinol, 5%, and neopentyl-*t*-butylcarbinol, 48%. (u) Trimethylacetyl chloride, in addition to the usual neopentyl alcohol and di-*t*-butyl ketone, gave about 1% trimethylacetaldehyde. (v) *t*-Butylacetyl chloride, in addition to *t*-butylneopentylcarbinol, and a trace of neopentylcarbinol, gave about 1% of *t*-butylacetaldehyde. (w) Triethylacetyl chloride and *n*-tributylacetyl chloride gave 2,2-diethyl-1-butanol, 89%, and 2,2-*n*-dibutyl-1-hexanol, 88%, respectively.

3. *t*-Amylmagnesium chloride was treated with the following substances with the indicated results. (a) Methyl *i*-propyl ketone gave methyl-*i*-propylcarbinol, 50%, the condensation product 2,3,6-trimethyl-3-heptene-5-one, 35 and 2% recovered ketone, *cf.* 2 (k) above. (b) Diethylacetyl chloride gave 2-ethyl-1-butanol, 74%, 3,3-dimethyl-5-ethyl-4-heptanol, 7%, and other products as yet unidentified. (c) Diethylacetaldehyde gave the same alcohols in 67 and 21% yields. (d) Ethylbutylacetyl chloride gave 2-ethyl-1-hexanol, 74% and 3,3-dimethyl-5-ethyl-4-nonanol, 15%. (e) Trimethylacetyl chloride gave neopentyl alcohol, 97%. (f) Lauroyl chloride gave lauryl alcohol, 54%, and 3,3-dimethyl-4-pentadecanol, 17%. (g) Methyl-*t*-butylneopentylacetyl chloride gave methyl-*t*-butylneopentylacetylaldehyde, 78%, and 2,4,4-trimethyl-2-*t*-butyl-1-pentanol, 19%. (h) The aldehyde in (g) was reduced to the primary alcohol, 90%, on prolonged heating. (i) Ethylbutylacetic acid was not changed by prolonged treatment with a large excess of the Grignard reagent. (j) Cinnamaldehyde gave no cinnamyl alcohol. The 1:4 addition product, 4,4-dimethyl-3-phenylhexanal, was found in 10% yield. (k) Mesityl oxide gave a very unmanageable mixture containing unreacted material, methyl-*i*-butylketone, a C_{11} diolefin probably related to 2,4,5,5-tetramethyl-2-heptene-4-ol, impure 4-methyl-3-pentene-2-ol, and 4,4,5,5-tetramethyl-2-heptanone, 16%, formed by 1:4 addition. By the bromoform reaction this saturated ketone gave 3,3,4,4-tetramethylhexanoic acid. (l) Isobutyraldehyde gave isobutyl alcohol, 84%. (m) Isobutyryl chloride, on addition of the Grignard reagent, gave the isobutyrate of isobutyl alcohol, 44%. (n) Acetyl chloride in ethyl ether gave methyl *t*-amyl ketone, 9%, 3,4-dimethyl-3-pentene-2-one, 9%, but no mesityl oxide.

4. *i*-Butylmagnesium chloride and trimethylacetyl chloride gave neopentyl alcohol, 61%, and 2,2,5-trimethyl-3-hexanol, 26%. In a similar reaction the Grignard iodide gave complications.

5. Neopentylmagnesium chloride with trimethylacetyl chloride gave no more than a trace of reduction but gave 2,2,5,5-tetramethyl-3-hexanone in 87% yield.

6. Excess of magnesium in the action of *t*-butylmagnesium chloride with diethylacetyl chloride did not increase the reduction.

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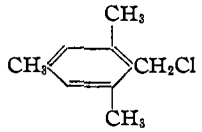
An Abnormal Reaction in the Sommelet Aldehyde Synthesis

BY REYNOLD C. FUSON AND J. J. DENTON

In a study of methods of making mesitaldehyde, hexamethylenetetramine was condensed with α^2-chloroisodurene (I) and the resulting quaternary ammonium salt decomposed in aqueous solution according to the procedure of Sommelet.[1] Instead of the expected aldehyde there was formed a white, solid base which proved to have the formula $C_{21}H_{30}N_2$. A Zerewitinoff determination showed the presence of two active hydrogen atoms. The most probable structure appeared to be that given in formula II.



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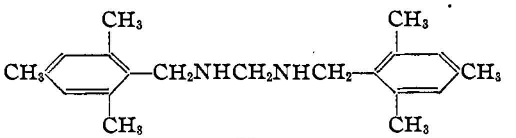

II

Evidence has now been accumulated which establishes the correctness of this formula. The action of acetic anhydride yielded an acetyl derivative which was identified as N-α^2-isodurylacetamide ($CH_3CONHCH_2C_9H_{11}$). Similarly, benzoylation led to the formation of N-α^2-isodurylbenzamide ($C_6H_5CONHCH_2C_9H_{11}$). The structures of these two amides were confirmed by synthesis from the parent amino compound, α^2-isodurylamine ($C_9H_{11}CH_2NH_2$).

This amine (isolated as the hydrohalide) was prepared in three different ways. Mesitonitrile, made from bromomesitylene by the Rosenmund–

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[1] Sommelet, *Compt. rend.*, **157**, 852, 1443 (1913).