The shift of λ_{max} by 6 mμ toward higher wave lengths in the diene is analogous to the difference between λ_{max} of cyclohexenylacetylene[3] (223 mμ) and that of cyclohexenylethylene[7] (230 mμ), a pair which shows, however, no appreciable difference in extinction.

DL-1-Cyclohexyl-3-butanol (III).—Two grams (0.013 mole) of the dienol (II) was hydrogenated completely over 100 mg. of platinum oxide in 100 ml. of ethanol. Hydrogen uptake at 26° and 750 mm.: calculated for two double bonds, 662 ml.; found (corrected for uptake by the catalyst), 622 ml. The saturated product was obtained in the theoretical yield and boiled at 84° at 4 mm.; n^{25}D 1.4670. Oxidation by sodium hypoiodite according to Shriner and Fuson[8] yielded iodoform.

Anal. Calcd. for $C_{10}H_{20}O$: C, 76.91; H, 12.91. Found: C, 77.26; H, 12.57.

1-Cyclohexyl-3-butanone (IV).—A solution of 1.1 g. of cyclohexylbutanol (III) in 10 ml. of glacial acetic acid and 0.82 g. of chromic anhydride was heated gently on the steam-bath for thirty minutes and permitted to stand overnight. The mixture, poured into 50 ml. of water, was extracted with petroleum ether, which was then washed and dried. The residue was evaporatively distilled at 16 mm. and 50° bath temperature; yield, 0.85 g. (76%); n^{20}D 1.4590; reported[9] n^{20}D 1.4586.

The **semicarbazone** of IV, recrystallized from aqueous methanol, melted at 166–168°; reported[9] m. p. 163°.

The **2,4-dinitrophenylhydrazone** of IV, recrystallized from methanol, melted at 106°; reported[9] m. p. 106°.

Trisnor-β-ionone (V).—A mixture of 1.8 g. (0.118 mole) of trisnor-β-ionol (II) and 4.55 g. of aluminum *t*-butoxide in 90 ml. of dry acetone plus 135 ml. of dry benzene were refluxed under nitrogen for forty-eight hours. After decomposition with 150 ml. of 2 *N* sulfuric acid, the reaction product was worked up in the customary manner. According to the spectral data, the crude distillate (1.5 g.) of b. p. 92–95° at 4 mm. consisted of five-sixth ketone and the rest starting material. The ketone was converted into the semicarbazone. After one recrystallization from ethanol, decomposition according to Heilbron[9] and subsequent evaporative distillation at 47° bath temperature and 12 mm. pressure yielded 0.77 g. (43% yield) of the pure ketone; n^{20}D 1.5500, λ_{max} 280 mμ, ϵ_{max} 26,700. The secondary maximum at 234 mμ, due to the presence of the dienol in the crude product was not completely eliminated.

Anal. Calcd. for $C_{10}H_{14}O$: 79.95; H, 9.39. Found: C, 79.57; H, 9.55.

The **semicarbazone**, melting after two recrystallizations at 201–203° (dec.), had a λ_{max} of 290 mμ, ϵ_{max} 45,000; it turns yellow on exposure to light.

Anal. Calcd. for $C_{11}H_{17}N_3O$: C, 63.74; H, 8.27; N, 20.27. Found: C, 63.58; H, 8.13; N, 19.78.

The **2,4-dinitrophenylhydrazone**, recrystallized three times from absolute ethanol, consisted of garnet-red crystals melting at 199–200° (dec.); λ_{max} 390 mμ, ϵ_{max} 30,000.

The **4-phenylsemicarbazone**, buff-colored platelets recrystallized from ethanol, m. p. 199–200° (dec.).

Catalytic Reduction of the Enynol I.—Various attempts to reduce selectively the triple bond of I with hydrogen over a 0.3% palladium–calcium carbonate catalyst in ethyl acetate yielded mixtures which were subjected to fractional distillation. The lowest boiling fractions, comprising less than 20% of the reduction product, showed, in typical runs, λ_{max} between 231 and 233.5 mμ with ϵ_{max} from 4000 to 6600 and n^{20}D of 1.4960, supposedly a mixture of one-fourth or less (5% of the total yield) of dienol with three-fourths non-conjugated carbinol of low refractive index (either compound III or trisnordihydroionol). The higher fractions, comprising the bulk of the mixture, converged toward λ_{max} 229 mμ with ϵ_{max} up to 11,600 and n^{20}D 1.5086, with starting material predominating. Similar results were obtained with Raney nickel in ethyl acetate, whereas no reduction at all was achieved with copper-zinc in alcohol.

Acknowledgment.—We thank Miss Bernice Hamerman for her able assistance in these experiments.

Summary

Lithium aluminum hydride serves for the partial hydrogenation of the triple bond to a double bond in cyclohexenylbutynol. The resulting trisnor-β-ionol was oxidized to trisnor-β-ionone. The ultraviolet absorption spectra of cyclohexenyl ethylenes and acetylenes are discussed.

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[7] Booker, Evans and Gillam, *J. Chem. Soc.*, 1453 (1940).

[8] Shriner and Fuson, "Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 2nd ed., 1940, p. 53–54.

[9] Heilbron, E. R. H. Jones and Richardson, *J. Chem. Soc.*, 287 (1949).

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

Grignard Reactions. XX.[1] Effect of Cuprous Chloride on the Reaction of *t*-Butylmagnesium Chloride and Trimethylacetyl Chloride

BY NEWELL C. COOK AND WILLIAM C. PERCIVAL

In a continuation of the study of the reaction between acid halides and Grignard reagents we have now found conditions which make it possible to obtain consistently high yields of a highly branched ketone from a reaction which heretofore has given mainly reduction products. In earlier attempts to prepare hexamethylacetone from *t*-butyl Grignard reagent and trimethylacetyl chloride[2] no ketone was formed using a one-to-one ratio of the Grignard reagent and the acid chloride. With a five-to-one ratio of reagents and using reverse addition at −10°, there was obtained a 32% yield. We have now shown that through the use of cuprous chloride with a one to one ratio of reactants, yields of 70 to 80% hexamethylacetone are readily obtained.

The role of cuprous chloride in such reactions was suggested when an 87% yield of 2,4,4-trimethyl-3-hexanone was obtained by treating *t*-amylmagnesium chloride and isobutyryl chloride in a copper reactor.[3] Previously, only 10 to

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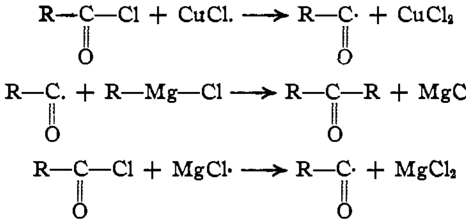
[1] For Paper XIX see Stehman, Cook and Whitmore, THIS JOURNAL, **71**, 1509 (1949).

[2] Whitmore, *Rec. trav. chim.*, **57**, 562 (1938).

[3] In the original note[1] this compound was erroneously reported as 2,4,4-trimethyl-3-pentanone.

15% yields had been realized from these reactions.[4] The reaction of *t*-butylmagnesium chloride and trimethylacetyl chloride, one of the most difficult tests of the beneficial effect of cuprous salts, was found to give hexamethylacetone in yields as high as 80% under cuprous chloride catalysis. We have confirmed our findings in several other syntheses of highly branched ketones to be reported later.

Kharasch[5] has shown that metallic ions such as the cuprous ion give rise to free radicals in Grignard reactions. If such were the case here the following could represent the · mechanism by which the cuprous chloride causes the formation of the hexamethylacetone.



$$\mathrm{R{-}\underset{\underset{O}{\|}}{C}{-}Cl + CuCl. \longrightarrow R{-}\underset{\underset{O}{\|}}{C}\cdot + CuCl_2}$$

$$\mathrm{R{-}\underset{\underset{O}{\|}}{C}. + R{-}Mg{-}Cl \longrightarrow R{-}\underset{\underset{O}{\|}}{C}{-}R + MgCl\cdot}$$

$$\mathrm{R{-}\underset{\underset{O}{\|}}{C}{-}Cl + MgCl\cdot \longrightarrow R{-}\underset{\underset{O}{\|}}{C}\cdot + MgCl_2}$$

The reactions tried to date using straight chain acid chlorides and Grignard reagents show that yields of ketones are improved but not as markedly as with highly branched reactants. It is believed that conditions such as temperature and more effective catalysts can be found which will give more satisfactory results. This work is being continued.

Experimental

The fractionation columns were of the total condensation variable take-off type packed with $^3/_{32}$ in. single turn glass helices. The dimensions (cm.) are for the packed section: column I, 70 × 1.5; column II, 90 × 2.2.

The Grignard reactors were of seven-liter capacity, water jacketed copper vessels (11″ × 8″) stirred with an off-center propeller (4″) driven by a $^1/_4$ hp. motor.

The *t*-butyl Grignard reagent (3.1 moles/l.) used in these reactions was synthesized in a large preparation and stored in a glass carboy under a nitrogen atmosphere. Only clear reagent was used in all runs.

The trimethylacetyl chloride, made by carbonation of *t*-butyl Grignard reagent and subsequent treatment of the trimethylacetic acid with thionyl chloride, had the following properties: b. p. 104°, $n^{20}\mathrm{D}$ 1.4123. The ethyl ether used was Mallinckrodt reagent grade.

The runs were either five or three mole reactions. Products from the five mole runs were fractionated in column I while those from the three mole runs were fractionated in column II. From several reactions using a variety of conditions it was established that with cuprous chloride yields of 70–80% hexamethylacetone could be obtained, and that reactions in glass without cuprous chloride gave only 1–2% hexamethylacetone. Even normal addition with cuprous chloride gave a 53% yield of ketone.

Reaction of *t*-Butylmagnesium Chloride and Trimethylacetyl Chloride.—Filtered *t*-butylmagnesium chloride (5 moles, 3 *M* solution) was added at reflux temperature over a one-hour period to 5 moles of trimethylacetyl chloride and 5 g. of cuprous chloride dissolved in 2 l. of anhydrous ethyl ether in a 7-l. Grignard reactor. A take-off condenser was then attached and warm water passed through the jackets of the reactor until the majority of the solvent had been stripped from the reactants. Steam was then passed through the reactor for a period of three days. The reaction mixture was drowned with ice, neutralized and ether extracted. The products were fractionated through a twenty-plate column, giving 1.3% *t*-butyl pivalate (b. p. 135°, $n^{20}\mathrm{D}$ 1.3920), 1.0% neopentyl alcohol (b. p. 112°, m. p. 50°), 71.6% hexamethylacetone (b. p. 153°, $n^{20}\mathrm{D}$ 1.4392) and 9.8% residue, calculated as trimethylacetyl radical.

Identification of Products.—Hexamethylacetone: by reduction with lithium aluminum hydride to the alcohol which was converted to the phenylurethan, m. p. 120–121°. *t*-Butyl pivalate: by neutral equivalent (4 *N* sodium ethylate), obs. 156, calcd. 158; molecular weight, obs. 146, calcd. 158; trimethylacetic acid from hydrolysis ester, anilide, m. p. 133–134°. Neopentyl pivalate: by hydrolysis and derivative of trimethylacetic acid (anilide m. p. 133–134°) and neopentyl alcohol (m. p. 50°)(phenylurethan m. p. 112–113°). Trimethylacetic acid: as the anilide, m. p. 133–134°. Neopentyl alcohol: as the phenylurethan, m. p. 112–113°.

All derivatives were established by mixed melting points with authentic samples.

Summary

The reaction of *t*-butylmagnesium chloride and trimethylacetyl chloride to form hexamethylacetone has been investigated. With the use of cuprous chloride as a catalyst yields of from 70 to 80% are obtained, using one to one ratios of reactants. The temperature of addition has little effect upon the reaction. Although good yields are obtained using normal addition, reverse addition gives better results. A free radical mechanism is postulated.

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[4] Whitmore and co-workers, THIS JOURNAL, **63**, 643 (1941).

[5] Kharasch, Nudenberg and Archer, *ibid.*, **65**, 495 (1943).