

in the traps. Titration^{10b} showed 1.52 moles of neopentylmagnesium chloride, a yield of 89.4%.

To the neopentylmagnesium chloride, 1.52 moles, was added, over a period of two hours, 231 g. (2.02 moles) of diisopropyl ketone. It took considerable time for the reaction to start. After about 35 cc. of the ketone had been added there was still no evidence of reaction. The reaction flask was heated until refluxing started. More ketone was added at this point, and the reaction between the ketone and the Grignard reagent started. The heat was removed and the rest of the ketone was added slowly. After all of the ketone had been added slow refluxing continued, without heating, for about five hours. The reaction mixture was allowed to stand overnight, and it was then stirred for twelve hours with enough heat to keep it refluxing. A sample of the reaction mixture was removed and a Gilman test¹⁴ was run on it. The test was negative. A check test gave the same result. Neopentylmagnesium chloride, itself, gives a positive Gilman test. The reaction being completed, a 220 cc. fraction was distilled from the reaction flask and carefully collected in a well-trapped system. This fraction contained neopentane. The products were

treated as usual. Fractionation of the oil layer gave the following products: diisopropyl ketone, 213.3 g. (1.87 moles); neopentyl-diisopropylcarbinol, 13.2 g. (0.071 mole) or 4%, b. p. 127° (60 mm.), n_D^{20} 1.4472. No reduction product could be found. The yield of enolization product, after correcting for the excess ketone used, was 90%.

Summary

1. The reactions of diisopropyl ketone with six Grignard reagents have been studied.

2. It has been shown that the enolization of a ketone in the Grignard reaction is not an inherent property of the ketone. The amount of enolization given by a particular ketone depends upon the Grignard reagent used.

3. A relation between the reduction given by the Grignard reagent and the presence and character of beta-hydrogen atoms in the Grignard reagent has been pointed out.

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

Abnormal Grignard Reactions. XI.^{1a} Sterically Hindered Aliphatic Carbonyl Compounds. I. Ketones Containing the Methyl-*t*-butylneopentylcarbinyl Group and their Bromomagnesium Enolates

BY FRANK C. WHITMORE AND DAVID I. RANDALL^{1b}

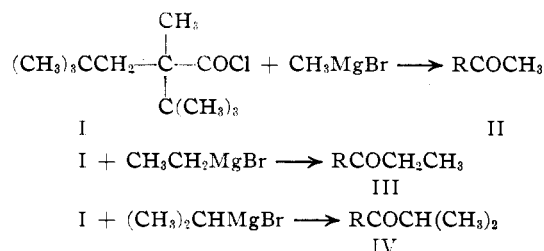
The effect of an adjacent mesityl group on the reactivity of the carbonyl of a ketone has been the subject of considerable interest during recent years. The investigations of this effect have been particularly centered around the behavior of mesityl ketones toward Grignard reagents.² In a few cases other ketones containing an aromatic group have been studied as to steric effects.^{2e} Until the present study no such sterically hindered ketones of the purely aliphatic series have been investigated.

There has now been made in this Laboratory a series of aliphatic sterically hindered ketones containing the methyl-*t*-butylneopentylcarbinyl group. When methyl-*t*-butylneopentylacetyl chloride (I)³ was added to an excess of methylmagnesium bromide, methyl methyl-*t*-butylneopentyl ketone (II) was the only product isolated.

(1) (a) Paper X. Whitmore and George, *THIS JOURNAL*, **64**, 1239 (1942). (b) Present address, Eastern Laboratory, Gibbstown, N. J.
(2) (a) Kohler, Fuson and Stone, *THIS JOURNAL*, **49**, 3181 (1927); (b) Kohler and Baltzly, *ibid.*, **54**, 4017 (1932); (c) Fuson, Fisher and Oakwood, *ibid.*, **52**, 5036 (1930); (d) Fuson, *et al.*, *J. Org. Chem.*, **4**, 111 (1939); (e) Smith and Guss, *THIS JOURNAL*, **59**, 804 (1937). These papers contain leading references to all other important work in this field.

(3) Whitmore and Laughlin, *ibid.*, **56**, 1129 (1934).

Ethylmagnesium bromide and isopropylmagnesium bromide reacted with methyl-*t*-butylneopentylacetyl chloride in the same way to give the corresponding alkyl methyl-*t*-butylneopentylcarbinyl ketones (III and IV).



R is the alkyl radical of I.

It is surprising that the action of methyl-*t*-butylneopentylacetyl chloride with isopropylmagnesium bromide gave no methyl-*t*-butylneopentylacetaldehyde or the corresponding primary alcohol. It will be recalled that the addition of this chloride to *t*-butylmagnesium chloride gave only methyl-*t*-butylneopentylacetaldehyde and its primary alcohol, with the former predominating.⁴

These ketones, like acetomesitylene,² show

(4) Whitmore, *et al.*, *ibid.*, **63**, 643 (1941).

much evidence of steric hindrance. The common carbonyl derivatives, such as the oximes, semicarbazones and 2,4-dinitrophenylhydrazones, could not be prepared. Methyl methyl-*t*-butylneopentylcarbiny ketone (II) does not give the haloform reaction. Enolization measurements made at 140° in dibutyl ether in a Kohler type^{2a} Grignard machine gave the following results:

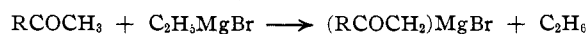
	% Enolization	% Addition
II	94	0
III	57	0
IV	25	0

While acetomesitylene is easily reduced to the corresponding carbinol with sodium and ethanol, ketone II could not be reduced by any of several methods tried. These included sodium and ethanol, sodium and moist benzene, aluminum isopropylate, hydrogen at 3000 pounds and 250° with Raney nickel, hydrogen at 45 pounds and 60° with Adams platinum oxide catalyst and, finally, hydrogen at 3400 pounds and 230° with copper calcium chromite. In the attempts using Raney nickel some splitting occurred. Water and unreacted ketone were the only products identified. It is thus shown that II is unique among ketones in its resistance to reduction.

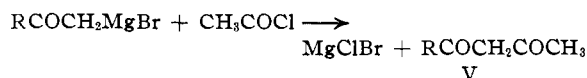
It has also been found that II is rather resistant to oxidation. Thus it was oxidized to methyl-*t*-butylneopentylacetic acid³ by a chromic acid-glacial acetic acid mixture only at temperatures of 90° and above.

The ethyl and isopropyl ketones, III and IV, were not as thoroughly investigated as II, because of the similarity of their behavior to that of II.

When II was added to an excess of ethylmagnesium bromide in ether, a bromomagnesium enolate precipitated. Enolates of this type react as true Grignard reagents.^{2a,b,5} The formation may be shown as



This enolate decomposed in water to give the original ketone. Acetyl chloride reacted with the enolate to give the beta-diketone, acetyl-(methyl-*t*-butylneopentylacetyl)-methane (V).

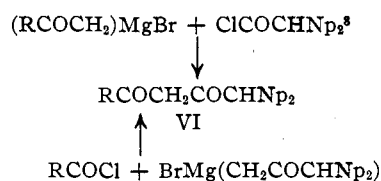


Several other diketones were made with other acid chlorides.

Treatment of the bromomagnesium enolate of

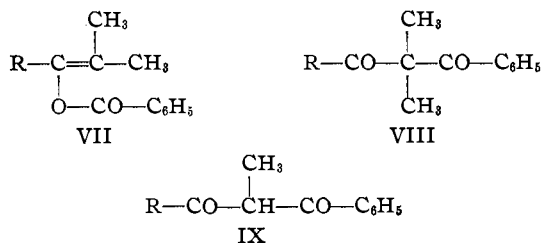
(5) Gilman and Jones, *THIS JOURNAL*, **63**, 1162 (1941).

II with dineopentylacetyl chloride⁶ gave a beta-diketone (VI) which is identical with the compound prepared by the action of methyl-*t*-butylneopentylacetyl chloride with the bromomagnesium enolate of methyl dineopentylcarbiny ketone.⁷



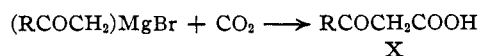
The bromomagnesium enolates of II and III gave only beta-diketone even with excess acid chloride. They thus differ from the enolates of aceto- and propio-mesitylene,^{2a,b} which give some tri-ketone with excess acid chloride.

The action of benzoyl chloride with the bromomagnesium enolate of IV gave a solid melting at 52°, which was rapidly hydrolyzed on treatment with base. The enol benzoate structure (VII), instead of the diketone structure (VIII), is probable for this compound since none of the true beta-diketones of this series could be split with alkali.



The enol benzoate structure (VII) is also supported by its low melting point (52°). This is much lower than would be predicted for the diketone structure (VIII), since the diketone (IX), with one less methyl group, melts at 115° (see below).

The enolates of II, III and IV gave the corresponding beta-keto acids on treatment with carbon dioxide. This reaction may be represented, in the case of II, as follows



These acids, on heating, regenerated the original ketones with liberation of carbon dioxide.

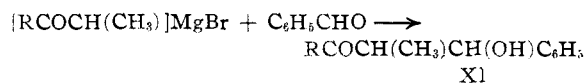
When benzaldehyde was added to the enolate of III a beta-ketol (XI) was obtained. The ketol

(6) Whitmore and Wilson, *ibid.*, **56**, 1397 (1934).

(7) Whitmore and Lester, *ibid.*, **64**, 1247 (1942).

(8) Np is neopentyl, $(\text{CH}_3)_3\text{CCH}_2$.

was oxidized^{2b} with chromic acid to the corresponding beta-diketone (IX).



Attempts to obtain the corresponding ketols from the enolates of II and IV by treatment with benzaldehyde were unsuccessful. The enolate of II and benzaldehyde gave an unmanageable gum. The enolate of IV was recovered as the original ketone.

We wish to thank R. S. George for his help in preparing this paper.

Experimental

The methyl-*t*-butylneopentylacetyl chloride (I) was prepared by the action of thionyl chloride with crude methyl-*t*-butylneopentylacetic acid.³ It had n_D^{20} 1.4648. All fractionations were done with the usual type⁹ of column unless otherwise specified.

Methyl Methyl-*t*-butylneopentylcarbinyl Ketone (3,5,5-trimethyl-3-*t*-butyl-2-hexanone) (II).—To 4 moles of 3.3 molar methylmagnesium bromide was added 271 g. (1.24 moles) of methyl-*t*-butylneopentylacetyl chloride with stirring over a period of four hours. Stirring was continued for twelve hours. The mixture was poured on ice and neutralized with hydrochloric acid. The product was extracted with ether and dried. Fractionation gave 223.5 g. (1.13 moles) of 91% of methyl methyl-*t*-butylneopentylcarbinyl ketone; b. p. 55° (3 mm.); n_D^{20} 1.4531–4. The colorless liquid had an odor resembling that of oil of cedar.

Anal. Calcd. for $\text{C}_{13}\text{H}_{26}\text{O}$: C, 78.8; H, 13.1; mol. wt., 198. Found: C, 78.7; H, 13.2; mol. wt., 191.

Oxidation of Methyl Methyl-*t*-butylneopentylcarbinyl Ketone (II).—A solution of 6.7 g. of chromic anhydride in 12 cc. of water and 50 cc. of glacial acetic acid was added slowly to 10 g. of the ketone in 500 cc. of glacial acetic acid. The temperature remained between 20 and 60°. No decoloration occurred and on dilution of the mixture with water no acid could be detected. That the oxidation had not taken place was shown by a 90% recovery of the original ketone. In a similar oxidation carried out at 90°, 16.3 g. of chromic anhydride was used for 10 g. of the ketone. After stirring for four hours on a steam-bath the mixture was diluted with 400 cc. of water. A 30% yield of crude acid separated. Crystallization from methyl alcohol gave methyl-*t*-butylneopentylacetic acid; m. p. and mixed m. p. 127–129°.

Attempted Reduction of Methyl Methyl-*t*-butylneopentylcarbinyl Ketone (II).—None of six different methods gave any reduction of the ketone. *In each case the starting material was recovered.*

Sodium and Ethanol.—To a solution of 20 g. of the ketone in 200 cc. of 95% ethanol was added during six hours 30 g. of sodium in small pieces. During the time of addition the reaction mixture was kept refluxing. The alcoholate was decomposed with water and the solution was neutralized with glacial acetic acid.

Sodium and Moist Benzene.—Over a period of three days 60 g. of finely divided sodium was added at intervals to 250 cc. of benzene containing the ketone and 85 cc. of sodium carbonate in 250 cc. of water. The mixture was stirred slowly during the time of addition. The benzene layer was separated and dried.

Aluminum Isopropylate.—In a 100-cc. flask were placed 7.5 g. of aluminum isopropylate, 15 g. of the ketone and 35 cc. of isopropyl alcohol. The reaction mixture was refluxed for four hours. No acetone was found.

Hydrogen and Raney Nickel.—The attempted hydrogenation of the ketone was done in a conventional type bomb under 3000 pounds of hydrogen. It was necessary to heat to 250° before a drop in pressure occurred. These rigorous conditions caused a partial splitting of the carbon skeleton.

Hydrogen and Adams Platinum Oxide Catalyst.—To 50 cc. of dioxane in a hydrogenation flask were added 10 g. of the ketone and 1 g. of Adams platinum oxide catalyst. The reaction mixture was shaken at 45 pounds pressure of hydrogen and 60° for five hours.

Hydrogen and Calcium Copper Chromite.—The attempted hydrogenation of 65 g. of the ketone dissolved in dioxane was done in a conventional type bomb at 3400 pounds hydrogen pressure. The bomb was shaken at 230° for forty hours.

Ethyl Methyl-*t*-butylneopentylcarbinyl Ketone (4,6,6-Trimethyl-4-*t*-butyl-3-heptanone) (III).—Ethylmagnesium bromide was prepared from 18.6 g. (0.77 gram-atom) of magnesium and 87.2 g. (0.8 mole) of ethyl bromide. To an ether solution of the Grignard reagent was added, over a period of one and one-half hours, 70.2 g. (0.32 mole) of methyl-*t*-butylneopentylacetyl chloride in 150 cc. of ether. The mixture was worked up as usual. Fractionation gave 53.6 g. (0.25 mole) or 79% of ethyl methyl-*t*-butylneopentylcarbinyl ketone; b. p. 85° (5 mm.); m. p. 15°; n_D^{20} 1.4550.

Anal. Calcd. for $\text{C}_{14}\text{H}_{28}\text{O}$: C, 79.17; H, 13.28. Found: C, 78.88; H, 13.33.

Isopropyl Methyl-*t*-butylneopentylcarbinyl Ketone (2,4,6,6-Tetramethyl-4-*t*-butyl-3-heptanone) (IV).—Isopropylmagnesium bromide was prepared from 2 gram-atoms of magnesium and 2 moles of isopropyl bromide. To an ether solution of the Grignard reagent was added 218 g. (1 mole) of methyl-*t*-butylneopentylacetyl chloride. Stirring was continued for eight hours. The material was worked up as usual. Fractionation gave 130.5 g. (0.58 mole) or 58% of isopropyl methyl-*t*-butylneopentylcarbinyl ketone; b. p. 77–87° (6 mm.); n_D^{20} 1.4589–90. The ketone is a viscous oil which crystallizes on standing; m. p. 38–39°.

Anal. Calcd. for $\text{C}_{15}\text{H}_{30}\text{O}$: C, 79.57; H, 13.35. Found: C, 79.8; H, 13.4.

No alcohol, olefin or methyl-*t*-butylneopentylacetaldehyde was found. It might be expected that the isopropyl Grignard reagent would give reduction.¹⁰

Preparation of Beta-diketones

The procedure was that recommended by Fuson.^{2d} The hindered ketone was added to an equal molar quantity of ethylmagnesium bromide in ether. Usually the bromo-

(9) Whitmore and Lux, *This Journal*, **54**, 3451 (1932).

(10) Whitmore, *et al.*, *ibid.*, **60**, 2788 (1938).

magnesium enolate of methyl methyl-*t*-butylneopentylcarbinyl ketone precipitated by the time the addition was completed. However, the enolates of the ethyl and isopropyl methyl-*t*-butylneopentylcarbinyl ketones rarely precipitated. An ether solution of the acid chloride was added and the reaction mixture was stirred and refluxed. The mixture was poured on ice and hydrochloric acid. The oil layer was separated and washed with 10% sodium carbonate solution. Copper derivatives, when made, were prepared by shaking an ether solution of the diketone with ammoniacal cupric acetate and then removing the ether.

Acetyl-(methyl-*t*-butylneopentylacetyl)-methane (5,7,7-Trimethyl-5-*t*-butyl-2,4-octadione) (V).—A solution of 0.10 mole of acetyl chloride in ether was added to 0.10 mole of the bromomagnesium enolate of methyl methyl-*t*-butylneopentylcarbinyl ketone. The reaction mixture was stirred for three hours. Decomposition and fractionation gave 0.07 mole or 70% of acetyl-(methyl-*t*-butylneopentylacetyl)-methane, n_D^{20} 1.4789; 2,4-dinitrophenylhydrazone, m. p. 181–182°; copper derivative, m. p. 166–168°. The liquid diketone gave a positive enol test with ferric chloride.

Anal. of 2,4-dinitrophenylhydrazone. Calcd. for $C_{21}H_{32}N_4O_8$: C, 59.96; H, 7.68. Found: C, 60.00; H, 7.61.

Benzoyl-(methyl-*t*-butylneopentylacetyl)-methane (4,6,6-trimethyl-4-*t*-butyl-1-phenyl-1,3-heptadione).—To 0.075 mole of the bromomagnesium enolate of methyl methyl-*t*-butylneopentylcarbinyl ketone was added 5.3 g. (0.038 mole) of benzoyl chloride. The reaction mixture was stirred for three hours and then treated as usual. Distillation from a Claisen flask gave 6.8 g. (0.023 mole) or 61% of benzoyl-(methyl-*t*-butylneopentylacetyl)-methane, b. p. 205–210° (8 mm.); crystallized from ligroin, m. p. 87–88.5°; 2,4-dinitrophenylhydrazone, m. p. 186–187°; copper derivative, m. p. 135–137°. The diketone produced a purple color with alcoholic ferric chloride.

Anal. Calcd. for $C_{20}H_{30}O_2$: C, 79.41; H, 9.99. Found: C, 79.5; H, 9.8.

Bis-(methyl-*t*-butylneopentylacetyl)-methane (2,2,4,8,10,10-Hexamethyl-4,8-di-*t*-butyl-5,7-undecadione).—An ether solution of 0.10 mole of the bromomagnesium enolate of methyl methyl-*t*-butylneopentylcarbinyl ketone was stirred and refluxed for twelve hours with 21.8 g. (0.10 mole) of methyl-*t*-butylneopentylacetyl chloride. The material was worked up as usual, and washed with 10% sodium carbonate solution. The basic washings yielded 11 g. of methyl-*t*-butylneopentylacetic acid. Evaporation of the ether from the oil layer gave 9.0 g. or 23% of bis-(methyl-*t*-butylneopentylacetyl)-methane which melted at 128–130° upon crystallization from ethanol. The diketone gave a blood red color with ferric chloride. The 2,4-dinitrophenylhydrazone could not be prepared.

Anal. Calcd. for $C_{25}H_{38}O_2$: C, 78.86; H, 12.72. Found: C, 78.51; H, 12.70.

Triethylacetyl-(methyl-*t*-butylneopentylacetyl)-methane (3,3-diethyl-7,9,9-trimethyl-7-*t*-butyl-4,6-decadione).—To 0.04 mole of the bromomagnesium enolate of methyl triethylcarbinyl ketone (3,3-diethyl-2-pentanone)¹¹ was added 8.7 g. (0.04 mole) of methyl-*t*-butylneopentylacetyl chloride. The mixture was worked up as usual. The

beta-diketone was precipitated as its copper salt. Decomposition of the copper salt with hydrochloric acid gave a 25% yield of diketone which melted at 129–131° on crystallization from ligroin. It gave a positive enol test with ferric chloride.

Dineopentylacetyl-(methyl-*t*-butylneopentylacetyl)-methane (2,2,8,10,10-Pentamethyl-4-neopentyl-8-*t*-butyl-5,7-undecadione) (VI).—To 0.075 mole of the enolate of methyl methyl-*t*-butylneopentylcarbinyl ketone was added 16.3 g. (0.075 mole) of dineopentyl acetyl chloride.^{6,7} The product was treated as usual. Distillation from a Claisen flask gave 12 g. (0.032 mole) or 42% of dineopentylacetyl-(methyl-*t*-butylneopentylacetyl)-methane, m. p. 90°, on crystallization from ethanol, along with small amounts of methyl methyl-*t*-butylneopentylcarbinyl ketone and dineopentylacetic acid. The same beta-diketone (VI) was prepared by the action of the enolate of methyl dineopentylcarbinyl ketone⁷ with methyl-*t*-butylneopentylacetyl chloride. A mixed melting point gave no depression.

1-Benzoyl-1-(methyl-*t*-butylneopentylacetyl)-ethane (1-Phenyl-2,4,6,6-tetramethyl-4-*t*-butyl-1,3-heptadione).—The enolate was prepared by the addition of 21 g. (0.1 mole) of ethyl methyl-*t*-butylneopentylcarbinyl ketone to an ether solution of ethylmagnesium bromide made from 2.4 g. of magnesium and 11.0 g. of ethyl bromide. To the resulting enolate was added 7.2 g. (0.051 mole) of benzoyl chloride. Decomposition and fractionation from a Claisen flask gave 6.0 g. (0.022 mole) or 43% of 1-benzoyl-1-(methyl-*t*-butylneopentylacetyl)-ethane; b. p. 166–169° (3 mm.); m. p. 115–116° on crystallization from ligroin. The beta-diketone was not split by refluxing for sixteen hours with 15% alcoholic potassium hydroxide and the copper salt could not be made. No enol test was obtained with ferric chloride.

Anal. Calcd. for $C_{21}H_{32}O_2$: C, 79.69; H, 10.18. Found: C, 79.71; H, 9.92.

Enol Benzoate (VII) of Isopropyl Methyl-*t*-butylneopentylcarbinyl Ketone (IV).—To a solution of 0.20 mole of the enolate of isopropyl methyl-*t*-butylneopentylcarbinyl ketone in dibutyl ether was added 14 g. (0.10 mole) of benzoyl chloride. The mixture was decomposed as usual. Distillation of the oil layer from a Claisen flask gave 21.5 g. (0.072 mole) or 72% of the enol benzoate; b. p. 177–180° (8 mm.); m. p. 50–52° after crystallization from ligroin. The ester gave no color test with ferric chloride, and it did not take up bromine from carbon tetrachloride.

Anal. Calcd. for $C_{22}H_{34}O_2$: C, 79.92; H, 10.38. Found: C, 80.2; H, 10.2.

Saponification of the ester took place readily. A solution of 2 g. of the enol benzoate and 5 g. of potassium hydroxide in 75 cc. of 95% ethanol was refluxed for one hour. Most of the ethanol was removed and 15 cc. of water was added. The mixture was extracted with ether. Evaporation of the ether gave isopropyl methyl-*t*-butylneopentylcarbinyl ketone. Acidification of the basic water layer gave benzoic acid. Although some beta-diketones are split by alkali, this compound was assumed to be an enol ester because of the ease with which it was saponified, and because of its low melting point (50–52°) as compared to that of 1-benzoyl-1-(methyl-*t*-butylneopentylacetyl)-ethane above.

(11) Unpublished work of C. E. Lewis of this Laboratory.

Preparation of the Beta-keto Acids

The beta-keto acids were prepared readily by passing excess carbon dioxide into an ether solution or suspension of the bromomagnesium enolate of the ketone. The product was decomposed by pouring on ice and hydrochloric acid. The ether layer was separated and extracted with several portions of 10% sodium carbonate solution. Acidification with cold hydrochloric acid precipitated the acids.

β -Keto- γ -methyl- γ -*t*-butyl- γ -neopentylbutyric Acid (4,6,6-Trimethyl-4-*t*-butyl-3-keto-heptanoic acid).—The enolate of methyl methyl-*t*-butylneopentylcarbonyl ketone was prepared by adding 0.10 mole of the ketone to ethylmagnesium bromide made from 2.7 g. of magnesium and 0.10 mole of ethyl bromide. Addition of carbon dioxide to the enolate gave 16.6 g. or 66% of the beta-keto acid; m. p. 116–117° after crystallization from ligroin. Prolonged heating on a steam-bath decomposed the acid giving carbon dioxide and methyl methyl-*t*-butylneopentylcarbonyl ketone.

α -Methyl- β -keto- γ -methyl- γ -*t*-butyl- γ -neopentylbutyric Acid (2,4,6,6-Tetramethyl-4-*t*-butyl-3-keto-heptanoic Acid).—The enolate of ethyl methyl-*t*-butylneopentylcarbonyl ketone was prepared by the addition of 5.4 g. of the ketone to a dibutyl ether solution of ethylmagnesium bromide made from 0.6 g. of magnesium and 3.0 g. of ethyl bromide. Addition of carbon dioxide to the enolate gave 3.0 g. or 48% of the beta-keto acid; m. p. 121–123° after crystallization from ether and ligroin. The acid decomposed rapidly at 100° to give ethyl methyl-*t*-butylneopentylcarbonyl ketone and carbon dioxide.

α,α -Dimethyl- γ -methyl- γ -*t*-butyl- γ -neopentylbutyric Acid (2,2,4,6,6-Pentamethyl-4-*t*-butyl-3-keto-heptanoic Acid).—Addition of carbon dioxide to 0.075 mole of the bromomagnesium enolate of isopropyl methyl-*t*-butylneopentylcarbonyl ketone in dibutyl ether gave 7.0 g. or 37% of the beta-keto acid; m. p. 100–102° after crystallization from ether and ligroin. The acid decomposed rapidly at 100° giving isopropyl methyl-*t*-butylneopentylcarbonyl ketone and carbon dioxide.

Preparation of Beta-ketol

Phenyl-(α -methyl- β -keto- γ -methyl- γ -*t*-butyl- γ -neopentylpropyl)-carbinol (1-Phenyl-2,4,6,6-tetramethyl-4-*t*-butyl-1-heptanol-3-one).—To a solution of 0.076 mole of the bromomagnesium enolate of ethyl methyl-*t*-butylneopentylcarbonyl ketone in dibutyl ether was added 8.0 g. (0.076 mole) of freshly distilled benzaldehyde. The prod-

uct was decomposed as usual. Distillation from a Claisen flask gave 6.4 g. or 26% of the ketol which solidified on cooling. It melted at 90–92° after crystallization from ligroin.

Anal. Calcd. for $C_{21}H_{34}O_2$: C, 79.17; H, 10.77. Found: C, 79.06; H, 10.61.

The ketol, 1.19 g., was oxidized by refluxing with 13 cc. of water, 2.5 cc. of concentrated sulfuric acid and 0.44 g. of potassium dichromate for four hours. A yield of 1.1 g. of 1-benzoyl-1-(methyl-*t*-butylneopentylacetyl)-ethane was obtained. It melted at 114–115° after crystallization from ligroin. A mixed melting point with the beta-diketone prepared above by the action of the enolate of ethyl methyl-*t*-butylneopentylcarbonyl ketone with benzoyl chloride gave no depression.

Summary

1. Three new aliphatic sterically hindered ketones, methyl, ethyl and isopropyl methyl-*t*-butylneopentylcarbonyl ketones, have been prepared from methyl-*t*-butylneopentylacetyl chloride and the appropriate Grignard reagents.

2. The bromomagnesium enolates of these ketones react, with few exceptions, as true Grignard reagents. Eleven new compounds, including beta-diketones, beta-keto acids and a beta-ketol, have been prepared from the bromomagnesium enolates.

3. The methyl, ethyl and isopropyl methyl-*t*-butylneopentylcarbonyl ketones gave no addition when run in the Grignard machine. The common carbonyl derivatives of these ketones could not be prepared. In general, the methyl-*t*-butylneopentylcarbonyl group exerts a steric influence on an adjacent carbonyl even greater than that of an adjacent mesityl group.

4. Methyl methyl-*t*-butylneopentylcarbonyl ketone is unique among ketones in its resistance to reduction and hydrogenation by known methods.

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