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

Abnormal Grignard Reactions. XII.[1] Sterically Hindered Aliphatic Carbonyl Compounds. II.[1] Ketones Containing the Dineopentylcarbinyl Group

BY FRANK C. WHITMORE AND CHARLES T. LESTER[2]

A rather systematic study of sterically hindered ketones of the aromatic series, especially those containing the mesityl group, has been made.[3] Aliphatic sterically hindered ketones, however, have received attention only recently.[1] The investigations have been concerned mainly with (1) the effect of different adjacent groups on the reactivity of the carbonyl and (2) the preparations and reactions of the halomagnesium enolates of these ketones.

In this Laboratory an attempt was made to prepare a tertiary alcohol by adding dineopentylacetyl chloride (I)[4] to a large excess of methylmagnesium bromide. Methane was evolved during the reaction, and the products were methyl dineopentylcarbinyl ketone (II) and bis-(dineopentylacetyl)-methane (IV). These changes may be represented as

$$\underset{\text{I}}{Np_2CHCOCl}\text{[5]} + CH_3MgBr \longrightarrow \underset{\text{II}}{Np_2CHCOCH_3} \qquad (1)$$

$$\text{II} + CH_3MgBr \longrightarrow \underset{\text{III}}{[Np_2CHCOCH_2]MgBr} + CH_4 \qquad (2)$$

$$\text{III} + \text{I} \longrightarrow \underset{\text{IV}}{Np_2CHCOCH_2COCHNp_2} \qquad (3)$$

Reaction 2 explains the evolution of the methane gas. Reaction 3 explains the formation of the beta-diketone. Both 2 and 3 are like reactions found with the mesityl ketones.[3] Reaction 3 was reduced to a minimum by the addition of the acid chloride to a large excess of methylmagnesium bromide. When the Grignard reagent was added to the acid chloride the beta-diketone (IV) was the principal product.

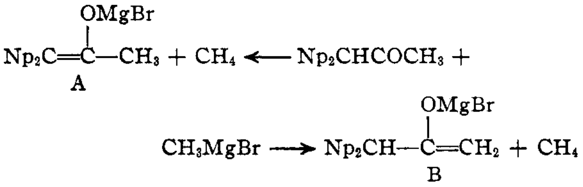
Methyl dineopentylcarbinyl ketone (II), like acetomesitylene, gave quantitative enolization with methylmagnesium bromide when run in a Grignard machine of the Kohler type.[3a] This ketone showed many other signs of steric hindrance. It formed a 2,4-dinitrophenylhydrazone with extreme difficulty and its reduction with aluminum isopropylate required boiling for eight days. With sodium hypobromite the ketone gave the dibromoketone. This reaction was surprising since Fuson has shown[6] that hindered ketones, which do not cleave to give haloform and acid, almost invariably give the tribromoketone.

Like acetomesitylene, methyl dineopentylcarbinyl ketone (II) was easily reduced with sodium and ethanol[7] and it reacted readily with bromine[6a] to give the monobromoketone. It was also hydrogenated at high temperature and pressure. The ease of reduction of this ketone was in sharp contrast to the behavior of methyl methyl-*t*-butylneopentylcarbinyl ketone which could not be reduced.[1]

The ketone (II), however, was not reduced by highly branched Grignard reagents.[8] It gave quantitative enolization with the isopropyl, isobutyl and *t*-butyl reagents.

Ethyl dineopentylcarbinyl ketone (V) was prepared in the same way as the methyl ketone. A small amount of the corresponding beta-diketone, 1,1-bis-(dineopentylacetyl)-ethane (VI), was also obtained. The ethyl ketone has not been as thoroughly investigated as the methyl ketone, since its behavior appeared to be almost identical with that of the methyl ketone.

The tertiary hydrogen of the dineopentylcarbinyl group presented an interesting problem. If this hydrogen is labile, the enolization of the methyl ketone (II) may be represented by either or both of the reactions



$$\underset{\text{A}}{Np_2C{=}\overset{OMgBr}{\overset{|}{C}}{-}CH_3} + CH_4 \longleftarrow Np_2CHCOCH_3 +$$

$$CH_3MgBr \longrightarrow \underset{\text{B}}{Np_2CH{-}\overset{OMgBr}{\overset{|}{C}}{=}CH_2} + CH_4$$

To test the lability of this tertiary hydrogen the

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(1) Whitmore and Randall, THIS JOURNAL, **64**, 1242 (1942).

(2) Present address: Calco Chemical Div., American Cyanamid Co., Bound Brook, N. J.

(3) (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 and co-workers, *J. Org. Chem.*, **4**, 111 (1939); (e) Fuson, Fugate and Fisher, THIS JOURNAL, **61**, 2362 (1939); (f) Smith and Guss, *ibid.*, **59**, 804 (1937); (g) Umnova, *J. Russ. Phys.-Chem. Soc.*, **54**, 881 (1913); (h) Löwenbein and Schuster, *Ann.*, **481**, 106 (1930).

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

(5) Np is neopentyl, $(CH_3)_3CCH_2$-.

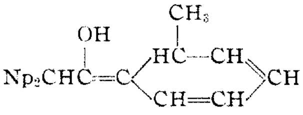
(6) (a) Fuson and Walker, THIS JOURNAL, **52**, 3269 (1930); (b) Gray, Walker and Fuson, *ibid.*, **53**, 3494 (1931); (c) Fuson, Farlow and Stehman, *ibid.*, **53**, 4097 (1931); (d) Fuson, Lewis and DuPuis, *ibid.*, **54**, 1114 (1932); (e) Fisher, Snyder and Fuson, *ibid.*, **54**, 3665 (1932).

(7) Klages and Allendorf, *Ber.*, **31**, 1008 (1898).

(8) Whitmore, *et al.*, THIS JOURNAL, **63**, 643 (1941).

phenyl (VII), *o*-tolyl (VIII) and *p*-tolyl (IX) dineopentylcarbinyl ketones were prepared. All three of these ketones showed quantitative addition of methylmagnesium bromide in the Grignard machine. No trace of enolization was detected. This indicates formula B for the enolate.

It seemed quite possible that the steric effect of the dineopentylcarbinyl group might exclude *normal addition*. The following possibilities were considered: 1,4-addition to form a diene, X[9]; 1,4-addition followed by rearrangement to produce an aromatic secondary alcohol (XI); 1,6-addition to form a quinoid (XII); 1,6-addition followed by rearrangement to produce an aromatic secondary alcohol (XIII); *normal addition* to form a tertiary alcohol (XIV).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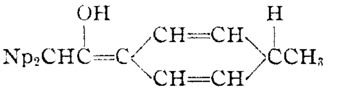
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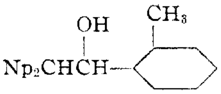
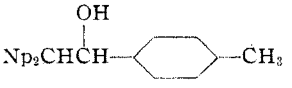

XI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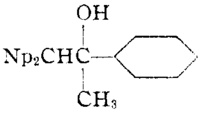
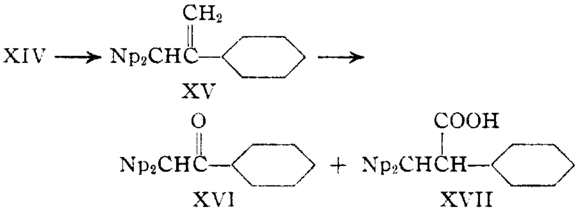

XIV

The product of the addition of the methyl Grignard reagent to phenyldineopentylcarbinyl ketone (VII) was isolated. When it was oxidized in acetic acid with chromium trioxide, the original phenyl ketone (VII) was the principal product of the oxidation. This eliminated X and XII. Compounds XI and XIII would give the same end-products when oxidized as the corresponding ketones. Accordingly the *o*- and *p*-tolyl ketones were oxidized. Even under vigorous conditions for seventy-two hours these compounds produced no phenyl ketone. The oxidation of XIV to produce the phenyl ketone and a high melting acid offers no unusual type of reaction. The reaction could proceed easily by the dehydration of XIV to produce an end methylene group, XV, which would then be oxidized to the phenyl ketone, XVI, and acid, XVII, much as dineopentylethylene is oxidized to dineopentyl ketone and dineopentylacetic acid.[10] All of this indicates



a very low degree of activity for the tertiary hydrogen in the dineopentylcarbinyl group. Other evidence of the difficulty with which this tertiary hydrogen is removed was found in the study of the reactions of the various ketones with bromine. The methyl and ethyl ketones reacted so vigorously with bromine that the reaction mixture had to be cooled in an ice-bath. The phenyl, *o*-tolyl and *p*-tolyl ketones, dissolved in carbon tetrachloride, were not brominated after ten hours of heating at 80°.

The dineopentylcarbinyl group has been found to exert a pronounced steric effect on an adjacent carbonyl group. In the reaction of ketones containing this group with Grignard reagents, however, the course of the reaction is dependent on the nature of the other group in the ketone. If this other group contains labile alpha-hydrogen, quantitative enolization occurs. If the other group does not contain such a hydrogen, normal addition occurs with the methyl Grignard reagent.

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

Experimental

The Grignard reagents for this investigation were all prepared by standard procedures. The dineopentylacetyl chloride (I)[4] was prepared from dineopentylacetic acid and thionyl chloride. The dineopentylacetic acid was obtained by the oxidation of 1,1-dineopentylethylene with 50% sulfuric acid and potassium dichromate.[10b] Unless otherwise specified all fractionations were carried out with high reflux ratios in columns developed in this Laboratory.[11]

Addition of Dineopentylacetyl Chloride to Methylmagnesium Bromide.—To 2.4 moles of methylmagnesium bromide was added 219 g. (1.0 mole) of dineopentylacetyl chloride; b. p. 103° (20 mm.); $n^{20}\mathrm{D}$ 1.4428–32. The products were worked up in the usual way. Fractionation gave 142.6 g. (0.72 mole) or 72% of methyl dineopentylcarbinyl ketone (II); b. p. 104° at 21 mm.; $n^{20}\mathrm{D}$ 1.4353–60 and 32 g. (0.17 mole) or 17% of the beta-diketone, bis-(dineopentylacetyl)-methane (IV)[12]; m. p. 96–97°.

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[9] Kohler and Nygaard, THIS JOURNAL, **52**, 4130 (1930).

[10] (a) Bartlett, Frazer and Woodward, *ibid.*, **63**, 495 (1941); (b) Whitmore and Surmatis, *ibid.*, **63**, 2200 (1941).

[11] Whitmore and Lux, *ibid.*, **54**, 3451 (1932).

[12] The beta-diketone will be thoroughly discussed in the next paper in this series, dealing with the reactions of the bromomagnesium enolates of the methyl and ethyl ketones.

The methyl ketone (II) readily absorbed bromine in carbon tetrachloride with the evolution of hydrogen bromide. In the Grignard machine it liberated one equivalent of methane. After five weeks of refluxing in a saturated solution of 2,4-dinitrophenylhydrazine, it gave a derivative, m. p. 137–138°.

Addition of Methylmagnesium Bromide to Dineopentylacetyl Chloride.—The Grignard reagent, 2 moles, was added in ten portions, each addition followed by refluxing and removing samples periodically to test for unreacted Grignard reagent, to 219 g. (1.0 mole) of dineopentylacetyl chloride. The addition was prolonged over a period of eight hundred forty-four hours. From this reaction was obtained 65 g. (0.33 mole) or 33% of the methyl ketone and 106 g. (0.156 mole) or 56% of the beta-diketone. Throughout the reaction period the samples removed gave positive Gilman[13] tests for the Grignard reagent. After the fifth portion was added, each subsequent addition of methylmagnesium bromide caused a rapid evolution of gas. By means of an Orsat analysis and a Dumas molecular weight determination a sample of this gas was identified as methane.

Hydrogenation of the Methyl Ketone (II).—A 50-g. sample of the ketone was hydrogenated by N. C. Cook of this Laboratory, using a zinc–copper chromite catalyst. A pressure of 1500 pounds of hydrogen for four hours at 200° and for an additional two hours at 230° was used. Fractionation gave 23.4 g. or 47% of methyl-(dineopentylcarbinyl)-carbinol; b. p. 113° at 20 mm.; n^{20}_{D} 1.4450–7. This product formed a 3,5-dinitrobenzoate; m. p. 97–98°.

Reduction of the Methyl Ketone (II) with Sodium and Ethanol.—By the action of 50 g. (2.1 gram-atoms) of sodium, cut in small pieces, on 25 g. (0.125 mole) of the ketone (II), dissolved in 500 cc. of 95% ethanol, was obtained 13.5 g. or 54% of methyl-(dineopentylcarbinyl)-carbinol; b. p. 113° at 20 mm.; n^{20}_{D} 1.4448–59. It gave a 3,5-dinitrobenzoate; m. p. and mixed m. p. 97–98°.

Reduction of the Methyl Ketone (II) with Aluminum Isopropylate.—The reduction was accomplished by heating at the boiling point for eight days, a mixture of 25 g. (0.125 mole) of the ketone, 13 g. (0.063 mole) of aluminum isopropylate and 18 g. (0.30 mole) of isopropyl alcohol. Fractionation gave 15.8 g. or 63% of the corresponding carbinol, b. p. 113° at 20 mm., n^{20}_{D} 1.4455–60; 3,5-dinitrobenzoate, m. p. and mixed m. p. 97–98°.

Reduction of the Methyl Ketone (II) with Branched Grignard Reagents.—A 20-g. sample of the ketone was added to an excess of each Grignard reagent. The gas evolved was tested for unsaturation by bubbling through a very dilute solution of potassium permanganate. After the evolution of gas ceased the mixture was worked up in the usual manner. Isopropyl-, isobutyl- and *t*-butylmagnesium halides were used. The permanganate solutions were not decolorized in any case showing the failure of the Grignard reagent to reduce the carbonyl.[8] No product except the ketone was found and the recovery was 85–90% in each case.

Reaction of the Methyl Ketone (II) with Sodium Hypobromite.—The sodium hypobromite was prepared from 200 g. of ice and water, 16 g. (0.4 mole) of sodium hydroxide and 32 g. (0.2 mole) of bromine. To this was added 10 g. (0.05 mole) of the ketone. This reaction gave 3 g. or 30% of unreacted ketone and 9.2 g. or 52% of the dibromoketone; m. p. 62–63°. No acid was found.

Mol. wt. Calcd. for $C_{13}H_{24}OBr_2$: 356. Found (cryoscopic): 353. *Anal.* Calcd. for $C_{13}H_{24}OBr_2$: Br, 44.9. Found: Br, 44.6.

Preparation of the Monobromoketone, $Np_2CHCOCH_2Br$.[5]—The monobromoketone was prepared by adding 80 g. (0.5 mole) of bromine to 100 g. (0.5 mole) of the methyl ketone (II). The mixture was cooled in an ice–salt-bath during the addition. The hydrogen bromide was removed by bubbling a stream of carbon dioxide through the mixture during the addition. From this reaction was obtained 105 g. or 76% of the monobromoketone; m. p. 33–34°.

Anal. Calcd. for $C_{13}H_{25}OBr$: Br, 28.9. Found: Br, 28.4.

The monobromoketone, 2.77 g. (0.01 mole), gave 1.8 g. of oil when it was refluxed with alcoholic potassium hydroxide. The oil was oxidized in 50 cc. of 95% acetic acid with 1 g. of chromium trioxide at room temperature to give 0.8 g. of dineopentylacetic acid[4]; m. p. and mixed m. p. 88–89°. A 5-g. sample of methyl dineopentylcarbinyl ketone (II) was not affected by such an oxidation mixture even at 50°.

Preparation of Ethyl Dineopentylcarbinyl Ketone (V).—In the same manner as in the case of the methyl ketone, 109 g. (0.5 mole) of dineopentylacetyl chloride, when added to 1.24 moles of methylmagnesium bromide, gave 81 g. or 76% of ethyl dineopentylcarbinyl ketone, b. p. 126° at 27 mm., n^{20}_{D} 1.4378–81 and 10 g. or 10% of the beta-diketone, 1,1-bis-(dineopentylacetyl)-ethane (VI).[12] In carbon tetrachloride a sample of the ethyl ketone absorbed bromine rapidly with the evolution of hydrogen bromide. A sample run in the Grignard machine liberated one equivalent of methane. All attempts to prepare a 2,4-dinitrophenylhydrazone or an oxime were unsuccessful.

Reaction of the Ethyl Ketone (V) with *t*-Butylmagnesium Chloride.—The same molar quantities of reactants, the same procedure and the same test for unsaturated gas were used as in the reaction of the methyl ketone with branched Grignard reagents above. The color of the potassium permanganate solution was not discharged, 87% of the ethyl ketone was recovered and no other product was found.

Preparation of the Monobromoethyl Ketone, $Np_2CHCOCHBrCH_3$.[5]—The procedure was the same as in the preparation of the monobromomethyl ketone above. From 21 g. (0.1 mole) of ethyl dineopentylcarbinyl ketone and 16 g. (0.1 mole) of bromine was obtained 20 g. of the monobromoketone; b. p. 90° (1 mm.), n^{20}_{D} 1.4663. This compound is so unstable that it could not be fractionated. Even when it was rapidly distilled extensive decomposition occurred in the later stages of the distillation.

Anal. Calcd. for $C_{14}H_{27}OBr$: Br, 27.5. Found: Br, 26.4.

Preparation of Phenyl Dineopentylcarbinyl Ketone (VII).—To 110 g. (0.5 mole) of dineopentylacetyl chloride was added 0.48 mole of phenylmagnesium bromide. The product was worked up in the usual manner to give 110 g. of phenyl dineopentylcarbinyl ketone; m. p. 64–65°.

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[13] Gilman and Schulze, This Journal, **47**, 2002 (1925).

A sample of this ketone showed quantitative addition and no enolization when run in the Grignard machine[3a] with methylmagnesium bromide. Attempts to prepare a 2,4-dinitrophenylhydrazone and an oxime were unsuccessful.

Mol. wt. Calcd. for $C_{18}H_{28}O$: 260. Found (cryoscopic): 268.

Preparation of *o*-Tolyl Dineopentylcarbinyl Ketone (VIII).—The *o*-tolyl bromide used to make *o*-tolylmagnesium bromide was prepared from *o*-toluidine as outlined in "Organic Syntheses."[14] From 0.21 mole of *o*-tolylmagnesium bromide and 55 g. (0.25 mole) of dineopentylacetyl chloride[4] was obtained 33 g. of oil. By repeated chilling and filtering the *o*-tolyl ketone, m. p. 32–33°, was isolated. The purification was so tedious that only as much ketone as was needed for immediate experimental purposes was purified. A sample of the ketone showed quantitative addition and no enolization when run in the Grignard machine with methylmagnesium bromide. The 2,4-dinitrophenylhydrazone and the oxime could not be prepared.

Mol. wt. Calcd. for $C_{19}H_{30}O$: 274. Found (cryoscopic): 283.

Preparation of *p*-Tolyl Dineopentylcarbinyl Ketone (IX).—The *p*-tolyl bromide used to prepare the *p*-tolylmagnesium bromide was made from *p*-toluidine.[15] From 0.112 mole of *p*-tolylmagnesium bromide and 27 g. (0.125 mole) of dineopentylacetyl chloride[4] was obtained 26.3 g. or 85% of the *p*-tolyl ketone; m. p. 78–79°. A sample of the ketone in the Grignard machine gave quantitative addition and no enolization with methylmagnesium bromide. The 2,4-dinitrophenylhydrazone and the oxime could not be prepared.

Mol. wt. Calcd. for $C_{19}H_{30}O$: 274. Found (cryoscopic): 285.

Attempted Bromination of the Aromatic Ketones.—A 0.025-mole sample of each of the aromatic ketones was dissolved in a separate portion of carbon tetrachloride. To each solution was added 8 g. (0.05 mole) of bromine. The mixtures were heated at 80° for ten hours. In each case the unchanged ketone was recovered quantitatively. The ketones were crystallized from methanol in the process of working up the reaction mixtures. The residues from these mother liquors were tested for bromine by sodium fusion. No bromine was found.

Oxidation of the Aromatic Ketones.—The oxidation of all three ketones (VII, VIII and IX) was first carried out at room temperature using 95% acetic acid and an equal weight of chromium trioxide. In each case the reaction mixture was treated as follows. The mixture was diluted with five volumes of water, extracted with an equal volume of ether, and the ether solution was washed repeatedly with water until the washings were free of acetic acid. The ether solution was then extracted with 30 cc. of 10% sodium hydroxide solution. The alkali layer was acidified with concentrated sulfuric acid and the solution was filtered. The ether solution was dried, the ether was removed on a steam-bath and the residue was crystallized from methanol.

The phenyl dineopentylcarbinyl ketone (VII) 6 g., was recovered quantitatively by this procedure; the *o*-tolyl ketone (VIII), 1 g., gave 0.1 g. of alkali soluble material, m. p. 104–39°, and 0.6 g. of unchanged ketone; the *p*-tolyl ketone (IX), 1 g., gave 0.2 g. of acid, m. p. 180–200°, and 0.6 g. of unchanged ketone. The acid oxidation products of the tolyl ketones were free of benzoic acid. Extraction with boiling water gave no benzoic acid and produced no change in the melting point range of the acid products.

The oxidation was repeated at 70–80°. After thirty-eight hours at this temperature the phenyl ketone (VII), 6 g., was recovered quantitatively. The *o*-tolyl ketone (VIII), 1 g., after seventy-two hours, gave 0.3 g. of unchanged ketone, 0.1 g. of acid, m. p. 132–68°, and 0.3 g. of dineopentylacetic acid,[4] m. p. and mixed m. p. 87–89°. The *p*-tolyl ketone (IX), 1 g., gave 0.4 g. of unchanged ketone and 0.4 g. of acid, m. p. 189–198°. From the oxidation of the tolyl ketones no trace of the phenyl ketone could be found.

Methylphenyl-dineopentylcarbinyl-carbinol (XIV).—Methylmagnesium iodide, 0.1 mole, and 13 g. (0.5 mole) of phenyl dineopentylcarbinyl ketone (VII) were refluxed in dibutyl ether.[16] Decomposition as usual gave 12.3 g. of oil. This oil was purified by distilling from a Claisen flask, b. p. 140–145° at 5 mm. It crystallized as a white solid, m. p. 42–43°. A total of 8.4 g. or 61% of pure product was obtained. A sample of this compound liberated one equivalent of methane in the Grignard machine with methylmagnesium bromide.

Mol. wt. Calcd. for $C_{19}H_{32}O$: 276. Found (cryoscopic): 284. *Anal.* Calcd. for $C_{19}H_{32}O$: C, 82.6; H, 11.6. Found: C, 82.4; H, 11.5.

A 1-g. sample of the solid tertiary carbinol (XIV) was oxidized at room temperature by the same procedure described under the oxidation of the aromatic ketones. At room temperature this sample gave 0.6 g. of phenyl dineopentylcarbinyl ketone (VII), m. p. and mixed m. p. 63–64°, and 0.17 g. of acid, m. p. 134–136°, probably having structure XVII. This is being studied further.

Summary

1. From dineopentylacetyl chloride and the appropriate Grignard reagents five new ketones, methyl, ethyl, phenyl, *o*-tolyl and *p*-tolyl dineopentylcarbinyl ketones, have been prepared.

2. The methyl and ethyl dineopentylcarbinyl ketones give quantitative enolization with Grignard reagents, including the highly branched types which frequently give reduction.

3. The phenyl, *o*-tolyl and *p*-tolyl dineopentylcarbinyl ketones add methyl Grignard reagent quantitatively without any trace of enolization. The phenyl ketone, which was the only aromatic ketone extensively investigated, gives the expected tertiary alcohol. It is very probable that the addition products of the *o*-tolyl and *p*-tolyl ketones are also the tertiary alcohols.

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(14) "Organic Syntheses," Coll. Vol. I, p. 131.

(15) *Ibid.*, p. 130.

(16) An attempt to add the methylmagnesium iodide in diethyl ether was unsuccessful.

4. The dineopentylcarbinyl group exerts a steric influence on an adjacent carbonyl similar to the effect of a mesityl group.

5. The tertiary hydrogen in ketones Np_2CHCOR,[5] in which R is alkyl or aryl, shows no sign of enolization either with Grignard reagents or with bromine. This inactivity of an α-hydrogen is apparently unique.

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Abnormal Grignard Reactions. XIII.[1] Sterically Hindered Aliphatic Carbonyl Compounds. III.[1] Compounds Derived from the Bromomagnesium Enolates of Alkyl Dineopentylcarbinyl Ketones

BY FRANK C. WHITMORE AND CHARLES T. LESTER[2]

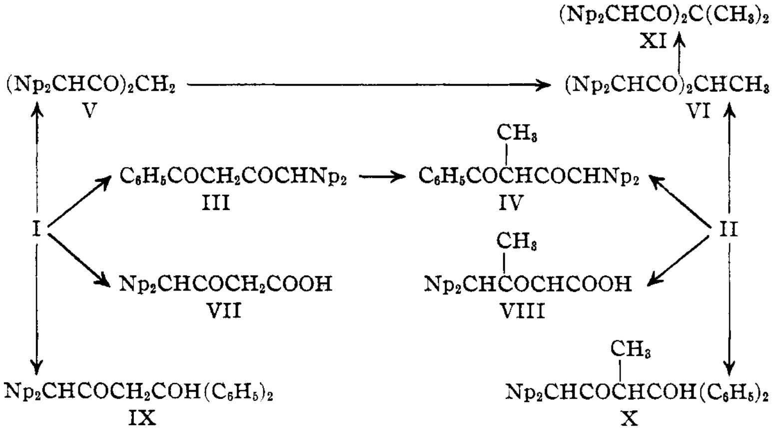
Many investigators have reported the formation of halomagnesium enolates from the action of Grignard reagents with ketones. Umnova,[3] Löwenbein and Schuster[4] and Kohler and Baltzly[5] have all reported such reactions. This particular reaction has been most thoroughly investigated by Fuson and co-workers[6] who have prepared and studied the reactions of many such enolates. They have shown that certain of these enolates react as true Grignard reagents. Gilman[7] has shown that the enolate of acetomesitylene gives the positive color test for a Grignard reagent. The preparations and reactions of bromomagnesium enolates containing the methyl-*t*-butylneopentylcarbinyl group have recently been studied in this Laboratory.[8]

It has been observed in a previous study[1] that methyl and ethyl dineopentylcarbinyl ketones react with Grignard reagents to form such enolates. These enolates also react as true Grignard reagents.

$$Np_2CHCOCH_3 + C_2H_5MgBr \longrightarrow \underset{\text{I}}{Np_2CHCOCH_2MgBr} + C_2H_6$$

$$Np_2CHCOCH_2CH_3 + C_2H_5MgBr \longrightarrow \underset{\text{II}}{Np_2CHCOCH(CH_3)MgBr} + C_2H_6$$

From these enolates the beta-diketones, III, IV V and VI, the beta-keto acids, VII and VIII, and the beta-ketols, IX and X, were prepared.



The steric influence of the dineopentylcarbinyl group is noticeable in the behavior of these beta-diketones. Many beta-diketones are cleaved by dilute alkali.[9] To cleave III and IV required six hours of refluxing with 50% alkali. The beta diketones, V and VI, moreover, were unaffected by refluxing with 60% alkali for twenty-four hours.

It has been shown that phenyl dineopentylcarbinyl ketone adds methylmagnesium bromide quantitatively, thus indicating the difficulty with which the tertiary hydrogen of the dineopentylcarbinyl group shifts to give the enolate.[1] An examination of the structure of the beta-diketone, XI, shows that it is like the phenyl ketone in that the only hydrogen available for enolization is the tertiary hydrogen of the dineopentylcarbinyl group. In the Grignard machine,[10] XI liberated 0.63 equivalent of methane indicating

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[1] Whitmore and Lester, THIS JOURNAL, **64**, 1247 (1942).

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[3] Umnova, *J. Russ. Phys.-Chem. Soc.*, **45**, 881 (1913).

[4] Löwenbein and Schuster, *Ann.*, **481**, 106 (1930).

[5] Kohler and Baltzly, THIS JOURNAL, **54**, 4017 (1932).

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