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 Np₂-CHCOR,[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.

STATE COLLEGE, PENNSYLVANIA
                          RECEIVED NOVEMBER 27, 1941

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

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.

Np₂CHCOCH₃ + C₂H₅MgBr ⟶
               Np₂CHCOCH₂MgBr + C₂H₆
                          I

Np₂CHCOCH₂CH₃ + C₂H₅MgBr ⟶
               Np₂CHCOCH(CH₃)MgBr + C₂H₆
                          II

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

(1) Whitmore and Lester, THIS JOURNAL, 64, 1247 (1942).
(2) Present address: Calco Chem. Div., American Cyanamid Co., Bound Brook, N. J.
(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).
(6) Fuson and co-workers, ibid., 52, 5036 (1930); 61, 2362 (1939); J. Org. Chem., 4, 111 (1939).
(7) Gilman and Jones, THIS JOURNAL, 63, 1162 (1941).
(8) Whitmore and Randall, ibid., 64, 1242 (1942).

(9) Bradley and Robinson, J. Chem. Soc., 2356 (1926).
(10) Kohler, Stone and Fuson, THIS JOURNAL, 49, 3181 (1927).

enolization and added 1.36 equivalents of the methyl Grignard reagent. This is the first case in which the tertiary hydrogen of the dineopentylcarbinyl group has been found to react as an enolizable hydrogen.[1]

We thank R. S. George of this Laboratory for help in the preparation of this paper.

Experimental

The bromomagnesium enolates of the methyl and ethyl dineopentylcarbinyl ketones were prepared according to the method of Fuson.[6] The products from the enolates were also prepared according to his directions.[6]

Benzoyl-(dineopentylacetyl)-methane (III).—From 0.2 mole of the enolate of methyl dineopentylcarbinyl ketone (I) and 28 g. (0.2 mole) of Eastman Kodak Co. White Label benzoyl chloride was obtained 24.6 g. or 41% of benzoyl-(dineopentylacetyl)-methane, m. p. 73–74°. It gave a strongly positive enol test with ferric chloride, and readily formed a 2,4-dinitrophenylhydrazone; m. p. 177–178°. A 10-g. sample of the beta-diketone, on refluxing with 25 cc. of 50% sodium hydroxide for six hours, gave 3.8 g. or 94% of benzoic acid, m. p. and mixed m. p. 121–122°, and 3.1 g. or 52% of methyl dineopentylcarbinyl ketone, b. p. 104–106° (20 mm.); $n^{20}D$ 1.4350–60.

1-Benzoyl-1-(dineopentylacetyl)-ethane (IV).—Benzoyl-(dineopentylacetyl)-methane (III), 7.5 g. (0.025 mole), was alkylated with sodium and methyl iodide according to the method of Weygand[11] to give 5.7 g. or 73% of 1-benzoyl-1-(dineopentylacetyl)-ethane, m. p. 81–82°. It gave a faintly positive enol test with ferric chloride. This compound was also prepared by the action of benzoyl chloride with the enolate of ethyl dineopentylcarbinyl ketone (II). From 7 g. (0.05 mole) of benzoyl chloride was obtained 6 g. or 39% of IV, m. p. and mixed m. p. 81–2°. Refluxing a 5-g. sample of the beta-diketone IV for six hours with 20 cc. of 50% sodium hydroxide gave 1.5 g. or 69% of benzoic acid and 1.9 g. or 59% of ethyl dineopentylcarbinyl ketone, b. p. 126° (27 mm.); $n^{20}D$ 1.4378.

Bis-(dineopentylacetyl)-methane (V) and 1,1-Bis-(dineopentylacetyl)-ethane (VI).—These compounds have been reported as by-products in the preparation of methyl and ethyl dineopentylcarbinyl ketones, respectively.[1] They have also been prepared in 68 and 49% yields, respectively, by the action of dineopentylacetyl chloride[12] with the corresponding bromomagnesium enolates.

A solution of 3.8 g. (0.01 mole) of bis-(dineopentylacetyl)-methane, m. p. 96–7°, in 25 cc. of carbon tetrachloride was treated with 1.6 g. (0.01 mole) of Dow bromine. The bromination proceeded rapidly with the evolution of hydrogen bromide giving 4 g. or 89% of the monobromo derivative, $(Np_2CHCO)_2CHBr$, m. p. 87–88°.

Anal. Calcd. for $C_{25}H_{47}O_2Br$: Br, 17.4. Found: Br, 16.5.

From 19 g. (0.05 mole) of bis-(dineopentylacetyl)-methane was obtained, by alkylation with sodium and methyl iodide,[11] 15 g. or 80% of 1,1-bis-(dineopentylacetyl)-ethane, m. p. and mixed m. p. 86–7°.

(11) Weygand, *Ber.*, **61**, 687 (1928).

(12) Whitmore and Wilson, This Journal, **56**, 1397 (1934).

Anal. Calcd. for $C_{26}H_{50}I_2$: C, 79.2; H, 12.7. Found: C, 79.0; H, 12.7.

Both beta-diketones, V and VI, gave strongly positive enol tests with ferric chloride and discharged the red color of a carbon tetrachloride solution of bromine with the evolution of hydrogen bromide. A 2-g. sample of each diketone was refluxed for twenty-four hours with 60% alkali. The diketones were recovered quantitatively and no cleavage products were found.

β-Keto-γ,γ-dineopentylbutyric Acid (VII) and α-Methyl-β-keto-γ,γ-dineopentylbutyric Acid (VIII).—From 0.01 mole of the enolate of methyl dineopentylcarbinyl ketone (I) and an excess of dry carbon dioxide gas was obtained 12.2 g. or 49% of the beta-keto acid (VII), m. p. 84–5° with decomposition. *Neut. equiv.* Calcd. for $C_{14}H_{26}O_3$: 242. Found: 243.5. A sample of the acid was dissolved in ether and placed in a bulb with a capillary tube. After the ether was evaporated, the acid was heated on a hot-plate until it began to decompose. The gas escaping from the tube produced a cloudiness in lime water. The liquid residue in the bulb had $n^{20}D$ 1.4358, corresponding to that of methyl dineopentylcarbinyl ketone. The keto acid also decomposed slowly at room temperature giving the ketone.

From 0.05 mole of the enolate of ethyl dineopentylcarbinyl ketone (II) and an excess of carbon dioxide was obtained 6.4 g. or 48% of beta-keto acid (VIII), m. p. 89–90° with decomposition. A sample of the acid decomposed on heating giving carbon dioxide and ethyl dineopentylcarbinyl ketone, $n^{20}D$ 1.4376. This acid also decomposed slowly at room temperature. *Neut. equiv.* Calcd. for $C_{15}H_{28}O_3$: 256. Found: 254.

Diphenyl-(β-keto-γ,γ-dineopentylpropyl)-carbinol (IX) and Diphenyl-(α-methyl-β-keto-γ,γ-dineopentylpropyl)-carbinol (X).—From 0.05 mole of the enolate of methyl dineopentylcarbinyl ketone (I) and 10 g. (0.05 mole) of Eastman Kodak Co. White Label benzophenone was obtained 11.2 g. or 56% of the beta-ketol IX, m. p. 87–88°. *Anal.* Calcd. for $C_{25}H_{36}O_2$: C, 82.1; H, 9.6; mol. wt., 380. Found: C, 81.8; H, 9.8; mol. wt., 373.

A 1-g. sample of the ketol was dissolved in 25 cc. of anhydrous ether and a stream of dry hydrogen chloride was passed through until the ether was evaporated. This produced a yellow solid, presumably the corresponding tertiary chloride, m. p. 73–74°, which gave a positive sodium fusion test for halogen. A sample of the ketol run in the Grignard machine with methylmagnesium bromide liberated one equivalent of methane at room temperature and another equivalent at the boiling point of dibutyl ether.

From 0.05 mole of the enolate of ethyl dineopentylcarbinyl ketone (II) and 10 g. of benzophenone was obtained 12 g. or 60% of the beta-ketol X, m. p. 122–123°. *Anal.* Calcd. for $C_{27}H_{38}O_2$: C, 82.2; H, 9.6; mol. wt., 394. Found: C, 82.0; H, 9.7; mol. wt., 388. A sample of this ketol also reacted with dry hydrogen chloride to form a yellow solid, presumably the tertiary chloride, m. p. 110–111°, which gave a positive sodium fusion test for halogen. The ketol liberated one equivalent of methane at room temperature and another at the boiling point of dibutyl ether when run in the Grignard machine with methylmagnesium bromide.

2,2-Bis-(dineopentylacetyl)-propane (XI).—Alkylation of 10 g. (0.03 mole) of 1,1-bis-(dineopentylacetyl)-ethane (VI) with sodium and methyl iodide[11] gave 8 g. or 76% of 2,2-bis-(dineopentylacetyl)-propane, m. p. 65–66°. *Anal.* Calcd. for $C_{27}H_{52}O_2$: C, 79.5; H, 12.7. Found: C, 79.8; H, 12.8. This compound gave a negative enol test with ferric chloride; it was unaffected by refluxing for twenty-four hours with 60% sodium hydroxide; it did not discharge the red color of a carbon tetrachloride solution of bromine. A sample run in the Grignard machine liberated 0.63 equivalent of methane and added 1.36 equivalents of methylmagnesium bromide. Both of these reactions occurred at the boiling point of dibutyl ether. No reaction took place at room temperature.

Summary

1. The bromomagnesium enolates of methyl and ethyl dineopentylcarbinyl ketones react as true Grignard reagents.

2. These enolates have been used to prepare several new compounds including beta-diketones, beta-keto acids and beta-ketols.

3. The diketones, bis-(dineopentylacetyl)-methane, 1,1-bis-(dineopentylacetyl)-ethane and 2,2-bis-(dineopentylacetyl)-propane, were not cleaved by refluxing with 60% alkali.

4. The reactions of 2,2-bis-(dineopentylacetyl)-propane emphasize the fact that the tertiary hydrogen of the dineopentylcarbinyl group is tightly bound and that this group exerts a pronounced steric effect on an adjacent carbonyl. This diketone is the only compound yet studied in which the tertiary hydrogen of the dineopentylcarbinyl group can be forced to react as an enol hydrogen.

STATE COLLEGE, PENNSYLVANIA

[COMMUNICATION No. 842 FROM THE KODAK RESEARCH LABORATORIES]

Action of Grignard Reagents on Certain Pentacenequinones, 6,13-Diphenylpentacene

BY C. F. H. ALLEN AND ALAN BELL

In continuation of the investigation of the behavior of polynuclear ketones with the Grignard reagent, 6,13-pentacenequinone, I, and 5,7,12,14-pentacenediquinone, XXI, have been examined.[1] The former is of particular interest because in one of the possible bond structures, all the double bonds radiate from the central ring. This arrangement would be expected to be the most stable of the possibilities, since, in accordance with the Fries rule, it has two normal naphthalene nuclei.[2] No such substance has yet been described. Since it contains a crossed conjugated system,[3]
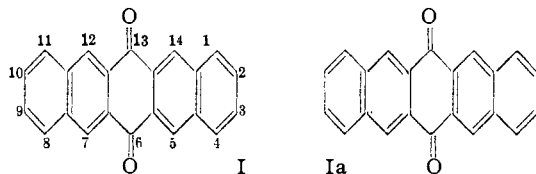
it would be expected to resemble dibenzalacetone in its behavior with phenylmagnesium bromide;

(1) Allen and Overbaugh, THIS JOURNAL, **57**, 740, 1322 (1935); Allen and Gilman, *ibid.*, **58**, 937 (1936); Allen and Bell, *ibid.*, **62**, 2408 (1940); Allen and McGibbon, *Can. J. Res.*, **B16**, 35 (1938).

(2) (a) Fries, Walter and Schilling, *Ann.*, **516**, 248 (1935). Also footnote 1, page 252. (b) Fieser in Gilman, "Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1938, Chap. 2, pp. 92, 107–110.

(3) Of course, the molecule actually contains two similar crossed conjugated systems, permitting a greater number of possible products, according to whether one or both react in each treatment.

the reaction should proceed stepwise, requiring two treatments with the Grignard reagent.[4]

Phenylmagnesium bromide reacts with the pentacenequinone to give mainly (70%) a diol IV as a result of 1,2-addition to the carbonyl groups, but, at the same time, a small amount (15%) of a diketone II is formed by 1,4-addition. The latter substance furnishes 5,14-diphenyl-6,13-pentacenequinone, III, on air oxidation of the alkaline solution. The formation of the diketone may be taken as evidence in favor of the location of the double bonds in one ring. The structure of the quinone III was determined by alkaline fusion, when 1,4-diphenylnaphthalene, 1,4-diphenylnaphthalene-2-carboxylic acid, and β-naphthoic acid were formed.

The bond structure of quinone III is written to correspond with I. When this quinone is treated with an excess of phenylmagnesium bromide, a mixture results from which a tetraphenylquinone V and the corresponding stereoisomeric diketones Va can be isolated. The structure of the quinone V was shown by cleavage with sodium amide, which gave only 1,4-diphenylnaphthalene. There was no trace of the diol VI, formed by 1,2-addition. This result would be expected in view of the known facts about hindrance to 1,2- and 1,4-addi-

(4) Allen and Blatt in Gilman, "Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1938, Chap. 6, p. 598.