concentrated sulfuric acid. Viscosities were run at 25° in a standard Ostwald viscometer. Care was taken not to heat the polymers while being dissolved.[8] Polymer was heated for various periods of time in an ampule similar to that used for determining weight loss, but fitted with a ground glass joint so that samples could be removed. The inherent viscosity of the heated polymer is plotted against time of heating in Figure 3.

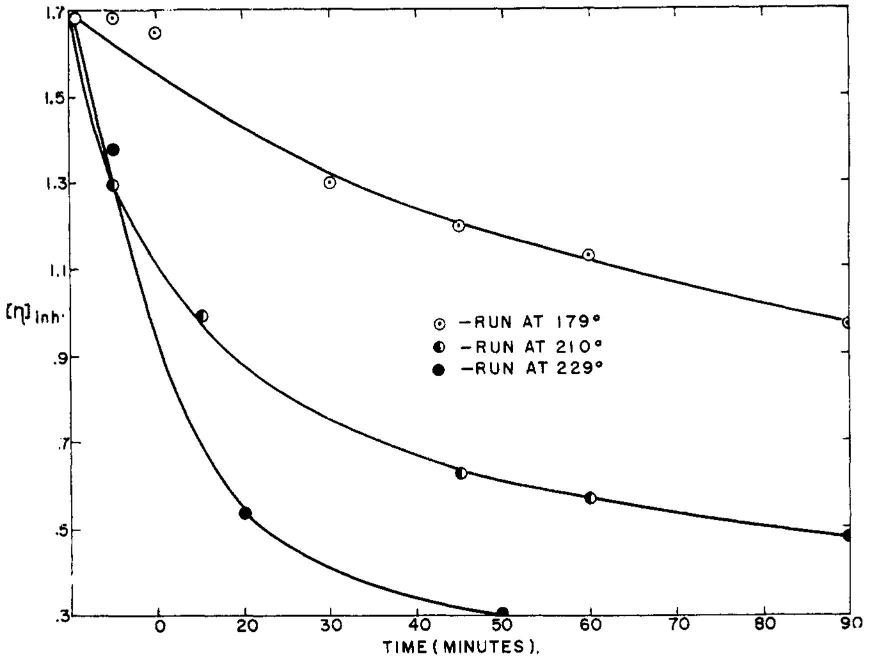

Fig. 3.—Effect of thermal degradation on $(\eta)_{\text{inh}}$ of propylene/SO_2 polymer.

At 229° the precipitous drop in inherent viscosity that accompanies very low weight loss (inherent viscosity is reduced by 50% when weight loss is only about 3%) suggests degradation by random cleavage or by splitting of weak links located randomly in the chain. In this respect the decomposition follows the alkaline hydrolysis of polyacrylonitrile[9] more closely than the pyrolyses of polystyrene[10] or polymethyl methacrylate.[11]

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[8] Inherent viscosity determinations were made by Dr. F. W. Billmeyer.

[9] J. R. McCartney, *Modern Plastics*, **30**, 118 (1953).

[10] H. H. G. Jellinek, *J. Phys. Chem.*, **56**, 707 (1952).

[11] N. Grassie and H. W. Melville, *Proc. Roy. Soc. (London)*, **199**, 1, 14, 24, 39 (1949).

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[CONTRIBUTION FROM THE ROLLIN H. STEVENS MEMORIAL LABORATORY OF THE DETROIT INSTITUTE OF CANCER RESEARCH AND FROM THE DEPARTMENT OF CHEMISTRY OF WAYNE UNIVERSITY]

Reactions of Organometallic Reagents with 2-Hydroxymethylenecyclohexanone and Its Isopropyl Ether[1,2]

BY ANDRE S. DREIDING AND STEWART N. NICKEL

RECEIVED MARCH 8, 1954

The condensation of three organometallic reagents (methylmagnesium iodide, methyllithium and phenylmagnesium bromide) with 2-hydroxymethylenecyclohexanone (I) resulted in 2-alkylidenecyclohexanones (IV and V), presumably by a nucleophilic attack at the hydroxymethylene carbon of the intermediate enolate salt II. The isopropyl ether of 2-hydroxymethylenecyclohexanone (VII) underwent mostly 1,4-addition with methylmagnesium iodide and phenyllithium to give 2-ethylidenecyclohexanone (IV) and 2-(α-isopropoxybenzyl)-cyclohexanone (VIIIb), respectively, while 1,2-addition to VII by methyllithium and lithium aluminum hydride produced cyclohexenecarboxaldehydes (XIa and XIc) related to the androtermone safranal.

2-Hydroxymethylene ketones and their ethers have been used as synthetic intermediates for the introduction of an alkyl group on either of the carbons alpha to the keto group.[3] They have, however, not been employed frequently in condensations with organometallic compounds to introduce alkyl groups at the carbonyl- or hydroxymethylene carbon. Under certain circumstances this reaction could offer promise for the ready preparation of intermediates in the synthesis of terpenes or polycyclic compounds. It was, therefore, made the subject of an exploratory study with 2-hydroxymethylenecyclohexanone and its isopropyl ether.

When an excess of methylmagnesium iodide was treated with 2-hydroxymethylenecyclohexanone (I) there was a copious evolution of methane and the major product was 2-ethylidenecyclohexanone (IV), identified by comparison with an authentic sample.[4] Since I has been shown to react with

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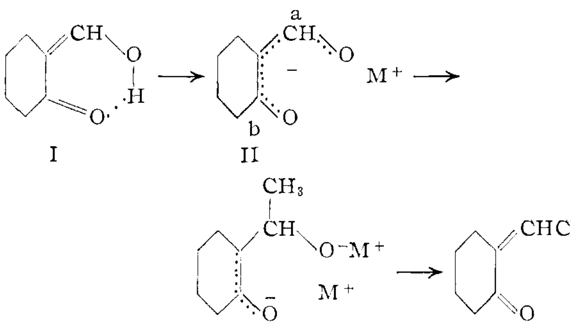
[1] Supported in part by institutional grants to the Detroit Institute of Cancer Research from the American Cancer Society, Inc., the American Cancer Society, Southeastern Michigan Division, and The Kresge Foundation.

[2] This work was abstracted in part from a dissertation submitted by Stewart N. Nickel to the Graduate School of Wayne University in partial fulfillment of the requirements for the degree of Master of Science.

[3] H. K. Sen and K. Mondal, *J. Ind. Chem. Soc.*, **5**, 609 (1928); W. S. Johnson and H. Posvic, THIS JOURNAL, **69**, 1361 (1947); J. W. Cornforth and R. Robinson, *J. Chem. Soc.*, 1855 (1949); A. L. Wilds and C. Djerassi, THIS JOURNAL, **68**, 1715 (1946); F. D. Gunstone and R. M. Heggie, *J. Chem. Soc.*, 1437 (1952); R. B. Woodward, F. Sondheimer, D. Taub, K. Heusler and W. M. McLamore, THIS JOURNAL, **74**, 4223 (1952); A. R. Pinder and R. Robinson, *J. Chem. Soc.*, 1224 (1952).

[4] G. Vavon and V. M. Mitchovitch, *Bull. soc. chim.*, [4] **45**, 961 (1929).



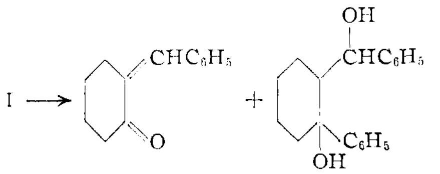
I II III IV

lithium aluminum hydride in ether to form primarily the enolate salt,[5] it is likely that the first step of the interaction of I with the Grignard reagent was also the formation of the enolate salt II. The reagent then attacked preferentially at the hydroxymethylene carbon (position a) and the reaction must have stopped at this stage for, if the dehydration had occurred during the Grignard reaction, then the resulting IV would have condensed further with the excess reagent. Thus the behavior of I in the Grignard reaction is similar to that of other enolizable β-dicarbonyl compounds[6] and differs from the reaction of I and other enolizable β-dicarbonyl compounds with lithium aluminum hydride,[5,7] where an intermediate loss of an oxygen atom permitted the reagent to attack both carbonyl carbons.

2-Hydroxymethylene-4-methylcyclohexanone reacted with methylmagnesium iodide in the same manner as I, the only isolated product being 2-ethylidene-4-methylcyclohexanone.

Since organolithium compounds are known to react differently at times from the corresponding Grignard reagents,[8] 2-hydroxymethylenecyclohexanone was condensed with methyllithium. In this case the reaction was the same as with the Grignard reagent: there was a copious evolution of a gas (probably methane) and the major product was a 25% yield of 2-ethylidenecyclohexanone (IV). The observed formation of 13% of cyclohexanone in this reaction may be due to a reverse aldol condensation suffered by the intermediate III during the isolation.

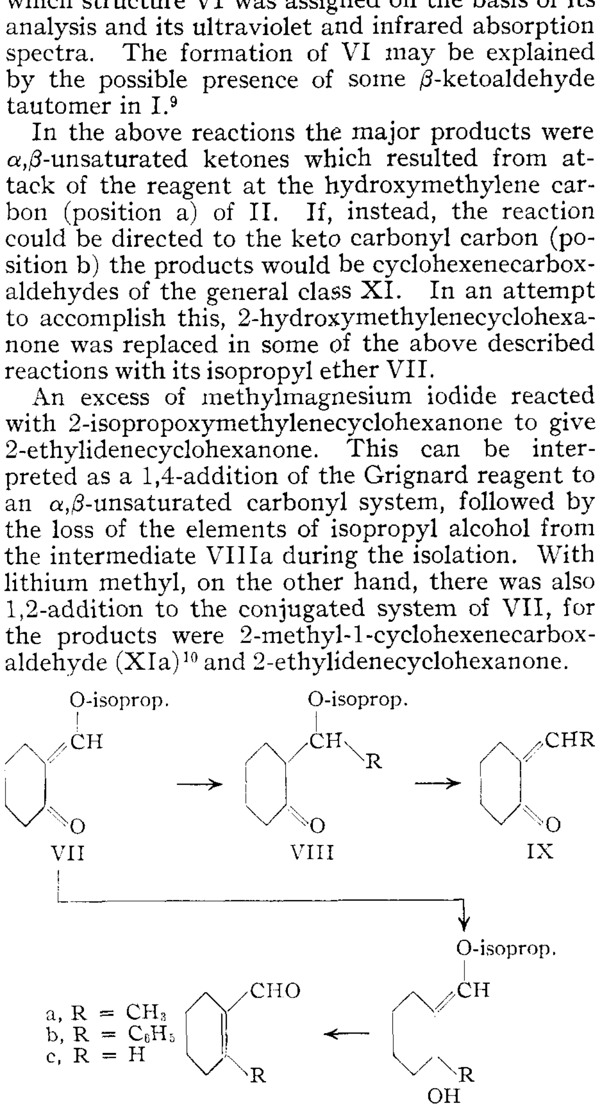
As expected from the preceding results, phenylmagnesium bromide condensed with I primarily at position a. Aside from the major product, 2-benzylidenecyclohexanone (V), there was also isolated a 9% yield of a by-product, m.p. 148–149°, to which structure VI was assigned on the basis of its analysis and its ultraviolet and infrared absorption spectra. The formation of VI may be explained by the possible presence of some β-ketoaldehyde tautomer in I.[9]



V VI

In the above reactions the major products were α,β-unsaturated ketones which resulted from attack of the reagent at the hydroxymethylene carbon (position a) of II. If, instead, the reaction could be directed to the keto carbonyl carbon (position b) the products would be cyclohexenecarboxaldehydes of the general class XI. In an attempt to accomplish this, 2-hydroxymethylenecyclohexanone was replaced in some of the above described reactions with its isopropyl ether VII.

An excess of methylmagnesium iodide reacted with 2-isopropoxymethylenecyclohexanone to give 2-ethylidenecyclohexanone. This can be interpreted as a 1,4-addition of the Grignard reagent to an α,β-unsaturated carbonyl system, followed by the loss of the elements of isopropyl alcohol from the intermediate VIIIa during the isolation. With lithium methyl, on the other hand, there was also 1,2-addition to the conjugated system of VII, for the products were 2-methyl-1-cyclohexenecarboxaldehyde (XIa)[10] and 2-ethylidenecyclohexanone.



VII VIII IX

a, R = CH_3
b, R = C_6H_5
c, R = H

XI X

Phenyllithium added to 2-isopropoxymethylenecyclohexanone largely in a 1,4-fashion. In this case, the immediate product of the reaction (VIIIb) did not lose isopropyl alcohol during the isolation and was obtained in a 40% yield. Its structure was deduced from its analysis, its ultraviolet and infrared absorption spectra and its ready conversion to the 2,4-dinitrophenylhydrazone of 2-benzylidenecyclohexanone. The isolation of a small amount of another carbonyl compound, which is considered to be 2-phenyl-1-cyclohexenecarboxaldehyde (XIb), as the 2,4-dinitrophenylhydrazone, indicated that there may also have been some 1,2-addition of phenyllithium to VII.[11]

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[5] A. S. Dreiding and J. A. Hartman, THIS JOURNAL, **75**, 939 (1953).

[6] E. P. Kohler and J. L. E. Erickson, *ibid.*, **53**, 2301 (1931); G. F. Woods, *ibid.*, **69**, 2549 (1947); G. F. Woods and I. W. Tucker, *ibid.*, **70**, 2174 (1948); G. F. Woods, P. H. Griswold, Jr., B. H. Armbrecht, D. L. Blumenthal and R. Plapinger, *ibid.*, **71**, 2028 (1949); A. Chaney and J. Astle, *J. Org. Chem.*, **16**, 57 (1951).

[7] A. S. Dreiding and J. A. Hartman, THIS JOURNAL, **75**, 3723 (1953).

[8] G. Wittig, "Newer Methods of Preparative Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1948, p. 588.

[9] G. Schwarzenbach and E. Felder, *Helv. Chim. Acta*, **27**, 1044 (1944); M. M. Bokadia and S. S. Deshapanda, *J. Ind. Chem. Soc.*, **27**, 548 (1950); **26**, 455 (1949).

[10] J. C. Lunt and F. Sondheimer, *J. Chem. Soc.*, 3361 (1950).

[11] R. B. Woodward and W. McLamore, THIS JOURNAL, **71**, 379 (1949), reported the condensation of the lithium derivative of α-picoline and of N-methylharman with VII. The nature of the products, obtained in unstated yields, indicated that there was at least some 1,2-addition to VII in both cases.

The lithium aluminum hydride reduction of VII, in contrast, proceeded almost exclusively by 1,2-addition to yield 1-cyclohexenecarboxaldehyde (XIc).[12]

In connection with the predominance of 1,4-addition to VII in the methyl Grignard and phenyllithium reactions as well as its persistence even with methyllithium it is interesting to note the recent observation of Hill, Walker and Hill[13] that even a simple enol ether reacted with a Grignard reagent, the nucleophilic attack occurring at the carbon which carried the oxygen. It is possible that enol ethers of β-dicarbonyl compounds are in general more susceptible to 1,4-addition than ordinary α,β-unsaturated carbonyl compounds. This is not in contradiction with the experiments of Woods and Tucker[6] since these reported reactions could have taken place by either 1,2- or 1,4-addition.

Some of the reactions described in this paper may be useful for the preparation of α,β-unsaturated ketones, difficultly available by other methods. For instance, the tendency for the introduction of two alkylidene groups in the condensation of an aldehyde with a ketone which has two reactive α-positions is avoided in the present method. Other reactions could be extended to the synthesis of aldehydes related to natural products. Thus 2-methyl-1-cyclohexenecarboxaldehyde (XIa) is structurally similar to β-cyclocitral and safranal, which has been shown to act as a male sex determining hormone (androtermone) with gametes of *Chlamydomonas eugamentos*.[14]

We are grateful to Dr. J. M. Vandenbelt and Mr. Bruce Scott of Parke, Davis and Co., for the measurement and valuable discussions of some of the ultraviolet and infrared absorption spectra mentioned in this paper.

Experimental[15]

Reactions with 2-Hydroxymethylenecyclohexanone (I). (a) **With Methylmagnesium Iodide.**—The addition of an ethereal solution (approximately 2 *M*) of 0.72 mole of methylmagnesium iodide to a stirred solution of 20 g. (0.159 mole) of 2-hydroxymethylenecyclohexanone (I)[16] (b.p. 39–40° at 0.1 mm.) in 200 cc. of ether at −10° was accompanied by a vigorous evolution of a gas (probably methane) and required 1 hour. After allowing the mixture to stand at −10° for another hour, 200 cc. of 5% hydrochloric acid was added with stirring and the aqueous layer was extracted with ether. The combined ethereal solutions were washed with several portions of 5% aqueous sodium hydroxide and then with saturated sodium chloride. Drying (sodium sulfate) and concentration left an oily residue which was distilled through a 6-inch Vigreux column to give, after a forerun of 6 g., 12 g. (61%) of 2-ethylidenecyclohexanone (IV), b.p. 68–70° (17 mm.), $n^{23}\mathrm{D}$ 1.4925 (reported[4] b.p. 77–79° at 10 mm., $n^{4}\mathrm{D}$ 1.4963), $\lambda^{\mathrm{alc}}_{\mathrm{max}}$ 250 mμ (ϵ 4,000). The colorless distillate darkened on standing at room temperature. This was also the case with the authentic sample of IV.

The 2,4-dinitrophenylhydrazone formed in 73% yield and crystallized from ethyl acetate as dark red blades, m.p. 219–220°, $\lambda^{\mathrm{alc}}_{\mathrm{max}}$ 216, 255 and 381 mμ (ϵ 17,900, 12,200 and 22,000); no depression of m.p. with an authentic sample.

Anal. Calcd. for $C_{14}H_{16}N_4O_4$: C, 55.25; H, 5.30. Found: C, 55.31; H, 5.35.

The semicarbazone crystallized from ethanol as colorless needles, m.p. 191–192° (reported for this derivative of IV,[4] m.p. 192°), $\lambda^{\mathrm{alc}}_{\mathrm{max}}$ 264 mμ (ϵ 11,590); no depression on admixture with an authentic sample.

(b) **With Methyllithium.**—To 43 g. (0.34 mole) of 2-hydroxymethylenecyclohexanone (I) in 100 cc. of ether was added, slowly and with stirring, an ethereal solution (approximately 2 *M*) of 1.36 moles of methyllithium at −40° over a period of two hours. After continued stirring at room temperature for 1 hour, 500 cc. of 5% hydrochloric acid was added and the product was isolated as in the preceding experiment. Fractionation yielded 4.5 g. (13%) of cyclohexanone, b.p. 55–63° (23 mm.), identified as the orange 2,4-dinitrophenylhydrazone, m.p. 162°, and 10.6 g. (25%) of 2-ethylidenecyclohexanone (IV), b.p. 85–90° (23 mm.), $n^{25}\mathrm{D}$ 1.4938. The 2,4-dinitrophenylhydrazone of the second fraction was dark red, m.p. 219–220°, and did not depress the m.p. of the derivative of the authentic sample of 2-ethylidenecyclohexanone (IV).

(c) **With Phenylmagnesium Bromide.**—To a stirred solution of 31 g. (0.25 mole) of 2-hydroxymethylenecyclohexanone (I) in 100 cc. of ether was added dropwise approximately 500 cc. of an ethereal solution of 0.83 mole of phenylmagnesium bromide at −10°. The addition, which took 2 hours, was followed by allowing the mixture to stand at room temperature for one hour and then decomposing with 5% hydrochloric acid. The product was worked up in the usual manner to give the following fractions: (1) 6.0 g. of biphenyl, m.p. 69.5°; (2) 22 g., b.p. 125–173° (1 mm.); (3) 6.5 g., b.p. 165–195° (0.3 mm.).

The second fraction represented 2-benzylidenecyclohexanone (V) (48% yield), which crystallized from petroleum ether as colorless needles, m.p. 54–55° (reported[17] m.p. 53°), $\lambda^{\mathrm{alc}}_{\mathrm{max}}$ 288 mμ (ϵ 16,850); $\lambda^{\mathrm{alc}}_{\mathrm{min}}$ 240 mμ (ϵ 2,300); $\lambda^{\mathrm{mineral\ oil}}_{\mathrm{max}}$ 5.97, 6.26 μ. The semicarbazone of V crystallized from ethanol as colorless needles, m.p. 195–197° dec. (reported[18] m.p. 197–200° dec.)

The 2,4-dinitrophenylhydrazone of V crystallized from ethyl acetate as dark red blades, m.p. 184–185°.

Anal. Calcd. for $C_{19}H_{18}N_4O_4$: C, 62.28; H, 4.95. Found: C, 62.50; H, 5.30.

The third fraction is considered to consist of **1-phenyl-2-(α-hydroxybenzyl)-cyclohexanol (VI)** (9.5%), which crystallized as flat colorless prisms from methanol, m.p. 148–148.7°. It did not give a color with alcoholic ferric chloride nor a precipitate with 2,4-dinitrophenylhydrazine solution.

Anal. Calcd. for $C_{19}H_{22}O_2$: C, 80.81; H, 7.85. Found: C, 80.60; H, 7.92.

The diol VI showed the following absorption characteristics: $\lambda^{\mathrm{alc}}_{\mathrm{max}}$ 260 mμ (ϵ 258) (typical spectrum of benzene ring); $\lambda^{\mathrm{mineral\ oil}}_{\mathrm{max}}$ 3.08 (s), 6.71 (m), 8.34 (m), 8.69 (m), 9.05 (m), 9.30 (m), 9.65 (w), 10.18 (s), 10.67 (w), 11.05 (m), 12.56 (m), 13.20 (m), 13.44 (s), 14.32 (s) μ (no carbonyl, but hydroxyl group present).

Reaction of 2-Hydroxymethylene-4-methylcyclohexanone with Methylmagnesium Iodide.—This Grignard reaction was conducted as described for I, but with 2-hydroxymethylene-4-methylcyclohexanone,[19] b.p. 44–45° (0.2 mm.). A part of the product was lost just before distillation and, therefore, the yield cannot be reported, but almost all of the saved portion distilled at 70–80° (21 mm.) (3.1 g.) and represented **2-ethylidene-4-methylcyclohexanone. The 2,4-dinitrophenylhydrazone** crystallized from ethyl acetate as dark red blades, m.p. 213.5–214° dec.

Anal. Calcd. for $C_{15}H_{18}N_4O_4$: C, 56.59; H, 5.70; N, 17.60. Found: C, 56.78; H, 5.81; N, 18.00.

An authentic sample of 2-ethylidene-4-methylcyclohexanone was prepared by the application of the method of Vavon

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[12] Since the completion of this experiment, P. Seifert and H. Schinz, *Helv. Chim. Acta*, **34**, 728 (1951), described the isolation of a 23% yield of XIc from the lithium aluminum hydride reduction of 2-isobutoxymethylenecyclohexanone.

[13] C. M. Hill, R. A. Walker and M. E. Hill, THIS JOURNAL, **73**, 1663 (1951).

[14] R. Kuhn, F. Moewus and G. Wendt, *Ber.*, **72B**, 1702 (1939).

[15] The melting points are not corrected. The analyses are by Micro-Tech Laboratories, Skokie, Ill.

[16] Pl. A. Plattner, P. Treadwell and C. Scholz, *Helv. Chim. Acta*, **28**, 771 (1945).

[17] O. Wallach, *Ber.*, **40**, 70 (1907).

[18] R. Poggi and P. Saltine, *Gazz. chim. ital.*, **62**, 678 (1932).

[19] K. v. Auwers, L. Fr. v. Sass and W. Wittekindt, *Ann.*, **444**, 195 (1925).

and Mitchovitch[4] to 4-methylcyclohexanone. It boiled at 103–105° (35 mm.) and yielded a 2,4-dinitrophenylhydrazone, m.p. 212–213°, which did not depress the m.p. of the product from the Grignard reaction.

Reactions of 2-Isopropoxymethylenecyclohexanone (VII). (a) **With Methylmagnesium Iodide.**—This reaction was conducted exactly as described in the first experiment with 30 g. (0.18 mole) of 2-isopropoxymethylenecyclohexanone (VII),[20] b.p. 72–73° (0.1 mm.), and 0.3 mole of methylmagnesium iodide. The reaction temperature was −50° and there was no evolution of gas. The crude product was distilled to give a forerun of 5 g., and the main fraction, 2-ethylidenecyclohexanone (IV), b.p. 58–64° (12 mm.), yield 15 g. (67%), $n^{25}\mathrm{D}$ 1.4908. The 2,4-dinitrophenylhydrazone of this sample melted at 219–220°.

(b) **With Methyllithium.**—The reaction (as described above) of 21 g. (0.13 mole) of VII with 0.2 mole of ethereal methyllithium at −50° yielded 16 g. of a colorless oil which was stirred with 45 cc. of a 40% aqueous solution of sodium bisulfite for a half-hour at room temperature. The crystalline sodium bisulfite addition compound of 2-methyl-1-cyclohexenecarboxaldehyde (XIa) was filtered and washed with ether; yield 10.3 g. (35%). The aldehyde XIa was recovered by treating the solid with dilute hydrochloric acid and ether extraction, yield of colorless oily residue 5.3 g. (34%), $n^{25}\mathrm{D}$ 1.5088 (reported[21] $n^{18}\mathrm{D}$ 1.5091). Since the yield of the sodium bisulfite addition compound from pure 2-methyl-1-cyclohexenecarboxaldehyde was only 65% it is possible that the crude product contained as much as 8.3 g. (53%) of XIa.

The 2,4-dinitrophenylhydrazone of XIa crystallized from ethyl acetate as bright red blades, m.p. 190–191°; $\lambda^{\mathrm{alc}}_{\mathrm{max}}$ 258, 292 and 385 mμ (ϵ 20,000, 11,850 and 35,400) (reported[21] m.p. 190–191°, $\lambda^{\mathrm{alc}}_{\mathrm{max}}$ 387 mμ, ϵ 29,500). This sample did not depress the m.p. of a sample of the same derivative kindly supplied by Dr. Lunt, m.p. 185°.[10] The semicarbazone crystallized from ethanol as colorless needles, m.p. 232–233° (reported[21] 232–233°).

The mother liquor from the filtration of the sodium bisulfite adduct of XIa was acidified and the organic material recovered by ether extraction, yield 3 g. (23%) of a light yellow oil, which was mostly 2-ethylidenecyclohexanone (IV). The 2,4-dinitrophenylhydrazone and the semicarbazone formed in high yields and melted at 219–220° and at 191–192°, respectively, alone and when mixed with authentic samples.

(c) **With Phenyllithium.**—The condensation of 5 g. (0.03 mole) of VII with an ethereal solution of phenyllithium (0.1 mole) was performed as in the preceding experiments at −60°. A 5-g. portion of the crude product (7.6 g.) was distilled through a short column to give two fractions: (1) b.p. 54° (20 mm.), yield 2 g.; and (2) b.p. 90–115° (0.03 mm.), yield 2.8 g. The first fraction did not yield a 2,4-dinitrophenylhydrazone and remained unidentified. The second fraction solidified partly and represented **2-(α-isopropoxybenzyl)-cyclohexanone** (**VIIIb**). It crystallized from petroleum ether as colorless needles, m.p. 71.5–72°, yield 1.9 g. (40%); $\lambda^{\mathrm{alc}}_{\mathrm{max}}$ 260 mμ (ϵ 260) (typical benzene spectrum); $\lambda^{\mathrm{mineral\ oil}}_{\mathrm{max}}$ 5.84 (s), 6.70 (w), 7.33 (w), 8.45 (w), 8.71 (m), 8.85 (s), 9.09 (s), 9.34 (m), 9.61 (w), 9.87 (s), 10.57 (w), 10.77 (w), 12.41 (m), 12.84 (m), 13.55 (m), 14.09 (m) μ.

Anal. Calcd. for $C_{16}H_{22}O_2$: C, 78.00; H, 9.00. Found: C, 78.04; H, 9.11.

The 2,4-dinitrophenylhydrazone of 2-(α-isopropoxybenzylcyclohexanone (**VIIIb**) precipitated as a yellow solid when the reagent was added to an alcoholic solution of VIIIb at room temperature, m.p. 150–155°. It was recrystallized from ethyl acetate as slender bright yellow blades, m.p. 171–172°.

Anal. Calcd. for $C_{22}H_{26}N_4O_5$: C, 61.96; H, 6.15; N, 13.14. Found: C, 62.24; H, 6.51; N, 13.64.

When the reaction of VIIIb with the reagent was performed at the boiling point of the solution, the dark red 2,4-dinitrophenylhydrazone of 2-benzylidenecyclohexanone (V) precipitated, m.p. 179–180°. After recrystallization from ethyl acetate, it melted at 184–185° alone and when mixed with the sample described above.

The oily material from the mother liquor of the crystallization of VIIIb formed a **2,4-dinitrophenylhydrazone**, which crystallized from ethyl acetate as maroon blades, m.p. 202–203°. This may be the derivative of **2-phenyl-1-cyclohexenecarboxaldehyde (XIb)**.

Anal. Calcd. for $C_{19}H_{18}N_4O_4$: C, 62.28; H, 4.95; N, 15.29. Found: C, 62.20; H, 4.89; N, 15.50.

(d) **With Lithium Aluminum Hydride.**—A solution of 26 g. (0.155 mole) of VII in a small amount of ether was added to a mixture of 6.68 g. (0.18 mole) of lithium aluminum hydride in 150 cc. of ether, which had been heated for a half-hour. After the addition (room temperature), the mixture was refluxed for 24 hours and then decomposed by the cautious addition of water, followed by 100 cc. of a saturated aqueous solution of sodium potassium tartrate.[22] The aqueous layer was extracted with ether and the combined ethereal solutions were washed with 5% hydrochloric acid and saturated sodium chloride solution. After drying and concentrating the residual 1-cyclohexenecarboxaldehyde (XIc) was distilled to give a colorless oil, b.p. 69–71° (18 mm.), $n^{25}\mathrm{D}$ 1.4928, yield 14 g. (82%) (reported b.p. 60–61° at 11 mm., $n^{19}\mathrm{D}$ 1,4914, yield 23%[12]; b.p. 61–63° at 24 mm., $n^{18}\mathrm{D}$ 1,4503[21]); $\lambda^{\mathrm{alc}}_{\mathrm{max}}$ 231 mμ (ϵ 13,000) (reported[21] $\lambda^{\mathrm{alc}}_{\mathrm{max}}$ 229 mμ (ϵ 12,100). The 2,4-dinitrophenylhydrazone of XIc crystallized from ethyl acetate as orange-red blades, m.p. 219–220° (reported[21] m.p. 219–220°). The semicarbazone of XIc crystallized from ethanol as colorless needles, m.p. 211–212° (reported m.p. 213–214°[21]); $\lambda^{\mathrm{alc}}_{\mathrm{max}}$ 265 mμ (ϵ 32,300); $\lambda^{\mathrm{alc}}_{\mathrm{infl}}$ 260 mμ (ϵ 31,700) (reported[21] $\lambda^{\mathrm{alc}}_{\mathrm{max}}$ 260 and 265 mμ (ϵ 28,500 and 31,700).

DETROIT, MICHIGAN

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[20] Prepared from I with isopropyl iodide and potassium carbonate in 82% yield. *Cf.* K. v. Auwers, *Ber.*, **71B**, 2082 (1938); W. S. Johnson and H. Posvic, THIS JOURNAL, **69**, 1361 (1947); R. B. Woodward and W. McLamore, *ibid.*, **71**, 379 (1949).

[21] I. Heilbron, E. Jones, D. Lewis, R. Richardson and F. Sondheimer, *J. Chem. Soc.*, 737 (1949).

[22] R. Nystrom and W. G. Brown, THIS JOURNAL, **70**, 3736 (1948).