

1-Aryluracils. The dehydrobromination of 1-aryl-5-bromodihydrouracils was accomplished by a procedure similar to the one described by Holysz.¹³ A solution of equimolar amounts of lithium chloride and 1-aryl-5-bromodihydrouracil in 50 ml. of *N,N*-dimethylformamide was heated on a steam cone for 3 hr. Water was now added to the contents to bring about precipitation. The precipitate was washed with distilled water over a Büchner funnel, air-dried, and recrystallized from dioxane as fine colorless needles. The ultraviolet absorption spectrum in methanol ($c = 20 \mu\text{g./ml.}$) was obtained on a Beckman Ratio Recording Spectrophotometer. **1-Phenyluracil:** 2.3 g. (0.009 mole) of 1-phenyl-5-bromodihydrouracil yielded 0.7 g. (44%) of 1-phenyluracil; m.p. 247°; $E_{\text{max}} = 11,100$ at 265 μ . Atkinson *et al.*⁸ reported m.p. 247°. **1-*p*-Chlorophenyluracil:** 2.4 g. (0.011 mole) of 1-*p*-chlorophenyl-5-bromodihydrouracil yielded 1.1 g. (45%) of 1-*p*-chlorophenyluracil; m.p. 258°; $E_{\text{max}} = 15,670$ at 264 μ .

Anal. Calcd. for $\text{C}_{10}\text{H}_7\text{ClN}_2\text{O}_2$: C, 53.90; H, 3.16; N, 12.59. Found: C, 53.85; H, 3.27; N, 12.58.

Acknowledgment. This work was supported by grant number CY-3231 from the U.S. Public Health Service.

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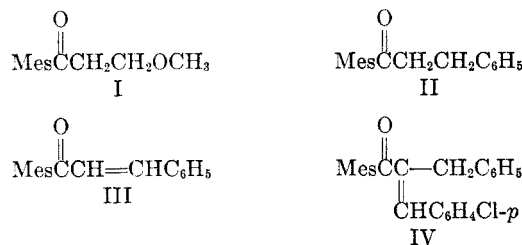
(13) R. P. Holysz, *J. Am. Chem. Soc.*, **75**, 4432 (1953).

Action of Grignard Reagents on β -Substituted Propiomesitylenes¹

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Received October 22, 1957

α -Hydrogen elimination reactions produced by the action of Grignard reagents on β -substituted mesityl ketones are followed by 1,4-addition of the Grignard reagent to the resulting α,β -unsaturated ketone. Thus β -methoxypropiomesitylene (I) reacts with two equivalents of phenylmagnesium bromide to give β -phenylpropiomesitylene (II).



The phenylated ketone proved to be identical with that prepared by catalytic hydrogenation of benzalacetomesitylene (III) according to the method of Barnes.³ The *p*-chlorobenzal derivative (IV) was made also.

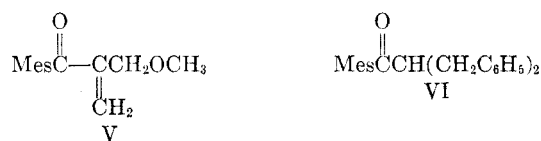
(1) This investigation was supported by a grant from the Office of Ordnance Research, U. S. Army (Contract No. DA-11-022-ORD-874).

(2) Socony-Vacuum Oil Co. Fellow, 1954-1955.

(3) R. P. Barnes, *J. Am. Chem. Soc.*, **57**, 937 (1935).

With mesitylmagnesium bromide β -methoxypropiomesitylene (I) yielded β -mesitylpropiomesitylene previously produced by condensing β -chloropropionyl chloride with mesitylene by the method of Friedel and Crafts⁴ and by catalytic hydrogenation of mesitoylmesitylacetylene.⁵

An interesting variant was furnished by 3-methoxyisopropenyl mesityl ketone (V),⁶ a product of the interaction of formaldehyde, acetomesitylene, and methanol. When this unsaturated ketone was allowed to condense with phenylmagnesium bromide the product was dibenzylacetomesitylene (VI).



This change differs from the preceding examples in that the enolate that loses the methoxide ion is formed by 1,4-addition of the Grignard reagent to an α,β -unsaturated ketone rather than by enolization of a saturated ketone. Presumably α -benzylvinyl mesityl ketone (VII) was formed as an intermediate.

In addition to the major product, dibenzylacetomesitylene, small amounts of mesitoic acid and dibenzyl ketone were isolated also. These compounds could be produced by air oxidation of the enolic form (VIII) of dibenzylacetomesitylene.



EXPERIMENTAL⁷

Reaction of β -methoxypropiomesitylene (I) with phenylmagnesium bromide. To a refluxing solution of phenylmagnesium bromide, prepared from 62.8 g. (0.4 mole) of bromobenzene, 9.6 g. (0.4 g.-atom) of magnesium, and 200 ml. of dry ether, was added with stirring 20.6 g. (0.1 mole) of β -methoxypropiomesitylene over a period of 10 min. The heating and stirring were continued for 5 hr. The reaction mixture was cooled in an ice bath and treated with a cold dilute solution of hydrochloric acid. The organic layer, after being washed with water and dried over anhydrous sodium sulfate, was freed of solvent by distillation, and the residual yellow oil was distilled through a 12-in. Vigreux column. The small amount of forerun solidified and had the odor characteristic of biphenyl. The main fraction was β -phenylpropiomesitylene, b.p. 149-153°/0.5 mm.; n_D^{20} 1.5570; yield 16.4 g. (65%).

(4) R. C. Fuson and C. H. McKeever, *J. Am. Chem. Soc.*, **62**, 2088 (1940).

(5) R. C. Fuson and J. S. Meek, *J. Org. Chem.*, **10**, 551 (1945).

(6) R. C. Fuson and C. H. McKeever, *J. Am. Chem. Soc.*, **62**, 999 (1940).

(7) All melting points are corrected; all boiling points are uncorrected.

The infrared spectrum⁸ of this compound is identical with that of a sample of β -phenylpropionemesitylene prepared according to the method of Barnes.³ It shows bands assignable to a hindered unconjugated ketone (1697 cm^{-1}) and to a mesityl group (852 cm^{-1}).

The *p*-chlorobenzal derivative (IV) was made by allowing a mixture of 1.0 g. (0.007 mole) of *p*-chlorobenzaldehyde, 0.6 g. (0.002 mole) of β -phenylpropionemesitylene (prepared by the method of Barnes or by the methoxyl elimination reaction), 50 ml. of ethanol, and 10 ml. of a 10% solution of sodium hydroxide to stand at room temperature for 22 hr. When the pale yellow reaction mixture was refrigerated white crystalline plates were deposited; m.p. 108–109.5°, after one recrystallization from ethanol.

Anal. Calcd.⁹ for $\text{C}_{25}\text{H}_{20}\text{OCl}$: C, 80.11; H, 6.18. Found: C, 80.09; H, 6.15.

The infrared spectrum of the compound, determined in carbon disulfide, shows absorption at 1655 cm^{-1} , assignable to the conjugated carbonyl function. Bands at 850, 820, and 695 cm^{-1} suggest the presence of mesityl as well as *p*-disubstituted- and monosubstituted benzene groups.

Reaction of β -methoxypropionemesitylene with mesitylmagnesium bromide. A Grignard reagent was prepared from 4.2 g. (0.18 g.-atom) of finely divided magnesium, 40 g. (0.2 mole) of freshly distilled bromomesitylene, 175 ml. of anhydrous ether, and a small crystal of iodine. To the refluxing solution was added, dropwise and with stirring, 10.3 g. (0.05 mole) of β -methoxypropionemesitylene in 150 ml. of anhydrous benzene. The heating and stirring were continued for 10 hr. The work-up was conducted as described in the previous experiment. Hot ethanol was added to the oily yellow residue, and the solution was refrigerated. The solid which separated was recrystallized from ethanol. Seven grams (50%) of white powdery material was obtained; m.p. 79.5–80.5°.

A mixed melting point determination with an authentic sample of β -mesitylpropionemesitylene⁶ showed no depression. The infrared spectrum (chloroform) of the compound exhibits strong bands at 1693 cm^{-1} and at 855 cm^{-1} . These can be assigned to the hindered carbonyl function and to the mesityl group, respectively.

Reaction of 3-methoxyisopropenyl mesityl ketone (V) with phenylmagnesium bromide. The reaction was conducted in an atmosphere of nitrogen. A Grignard reagent was prepared from 11.3 g. (0.072 mole) of bromobenzene, 1.7 g. (0.07 g.-atom) of magnesium, and 50 ml. of dry ether. To the Grignard solution was added, dropwise and with stirring, a solution containing 3.9 g. (0.018 mole) of the methoxy ketone, 50 ml. of dry ether, and 75 ml. of dry benzene. One hour was required for the addition. The reaction mixture, grey-white because of suspended solid material, was heated under reflux for 10 hr., and then allowed to stand overnight at room temperature. The suspension was cooled in an ice-bath and hydrolyzed with cold dilute hydrochloric acid. The work-up was conducted in the usual manner.

A portion of the oily residue was taken up in hot ethanol, and the solution cooled in the refrigerator. Pale yellow prisms separated; m.p. 81–83°. Recrystallization from an ethanol-water mixture gave white pellets, m.p. 83.5–85°.

Anal. Calcd. for $\text{C}_{25}\text{H}_{26}\text{O}$: C, 87.67; H, 7.65. Found: C, 87.84; H, 7.75.

The carbonyl region of the infrared spectrum (carbon disulfide) of the compound contains a strong band at 1700 cm^{-1} . A band at 854 cm^{-1} is assignable to a mesityl group, and a mono-substituted benzene nucleus is indicated by strong absorption at 750 and 700 cm^{-1} .

Addition of cyclohexane to the remainder of the oily

(8) The infrared spectra were determined and interpreted by Mr. James Brader, Mrs. Louise Griffing, Mr. Sy Portnow, and Mr. Brian Cloonan.

(9) The microanalyses were performed by Mr. J. Nemeth, Mrs. R. Maria Benassi, Mr. Rolo Nasset, Miss Claire Higham, Mrs. Ruby Ju, and Mrs. Stingl.

residue caused the separation of white, star-like crystals, m.p. 151–153°. A mixture melting point determination and the infrared spectrum showed the compound to be mesitoic acid. The cyclohexane solution from which the mesitoic acid had been removed, was subjected to chromatographic treatment. Three products, biphenyl, dibenzylacetomesitylene, and a yellow oil were obtained. The infrared spectrum (carbon disulfide) suggested that the liquid was dibenzyl ketone. The oxime formed silky white needles, m.p. 120–120.5°; no mixture melting point depression was observed with an authentic sample of the oxime of dibenzyl ketone. The total yield of dibenzylacetomesitylene was 2.2 g. About 0.1 g. of mesitoic acid and a similar amount of dibenzyl ketone were isolated.

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Isolation of Carbonyl Compounds under Neutral Conditions Using the Girard Reagent

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Received October 30, 1957

In the course of an investigation of the constituents of an essential oil, an attempt was made to isolate the carbonyl compounds present by means of the Girard "T" reagent.¹ The literature indicated that this reagent was suitable for the isolation of aldehydes as well as ketones.^{2,3} However, application of this procedure resulted in a much lower yield than was indicated by analysis of the oil for carbonyl compounds by the standard hydroxylamine hydrochloride procedure.

Studies using citral as a model carbonyl compound showed that the Girard complex formed smoothly but that the acid regeneration procedure failed to yield any detectable amount of citral. The product had an infrared spectrum indicative of the presence of a complex mixture containing *p*-cymene. This finding is not surprising in view of the known instability of citral in the presence of strong acids and the occurrence of *p*-cymene in the decomposition products.⁴

It has been found that regeneration of a carbonyl compound from its Girard complex can be effected by merely adding a large excess of aqueous formaldehyde to the neutral solution of the complex. In the case of stable carbonyl compounds, the

(1) A. Girard and G. Sandulesco, *Helv. Chim. Acta*, **19**, 1095 (1936).

(2) E. Lederer and G. Nachmias, *Bull. soc. chim. France*, **400** (1949). These authors' results in recovering citral from its Girard derivative in 89 per cent yield by acid hydrolysis could not be repeated. Using their procedure, a small yield of organic material containing no detectable (infrared spectrum) citral was recovered.

(3) A. Weissenberg and D. Ginsburg, *Bull. Research Council Israel, Sect. A.*, **5A**, 268 (1956).

(4) J. L. Simonsen and L. N. Owen, *The Terpenes*, 2nd ed., Cambridge Univ. Press, Vol. I, p. 91 (1947).