The infrared spectrum[8] of this compound is identical with that of a sample of β-phenylpropiomesitylene 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-phenylpropiomesitylene (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 $C_{25}H_{23}OCl$: 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-methoxypropiomesitylene 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-methoxypropiomesitylene 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-mesitylpropiomesitylene[5] 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 $C_{25}H_{26}O$: 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 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.

NOYES CHEMICAL LABORATORY
UNIVERSITY OF ILLINOIS
URBANA, ILL.

---

[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 Nesset, Miss Claire Higham, Mrs. Ruby Ju, and Mrs. Stingl.

Isolation of Carbonyl Compounds under Neutral Conditions Using the Girard Reagent

C. L. TEITELBAUM

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).

yields are comparable to those obtained by the use of mineral acid. However, in the case of relatively unstable aldehydes, the yields from the new procedure are distinctly superior. Typical results are given in Table I.

TABLE I

Carbonyl Compound	Regeneration Procedure	Yield, %
Citral	CH_2O	81
	HCl	10^a
n-Octanaldehyde	CH_2O	78
	HCl	64
Acetophenone	CH_2O	72
	HCl	84
Benzaldehyde	CH_2O	50
	HCl	27^b
2-Octanone	CH_2O	96
	HCl	85

[a] Product was a complex mixture exhibiting the major infrared spectral bands of *p*-cymene. [b] The product consisted of a mixture of solid (apparently benzoic acid) and liquid (solution of benzoic acid in benzaldehyde).

An attempt was also made to eliminate the use of acetic acid as catalyst for formation of the Girard complex. It was found that a cation exchange resin[5] is equally efficient as a catalyst and can be readily removed by decantation, leaving a neutral solution. This avoids the troublesome necessity of neutralizing the acetic acid and eventually extracting traces of it from both the carbonyl and non-carbonyl products.

These modifications of the Girard procedure have proven to be of particular value in isolating carbonyl compounds from mixtures where it is desirable to avoid acidic conditions.

EXPERIMENTAL

Girard "T" reagent (50 g.),[6] 25 g. carbonyl compound, 1 g. cation exchange resin,[5] and 100 ml. ethanol were placed in a flask. The mixture was refluxed 1 hr., during which time the Girard reagent dissolved; the solution was then decanted from the exchange resin into 400 ml. of water. The resulting solution was divided into two equal aliquots. To one half was added 100 ml. 37% formalin solution, and to the other half 50 ml. concentrated hydrochloric acid. Both solutions were allowed to stand overnight at room temperature. Each solution was extracted with pentane and the extract was washed five times with water and dried over anhydrous sodium sulfate. The pentane was evaporated from each extract by heating on a water bath and briefly applying water aspirator vacuum to remove the last traces of solvent. A control experiment demonstrated that the evaporation procedure does not cause any significant loss of the carbonyl compounds used in this work. The recovered carbonyl compound was checked for purity by means of its infrared spectrum.

Acknowledgment: The technical assistance of John Lenard is gratefully acknowledged.

BATTELLE MEMORIAL INSTITUTE
COLUMBUS 1, OHIO

---

[5] Amberlite IRC 50, Rohm & Haas Co.

[6] Arapahoe Chemicals, Inc.

Preparation of 3-Hydroxymethyl-5-pyrazolone from 3-Carbethoxy-5-pyrazolone[1]

TAKUO OKUDA AND CHARLES C. PRICE

Received October 28, 1957

A compound believed to be 3-hydroxymethyl-5-pyrazolone has been previously synthesized by Gillespie and Price[2] by condensation of ethyl tetronate with hydrazine hydrate. The preparation of the same compound from 3-carbethoxy-5-pyrazolone[3] through reduction with lithium aluminum hydride confirms the structure assigned earlier.

EXPERIMENTAL

Reduction of 3-carbethoxy-5-pyrazolone to 3-hydroxymethyl-5-pyrazolone. 3-Carbethoxy-5-pyrazolone[3] (10 g., 0.0641 mole) was placed in a Soxhlet extractor mounted on a flask containing a solution of 5 g. (0.132 mole) of lithium aluminum hydride in 400 ml. of dry ether. The ether was refluxed with stirring for 7 hr. After cooling, 14 ml. of ethyl acetate was added with stirring, and then 5 ml. of water. The solid precipitate was filtered after standing overnight. The filtrate gave only a negligible amount of oily residue when the solvent was removed by distillation. The filtered precipitate was extracted with ethanol using a Soxhlet extractor for 6 hr. The ethanol was distilled from the extract *in vacuo* leaving a viscous residue which was cooled to 0° for a week. The resulting crystalline precipitate was filtered with suction. The viscous filtrate gave no more crystalline produce on further concentration and cooling. Attempts to make picrate and benzoyl derivatives from the filtrate also failed.

The filtered product, which weighed 1.2 g., showed the presence of lithium by flame color test. The material was dissolved in 2 ml. of water and the solution was neutralized with acetic acid. On scratching the wall of the container, 0.35 g. of crystals precipitated. Recrystallized from *ca.* 1 ml. of ethanol, the material melted at 156–158° and showed no melting point depression when mixed with a sample of Gillespie's material. The two samples also had the same infrared spectra with the following major characteristics (in potassium bromide, wave length and % absorption): 2.93 (61), 3.45 (67), 3.6 (72), 6.15 (87), 6.49 (71), 6.61 (78), 6.87 (74), 7.90 (39), 8.18 (35), 8.51 (50), 9.34 (38), 9.59 (65), 9.92 (42), 10.20 (37), 12.2 (58), 12.9 (56), 14.0 (52).

JOHN HARRISON LABORATORY OF CHEMISTRY
UNIVERSITY OF PENNSYLVANIA
PHILADELPHIA 4, PENNA.

---

[1] Supported in part by U. S. Public Health Service Grant CY 2714.

[2] J. F. Gillespie and C. C. Price, *J. Org. Chem.*, **22**, 780 (1957).

[3] R. v. Rothenburg, *J. Prakt. Chem.*, [2] **51**, 53 (1895).

Dimeric Pyrolysis Products of Polypropylene Oxide

ALLEN NOSHAY AND CHARLES C. PRICE

Received September 19, 1957

Price and St. Pierre[1] have reported that the py-

---

[1] C. C. Price and L. E. St. Pierre, *J. Am. Chem. Soc.*, **78**, 3432 (1956).