

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 ₂ O	81
	HCl	10 ^a
<i>n</i> -Octanaldehyde	CH ₂ O	78
	HCl	64
Acetophenone	CH ₂ O	72
	HCl	84
Benzaldehyde	CH ₂ O	50
	HCl	27 ^b
2-Octanone	CH ₂ O	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 resin⁵ 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.

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Preparation of 3-Hydroxymethyl-5-pyrazolone from 3-Carbethoxy-5-pyrazolone¹

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A compound believed to be 3-hydroxymethyl-5-pyrazolone has been previously synthesized by Gillespie and Price² by condensation of ethyl tetronate with hydrazine hydrate. The preparation of the same compound from 3-carbethoxy-5-pyrazolone³ 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-pyrazolone³ (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 product 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).

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

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Dimeric Pyrolysis Products of Polypropylene Oxide

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Price and St. Pierre¹ have reported that the py-

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