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.

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(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).

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(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-

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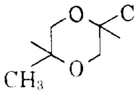
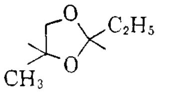
(1) C. C. Price and L. E. St. Pierre, *J. Am. Chem. Soc.*, **78**, 3432 (1956).

rolysis of polypropylene oxide in the presence of *p*-toluenesulfonic acid produced propionaldehyde, propionic and acrylic acids, and dimethyldioxane. Dr. R. K. Summerbell has suggested to us[2] that the properties we reported for the latter substance indicated it to be the isomeric 2-ethyl-4-methyldioxolane. We have therefore reinvestigated the identity of this pyrolysis fraction and find it does indeed contain considerable quantities of 2-ethyl-4-methyldioxolane (II), as well as an isomer, probably *trans*-2,5-dimethyldioxane (I).


I


II

The presence of II was proven by the acid hydrolysis of the pyrolysis product in the presence of 2,4-dinitrophenylhydrazine to produce propionaldehyde 2,4-dinitrophenylhydrazone, by infrared spectra, by vapor chromatography,[3] and by nuclear magnetic resonance.[4]

The latter three measurements also indicated the presence of an isomer, probably *trans*-2,5-dimethyldioxane, in roughly equal amounts.

Since II is readily prepared by acid-catalyzed condensation of propylene glycol with propionaldehyde, it is not clear whether this compound is a direct product of pyrolysis or is formed from the glycol and aldehyde as a secondary product.

EXPERIMENTAL

Pyrolyses. A 29-g. sample of polypropylene oxide and 0.3 g. of *p*-toluene sulfonic acid were heated together in a sand bath at 270–330° to give 25.5 g. of yellow distillate and 2 g. of black residue. Redistillation through a 6-inch Vigreux column gave 8.5 g., b.p. 51–87°; 10 g., b.p. 87–113° and 3.0 g., b.p. 113–165°. Two redistillations of the main fraction gave three fractions corresponding to dimer, 0.5 g., b.p. 117–120°, n_D^{28} 1.4073; 2.5 g., b.p. 121–123°, n_D^{28} 1.4088; 1.5 g., b.p. 123–128°, n_D^{28} 1.4102.

A similar pyrolysis of 114 g. of polypropylene oxide (Ucon "2025," Carbide Chemicals Corporation) gave the following dimer fractions, after three redistillations: 1.5 g., b.p. 117–119°, n_D^{19} 1.4090; 2.0 g., b.p. 119–120°, n_D^{19} 1.4112; 2.0 g., b.p. 120–122, n_D^{19} 1.4130; 1.5 g., b.p. 122–125°, n_D^{19} 1.4141.

The infrared spectra of all seven dimer samples were almost identical, except for changes in relative intensity of bands, and all were very similar to the spectra reported earlier by St. Pierre.[1]

The infrared spectrum of 2-ethyl-4-methyldioxolane, b.p. 117.5°, n_D^{20} 1.4048, prepared by condensation of propionaldehyde and propylene glycol,[3] was similar to the dimer fractions, except for the absence of bands at 7.86 μ and 11.86 μ. These are the only two major bands for *trans*-2,5-dimethyldioxane[5] not present also in the dioxolane. The strong band in *cis*-2,5-dimethyldioxane at 8.23 μ is almost entirely absent in the pyrolysis product. The bands at 7.1, 9.65, 10.75, and 11.03 μ in the dioxolane are considerably weaker in pyrolysis product fractions boiling at 122–125° than those boiling at 117–119°. A rough approximation from band intensities would suggest that the main components of the pyrolysis are 2-ethyl-4-methyl dioxolane and *trans*-2,5-dimethyldioxane in roughly equal amounts.

The fact that the dimer fractions are not pure dioxolane is further supported by the spread in boiling point and refractive index.[6] Assuming a two component mixture and a linear relation between composition and refractive index, the material from the second pyrolysis would be about 40% dioxolane and 60% dioxane. From this same material, vapor chromatography[3] gave a fraction identified as the dioxolane (55%) and another fraction, probably the dioxane (45%).

A comparison of the nuclear magnetic resonance spectrum[4] of the pyrolysis product with the markedly different spectra of 2-ethyl-4-methyldioxolane and *trans*-2,5-dimethyldioxane was entirely consistent with the conclusion that the pyrolysis mixture contained roughly equal amounts of these isomers.

It was also noted that the synthetic dioxolane crystallized in a Dry Ice–acetone bath whereas none of the dimer fractions did so.

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[2] Private communication.

[3] Courtesy of Dr. L. E. St. Pierre, Research Laboratories, General Electric Company, Schenectady, N. Y.

[4] Courtesy of Dr. J. D. Roberts, California Institute of Technology, Pasadena, Calif.

[5] Samples of *trans*-2,5-dimethyldioxane and the mixed *cis-trans* isomers were kindly supplied by R. K. Summerbell and D. Dalton, Northwestern University.

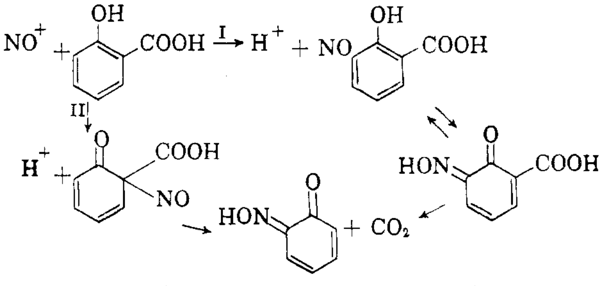
[6] E. Augdahl, *Acta Chem. Scand.*, 9, 1237 (1955) has reported *trans*-2,5-dimethyldioxane, b.p. 121.5°, n_D^{22} 1.4147.

Nitrosodecarboxylation

RONALD A. HENRY

Received September 16, 1957

The addition of sodium nitrite to an aqueous ethanolic solution of salicylic acid causes an immediate and rapid evolution of carbon dioxide; some 2-nitrophenol can be distilled from the resulting solution. This decarboxylation could conceivably occur by either of the following reaction paths:



The resulting *ortho*-quinone monoxime or 2-nitrosophenol would then be oxidized by excess nitrite to the 2-nitrophenol. From the nature of the product recovered, it is not possible to differentiate between these two routes. Similarly, the formation of 2-nitro-4-methylphenol from sodium nitrite and 5-methylsalicylic acid does not permit a differentiation between the two mechanisms. However, a determination of the products formed in the reac-