

The solution remaining in the reaction flask after the steam distillation was washed into a volumetric flask and diluted to 1 l. The amount of dichromate anion remaining in this solution was determined on a 50-ml. aliquot by the procedure of Kolthoff and Sandell.⁹ The difference between the dichromate value so obtained and that obtained from 5.00 ml. of the original chromic acid oxidizing mixture, which had been carried through the entire procedure but without the addition of any organic material, gave the values of $\text{Cr}_2\text{O}_7^{2-}$ consumed that are recorded in the table.

(9) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," 3rd ed., The Macmillan Co., New York, N. Y., 1952, p. 594.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF WISCONSIN
MADISON 6, WISCONSIN

β -Propiolactone. XV. Use in the Diene Synthesis

By T. L. GRESHAM, J. E. JANSEN AND F. X. WERBER

RECEIVED SEPTEMBER 14, 1953

β -Propiolactone may be used in place of acrylic acid as the dienophile component in the Diels-Alder diene synthesis. Cyclohexene-4-carboxylic acid (from butadiene) and the corresponding substituted adducts from isoprene and cyclopentadiene have thus been prepared in excellent yield.

A catalyst (potassium carbonate) known to aid polymerization of the lactone to a polyester and assist in the pyrolysis of the latter to acrylic acid,¹ was used to accelerate the reaction. In the absence of such a catalyst a major portion of the lactone was recovered as its polymer (polyester), as evidenced by the formation of acrylic acid during distillation of the crude reaction product.

Experimental

Butadiene and β -Propiolactone.—Following is one set of conditions which gave the optimum yield. In a chilled 2900-ml. stainless steel autoclave were placed 576 g. of β -propiolactone (97% purity, 7.75 moles), 500 g. of butadiene (9.25 moles), 6 g. of potassium carbonate and 2 g. of hydroquinone. The mixture was heated to 200°; exothermic reactions took place at about 100° and 200°, raising the temperature to 270° for a short time. The temperature was maintained at 200° for 1.5 hours. The crude reaction product was distilled; 937 g. of cyclohexene-4-carboxylic acid (96% of theory, based on the β -propiolactone content of the starting material) was obtained, b.p. 126° (16 mm.). The product was identical in every respect with that produced by reaction of acrylic acid and butadiene.²

Isoprene and β -Propiolactone.—Potassium carbonate, 5 g., and 1 g. of hydroquinone were heated to 170° in a 2900-ml. stainless steel autoclave. A mixture of 432 g. of β -propiolactone (97% purity, 5.82 moles) and 476 g. (7.0 moles) of isoprene was pumped in. The temperature rose to 205° and was maintained there during the addition, which took one hour. The resulting reaction mixture, on distillation, gave 750 g. of a mixture of methylcyclohexene-carboxylic acids,³ b.p. 93° (0.9 mm.), 129° (10 mm.), m.p. 75–90° (lit.⁴ 97–98° for a single acid, after recrystallization).

Anal. Calcd. for $\text{C}_8\text{H}_{12}\text{O}_2$: neut. equiv., 140.2. Found: neut. equiv., 141.9.

(1) T. L. Gresham, J. E. Jansen and F. W. Shaver, *THIS JOURNAL*, **70**, 998 (1948).

(2) F. X. Werber, J. E. Jansen and T. L. Gresham, *ibid.*, **74**, 532 (1952).

(3) J. S. Meek and co-workers (Abstracts, 115th American Chemical Society Meeting, San Francisco, Calif., 1949, p. 59L) state that the reaction of acrylic acid with isoprene gives "predominantly" the para isomer (1-methylcyclohexene-4-carboxylic acid).

(4) French Patent 672,025, to Société M. Naef & Cie. (C. A., **24**, 2243 (1930)).

Dicyclopentadiene and β -Propiolactone.—A mixture of 241 g. of β -propiolactone (97% purity, 3.25 moles) and 300 g. of dicyclopentadiene (technical) were pumped into a 1-l. stainless steel bomb at 180° and containing 5 g. of potassium carbonate and 7 g. of hydroquinone. The temperature was maintained at 170–180° for a total of 1.25 hours, including the addition period. The crude reaction product was distilled. About 23% of the dicyclopentadiene was recovered; 415.3 g. of 3,6-endomethylenecyclohexene-4-carboxylic acid (92.5% of theory, based on β -propiolactone) was recovered. It boiled at 120.5–121.5° (10 mm.) (lit.⁵ 132–134° (22 mm.)), n_D^{25} 1.4955.

Anal. Calcd. for $\text{C}_8\text{H}_{10}\text{O}_2$: neut. equiv., 138.2. Found: neut. equiv., 144.1.

Acknowledgment.—The authors wish to thank Mr. Harry Davis and associates for carrying out the pressure reactions.

(5) O. Diels and K. Alder, *Ann.*, **460**, 98 (1928).

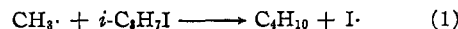
B. F. GOODRICH RESEARCH CENTER
BRECKSVILLE, OHIO

Free Radical Displacement Reactions

By J. L. FRANKLIN AND G. R. L. SHEPHERD

RECEIVED AUGUST 27, 1953

A study of the system, methyl-isopropyl iodide-helium at 8–9 mm. and 300–330° has demonstrated the relatively small contribution of the reaction



either in the gas phase or as a heterogeneous reaction. Although the above was the reaction sought, the extraction of hydrogen or iodine atoms by the methyl radical was believed to be the favored reaction in view of the probable activation energy of (1) associated with inversion of the iodide. Methyl radicals were produced by the reaction of sodium vapor and methyl bromide in a modification of the Polanyi "sodium flame" technique.¹ The radicals thus formed were transported at high velocity on a helium stream into a reactor section where they came in contact with isopropyl iodide. The reactor section contained silver gauze, which served as a means of detection for any iodine displaced according to reaction 1.

Experimental

A helium stream was saturated with sodium in a heated Pyrex U-tube and then introduced through a 1-mm. jet into the preheater consisting of a 6" section of 25-mm. Pyrex tubing. In the preheater the sodium reacted with methyl bromide, carried on a second helium stream, to form methyl radicals and sodium bromide with the emission of the characteristic yellow sodium radiation when the mixing zone was illuminated with a sodium resonance lamp. The radicals thus generated were carried very rapidly through a jet of 2 mm. diameter into the reactor zone. The high gas velocities prevailing in the jets prevented backmixing. Depending on the experiment, an additional helium stream brought either isopropyl iodide or iodine into the reactor. In the preliminary experiments iodine was employed as a means of identifying methyl radicals by the formation of methyl iodide. In the investigation of the displacement reaction itself the iodine was replaced with isopropyl iodide. The reactor itself consisted of a 5.5" length of 25-mm. Pyrex tubing electrically wound. After being treated with acid and sodium cyanide solution to remove all traces of oxide and sulfide, silver gauze was placed in the reactor to detect any displaced iodine. Deposits on the gauze were subsequently analyzed for iodine polarographically, after the io-

(1) E. Horn, M. Polanyi and D. W. G. Style, *Trans. Faraday Soc.*, **30**, 189 (1934).