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 $Cr_2O_7^-$ 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

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 $C_8H_{12}O_2$: 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, 2213 (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.)), $n^{25}D$ 1.4955.

Anal. Calcd. for $C_8H_{10}O_2$: 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).

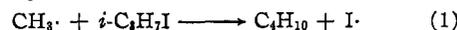B. F. GOODRICH RESEARCH CENTER
BRECKSVILLE, OHIO

Free Radical Displacement Reactions

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

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

$$CH_3\cdot + i\text{-}C_3H_7I \longrightarrow C_4H_{10} + I\cdot \qquad (1)$$

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 activational 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).

dine had been oxidized to iodate, by the method of Evans, et al.[2] From the reactor the reaction products were pumped through a Dry Ice trap and 4 liquid nitrogen traps where the condensable products were collected for analysis by mass spectrometer. Helium and non-condensable gases were removed by a vacuum pump controlled by a manometer to produce the desired pressure in the range of 6.2 to 8.7 mm. Flow rates of helium and methyl bromide were controlled by very small jets operating at sonic velocity. Prior to an experiment the system was evacuated with diffusion pumps to less than 10^{-5} mm.

Materials.—Helium was obtained from the Mathieson Chemical Company and was stated to be of 99.9% purity. Any traces of oxygen present were removed by adsorption on activated carbon at liquid nitrogen temperatures. The methyl bromide, obtained from the Mathieson Company was used directly. Its purity was stated to be 99.4%. The isopropyl iodide used was a mid boiling point fraction (89.2°) from a distillation of "Eastman Grade" isopropyl iodide.

In the initial experiments, iodine was introduced into the reactor section to determine the relative concentration of methyl radicals available for reaction. (Zero activation energy was assumed for the reaction between methyl radicals and molecular iodine.) The resulting methyl iodide was determined by mass spectrometric analyses of the condensed product. The first two columns in the table summarize the calibration runs. In the remainder of the experiments the reactor was loosely packed with silver gauze and isopropyl iodide was brought into the reactor in place of iodine.

the detection of iodine in the system. The rate constants reported in the preceding reference were determined over an interval of 400–490° and result in an unreasonably low activational energy, which the authors attribute to recombination at the higher temperatures. However, this factor should not greatly affect the present comparison.

On the basis of the simple collision theory, it is estimated that the methyl concentrations and reaction times employed were sufficient for the detection of the displacement reaction only if the corresponding activational energy does not exceed 10 to 15 kcal. From the very meager indications of displacements (0.05–1.5% of the methyl radicals entering the reactor) it is concluded only that appreciable displacement does not occur in the homogeneous phase or on the silver surface at these temperatures. Small amounts of methyl iodide were found in the products of reaction which might have been formed by the reaction of methyl radicals and iodine atoms or by extraction from the isopropyl iodide. With the primary methyl radical it appears that the expected extraction (of hydrogen and perhaps iodine) reactions predominated over the displacement of iodine.

	Calibration		Displacement study			
Reactor temp., °C.	304	304	304	304	327	326
Helium circulated:						
Total, moles/sec. × 10⁴	3.12	3.25	3.28	3.32	3.40	3.23
Over sodium, moles/sec. × 10⁴	0.49	0.49	0.49	0.49	0.49	0.49
Partial pressures, mm.:						
Methyl bromide	.08	.09	.09	.06	.06	.05
Sodium	.03	.06	.03	.03	.03	.03
Iodine	.02	.03	0	0	0	0
Isopropyl iodide	0	0	0.04	0.17	0.36	0.22
Mmoles charged:						
Methyl bromine	28.2	24.1	52.9	34.9	19.2	23.2
Sodium	12.4	19.6	14.9	14.5	9.1	11.2
Iodine	6.6	6.9	0	0	0	0
Isopropyl iodide	0	0	31.7	121.3	141.7	128.0
Yield of methyl radicals:						
Mmoles to reactor	0.17	0.18	0.36[a]	0.36[a]	0.20[a]	0.29[a]
Mole % of sodium charge	2.5	2.6	....	....	.....	....
Methyl iodide recovered, mmoles	0.17	0.18	0.06	Trace	0.02	....
Mmoles I deposited on silver wire	.....	...	0.0047	0.0055	0.0063	0.0079
% Displacement (after corrn. for thermal dec.)	.....	...	1.3	1.5	0.05	0.81
Duration of exp., sec.	10,800	9000	17,800	18,000	9900	14,400

[a] Based on first two calibration runs.

In the displacement study the amount of iodine deposited on the silver gauze was considered to be a measure of the displacement reaction after correction for thermal effects based on "blank runs" with isopropyl iodide in the presence of the silver gauze. At 304° the thermal decomposition of the iodide was negligible, but at 327° the decomposition proceeded to an extent equivalent to 1.4% of the methyl radicals reaching the reactor section. At much higher temperatures (385°) the formation of iodine was 16-fold that predicted from the velocity constants of Butler, Mandell and Polanyi[3]; thus, the silver gauze appeared quite effective for

(2) R. M. Evans, W. F. Hanson, Jr., and P. K. Glasoe, Ind. Eng. Chem., Anal. Ed., 14, 314 (1942).

(3) E. T. Butler, Erna Mandell and M. Polanyi, Trans. Faraday Soc., 41, 298 (1945).

Perfluorinated Alkene, Alkyne and Cycloalkene

BY ALBERT L. HENNE AND KAZI ABDUL LATIF

The synthesis of perfluoro-2-butene, $CF_3-CF=CFCF_3$ and of perfluorocyclopentene,