The carbon tetrachloride layer was separated and the solvent was removed by distillation at room temperature under reduced pressure. The gummy residue was dissolved in hot alcohol and cooled. By diluting with more alcohol a gummy precipitate formed. This was removed and the solution concentrated and allowed to stand in the refrigerator. After standing several weeks about 0.5 g. of needles of 2-hydroxy-4′,5-dimethylbenzophenone formed, which after recrystallization from alcohol melted at 88–90° and a mixed melting point with a known sample prepared as described above showed no depression. No other definite products could be isolated from the mother liquor.

Summary

Treatment of 2-phenyl-4-*p*-tolyl-6-methylcoumarin with phenylmagnesium bromide yielded a substituted pyranol-2 which was converted to 6-methyl-3-phenyl-4-(*p*-tolyl)-flavylium perchlorate, ferrichloride and chloride-hydrochloride. These same salts were also obtained from 2,3-diphenyl-4-(*p*-tolyl)-6-methyl-1,4-benzopyran-4-ol which was synthesized by the reaction between *p*-tolylmagnesium bromide and 6-methyl-2,3-diphenylchromone.

This formation of identical flavylium salts from a pyranol-2 and a pyranol-4 constitutes additional evidence in favor of the viewpoint that the flavylium salts contain a mobile allylic system.

URBANA, ILLINOIS RECEIVED MARCH 21, 1941

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE INSTITUTE OF TECHNOLOGY OF THE UNIVERSITY OF MINNESOTA]

The Preparation and the Vapor Pressures of Cyclobutene and Cyclobutane*

BY G. B. HEISIG

Cyclobutene and cyclobutane have been prepared by the following series of reactions: (1) cyclobutanedicarboxylic ethyl ester from trimethylene bromide, ethyl malonate and sodium ethylate by the Perkin reaction, yield 25%[1]; (2) cyclobutane dicarboxylic acid from the ester, yield 25%[2]; (3) cyclobutane carboxylic acid by the decarboxylization of the dicarboxylic acid, yield 92%[3]; (4) acid chloride of the monocarboxylic acid by treatment with thionyl chloride, yield 84.7%[4]; (5) acid amide by the action of ammonia, yield 79%[2]; (6) cyclobutylamine by the Hoffman rearrangement of the acid amide, 22%[2]; (7) trimethylcyclobutylammonium iodide, yield 85%[5]; (8) trimethylcyclobutylammonium hydroxide, degradation to cyclobutene and butadiene, bromination, removal of the butadiene as tetramethyldiaminobutene, and distillation of the 1,2-dibromocyclobutene, yield 48%[5]; (9) cyclobutene, yield 85%[5]; (10) cyclobutane 100%.[5]

The small over-all yield (9.9%) is due largely to the low yields of cyclobutane dicarboxylic ester and to the difficulty in obtaining the amine from cyclobutane carboxylic acid.

Efforts to improve the yield of the dicarboxylic ester by changing the rate of the addition of the reagents, the temperature, the length of time of standing after mixing the reagents, and the rate of agitation were unsuccessful. It was found simpler to saponify the malonic and cyclobutyl dicarboxylic ethyl esters and to separate the malonic and cyclobutyl dicarboxylic acids by precipitating barium malonate according to the method of Sugden and Wilkens than to follow the directions of Perkin. The yield (23%) of pure acid was eventually the same in either case.[6]

A six-fold increase in the yield of amine from the monocarboxylic acid was obtained by carrying out a modified Curtius rearrangement according to the general method described by von Braun and modified by Oesterlin.[7]

To 28.4 g. of the monocarboxylic acid (0.284 mole) in a 500-cc. distilling flask were added 200 cc. of chloroform, 50 cc. of concd. sulfuric acid, and solid sodium azide (0.31 mole) in such portions as to maintain the mixture at 40–50°. After standing for two days at room temperature, water was added, and the aqueous layer was boiled to remove the chloroform. An aqueous solution containing 160 g. of potassium hydroxide was then added to render the solution alkaline, and the amine was distilled into 50 cc. of concd. hydrochloric acid. On evaporating the concentrated

---

* Original manuscript received February 16, 1939.

[1] Perkin, *J. Chem. Soc.*, **51**, 1-28 (1887).

[2] Böeseken, *Rec. trav. chim.*, **37**, 261 (1919).

[3] Zelinsky and Cutt, *Ber.*, **40**, 4744 (1907).

[4] Perkin and Sinclair, *J. Chem. Soc.*, **61**, 41 (1892).

[5] Willstätter and Bruce, *Ber.*, **40**, 3979 (1907).

[6] Sugden and Wilkens, *J. Chem. Soc.*, 146 (1927).

[7] Von Braun, *Ann.*, **490**, 125 (1931); Oesterlin, *Angew. Chem.*, **45**, 536 (1932).

hydrochloric acid, white crystals of the hydrochloride were obtained. The dried product weighed 29.09 g., corresponding to a yield of 95%. A total yield of 92% of amine hydrochloride was obtained from 0.883 mole of the acid, compared with a yield of 14.7% of the amine obtained by the other workers.

An attempt to shorten the time required to prepare trimethylcyclobutylammonium iodide by methylating the amine with dimethyl sulfate gave the same yield of an inferior product.

Preparation of Pure Cyclobutene.—The pure dibromide (70 g.) prepared as described by Willstätter and Bruce[5] was dissolved in an equal volume of ethanol, dropped slowly into a boiling mixture of 75 g. of zinc dust and 35 cc. of ethanol, and agitated with a mechanical stirrer fitted with a mercury seal. The effluent gases were passed successively through a reflux condenser (Allihn), drying tube filled with calcium chloride into a trap immersed in liquid air. The gas was collected in an evacuated sphere fitted with a breaking device. The yield was very nearly quantitative (96%). The remainder of the cyclobutene was used for the preparation of cyclobutane.

Purification of Cyclobutene.—After drying the cyclobutene with sodium (−80°), the sample was distilled three times from a trap at −182°. Only the middle portion was taken in each case. The vapor pressure was then determined at −36.4° and −5.1°. After three further distillations, the vapor pressures of the sample checked those previously obtained at the same temperatures, and the vapor pressures of the low, middle and high boiling fractions were identical at the same temperature. A portion of this sample was used to determine the vapor pressure at various temperatures.

Purification of Cyclobutane.—The sphere containing the cyclobutane prepared by the reduction of cyclobutene was sealed to the apparatus, and the contents transferred to an evacuated trap containing bright sodium. Cyclobutane was dried over the sodium at the temperature of melting ice for four days. After several distillations from a temperature of −80 to −182°, the gas was distilled in a Podbielniak precision still. A small amount of butane, due undoubtedly to the use of an excess of hydrogen in the reduction, was removed. The sample dried by passing through phosphorus pentoxide freed from the trioxide was distilled repeatedly until the vapor pressure of all fractions was the same at 0° and at the sublimation point of carbon dioxide. Portions were used for the determination of the vapor pressure and the action with radon.

Vapor Pressures of Cyclobutene and Cyclobutane.—The vapor pressures of these gases were determined using the apparatus and method previously described.[8] The calculated and observed values are found in Tables I and II.

TABLE I

VAPOR PRESSURES OF CYCLOBUTENE AT VARIOUS TEMPERATURES

t_c	Mm. Hg Exptl. at 0°	Mm. Hg Calcd. at 0°
−77.1	8.7	9.0
−62.9	26.5	26.5
−55.0	44.5	44.3
−46.8	74.0	72.6
−37.7	120.9	120.7
−30.7	175.2	174.0
−17.9	322.2	321.8
−13.0	404.0	400.7
− 5.1	564.6	561.8
− 2.1	635.9	635.2
− 0.2	685.7	685.7
+ 1.9	742.1	745.0
2.4		760.0

$$\log P_{\text{mm.}} = 7.5728 - (1292.7/T)$$

TABLE II

VAPOR PRESSURE OF CYCLOBUTANE AT VARIOUS TEMPERATURES

T_v	Mm. Hg at 0° Exptl.	Mm. Hg at 0° Calcd.
−74.4	6.1	7.0
−70.92	8.1	9.1
−57.66	21.2	23.1
−50.42	34.8	36.8
−37.5	78.1	78.1
−28.44	126.3	126.6
−18.7	205.1	204.0
− 9.74	309.6	307.6
− 0.72	454.4	451.5
+ 4.2	553.4	550.7
8.09	643.0	641.3
9.76	685.1	685.0
13.08	774.0	776.0

$$\log_{10} P = 7.5330 - (1328.9/T)$$

Acknowledgment is made of financial aid from the Graduate School in carrying out this work.

Summary

The synthesis of cyclobutane as originally carried out by Willstätter and his co-workers has been simplified by eliminating the preparation of the acid chloride of cyclobutylcarboxylic acid, its acid amide and the Hoffman rearrangement, thereby increasing the yields three-fold. Attempts to improve the yield of ethyl cyclobutyldicarboxylic ester were unsuccessful. The vapor pressures of cyclobutene and cyclobutane were determined and fitted to an equation.

MINNEAPOLIS, MINN. RECEIVED APRIL 21, 1941

---

[8] Heisig, THIS JOURNAL, **55**, 2311 (1933).