After removal of the solvent, the residue crystallized. The crude product was dissolved in 8 ml of ethyl acetate and filtered, and the filtrate was diluted with 10 ml of hexane. On standing, 0.8 g of product separated: mp 85°, R_f 0.88.

Anal. Calcd for $C_{17}H_{18}N_2O_4$: C, 64.95; H, 5.77; N, 8.91. Found: C, 65.12; H, 5.93; N, 8.98.

A sample of this compound was hydrolyzed in 6 *N* hydrochloric acid by heating for 16 hr at 110°, and the hydrolysate was chromatographed. Only two spots (R_f 0.13 and 0.45), corresponding to those for glycine and 3-hydroxypicolinic acid, respectively, could be detected.

3-Hydroxypicolinylglycine Ethyl Ester.—Hydrogen gas was bubbled through a solution of 314 mg (1 mmole) of 3-benzyloxypicolinylglycine ethyl ester dissolved in 10 ml of 50% ethanol containing 100 mg of 5% palladium on charcoal for 4 hr while stirring at room temperature. The catalyst was removed by filtration and washed with ethanol. The filtrate and washing were combined and concentrated under vacuum; the residue obtained crystallized. It was dissolved in 2 ml of ethyl acetate and a small amount of insoluble material was removed by centrifugation, after which the solution was diluted with 20 ml of hexane. A yield of 120 mg of a pure product melting at 90–91° was obtained.

Anal. Calcd for $C_{10}H_{12}N_2O_4$: C, 53.57; H, 5.39. Found: C, 53.82; H, 5.60.

A sample of this product, when chromatographed, showed a single spot strongly fluorescent under ultraviolet light that gives a positive reaction with ferric chloride solution. It had a R_f 0.9.

Acknowledgment.—The author wishes to express his thanks to Dr. Miklos Bodanszky for advice and interest in this work.

A Simple Synthesis of Cyclopropene[1]

G. L. Closs[2] and K. D. Krantz

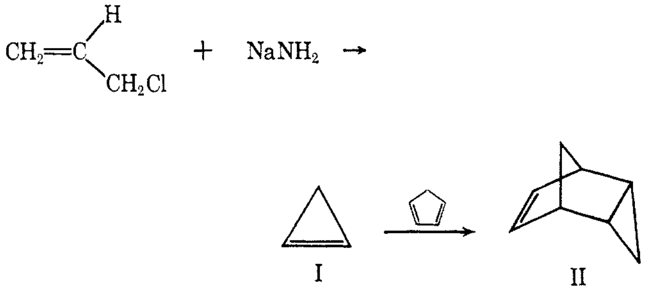
Department of Chemistry,
The University of Chicago,
Chicago, Illinois 60637

Received October 26, 1965

Recently in our laboratory the need arose to prepare a sample of cyclopropene (I). Since the known synthesis of this hydrocarbon is extremely laborious,[3] we were tempted to extend the method of Fisher and Applequist,[4] who recently prepared 1-methylcyclopropene from methallyl chloride and sodium amide in tetrahydrofuran.

It was found that I is indeed obtained when allyl chloride is added dropwise to a suspension of sodium amide under conditions where the unstable hydrocarbon can readily escape the reaction mixture. Cyclopropene was identified by its nmr spectrum[5] and its Diels–Alder reaction with cyclopentadiene at 0°, resulting in the formation of the tricyclic hydrocarbon II.[6] Although the yield of I did not exceed 10% under a variety of reaction conditions tried, the simplicity of the procedure and the ready availability of the starting materials make this reaction a practical synthesis, superior to the older method. No detailed study of the other reaction products has been made, but it appears that the main product is allylamine.

As has been pointed out before,[4] the mechanism of the reaction is probably closely related to that of several previously described reactions in which vinylcarbenes were shown to cyclize to cyclopropene derivatives.[7]



Experimental Section

A three-neck flask (100–150 ml) was equipped with magnetic stirrer, addition funnel, nitrogen inlet capillary, and a jacketed column (condenser, ~20 in.) filled with glass helixes. The column was cooled with circulating ice–water. Connected to the column was a small gas wash flask filled with 2 *N* sulfuric acid. The wash flask was connected with a trap held at liquid nitrogen temperature. Because of the instability of cyclopropene it was found advantageous to keep the dead volume of the system to a minimum, allowing the product to reach the trap in a minimum time.

The flask was charged with commercial sodium amide (Fisher, 12 g, 0.3 mole) and mineral oil (20 ml) and was heated to 80°. To the stirred suspension was added dropwise allyl chloride (23 g, 0.3 mole) diluted with mineral oil (15 ml). A steady stream of gas evolved from the reaction mixture. After addition was complete (2–4 hr) and the gas evolution became slower, a slow rate of nitrogen was passed through the system to sweep the product into the trap. Heating was continued for another 2 hr. The cyclopropene collected in the trap was contaminated with allyl chloride (this contamination increases when nitrogen is passed too fast through the system). Purification of the product can be accomplished by vapor phase chromatography as described previously.[6] The use of other solvents, such as tetrahydrofuran or dimethoxydiethylene glycol, did not improve the yield and the product was found to be less pure.

In another experiment the sulfuric acid washing flask was eliminated and the gas stream was directly led into a solution of cyclopentadiene (6.6 g, 0.1 mole) in *n*-pentane (40 ml) held at 0°. After completion of the reaction the solvent was removed and distillation of the remainder afforded pure tricyclooctene (II) (3.2 g, 10%), mp 30–31° (lit.[6] mp 30–32°). The nmr spectrum of II was identical with that reported.[6]

Acknowledgment.—We are indebted to Dr. Applequist for making his results available to us before publication.

---

[1] Supported by National Science Foundation Grant GP-4214.

[2] A. P. Sloan Foundation Fellow, 1962–1966.

[3] N. Y. Dem'yanov and M. N. Doyarenko, *Chem. Ber.*, **56**, 2002 (1923); M. J. Schlatter, *J. Am. Chem. Soc.*, **63**, 1733 (1941).

[4] F. Fisher and D. E. Applequist, *J. Org. Chem.*, **30**, 2089 (1965).

[5] K. B. Wiberg and B. J. Nist, *J. Am. Chem. Soc.*, **83**, 1226 (1961).

[6] K. B. Wiberg and W. J. Bartley, *ibid.*, **82**, 6375 (1960).

[7] G. L. Closs and L. E. Closs, *ibid.*, **83**, 1003, 2015 (1961); **85**, 99 (1963); G. L. Closs, L. E. Closs, and W. A. Böll, *ibid.*, **85**, 3796 (1963).