Anal. Calcd. for $C_9H_8N_2O$: C, 67.48; H, 5.03; N, 17.49. Found: C, 67.65; H, 5.17; N, 17.66.

1-Aminocarbostyril was heated under reflux overnight with 1 *N* sodium hydroxide or 10% potassium hydroxide in 95% ethyl alcohol and was recovered unchanged.

Sodium 2-[2-(2-Carboxyvinyl)-phenyl]-hydrazinosulfonate (IV) and Dilute Sodium Hydroxide.—A solution of 1.4 g. (0.005 mole) of IV and 100 ml. of 0.1 *N* sodium hydroxide was refluxed under a nitrogen atmosphere for 2 hours. After cooling, 2 ml. of acetic acid and 1 ml. of 6 *N* hydrochloric were added, and the solution was then concentrated to 25 ml. by heating under reduced pressure. On cooling, 0.2 g. of *trans*-cinnamic acid was removed by filtration. The filtrate was concentrated to dryness, and the residue was recrystallized from ethyl alcohol–ether to give a small yield of 3-indazoleacetic acid hydrochloride.

Sodium 2-(4-Benzyloxyphenyl)-hydrazinosulfonate and Dilute Sodium Hydroxide.—A solution of 1.5 g. (0.005 mole) of sodium 4-benzyloxy-2-phenylhydrazinosulfonate[11] and 100 ml. of 0.1 *N* sodium hydroxide was heated under reflux for 3 hours. After cooling, the solution was extracted with ether. The ether extract was then extracted with dilute hydrochloric acid. The ether layer was washed with water and dried with anhydrous magnesium sulfate. After evaporation of the ether, about 300 mg. of benzylphenyl ether was obtained. The acidic extract was concentrated to dryness, and the residue recrystallized from ethyl alcohol–ether mixture to give about 50 mg. of 4-benzyloxyphenylhydrazine hydrochloride.

(11) Prepared by H. L. Breunig of this laboratory according to the general procedure of J. Altschul, *Ber.*, **25**, 1842 (1892), m.p. 335°.

INDIANAPOLIS 6, INDIANA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF KANSAS]

Studies on Allylpyrroles and Related Pyrrole Derivatives[1]

BY PAUL A. CANTOR AND CALVIN A. VANDERWERF

RECEIVED JUNE 17, 1957

Contrary to the generally accepted principle that alkylation of alkali metal salts of pyrrole occurs at the 1-position and alkylation of pyrrylmagnesium halides at the 2-position, both pyrrylpotassium and pyrrylmagnesium bromide yield predominantly 2-allylpyrrole in reaction with allyl bromide. The obvious explanation that, in the reaction of pyrrylpotassium with allyl bromide, the initial product is 1-allylpyrrole, which then undergoes a Claisen type rearrangement to 2-allylpyrrole, appears to be substantiated by the fact that reaction of propargyl bromide with pyrrylpotassium yields 1-propargylpyrrole, in which spatial features are less favorable for rearrangement. On the other hand, this explanation is vitiated by the facts (1) that reaction of pyrrylpotassium with crotyl bromide gives the product with an unrearranged side chain, 2-crotylpyrrole, and (2) that authentic 1-allylpyrrole, formed by pyrolysis of 3-(1-pyrryl)-propyl acetate, cannot be made to rearrange under the conditions of the synthesis of 2-allylpyrrole.

Studies on Allylpyrroles and Related Pyrrole Derivatives

Over the years, it has come to be a generally accepted principle of pyrrole chemistry that alkylation of an alkali metal salt of pyrrole produces the corresponding 1-alkylpyrrole, whereas similar reaction of a pyrrylmagnesium halide[2] forms a 2-alkylpyrrole or a mixture of 2- and 3-alkyl derivatives. This generalization has, in fact, become a guiding principle in the assignment of structure of alkylpyrroles; it was largely on this basis that Ciamician and Dennstedt[3] named the product they obtained by reaction of pyrrylpotassium with allyl bromide in ether as 1-allylpyrrole, and Hess[4] reported 2-allylpyrrole as the product of the reaction between pyrrylmagnesium bromide and allyl bromide in ether solution.

Our early studies indicated, however, that the two products were identical; this apparent discrepancy in the literature, together with the interesting possibilities for rearrangement of 1-allylpyrrole, prompted us to undertake an investigation of the 1-allylpyrroles and related pyrrole derivatives.

(1) This investigation was performed as a part of American Petroleum Institute Research Project 52 on "Nitrogen Constituents of Petroleum," which is conducted at the University of Kansas in Lawrence, Kan., and at the Bureau of Mines Experiment Stations in Laramie, Wyo., and Bartlesville, Okla.

(2) This term is meant to apply to the type of product obtained by reaction between a Grignard reagent such as ethylmagnesium bromide and pyrrole, with no suggestion as to specific structure, which is still a matter of controversy. See M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall, Inc., New York, N. Y., 1954, pp. 75–80, for a review of the problem; and W. Herz, *J. Org. Chem.*, **22**, 1260 (1957), for proof of the nature of the reaction of 1-alkylpyrroles with acyl halides in the presence of a Grignard reagent.

(3) G. L. Ciamician and M. Dennstedt, *Ber.*, **15**, 2581 (1882).

(4) K. Hess, *ibid.*, **46**, 3125 (1913).

Results

Following are the salient results of the investigation: (1) The major product obtained by reaction of pyrrylpotassium with allyl bromide[3] was shown to be identical with that obtained by reaction of pyrrylmagnesium bromide with allyl bromide; this compound was assigned the structure 2-allylpyrrole on the basis of: (a) presence of a strong infrared absorption band in the region 3400 cm.$^{-1}$, characteristic of a free N–H group; (b) partial catalytic hydrogenation to a propylpyrrole which differed from authentic 1-propylpyrrole and was identical with 2-propylpyrrole, prepared by reaction of pyrrylmagnesium bromide with *n*-propyl bromide;[5] and (c) complete catalytic hydrogenation in acetic acid with platinic oxide catalyst to 2-propylpyrrolidine, the melting point of whose benzenesulfonamide corresponded to that reported[6] for the benzenesulfonamide of 2-propylpyrrolidine.

(2) The new compound 1-allylpyrrole was synthesized by pyrolysis of 3-(1-pyrryl)-propyl acetate, obtained by reaction of pyrrylpotassium with 3-bromopropyl acetate.[7] Its structure was proved by catalytic hydrogenation to the known 1-propylpyrrole.

(3) Reaction of pyrrylpotassium with propargyl

(5) M. Dennstedt, *ibid.*, **25**, 3636 (1892).

(6) R. Lukeš, F. Šorm and Z. Arnold, *Collection Czechoslov. Chem. Communs.*, **12**, 641 (1947).

(7) F. F. Blicke and E. S. Blake, THIS JOURNAL, **53**, 1015 (1931).

bromide afforded as the only isolable product 1-propargylpyrrole, which could be hydrogenated catalytically, under carefully controlled conditions, to 1-allylpyrrole and, further, to 1-propylpyrrole.

(4) Reaction of pyrrylpotassium with crotyl bromide afforded as the only isolable product 2-crotylpyrrole [1-(2-pyrryl)-2-butene]. The structure was proved (a) by catalytic hydrogenation first to a butylpyrrole, identical with a sample of 2-butylpyrrole, prepared by reaction of pyrrylmagnesium bromide with *n*-butyl bromide, and then to a 2-butylpyrrolidine, identical with a sample prepared by catalytic hydrogenation of 2-butylpyrrole; and (b) by carefully controlled ozonolysis according to the method of Wibaut and Guljé[8] with isolation of 3-pentenoic acid.

(5) Treatment of 1-allylpyrrole under environmental conditions simulating those which obtained in the synthesis of 2-allylpyrrole by reaction of pyrrylpotassium with allyl bromide afforded no trace of 2-allylpyrrole.

Discussion of Results

Much of the latter part of the present investigation was undertaken in an attempt to shed some light on the unique behavior of allylic type bromides in affording predominantly 2-substituted pyrrole derivatives upon reaction with pyrrylpotassium under conditions identical with those which for saturated alkyl and propargyl bromides give almost exclusively 1-alkylation. On the basis of the present results, this behavior is still unexplained.

The obvious assumption is, of course, that the reaction of allylic bromides with pyrrylpotassium proceeds first in the usual manner to afford a 1-substituted product, followed by a Cope or Claisen type rearrangement of the 1-allylic derivative to yield the final 2-substituted product. This explanation is given credence by the fact that reaction of pyrrylpotassium with propargyl bromide, which would produce an initial product, 1-propargylpyrrole, wherein the rearrangement to the 2-derivative would be unfavorable sterically, does indeed yield 1-propargylpyrrole as the only isolable product.[9] It is however, rendered untenable by the facts that the product (2-crotylpyrrole) of the reaction of pyrrylpotassium with crotyl bromide bears the unrearranged side chain and that authentic 1-allylpyrrole cannot be induced to rearrange under the conditions employed in the synthesis of 2-allylpyrrole.

If pyrrylpotassium may be formulated as an ionic, though not necessarily highly dissociated compound, then the resonant anion might be regarded as a special type of ambident ion. The reaction of allyl bromide with pyrrylpotassium should possess greater SN1 character than the corresponding reaction for *n*-propyl bromide[10] (although it would be expected to be slight for either halide in this reaction), and in such a case Kornblum's[11] principle would predict, therefore, that the percentage of attack at the nitrogen (1-position) should be greater for allyl bromide than for *n*-propyl bromide. This prediction is contrary to the observed results.

Experiments designed to test other possible explanations for the anomalous behavior of allyl-type halides in reaction with pyrrylpotassium are in progress in our laboratories.

Experimental[12]

Ciamician's Allylpyrrole.—This compound was prepared exactly as described[3] except that the reaction was run in an atmosphere of nitrogen. From 39.0 g. (1.00 mole) of potassium, 121 g. (1.00 mole) of allyl bromide and 300 ml. of pyrrole, 32 g. (30%) of pure 2-allylpyrrole (Ia), b.p. 83–84° (24 mm.), 97–98° (40 mm.), 105–106° (48 mm.), $n^{30}D$ 1.5112, was obtained upon careful fractional distillation of the reaction product. The infrared spectrum of the pure compound showed a strong absorption peak at 3400 cm.$^{-1}$. Under no conditions was it possible to avoid formation of a considerable amount of tarry material, perhaps polymerized allylpyrroles, which remained in the flask after distillation of the crude reaction mixture. Total loss of 2-allylpyrrole should, however, be expected to be greater than that of 1-allylpyrrole, as all observations point to the fact that the former is much more readily polymerized than the latter.

This reaction was repeated with 0.75-mole quantities of pyrrylpotassium and of allyl bromide. The entire oil layer isolated from the reaction mixture was dried and then hydrogenated catalytically in a Parr apparatus under a pressure of 3 atm. of hydrogen in the presence of 100 mg. of platinic oxide. Careful fractional distillation of the hydrogenated material, after removal of catalyst and solvent, yielded 0.42 mole (56%) of 2-propylpyrrole, b.p. 178–179° (740 mm.), and 0.072 mole (9.6%) of 1-propylpyrrole, b.p. 148–149° (740 mm.). The actual ratio of 2- to 1-alkylation in the reaction is therefore approximately 6:1. These results were essentially unchanged whether the reaction was run in ether, toluene or an excess of pyrrole.

Hess' Allylpyrrole.—Reaction of one-mole quantities of pyrrylmagnesium bromide and allyl bromide according to the method of Hess[4] afforded 20 g. (19%) of 2-allylpyrrole (Ib), b.p. 82–83° (24 mm.), 97–98° (40 mm.), 104–105° (48 mm.), $n^{30}D$ 1.5110. Considerable tarry residue remained in the distillation flask, but no other product could be isolated. The infrared spectrum of the 2-allylpyrrole (Ib) was identical to that of the 2-allylpyrrole (Ia) obtained by the method of Ciamician.[3]

Partial Hydrogenation of 2-Allylpyrrole.—A solution of 21 g. (0.20 mole) of Ia in 100 ml. of ether with 100 mg. of suspended platinic oxide was shaken under hydrogen pressure of 3 atm. in a standard Parr low-pressure hydrogenation apparatus until 0.20 mole of hydrogen had been absorbed. After removal of the catalyst and the solvent, the residue was distilled under vacuum to yield 17 g. (81%) of pure 2-propylpyrrole (IIa), b.p. 92–93° (23 mm.), 179–180° (749 mm.), $n^{30}D$ 1.4873. The infrared spectrum of the IIa was identical to that of a sample of 2-propylpyrrole obtained by reaction of *n*-propyl bromide with pyrrylmagnesium bromide.[5]

Anal. Calcd. for $C_7H_{11}N$: C, 77.0; H, 10.2; N, 12.8. Found: C, 77.2; H, 10.0; N, 13.0.

Similar catalytic hydrogenation of 14 g. (0.12 mole) of Ib yielded 11 g. (80%) of 2-propylpyrrole (IIb), b.p. 91–92° (23 mm.), 179–180° (749 mm.), $n^{27}D$ 1.4871. The infrared spectrum of IIb was identical to those of IIa and of the synthetic sample of 2-propylpyrrole.

Anal. Calcd. for $C_7H_{11}N$: C, 77.0; H, 10.2; N, 12.8. Found: C, 77.0; H, 10.0; N, 12.7.

2-Propylpyrrolidine.—A solution of 11 g. (0.1 mole) of

(8) J. P. Wibaut and J. Guljé, *Proc. Koninkl. Nederland. Akad. Wetenschap.*, **54B**, 330 (1951).

(9) The fact that phenyl propargyl ethers do not rearrange as do the phenyl allyl ethers is well established; see S. G. Powell and R. Adams THIS JOURNAL, **42**, 646 (1920), and C. D. Hurd and F. L. Cohen, *ibid.*, **53**, 1068 (1931).

(10) The ratio of the unimolecular reactivity of allyl chloride to that of *n*-propyl chloride is at least significantly greater than the ratio of the bimolecular reactivity of allyl chloride to that of *n*-propyl chloride; see C. A. Vernon, *J. Chem. Soc.*, 423 (1954).

(11) See N. Kornblum, R. A. Smiley, R. K. Blackwood and D. C. Iffland, THIS JOURNAL, **77**, 6269 (1955).

(12) Boiling points and melting points are uncorrected. Infrared spectra were determined with a Perkin–Elmer model 21 double beam spectrophotometer in 0.025-mm. sodium chloride cells. Microanalyses by Schwarzkopf Microanalytic Laboratory.

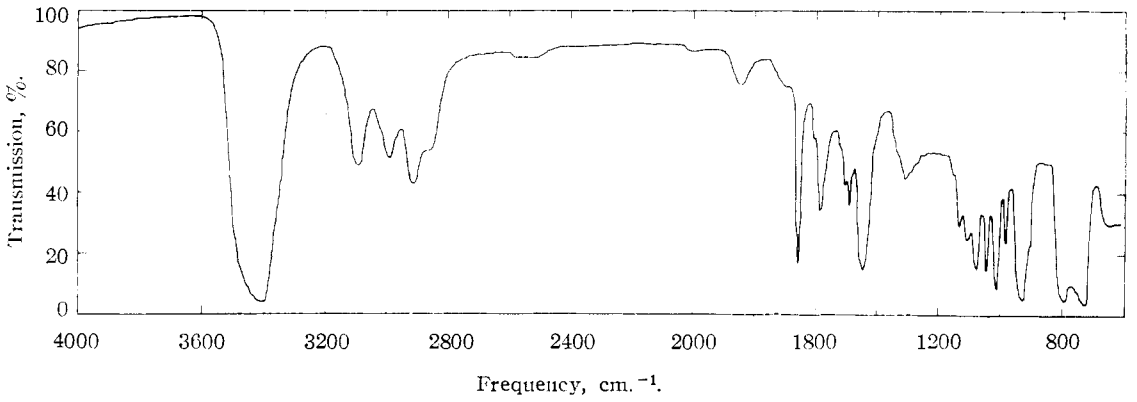

Fig. 1.—Infrared spectrum of 2-allylpyrrole.

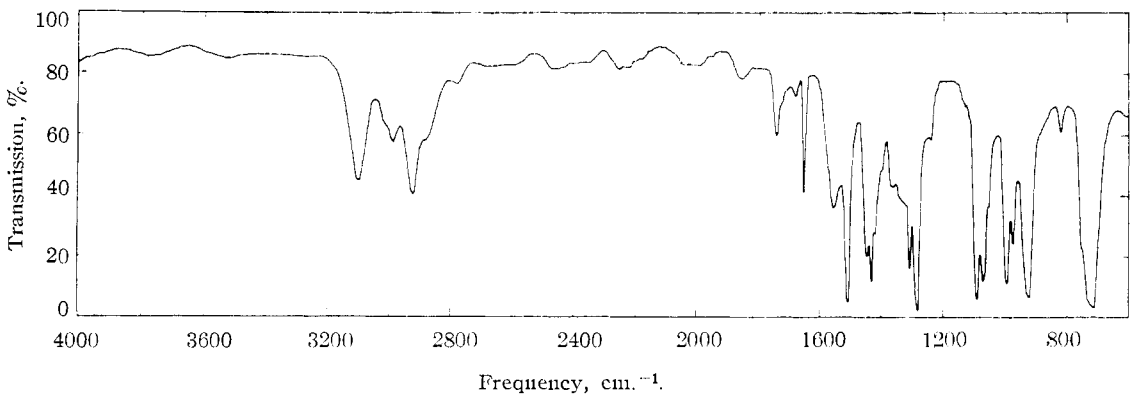

Fig. 2.—Infrared spectrum of 1-allylpyrrole.

IIa in 50 ml. of glacial acetic acid, with 800 mg. of suspended platinic oxide, was shaken under a hydrogen pressure of 3 atm. in a standard Parr hydrogenation apparatus. After 5 hours, hydrogen absorption stopped with a total addition of 0.18 mole. After removal of the catalyst by filtration, 50 ml. of concentrated hydrochloric acid was added to the filtrate and the resulting solution was concentrated to 35 ml. on a steam-bath. Cautious addition of 100 ml. of 50% aqueous potassium hydroxide brought about the separation of a dark red oil which was isolated by decantation, taken up in ether, and the ether solution dried over anhydrous magnesium sulfate. The ether was removed and the residue was distilled to give 9.0 g. (81%) of 2-propylpyrrolidine (IIIa), b.p. 145–146° (739 mm.), $n^{28}D$ 1.4473, m.p. of benzenesulfonamide 67.0–68.2° (lit.[6] 68.5°). Similar treatment of 10.7 g. of IIb afforded 8.8 g. (80%) of 2-propylpyrrolidine (IIIb), b.p. 144° (740 mm.), $n^{25}D$ 1.4478, m.p. of benzenesulfonamide 67.5°.

A mixture of the benzenesulfonamides of IIIa and IIIb melted at 67.1–68.2°.

1-Allylpyrrole.—A total of 60 g. of 3-(1-pyrryl)-propyl acetate, prepared by the method of Blicke and Blake,[7] was allowed to drop, at the rate of 5 g./hr., into a vertical 18″ long, 18-mm. diameter, quartz-chip-packed quartz column heated to 500–515°. The issuing vapor was condensed, the dark condensate taken up in ether, and the ether solution washed first with three 100-ml. portions of 10% sodium bicarbonate solution and then with two 100-ml. portions of water. It was then dried over anhydrous calcium sulfate and the ether removed. Distillation of the residue gave 15 g. (42%) of 1-allylpyrrole, b.p. 50° (22 mm.), 66° (48 mm.), $n^{30}D$ 1.4927. The infrared spectrum showed no absorption in the region 3300–3400 cm.$^{-1}$.

Anal. Calcd. for C_7H_9N: C, 78.5; H, 8.5; N, 13.1. Found: C, 78.6; H, 8.5; N, 13.0.

The absorption bands in the infrared spectra of pure 2-allylpyrrole and of 1-allylpyrrole are compared in Table I and the respective infrared spectra are shown in Figs. 1 and 2.

TABLE I

ABSORPTION BANDS IN INFRARED SPECTRA OF 2-ALLYLPYRROLE AND 1-ALLYLPYRROLE[a]

2-Allylpyrrole	1-Allylpyrrole	2-Allylpyrrole	1-Allylpyrrole	2-Allylpyrrole	1-Allylpyrrole
3400	..	1505	1510	1080	1090 }
3090	3100	1490	..		1070 }
2990	2990	1442	1443	1046	..
2910	2923		1429	1012	..
2855	2880	..	1363	984	995 }
1850	1860	1310	1305		975 }
1710	1740	1290	1280	930	925
1660	1680 }	1245	1240	905	..
	1650 }			795	820
1585	1555	1135	..	726	715
		1110	..	650	..

[a] Values are frequencies in cm.$^{-1}$.

Hydrogenation of 1-Allylpyrrole to 1-Propylpyrrole.—A solution of 5.4 g. (0.050 mole) of 1-allylpyrrole in 50 ml. of ether, with 50 mg. of suspended platinic oxide, was shaken with hydrogen at a pressure of 3 atm. in a standard Parr low pressure hydrogenation apparatus. Hydrogenation was complete in 10 minutes. The catalyst and ether were removed and the residue was distilled to give 4.0 g. (80%) of 1-propylpyrrole, b.p. 145–146.5° (740 mm.). The infrared spectrum of the product was identical with that of a synthetic sample of 1-propylpyrrole prepared by reaction of pyrrylpotassium with *n*-propyl bromide.[13]

1-Propargylpyrrole.—Pyrrylpotassium, prepared by addition of 30 g. (0.75 mole) of potassium to 280 ml. of pyrrole, was treated cautiously with 90 g. (0.75 mole) of propargyl bromide. The reaction mixture was refluxed for 1 hour, then decomposed with water. The oily layer which

(13) C. U. Zanetti, *Ber.*, **22**, 2515 (1889).

separated was taken up in ether and the ether solution dried over anhydrous calcium sulfate. After removal of the ether, the residue was distilled under reduced pressure to afford 20 g. (27%) of 1-propargylpyrrole, b.p. 70° (23 mm.), $n^{20}D$ 1.5095.

Anal. Calcd. for C_7H_7N: C, 80.0; H, 6.7; N, 13.3. Found: C, 80.0; H, 6.8; N, 13.2.

Hydrogenation of 1-Propargylpyrrole to 1-Allylpyrrole.—A solution of 10.0 g. (0.100 mole) of 1-propargylpyrrole in 50 ml. of ether, with 100 mg. of suspended platinic oxide, under a hydrogen pressure of 2 atm. was shaken in a standard Parr hydrogenation apparatus until 0.1 mole of hydrogen had been absorbed. The catalyst was removed by filtration and the ether by evaporation. Distillation of the residue under vacuum yielded 7 g. (60%) of 1-allylpyrrole, b.p. 49–50° (22 mm.), $n^{27}D$ 1.4950. The infrared spectrum of the product was identical with that of the 1-allylpyrrole prepared by pyrolysis of 3-(1-pyrryl)-propyl acetate.

2-Crotylpyrrole.—To a well-stirred, ice-cold solution of pyrrylpotassium, prepared from 40 g. (1.0 mole) of potassium and 268 g. (4.00 moles) of pyrrole, 102 g. (0.750 mole) of crotyl bromide was added dropwise. After addition was complete, the reaction mixture was refluxed for 1.5 hr., then cooled on an ice-bath and finally ice-cold water was added. The contents of the flask were transferred to a separatory funnel, the oil layer was removed and the water layer was extracted with an equal volume of ether. After drying of the combined extracts with magnesium sulfate, the ether was removed and the residue was distilled to give 55 g. (61%) of pure 2-crotylpyrrole, b.p. 90–92° (11 mm.), $n^{25}D$ 1.5088.

Anal. Calcd. for $C_8H_{11}N$: C, 79.2; H, 9.2; N, 11.6. Found: C, 79.2; H, 9.5; N, 11.5.

This reaction was repeated with 0.75-mole quantities of pyrrylpotassium and of crotyl bromide. The oil layer isolated from the reaction mixture was dried over magnesium sulfate and then hydrogenated catalytically in a Parr apparatus under a hydrogen pressure of 3 atm. in the presence of 100 mg. of platinic oxide. Careful fractional distillation of the residue, after removal of catalyst and solvent, yielded 0.45 mole (60%) of 2-butylpyrrole, b.p. 90–91° (25 mm.), and 0.057 mole (7.6%) of 1-butylpyrrole, b.p. 76–77° (24 mm.). The actual ratio of 2- to 1-alkylation in the reaction is therefore approximately 8:1.

Hydrogenation of 2-Crotylpyrrole to 2-Butylpyrrole.—Exactly 12.0 g. (0.1 mole) of 2-crotylpyrrole was dissolved in 50 ml. of ether, 100 mg. of platinic oxide was added and the suspension was shaken under a hydrogen pressure of 3 atm. until 0.1 mole of hydrogen had been absorbed (45 min.). The catalyst was filtered from the pale yellow solution and the solution was then dried over anhydrous calcium sulfate. Distillation of the ether-free residue yielded 11 g. (88%) of pure 2-butylpyrrole (IVa), b.p. 90–91° (24–25 mm.), $n^{28}D$ 1.4854. This product gave an infrared spectrum identical with that for a sample of 2-butylpyrrole (IVb) prepared by reaction of pyrrylmagnesium bromide with *n*-butyl bromide according to the general method of Hess.[4]

Hydrogenation of 2-Butylpyrrole to 2-Butylpyrrolidine.—Hydrogenation of 10 g. of IVa according to the procedure described for 2-propylpyrrole yielded 9.5 g. (94%) of 2-butylpyrrolidine, b.p. 170–171° (741 mm.), $n^{25}D$ 1.4479. Hydrogenation of IVb yielded the identical product.

Ozonolysis of 2-Crotylpyrrole.—A mixture of 5% ozone in oxygen was passed into a solution of 12.1 g. (0.10 mole) of 2-crotylpyrrole in 100 ml. of carefully purified methylene chloride at −60° until slightly more than 0.1 mole of ozone had been absorbed. Ozone absorption was complete during this period, with no ozone present in the exit gas.

The dark red solution containing the ozonide was warmed to 0°, transferred to an addition funnel equipped with a pressure equalizer and added cautiously, with stirring, to a solution of 22 g. (0.20 mole) of 30% hydrogen peroxide and 1 ml. of concentrated sulfuric acid in 100 ml. of distilled water. The methylene chloride was removed by distillation and the aqueous solution was refluxed for 15 minutes.

After being cooled to room temperature, the contents of the flask were extracted five times with a total of 1000 ml. of ether. The ether solution was extracted with 250 ml. of 10% aqueous sodium hydroxide. All the colored material was extracted into the aqueous layer during this operation.

After acidification with 10% sulfuric acid, the aqueous solution was re-extracted with 500 ml. of ether. The ether solution was dried and the ether removed under reduced pressure leaving a residue consisting of 1.5 g. of a liquid acid which formed a *p*-bromophenacyl ester, m.p. 86.1–87.3° (lit.[14] value for 3-pentenoic acid 87–88°) and an amide, m.p. 66.0–67.3° (lit.[14] 69–70°).

Attempted Rearrangement of 1-Allylpyrrole.—Rearrangement of 1-allylpyrrole was attempted as: (1) A mixture of 5 g. of potassium, 15 g. of 1-allylpyrrole and 250 ml. of toluene was refluxed for 4 hr. with stirring, then cooled, and cold water added cautiously. The oil layer was separated, the water layer extracted with an equal volume of ether, and the combined organic fractions were dried over anhydrous calcium sulfate. After removal of the ether, the residue was distilled under reduced pressure. (2) A mixture of 15 g. of potassium amide, 15 g. of 1-allylpyrrole and 100 ml. of benzene was treated as described for the mixture in (1). (3) A mixture of 15 g. of pyrrylpotassium, 5 g. of potassium bromide, 15 g. of 1-allylpyrrole and 100 ml. of benzene was treated as described for the mixture in (1).

In every case only 1-allylpyrrole was recovered; infrared spectra gave no evidence for the presence of any 2-allylpyrrole.

(14) K. V. Auwers, *Ann.*, **432**, 70 (1923).

LAWRENCE, KANSAS

[COMMUNICATION FROM THE B. F. GOODRICH RESEARCH CENTER]

The Synthesis and Reactions of Some Cyclic Imides[1]

BY C. M. HENDRY

RECEIVED AUGUST 20, 1957

The synthesis of simple five and six-membered cyclic imides through ring closure has been studied. A new catalyzed, low temperature ring closure was found and applied to the synthesis of 1,3-thiazanedione-2,4 and succinimide; these imides were prepared from β-thiocyanatopropionic acid and β-cyanopropionic acid, respectively. Some reactions of 1,3-thiazanedione-2,4 have been investigated. The previously reported acid-catalyzed, high temperature ring closure of β-cyanopropionic acid also was examined. β-Sulfopropionimide has been synthesized for the first time. The ease with which cyclic imides are formed depends upon the size and constitution of the ring.

The reaction of carboxylic acids with nitriles to form imides is a general reaction.[2] This reaction as well as the reaction of carboxyamides with carboxyl groups may be employed to synthesize succinimide[3] (III); this type of ring closure requires high temperature and mineral acid catalysis. Five-membered cyclic imides containing a sulfide linkage, such as thiazolidinedione-2,4 (I), are much more easily formed than the succinimide ring, by

(1) Paper presented before the Division of Organic Chemistry at the National Meeting of the American Chemical Society, April 11, 1957.

(2) F. C. Whitmore, "Organic Chemistry," D. Van Nostrand Co., Inc., New York, N. Y., 1937, p. 501.

(3) M. T. Bogert and D. C. Eccles, THIS JOURNAL, **24**, 20 (1902).