210° dec.; λ_{max} 253 mμ (log ε 3.65), 312 (3.73); pK'_a 7.0, 13.5 (66% dimethylformamide).

Anal. Calcd. for $C_9H_8N_2O_3$: C, 56.25; H, 4.20; N, 14.58. Found: C, 55.82; H, 4.33; N, 14.71.

2-Carbamylmethylindazole.—A solution of 20.4 g. (0.1 mole) of ethyl 2-indazoleacetate[5] dissolved in 50 ml. of methyl alcohol was added to 200 ml. of saturated ammoniacal methyl alcohol and allowed to stand at room temperature overnight. The solid that separated was collected and recrystallized from ethyl alcohol, m.p. 205°, λ_{max} 274 mμ (log ε 3.82); 6.5 g. (37%) yield.

Anal. Calcd. for $C_9H_9N_3O$: C, 61.70; H, 5.18; N, 23.99. Found: C, 61.66; H, 4.87; N, 24.24.

2-Cyanomethylindazole.—A solution of 8.8 g. (0.05 mole) of 2-carbamylmethylindazole, 9.5 g. (0.05 mole) of *p*-toluenesulfonyl chloride and 9 g. of pyridine was heated on a steam-bath for 0.5 hour. The solution was added to ice-water, and the solid that formed was washed with water and recrystallized from 50% aqueous ethyl alcohol. The solid (5 g.) that was deposited on cooling was air-dried and then recrystallized from ethyl acetate–petroleum ether to give 4 g. (50% yield) of 2-cyanomethylindazole, m.p. 82°, λ_{max} 274 mμ (log ε 3.81).

Anal. Calcd. for $C_9H_7N_3$: C, 68.77; H, 4.49; N, 26.74. Found: C, 68.84; H, 4.47; N, 26.77.

2β-Carbamylethylindazole.—A mixture of 11.8 g. (0.1 mole) of indazole, 7.1 g. (0.1 mole) of acrylamide, 1 ml. of 40% benzyltrimethylammonium hydroxide and 100 ml. of *t*-butyl alcohol was allowed to stand near a steam-bath (reaction temperature about 50°) overnight and then at room temperature for 2 days. The solid that formed was collected and air-dried. It melted over a range starting at 135°, and examination of the ultraviolet spectrum indicated about 15% of the 1-isomer. The product was recrystallized from ethyl alcohol and 9.5 g. (50% yield) of 95% pure 2-isomer melting near 165° was obtained. A sample was recrystallized from ethyl acetate and then ethyl alcohol to give pure 2β-carbamylethylindazole, m.p. 185–187°, λ_{max} 274 mμ (log ε 3.81).

Anal. Calcd. for $C_{10}H_{11}N_3O$: C, 63.47; H, 5.86; N, 22.21. Found: C, 63.36; H, 6.10; N, 22.58.

2-β-Aminoethylindazole Dihydrochloride (IX). (a) **Reduction of 2-Cyanomethylindazole.**—A mixture of 3.6 g. (0.023 mole) of 2-cyanomethylindazole, 0.1 g. of Adams catalyst and 25 ml. of acetic anhydride was shaken with hydrogen in a Parr apparatus. Following the theoretical uptake of hydrogen (about 6 hours) the catalyst was removed by filtration, water was added, and the solvents removed by heating under reduced pressure. The resulting oil was treated with excess picric acid in ethyl alcohol, and 3 g. (30% yield) of 2β-acetylaminoethylindazole picrate separated. It was recrystallized from ethyl alcohol, m.p. 182°.

Anal. Calcd. for $C_{17}H_{16}N_6O_8$: C, 47.22; H, 3.73; N, 19.44. Found: C, 47.27; H, 3.99; N, 19.63.

The above picrate was shaken for 5 minutes with a mixture of 50 ml. of nitrobenzene and 50 ml. of concentrated hydrochloric acid. The acid extract was warmed on a steam-bath for 5 hours and then concentrated to dryness by heating under reduced pressure. The residue was recrystallized from a methyl alcohol–ether mixture containing a small amount of hydrogen chloride. The yield of compound IX was 1 g. (60%), m.p. 212° dec. (capillary), λ_{max} 274 mμ (log ε 3.81), pK_a' 8.2 (66% dimethylformamide).

Anal. Calcd. for $C_9H_{11}N_3 \cdot 2HCl$: C, 46.17; H, 5.60; N, 17.95. Found: C, 46.31; H, 5.64; N, 18.23.

(b) **2β-Carbamylethylindazole and Sodium Hypochlorite.**—A mixture of 4 g. (0.02 mole) of 2β-carbamylethylindazole and 4 g. (0.1 mole) of sodium hydroxide in 30 ml. of ice-water containing 1.5 g. (0.02 mole) of chlorine was stirred at room temperature for 2 hours. Then the reaction was warmed on a steam-bath for 1 hour during which time solution was effected. The solution was extracted four times with 50 ml. of ethyl acetate, and the extracts were dried with anhydrous magnesium sulfate. Ether containing hydrogen chloride was added, and the mixture was allowed to stand for several days. The solid was collected and was recrystallized from ethyl alcohol to give 3 g. (64% yield) of IX, m.p. 215° dec. (capillary).

Anal. Calcd. for $C_9H_{11}N_3 \cdot 2HCl$: C, 46.17; H, 5.60; N, 17.95. Found: C, 46.33; H, 5.72; N, 17.66.

1β-Carbamylethylindazole.—A mixture of 7 g. (0.037 mole) of 1β-carboxyethylindazole[3] and 7 g. of urea was heated at 190° for 2 hours. After cooling about 50 ml. of 1 *N* sodium hydroxide was added, and the mixture was extracted with two 100-ml. portions of ethyl acetate. The ethyl acetate solution was dried and then concentrated to dryness by heating on a steam-bath. The solid that resulted was recrystallized from ethyl acetate to give 4 g. (57% yield) of 1β-carbamylethylindazole, m.p. 143°; λ_{max} 253 mμ (log ε 3.59), 290 (3.69).

Anal. Calcd. for $C_{10}H_{11}N_3O$: C, 63.47; H, 5.86; N, 22.21. Found: C, 63.85; H, 6.05; N, 22.07.

1β-Aminoethylindazole dihydrochloride (VIII) was prepared from 4 g. of 1β-carbamylethylindazole according to the second procedure described above for the preparation of compound IX. The product was recrystallized from alcohol–water mixture to give 3.7 g. (77% yield) of VIII, m.p. 180° dec. (capillary); λ_{max} 251 mμ (log ε 3.58), 289 (3.64); pK_a' 8.4 (66% dimethylformamide).

Anal. Calcd. for $C_9H_{11}N_3 \cdot 2HCl$: C, 46.17; H, 5.60; N, 17.95. Found: C, 46.43; H, 6.01; N, 18.05.

INDIANAPOLIS 6, INDIANA

[CONTRIBUTION FROM THE LILLY RESEARCH LABORATORIES]

Reinvestigation of the Fischer Indazole Synthesis

BY C. AINSWORTH

RECEIVED OCTOBER 23, 1957

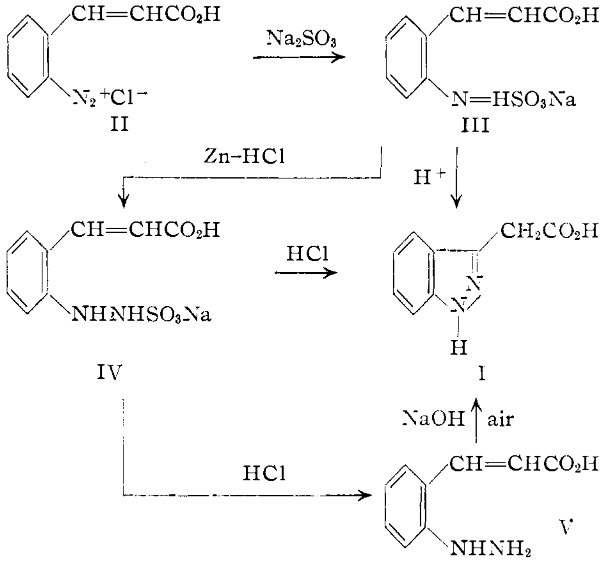
The Fischer synthesis of 3-indazoleacetic acid has been reinvestigated, and the intermediate described as *o*-hydrazinocinnamic acid has been shown to be 2,3-dihydro-3-indazoleacetic acid. Sodium 2-(substituted phenyl)-hydrazinosulfonates have been found to undergo carbon–nitrogen cleavage under basic conditions.

Preliminary to the synthetic approach used for the preparation of 3β-aminoethyl-5-hydroxyindazole,[1] we reinvestigated some of the studies of Fischer and co-workers.[2] The work in question described the preparation of 3-indazoleacetic acid (I) from different intermediates obtained by the reduction of 2-(2-carboxyvinyl)-benzenediazonium chloride (II) as illustrated in the reaction scheme

---

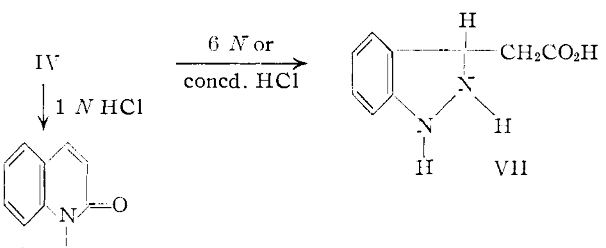
[1] C. Ainsworth, THIS JOURNAL, **79**, 5245 (1957).

[2] (a) E. Fischer, *Ber.*, **14**, 478 (1881); (b) E. Fischer and H. Kuzel, *Ann.*, **221**, 261 (1883); (c) E. Fischer and J. Tafel, *ibid.*, **227**, 303 (1885).



In his discussion Fischer stated that certain discrepancies existed in his observations. For example, he was mystified by the finding that reduction of compound V with sodium amalgam gave rise to I.

The conversion of the type represented by III to I was discussed in a previous[1] publication. The present communication deals mainly with the reactions of compound IV. This material was prepared according to the method of Fischer[2b] and first was treated with acid of varying concentration. It was converted with 1 *N* hydrochloric acid to 1-aminocarbostyril (VI),[2a,2b] while 6 *N* or concentrated hydrochloric acid yielded a product having the correct analysis for V but having a melting point of 185° rather than that of 171° dec. reported[3] by Fischer. The physical data obtained for this product, however, are not in agreement with those of structure V but correspond to that expected for VII.[4] The *pK*'a values are 2.9 (carboxylic acid) and 5.7 (amine) in water, and 4.8 and 6.8 in 66% dimethylformamide solution. A zwitterion is indicated for the neutral material since the infrared spectrum shows weak absorption in the 6.2 μ region, whereas the hydrochloride salt has strong absorption at 5.8 μ (carboxyl carbonyl). It was somewhat perplexing, however, to find that the ultraviolet spectrum obtained in methyl alcohol, under normal conditions, is identical with that of 3-indazoleacetic acid (I). Only when a solvent free of oxidizing agent was used, and the determination made soon after solution, was the problem resolved. Under such conditions the chromophoric absorption corresponds to that expected for VII.[5] The ultraviolet spectra in Fig. 1 show that the admission of a small quantity of air brought about the oxidative transformation of VII to I in aqueous solution. The conversion was complete in less than one day and was very much faster in alcohol.



Fischer mentioned that V was difficult to recrystallize and that the analysis was performed on the crude material. He reported a melting point of 171° dec. for the product V and a melting point of 168–170° dec. for I, but apparently did not consider that the two materials might have been the same. In view of the finding that compound VII is so easily oxidized, it seems possible that these samples were both I.

Next, compound IV was treated with dilute aqueous sodium hydroxide under a nitrogen atmosphere, and the reaction was followed by ultraviolet analysis. The data obtained for a sample heated under reflux for two hours revealed that chemical change had taken place. When the reaction was made acidic and concentrated, an insoluble product separated. The filtrate showed no cinnamic acid-type absorption, but indicated the presence of indazoleacetic acid that subsequently was isolated in the pure state. *Surprisingly, the acid-insoluble material from this reaction was found to be unsubstituted cinnamic acid.* This type of reaction, involving a cleavage of the carbon–nitrogen bond, was substantiated by the finding that sodium 2-(4-benzyloxyphenyl)-hydrazinosulfonate, heated for two hours with 0.1 *N* sodium hydroxide, was converted to benzylphenyl ether, together with some of the normal hydrolysis product 4-benzyloxyphenylhydrazine.

It appears that this type of reaction falls into a larger classification represented by the equation

$$\mathrm{ArNHNHZ} \xrightarrow{\text{base}} \mathrm{ArH} + \mathrm{N_2} + \mathrm{ZH}$$

where Ar is aryl[6] or aroyl[7] and Z is sulfonate or tosyl, etc.

The aminocarbostyril VI was unchanged when subjected to dilute aqueous base or to strong alkali in 95% ethyl alcohol for a relatively long heating period. Thus, we were not able to obtain *o*-hydrazinocinnamic acid (V). The assignment of structure VII, rather than V, to the hydrolytic product of IV, and the finding that this product is so readily oxidized to I by air, leads to the proposal that Fischer's material thought to be V may well have contained considerable amounts of I and that the latter was unaffected by sodium amalgam.

Acknowledgment.—The analyses were performed by W. L. Brown, H. L. Hunter, G. M.

---

[3] The only other reference found in the literature to *o*-hydrazinocinnamic acid was that of K. von Auwers and E. Frese, *ibid.*, **450**, 273 (1926), who prepared the material according to the procedure of Fischer but reported a melting point of 196–197°.

[4] R. C. Elderfield, "Heterocyclic Compounds," Vol. V, John Wiley and Sons, Inc., New York, N. Y., 1957, p. 166, reasoning by analogy with the transformation of benzimidazolines to benzimidazoles, proposed compound VII as an intermediate to explain some of Fischer's findings.

[5] The ultraviolet spectrum is considerably different from that characteristic of a cinnamic acid. The curve resembles that of 2-methylindoline but shifted to slightly shorter wave length; H. Kondo and H. Katsura, *Ber.*, **73**, 1424 (1940).

[6] R. Escales, *ibid.*, **18**, 893 (1885), found that β-phenylsulfonylphenylhydrazine was decomposed with base into benzene, nitrogen and benzenesulfinic acid.

[7] J. S. McFadyen and T. S. Stevens, *J. Chem. Soc.*, **139**, 584 (1936).

Maciak and Gloria Beckmann. The physical studies so important to this investigation were conducted by H. E. Boaz, D. O. Woolf, Jr., and L. G. Howard.

Experimental[8]

2-(2-Carboxyvinyl)-benzenediazonium chloride (II) was prepared according to the method reported by Fischer[2b] using *o*-aminocinnamic acid.[9] It was recrystallized from concentrated aqueous solution and was unstable above 100°; λ_{max} 272 mμ (log ε 4.16), 334 (3.28); infrared (Nujol mull) 4.41m (N≡N), 5.89s (C═O), 6.12m (C═C).

Anal. Calcd. for $C_9H_7ClN_2O_2$: C, 51.32; H, 3.35. Found: C, 51.40; H, 3.60.

Sodium 2-[2-(2-Carboxyvinyl)-phenyl]-hydrazinosulfonate (IV).—A stirred solution of 12 g. (0.06 mole) of *o*-aminocinnamic acid hydrochloride[10] [λ_{max} 235 mμ (log ε 4.22), 277 (4.07), 354 (3.75)], 5 ml. (0.06 mole) of concentrated hydrochloric acid and 30 ml. of water was cooled to 0°, and 4.5 g. (0.06 mole) of sodium nitrite was added. After 5 minutes a solution of 18 g. (0.18 mole) of sodium sulfite in 50 ml. of water was added, and the solution became orange in color. In about 2 minutes 5 ml. of concentrated hydrochloric acid was added, followed immediately with 10 g. of zinc dust. The color changed from orange to yellow. After 5 minutes the excess zinc was removed by filtration, and the filtrate was warmed to about 50°, saturated with sodium chloride and then treated with 20 ml. of acetic acid. The solid that separated on cooling was recrystallized from a small volume of water, and 3.5 g. (20% yield) of IV was obtained as a yellow solid, m.p. 210° dec.; λ_{max} 235 mμ (log ε 4.22), 277 (4.07), 354 (3.75); infrared (Nujol mull) 5.92ms (C═O), 6.14s (C═C).

Anal. Calcd. for $C_9H_9N_2NaO_5S$: C, 38.57; H, 3.24; N, 10.00. Found: C, 38.82; H, 3.31; N, 9.74.

2,3-Dihydro-3-indazoleacetic Acid (VII).—A solution of 5.4 g. (0.02 mole) of IV and 10 ml. of 6 *N* or concentrated hydrochloric acid was heated on a steam-bath for 2 hours. After concentrating to dryness by heating under reduced pressure, the residue was dissolved in 20 ml. of water and was treated with 5 g. of sodium acetate. The product that separated on cooling was recrystallized from 200 ml. of 50% aqueous ethyl alcohol, and 1.5 g. (42% yield) of VII was obtained as an amphoteric white solid, m.p. 185°; λ_{max} 274 mμ (log ε 3.27) (water); infrared (Nujol mull) medium intensity bands at 3.21, 6.48, 6.75, 7.69, 7.86, 8.25, 9.50, 10.67, 10.85, 12.70, 13.20, 13.51, 13.73 and 14.32 μ; pK'_a 2.9, 5.7 (water), 4.8, 6.8 (66% dimethylformamide).

Anal. Calcd. for $C_9H_{10}N_2O_2$: C, 60.66; H, 5.66; N, 15.72. Found: C, 60.76; H, 5.75; N, 15.54.

The hydrochloride salt was recrystallized from an ethyl alcohol-ether mixture, m.p. 172° dec. (capillary); infrared (Nujol mull) medium-strong bands at 3.22, 5.82, 6.23, 6.30, 6.72, 7.68, 7.75, 7.92, 8.16, 8.43, 9.76, 10.04, 12.36, 12.98, 13.25, 13.46, 13.90 and 14.86 μ.

Anal. Calcd. for $C_9H_{10}N_2O_2 \cdot HCl$: C, 50.36; H, 5.17; N, 13.05. Found: C, 50.06; H, 5.37; N, 12.78.

3-Indazoleacetic Acid (I).—A slow stream of air was bubbled into a solution of 1.8 g. (0.01 mole) of VII and 100 ml. of 0.25 *N* sodium hydroxide for 48 hours. Addition of 4 ml. of 6 *N* hydrochloric acid caused a solid to separate that was collected and recrystallized from water. The yield of I was 1 g. (57%), m.p. 168° dec. (capillary); λ_{max} 252 mμ (log ε 3.60), 287 (3.73); infrared (Nujol mull) 2.94, 3.12mw (N–H), 5.78, 5.84s (carboxyl carbonyl), 6.11w (C═N).

Anal. Calcd. for $C_9H_8N_2O_2$: C, 61.63; H, 4.58; N, 15.90. Found: C, 61.75; H, 4.90; N, 16.16.

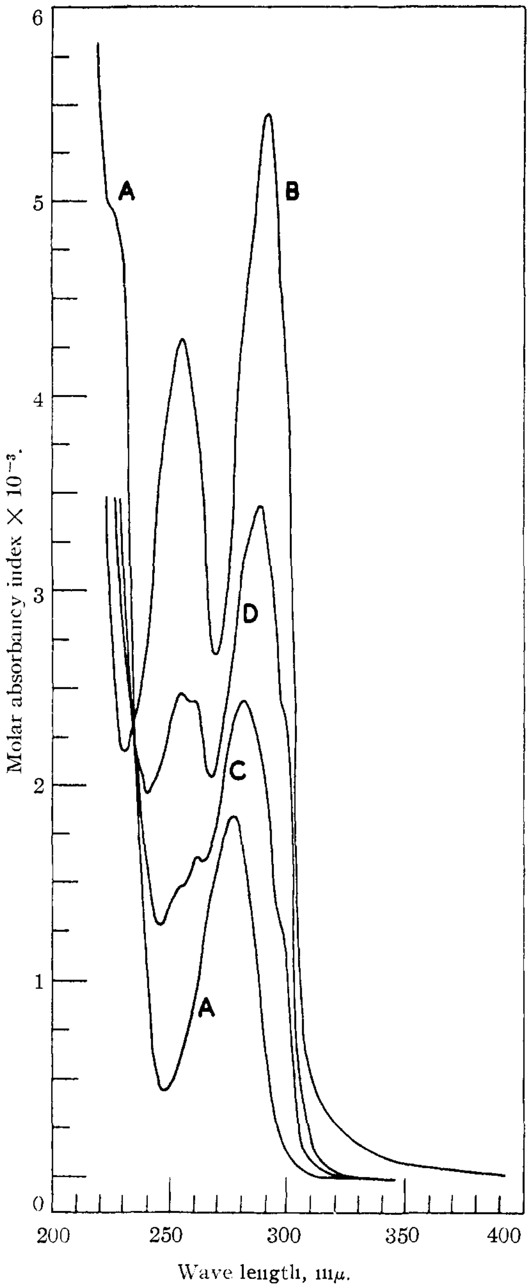


Fig. 1.—Ultraviolet absorption curves obtained in water for 2,3-dihydro-3-indazoleacetic acid (VII) (curve A); 3-indazoleacetic acid (I) (curve B); compound VII, 10 minutes after the admission of air (curve C); compound VII, 60 minutes after admission of air (curve D).

The hydrochloride was recrystallized from an ethyl alcohol-ether mixture, m.p. 185° dec. (capillary).

Anal. Calcd. for $C_9H_8N_2O_2 \cdot HCl$: C, 50.83; H, 4.27; N, 13.18. Found: C, 51.07; H, 4.37; N, 13.23.

1-Aminocarbostyril (VI).—A solution of 2.8 g. (0.01 mole) of IV and 50 ml. of 1 *N* hydrochloric acid was heated under reflux overnight. After the mixture was concentrated to dryness by heating under reduced pressure the residue was dissolved in 10 ml. of water and was treated with 2 g. of sodium acetate. The product that separated was recrystallized from water to give 0.25 g. (15% yield) of VI, m.p 130° (lit.[2a,2b] m.p. 127°); λ_{max} 228 mμ (log ε 4.56), 270 (3.69), 330 (3.68); infrared (Nujol mull) 3.02, 3.12w (N–H), 6.00s (C═O), 6.06s (C═C).

---

[8] Unless otherwise stated, the melting points were determined with a Fisher–Johns assembly and are uncorrected. The ultraviolet spectra, unless otherwise indicated, were determined in ethyl alcohol.

[9] The *o*-nitrocinnamic acid used as starting material is best prepared according to the method of E. C. Taylor, Jr., and E. J. Stojny, This Journal, **78**, 5104 (1956). For a leading reference concerning the reduction of nitrocinnamic acids, see E. R. Blout and D. C. Silverman, *ibid.*, **66**, 1442 (1944).

[10] F. Tiemann and J. Oppermann, *Ber.*, **13**, 2056 (1880), did not record the melting point of this compound; we found it to be 188° dec.

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.

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

---

[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).

[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).