80.3 g of this product, containing ca. 62.7 g (0.55 mol) of 15, in 350 ml of dry benzene was added dropwise over 4 hr to 1 l. of dry benzene, to which was added at the beginning of the reaction and at hourly intervals ca. one-fourth of a total of 250 g (0.569 mol) of lead tetraacetate.¹¹ The reaction was exothermic and maintained itself at $ca. 35-40^{\circ}$. The yellow reaction mixture was filtered to remove lead diacetate, which was washed with 4×100 ml of benzene. The combined benzene layers were washed with 4×1 l. of water, dried over sodium sulfate, filtered, and evaporated. The 153.2 g of residue was distilled under reduced pressure to afford benzene (78 g), starting material (4 g), and 58 g, bp 70-165° (3.5-5.5 mm), which was redistilled to afford 17.1 g of starting material, bp $32-45^{\circ}$ (1-2 mm), and 29.1 g (31%) of crude 8, bp $85-145^{\circ}$ (1.5-2.5 mm). When placed in the freezer with a small amount of ether, this product solidified to afford, after recrystallization from ether in the cold, 13.4 g (14%) of pure 8: mp 26–27°; bp 222°; uv max (cyclohexane) 299 m μ (ϵ 84); ir (film) 5.70 and 5.80 μ ; nmr (CDCl₃) δ 1.67 (s, 3, H₃C−C ≤), 2.12 (s, 3, H₃CCOO−), and 2.18 ppm (s, 6, 2 H₃CCO−). Anal. Calcd for C₈H₁₂O₄: C, 55.81; H, 7.02. Found: C, 55.69; H, 6.90.

Pyrolysis of 8.-Using an apparatus of the type previously described,¹ 9.74 g (0.056 mol) of 8 in a 25-ml flask was refluxed at a pot temperature of 240° through a heating column at 380-400° for 7 hr. There was obtained 3.94 g of yellow distillate and a dark, solid pot residue. The distillate was found by vpc analysis to be ca.75% acetic acid (ca.95% yield), ca.10% 8, and ca. 15% of an unidentified substance which was not 10. Ultraviolet spectra of all product fractions indicated that 10 was not present in significant amounts. Effluent gas, including the nitrogen run through the system, was collected during much of the pyrolysis. Vpc analysis of this gas indicated that a maximum of 25% of the theoretical amount of carbon monoxide required for formation of 10 could have been produced.

Registry No.—7, 34564-51-7; 8, 34564-52-8; 9, 34564-53-9; 15,815-57-6.

Acknowledgment.-R. A. A. was a recipient of financial support under the terms of an institutional research training grant from the U.S. Public Health Service, summer, 1971.

A Rational Synthesis of 2-Aminoindazole

K. SAKAI AND J.-P. ANSELME*1

Department of Chemistry, University of Massachusetts at Boston, Boston, Massachusetts 02116

Received December 29, 1971

As a part of our investigation of the chemistry of N-nitrenes,² it was of interest to study the oxidation of 2-aminoindazole (1). This report of the rational synthesis of 1 and of its oxidation is prompted by the recent disclosure of the preparation of both 1- and 2-aminoindazole by the amination of indazole with hydroxylamine-O-sulfonic acid.3

The scheme used for the preparation of 1 is based on the cyclization of an o-nitreno benzaldimine derivative.4a,b The failure of our initial attempts to de-

 (2) K. Sakai and J.-P. Anselme, *Tetrahedron Lett.*, 3851 (1970); K.
 Sakai, A. Tanaka, G. Koga, and J.-P. Anselme, J. Chem. Soc. Jap., Pure Chem. Sect., 92, 1065 (1971).

(a) D. S. C. James, S. Brabbury, D. C. Horwell, M. Keating, C. W. Rees, and R. C. Storr, Chem. Commun., 828 (1971).
(4) (a) L. Krbechek and H. Takimoto, J. Org. Chem., 29, 1150 (1964);
(b) P. A. S. Smith in "Nitrenes," W. Lwowski, Ed., Wiley, New York, N. Y., 1970, p 139; (c) J. I. G. Cadogan and R. J. G. Searle, Chem. Ind. (London), 1000 (1994); 1282 (1963).

oxygenate N-(o-nitrobenzal)aminophthalimide (4) to 2⁴ led us to generate the nitrene from the corresponding azide. In this fashion, 1 was obtained in 94% yield from 3 as yellow crystals, mp 96-97°, as illustrated in Scheme I.



Although 3 was also prepared by the diazotization and azidation of 7, it was best obtained by the condensation of o-azidobenzaldehyde (5) with N-aminophthalimide (6). o-Azidobenzaldehvde was synthesized in one step by the diazotization and azidation of o-aminobenzaldazine.

Since Rees and his group^{3,5} have extensively investigated the oxidation of 1, we will only briefly describe our results carried out under different experimental conditions. Besides trace amounts of indazole (12), 2,2'-biindazole (13) was the main product obtained from the oxidation of 1 with mercuric oxide in refluxing n-butyl alcohol for 96 hr; in addition, an unstable crude compound exhibiting absorption in the triple bond region was also isolated as a very minor component which may perhaps be the product of the fragmentation of the N-nitrene. Addition of a catalytic amount of sodium methoxide gave essentially the same results, although only 2 hr were required in this case. In benzene at room temperature, oxidation with lead tetraacetate gave 12.

Our results, in conjunction with those of Rees and his students,^{3,5} indicate that, under those conditions, fragmentation of 2-indazolyl nitrene (8) is not favored, occurring at best only to a minor extent. In view of the difference between Rees' results² and ours, it seems likely that the formation of the tetrazane 10⁶ and of the tetrazene 11 does not proceed via the N-nitrene 8. Scheme II outlines possible routes which may help explain the products obtained by us. Evidently, the conditions of our oxidations would preclude any possibility of isolation of the 1,2,3-benzotriazine isolated by Rees only in the strict absence of nucleophiles.³

⁽¹⁾ Fellow of the A. P. Sloan Foundation.

⁽³⁾ D. J. C. James, S. Bradbury, D. C. Horwell, M. Keating, C. W. Rees,

⁽⁵⁾ Private communication from C. W. Rees.
(6) D. J. Anderson, T. L. Gilchrist, and C. W. Rees, Chem. Commun., 800 (1971).



Experimental Section⁷

N-(o-Nitrobenzal)aminophthalimide (4) was prepared in 90% yield by overnight reflux of equimolar amounts (0.1 mol) of N-aminophthalimide and o-nitrobenzaldehyde in 250 ml of ethanol containing a catalytic amount of acetic acid. The pale yellow analytical sample, mp 227-229°, was obtained by crystallization from benzene-ethanol. *Anal.* Calcd for $C_{15}H_9N_8O_4$: C, 61.02; H, 3.07; N, 14.23.

Found: C, 60.99; H, 3.22; N, 14.12

N-(o-Aminobenzal)aminophthalimide (7), mp 189-191°, was obtained in 90% yield by hydrogenation of 4 over Pd/C in ethanol until the theoretical amount of hydrogen was absorbed. The analytical sample was obtained as pale yellow crystals after crystallization from benzene-ethanol. Anal. Calcd for $C_{15}H_{11}N_3O_2$: C, 67.91; H, 4.18; N, 15.84.

Found: C, 68.04; H, 4.30; N, 15.53.

N-(o-Azidobenzal)aminophthalimide (3) was synthesized by diazotization of 7 with sodium nitrite in a mixture of acetic acid and hydrochloric acid, followed by the addition of sodium azide. The yield of product, identical with material prepared by the alternate route described below, was 34%. Compound **3** was also obtained in 67% yield by the condensa-

tion of o-azidobenzaldehyde with N-aminophthalimide in the presence of catalytic amounts of acetic acid in ethanol. Recrystallization from ethanol-benzene gave the analytically pure pale yellow sample, mp 170–171°. Anal. Calcd for $C_{15}H_9N_5O_2$: C, 61.85; H, 3.12; N, 24.05.

Found: C, 61.77; H, 3.32; N, 24.10.

o-Azidobenzaldehyde (5).-o-Aminobenzaldazine (31 mmol) was diazotized at 0° in a mixture of 150 ml of acetic acid and 50 ml of concentrated hydrochloric acid by the addition of an aqueous solution of 87 mmol of sodium nitrite in 30 ml of water. The mixture was stirred for 0.5 hr at 0°, then an aqueous solution of 130 mmol of sodium azide in 40 ml of water was slowly added while the temperature was kept at 0°. Stirring was continued for an additional 0.5 hr at that temperature, then for 15 min at room temperature. After addition of 200 ml of water and extraction with ether, the ethereal extract was washed successively with water, 5% sodium hydroxide solution, and water. The organic phase was dried and evaporated to give 4.3 g (48%) of o-azidobenzaldehyde, mp 34-36° (lit.⁸ mp 35-36.5°)

2-(N-Phthalimido)indazole (2).-Cyclization of 1 g of 3 was achieved by heating in 60 ml of o-dichlorobenzene at 140-145° for 1.5 hr. After the evolution of nitrogen had subsided, the solvent was removed at $\sim 100^{\circ}$ under reduced pressure. Recrystallizaof the residue from benzene-ethanol gave 0.81 g (97%) of white product, mp 262-263°

Anal. Calcd for C15H9N3O2: C, 68.43; H, 3.44. Found: C, 68.13; H, 3.65.

2-Aminoindazole (1).—A solution of 4.5 g (0.017 mol) of 2 in 150 ml of ethanol containing an excess (2.1 g) of hydrazine was warmed for ~ 0.5 hr; a white precipitate was formed very rapidly. Then an excess of concentrated hydrochloric acid was added and the mixture was again warmed for ~ 15 min. The insoluble phthalhydrazide (1.89 g) was filtered and the filtrate was concentrated to remove the alcohol. The residue was then made alkaline with concentrated ammonium hydroxide and extracted with several portions of ether. The ethereal extract was dried and evaporated to give $2.19 ext{ g} (97\%)$ of essentially pure 2-aminoindazole as very pale yellow crystals, mp 95-96°. Recrystallization from benzene-ethanol (9:1) gave the analytically pure sample, mp 96-97°.

Anal. Calcd for $C_7H_7N_3$: C, 63.14; H, 5.29; N, 31.56. Found: C, 63.38; H, 5.22; N, 31.59.

Oxidation of 2-Aminoindazole. A. Yellow Mercuric Oxide. A mixture of 0.25 g (1.9 mmol) of 1 and 0.50 g (2.3 mmol) of yellow mercuric oxide in 30 ml of n-butyl alcohol was heated to reflux for 4 days; during this time, a total of 43 ml of gas was collected. Evaporation of the solvent gave a solid-liquid mixture whose infrared spectrum exhibited absorption in the triple-bond region (-CN?). Crystallization of this mixture from benzene gave 0.15 g of yellow crystals, mp 254-256°, which upon several recrystallizations from benzene-ethanol gave a pure sample of 2,2'-biindazole, mp 267-268° dec (lit.³ mp 268°). Work-up of Work-up of the filtrate gave trace amounts of recovered 1 and of indazole, which was isolated by sublimation and identified as its picrate, mp 134-136° (lit.⁹ mp 136°).

When a catalytic amount of sodium methoxide was added, essentially the same results were obtained in 2 hr instead of 4 days.

Lead Tetraacetate.--- A mixture of 0.65 g (4.9 mmol) of 1 В. and 2.2 g of lead tetraacetate in 25 ml of benzene was stirred at 0° until the initial reaction had subsided, then at room temperature for 40 min, and finally heated at reflux for an additional 20 The precipitated lead diacetate was removed and washed min. with ether. The combined filtrate was washed successively with water, 10% sodium bicarbonate solution, and water. Evaporation of dried solution in vacuo left 0.45 g of a reddish mass. Sublimation of part of this material showed it to consist essentially of indazole, identified as its picrate.

Registry No.-1, 33334-11-1; 2, 34638-59-0; 3, 34638-60-3; 4, 32387-06-7; 5, 16714-25-3; 7, 34608-92-9.

Acknowledgment.—The generous support of this work by the National Institutes of Health under Grant GM 13689-05 is hereby acknowledged with deep appreciation.

⁽⁷⁾ All melting points are uncorrected. Analyses were performed by the Microchemical Laboratory of Belmont, Mass.

⁽⁸⁾ E. Bamberger and E. Demerth, Ber., 34, 1334 (1901).

⁽⁹⁾ E. Fischer and O. Seuffert, Ber., 34, 797 (1901).