$-30°$ was added 6.66 g. (0.05 mole) of aluminum chloride in three portions during a 5-min. period. After 2 hr. below $-20°$, the mixture was poured into ice water and stirred 5 min. The organic layer was extracted three–times with water and the extracts and water layer combined. Treatment of the aqueous solution with zinc dust and subsequent extraction with chloroform gave 1.37 g. (37%) of ferrocene (infrared comparison).

A similar reaction with ethyl oxalyl chloride gave 64% ferrocene (infrared comparison) upon reduction of the aqueous layer.

Reaction of Ferrocene and Aluminum Chloride with Chloroacetal.—Chloroacetal (15.3 g.; 0.1 mole) was added dropwise during an 80-min. period to 9.3 g. (0.05 mole) of ferrocene and 13.3 g. (0.10 mole) of aluminum chloride in 65 ml. of ethylene dichloride under nitrogen at $-20°$. After 30 min., the mixture was warmed to $-5°$, added to ice, and the aqueous layer extracted with chloroform. After removal of solvent from the combined organic layers, the residue (5.92 g.) was extracted with 120 ml. of petroleum ether (b.p. 30–60°) in 20-ml. portions and each portion added to 180 g. of alumina and eluted with petroleum ether to give 1.75 g. (19%) of ferrocene. Continued elution with the usual solvents removed distinct fractions (oils), the infrared spectra of which suggested that the ferrocenes present were monosubstituted. Reduction of the aqueous layer with zinc dust, extraction with chloroform, and removal of solvent left moist solid, which when extracted with methanol left 3.04 g. (33%) of crude ferrocene. Removal of methanol and chromatography of the residue (2.73 g.) gave 4% ferrocene and 1.65 g. of solid, m.p. 14–21°, the infrared spectrum of which showed strong bands at 9 and 10 μ (a monosubstituted ferrocene).

1,1′-Bis(*p*-fluorobenzoyl)ferrocene.—A mixture of 37.1 g. (0.263 mole) of *p*-fluorobenzoic acid and 48 ml. (0.658 mole) of thionyl chloride in 25 ml. of benzene was refluxed 7 hr. Volatile material was removed *in vacuo*, 90 ml. of dry methylene chloride was added, and the solution was treated with 31.1 g. (0.233 mole) of powdered anhydrous aluminum chloride. To the mixture in an ice bath was then added dropwise a solution of 17.3 g. (0.093 mole) of ferrocene in 90 ml. of methylene chloride during a 1.5-hr. period, and the mixture was stirred overnight at room temperature. The solution was poured onto ice, stirred 4 hr., and the aqueous phase washed with chloroform. The organic phases were combined, washed twice with water and once with 5% sodium hydroxide solution, dried, and evaporated *in vacuo*. Crystallization of the residue from 150 ml. of toluene yielded 30.4 g. (76%) of 1,1′-bis(*p*-fluorobenzoyl)ferrocene, m.p. 129–130.5°; λ_{max} (log ϵ) 472 (2.83), 350 (3.29), 250 mμ (4.28).

Anal. Calcd. for $C_{24}H_{16}F_2FeO_2$: C, 67.00; H, 3.75; Fe, 12.98. Found: C, 66.95; H, 3.86; Fe, 13.63.

1,1′-Bis(*n*-butyryl)ferrocene.—The reaction of *n*-butyryl chloride, aluminum chloride, and ferrocene was carried out by the method employed by Vogel, *et al.*, for the preparation of 1,1′-dicaprylylferrocene.[10] 1,1′-Dibutyrylferrocene, m.p. 73.0–74.5°, was obtained in 77% yield; lit.[18] m.p. 74–75°.

Acknowledgment.—We are grateful to Mr. Richard Thivierge for technical assistance.

[18] A. N. Nesmeyanov and N. A. Vol'kenau, *Dokl. Akad. Nauk SSSR*, **107**, 262 (1956).

---

o-Nitrosobenzamide. A Possible Intermediate in the von Richter Reaction

KHAIRAT M. IBNE-RASA AND EDWARD KOUBEK

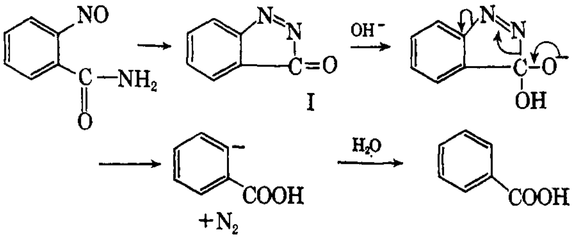
Metcalf Chemical Laboratories, Brown University, Providence 12, Rhode Island

Received May 29, 1963

The previously unknown *o*-nitrosobenzamide has been synthesized and its behavior under the conditions of the von Richter reaction studied; the conditions of the von Richter reaction employed were those established by the research of Bunnett and his group.[1] This work was undertaken because of our interest in the peroxy acid oxidations of aromatic amines[2] and of nitrosobenzenes,[3] and because *o*-nitrosobenzamide has been implicated as an intermediate in the von Richter reaction.[4]

o-Nitrosobenzamide was obtained in excellent yield by oxidizing *o*-aminobenzamide with peroxyacetic acid in ethanolic medium at *ca.* 0°. These conditions previously have been shown[2] to favor the formation of nitrosobenzenes as the chief products of the peroxyacetic acid oxidation of aromatic amines. The amido group in the present substrate did not cause any complications. Its indifference to peroxyacetic acid was foreseen on mechanistic grounds[2] and by analogy with the peroxyacetic acid oxidation of nicotinamide to nicotinamide N-oxide in 82% yield.[5] The elemental and spectral analyses of the reaction product confirmed it to be the desired nitrosobenzamide.[2,6]

A recently proposed mechanism for the von Richter reaction[4] requires that *o*-nitrosobenzamide should give benzoic acid and nitrogen gas according to the following reaction sequence.



When *o*-nitrosobenzamide was treated with cyanide ion or hydroxide ion in aqueous ethanolic medium at 150°, the von Richter reaction conditions,[1] benzoic acid was formed with evolution of nitrogen gas as predicted by the Rosenblum mechanism.[4] The yield of isolated benzoic acid was 20% with cyanide ion and 45% with hydroxide ion. The reported yields of benzoic acids from the von Richter reaction range between 10 and 40%.[1] The isolated product melted at 122° and its ultraviolet spectrum in water was superimposable with that of an authentic sample of benzoic acid.

A transient red color appeared immediately upon addition of base to the aqueous ethanolic solutions of *o*-nitrosobenzamide. This color may be attributable to the formation of 3-indazolone, the intermediate I. The preparation of I (in solution) by independent synthesis and its hydrolysis to benzoic acid and nitrogen gas has been reported recently.[7] The solutions of I in acetonitrile were reported to have deep red color.[7]

Experimental

Materials.—*o*-Aminobenzamide (Matheson Coleman and Bell, practical grade) was purified by treatment with decolorizing

---

[1] (a) J. F. Bunnett, J. F. Cormack, and F. C. McKay, *J. Org. Chem.*, **15**, 481 (1950); (b) J. F. Bunnett, M. M. Rauhut, D. Knutson, and G. E. Bussell, *J. Am. Chem. Soc.*, **76**, 5755 (1954); (c) J. F. Bunnett and M. M. Rauhut, *J. Org. Chem.*, **21**, 934 (1956).

[2] K. M. Ibne-Rasa and J. O. Edwards, *J. Am. Chem. Soc.*, **84**, 763 (1962).

[3] K. M. Ibne-Rasa, C. G. Lauro, and J. O. Edwards, *ibid.*, **85**, 1165 (1963).

[4] M. Rosenblum, *ibid.*, **82**, 3796 (1960).

[5] E. C. Taylor, Jr., and A. J. Crovetti, *Org. Syn.*, **37**, 63 (1957).

[6] K. Nakamoto and R. E. Rundle, *J. Am. Chem. Soc.*, **78**, 1113 (1956).

[7] E. F. Ullman and E. A. Bartkus, *Chem. Ind.* (London), 93 (1962).

charcoal and recrystallization from ethanol to m.p. 109–111°; lit.[8] m.p. 109–111.5°. Commercial peroxyacetic acid solutions, generously donated by BECCO, were used.

Preparation of o-Nitrosobenzamide.—To absolute ethanol (40 ml.), previously saturated with anhydrous sodium acetate, was added ~40% peroxyacetic acid (20 ml.). The mixture was centrifuged and the supernatant liquid cooled to 0°. To the cooled solution was added a solution of o-aminobenzamide (1.4 g.) in ethanol (20 ml.), and the reaction mixture was allowed to stand for about 1 hr. The solution was then evaporated at room temperature (reduced pressure) to lower volume (about 15 ml.); the precipitated solid was removed by filtration, and washed first with cold ethanol (—10°) and then with ether. The product (1.3 g., 85%) was a pale green solid, m.p. 220° dec. It was stored at −10° in the absence of light until used. Absorption (in ethanol): λ_{max} at 750 (1.40; 0.01 M solution), 310 (3.67), and 285 mμ (log ε 3.71). Selected infrared maxima (KBr): 6.7 and 7.9 μ.

Anal. Calcd. for $C_7H_6N_2O_2$: C, 56.00; H, 4.03; N, 18.66. Found: C, 56.51; H, 4.25; N, 18.36. The elemental analysis was done by Dr. S. M. Nagy at Massachusetts Institute of Technology.

Reaction of o-Nitrosobenzamide with Cyanide Ion.—o-Nitrosobenzamide (2.0 g.) was heated with an equivalent amount of potassium cyanide (or sodium hydroxide) in 60 ml. of 50% aqueous ethanol in a sealed tube at 140–160° for 1.25 hr. The resulting brownish solution was acidified with hydrochloric acid and repeatedly treated with decolorizing charcoal until colorless. The clear solution was then made basic, evaporated to near dryness, and acidified with hydrochloric acid, and the resulting precipitate was removed by filtration. This precipitate was then sublimed once and the yellowish sublimate recrystallized from water. The resulting benzoic acid melted at 122°. Its ultraviolet spectrum in aqueous medium was identical with that of an authentic sample of benzoic acid, and it did not depress the melting point of authentic benzoic acid. The yield of the isolated product was 20% with cyanide ion and 40% with hydroxide ion. The reaction was accompanied by the evolution of a gas, which was dried with liquid nitrogen and then shown to be nitrogen by mass spectral analysis.

Acknowledgment.—The authors wish to thank Professors J. F. Bunnett and J. O. Edwards for their kind interest in this work. Professor Bunnett directed our attention to ref. 4. This work was supported in part by the U. S. Atomic Energy Commission, Contract 1983. The gas analysis was performed at Harvard University through the courtesy of Dr. G. O. Dudek.

[8] I. M. Heilbron, "Dictionary of Organic Compounds," Vol. I, Oxford University Press, New York, N. Y., 1934, p. 37.

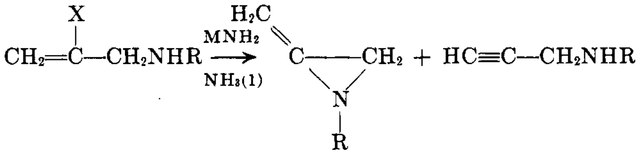
Amines Derived from Dihalopropenes. V.[1a] Reaction of 2-Haloallylamines with Various Bases[1b]

ALBERT T. BOTTINI, BARBARA J. KING, AND ROBERT E. OLSEN[1c]

Chemistry Department, University of California, Davis, California

Received May 20, 1963

An N-alkylallenimine III is obtained as the main product from the reaction of an N-(2-bromoallyl)-alkylamine I with sodium amide in liquid ammonia,[2,3] but the only discernible product from the reaction of N-(2-chloroallyl)ethylamine (IIa, R = C_2H_5) with potassium amide in liquid ammonia was N-ethylpropargylamine (IVa, R = C_2H_5). In order to determine if the course of the reaction of an N-(2-haloallyl)alkylamine with amide in liquid ammonia was influenced by the alkyl metal cation,[4] we examined the reactions of the N-(2-haloallyl)ethylamines with the common alkali metal amides in liquid ammonia. Reactions were carried out on a small scale, and the yields and product compositions were determined by gas–liquid partition chromatography (g.l.p.c.).



I, X = Br III IV
II, X = Cl

We observed no significant difference in the yields or product compositions from reactions of N-(2-bromoallyl)ethylamine (Ia, R = C_2H_5) with lithium amide, sodium amide, and potassium amide. Using a constant amide–Ia mole ratio of 1.2, which Pollard and Parcell found gave optimum yields of allenimines from N-(2-bromoallyl)alkylamines,[2] initial Ia concentrations of 0.25 and 0.5 M, and reaction times of 4.5 to 5 hr., imine–amine mixtures consisting of 75–82% N-ethylallenimine (IIIa, R = C_2H_5) were obtained in yields of 48–62%. As the 2,3-dibromopropene used for the preparation of Ia and other N-(2-bromoallyl)alkylamines contained less than 1.5% of the isomeric 1,3-dibromopropenes,[5] we could estimate that the Ia contained less than 2% of the isomeric N-(3-bromoallyl) ethylamines, which yield only the propargylamine under the reaction conditions used for allenimine formation.[6] Thus, most of the IVa was formed from dehydrobromination of Ia.

The product compositions obtained from all reactions of N-(2-chloroallyl)ethylamine (IIa) with any of the three alkali metal amides were identical and consisted of <1% IIIa and >99% IVa. Under the same reaction conditions used for Ia, treatment of IIa at an initial concentration of 0.5 M with potassium amide gave yields of 50–56% based on IIa, while use of lithium amide or sodium amide gave yields of 20–29%. When the amide–IIa ratio was increased to more than 2, yields of IVa from reactions of potassium amide with IIa at an initial concentration of 0.4 M were increased to over 80%. Comparable yields were also obtained using sodium amide, but reaction times of 9–10 hr. were required instead of 5 hours.

Reactions of N-(2-bromoallyl)methylamine, N-(2-bromoallyl)isopropylamine, and N-(2-bromoallyl)-hexylamine were carried out on a preparative scale with 0.8–1.5 moles of the amine using sodium amide–I ratios of 1.2. These reactions gave 46–70% yields of mixtures of three to four parts of the corresponding

[1] (a) Part IV: A. T. Bottini, V. Dev, and M. Stewart, *J. Org. Chem.*, **28**, 156 (1963); (b) acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research; (c) American Chemical Society Petroleum Research Fund Fellow, 1961.

[2] C. B. Pollard and R. F. Parrell, *J. Am. Chem. Soc.*, **73**, 2925 (1951).

[3] A. T. Bottini and J. D. Roberts, *ibid.*, **79**, 1462 (1957).

[4] See W. H. Puterbaugh and C. R. Hauser, *J. Org. Chem.*, **24**, 416 (1959).

[5] Treatment of the 2,3-dibromopropene with lithium aluminum hydride in ether gave a mixture of 1- and 2-bromopropenes that was 98.8% 2-bromopropene as determined by g.l.p.c. See L. F. Hatch, P. D. Gardner, and R. E. Gilberg, *J. Am. Chem. Soc.*, **81**, 5943 (1959), for an earlier application of a method similar to that used by us.

[6] A. T. Bottini, B. J. King, and J. M. Lucas, *J. Org. Chem.*, **27**, 3688 (1962).