less readily to yield *p*-indoaniline dyes by elimination of the para-substituent. The ease with which the elimination coupling occurred appeared to be influenced by the presence of other substituents in the phenol ring. No evidences of *o*-indoaniline dye formation were observed with any of the phenols studied.

ROCHESTER 4, N. Y. RECEIVED DECEMBER 20, 19

[DEPARTMENT OF CHEMISTRY AND PURDUE RESEARCH FOUNDATION, PURDUE UNIVERSITY]

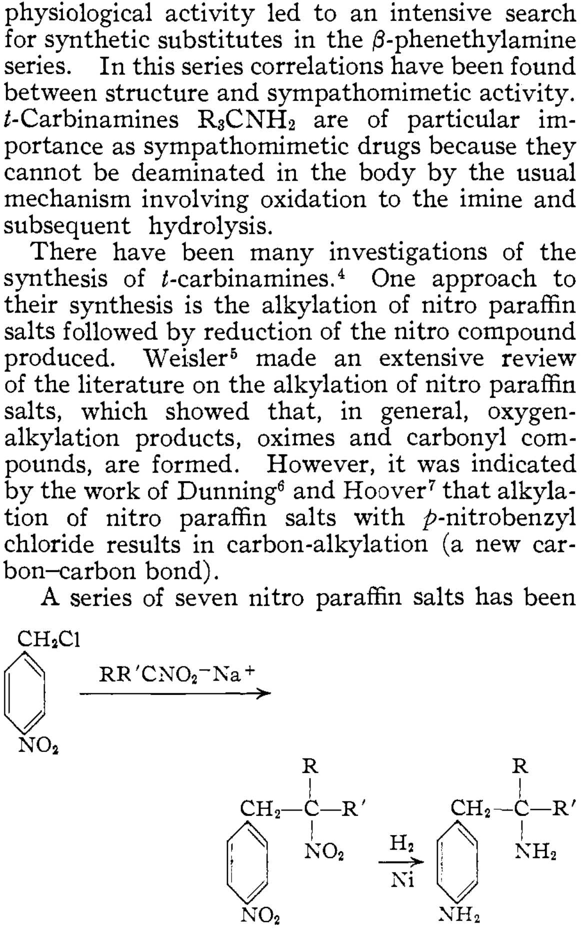
Carbon Aralkylations of Nitro Paraffins[1]

BY H. B. HASS, E. JANET BERRY[2] AND MYRON L. BENDER[3]

The isolation of adrenalin and discovery of its physiological activity led to an intensive search for synthetic substitutes in the β-phenethylamine series. In this series correlations have been found between structure and sympathomimetic activity. *t*-Carbinamines R_3CNH_2 are of particular importance as sympathomimetic drugs because they cannot be deaminated in the body by the usual mechanism involving oxidation to the imine and subsequent hydrolysis.

There have been many investigations of the synthesis of *t*-carbinamines.[4] One approach to their synthesis is the alkylation of nitro paraffin salts followed by reduction of the nitro compound produced. Weisler[5] made an extensive review of the literature on the alkylation of nitro paraffin salts, which showed that, in general, oxygen-alkylation products, oximes and carbonyl compounds, are formed. However, it was indicated by the work of Dunning[6] and Hoover[7] that alkylation of nitro paraffin salts with *p*-nitrobenzyl chloride results in carbon-alkylation (a new carbon–carbon bond).

A series of seven nitro paraffin salts has been treated with *p*-nitrobenzyl chloride, forming carbon-alkylation products in every case. No effort was made to isolate products of oxygen-alkylation. The products, dinitro compounds, were then reduced to the corresponding diamines. The over-all scheme is shown in Fig. 1.



R and R' = H, alkyl, or cycloalkyl

Fig. 1.

The dinitro compounds and diamines prepared in this manner, together with their physical constants and analyses, are summarized in Tables I and II. The experimental procedures for only one alkylation and one reduction are described in the experimental section. They are, however, representative of the methods used in all the alkylations and reductions.

Experimental[8]

Materials.—Nitroethane (n^{20}D 1.3915), 1-nitropropane (n^{20}D 1.4013), 2-nitropropane (n^{20}D 1.3940), 1-nitrobutane (n^{20}D 1.4110), and 2-nitrobutane (n^{22}D 1.4037) were re-rectified Commercial Solvents Corporation products. Nitrocyclohexane was a re-rectified du Pont product. Nitrocyclopentane was prepared according to the directions of Shechter.[9] *p*-Nitrobenzyl chloride was an Eastman Kodak Company product.

Preparation of 2-Nitro-1-(*p*-nitrophenyl)-butane.—Sodium (3.4 g., 0.15 mole) was dissolved in 300 ml. of ethanol. Freshly distilled 1-nitropropane (65 g., 0.73 mole)[10] and then *p*-nitrobenzyl chloride (25 g., 0.15 mole) were added. After refluxing for eight hours,[11] the mixture was filtered to remove the sodium chloride. The filtrate was evaporated to a yellow oil. This oily residue formed a yellow solid after cooling and stirring with a small amount of ethanol. Recrystallization from ethanol gave 16.5 g. of 2-nitro-1-(*p*-nitrophenyl)-butane; yield 50.6%; m. p. 64-65°.

Preparation of 1-(*p*-Aminophenyl)-2-butylamine.—2-Nitro-1-(*p*-nitrophenyl)-butane (16.5 g., 0.074 mole), 5 g. of Raney nickel, and 300 ml. of ethanol were placed in a hydrogenation bomb. The reaction mixture was subjected to hydrogen at 1200 p. s. i. and 60-70° for eight hours. The catalyst was filtered from the reaction mixture, ethanol was removed under reduced pressure, and the residue was distilled. Nine grams of 1-(*p*-aminophenyl)-2-butylamine was obtained; b. p. 110° (1 mm.); n^{20}D 1.5642; yield 74.4%.

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[1] Based on a thesis by E. Janet Berry, submitted to the Faculty of Purdue University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1946.

[2] du Pont Fellow, 1944-1946; present address: Standard Oil Development Company, New York, N. Y.

[3] E. K. Lilly Fellow, 1947, American Cyanamid Company Fellow, 1947-1948; present address: Harvard University, Cambridge, Massachusetts.

[4] See Ritter and Kalish, THIS JOURNAL, **70**, 4048 (1948), for a list of references.

[5] Weisler, Doctoral Thesis, University of Rochester, 1939.

[6] Dunning, reported by Weisler, reference 5.

[7] Hoover, Doctoral Thesis, Purdue University, 1941.

[8] All melting points are corrected; microanalyses by Miss Theta Spoor, University of Illinois, Urbana, Illinois, and Mr. H. Galbraith and Miss L. Roth of Purdue University.

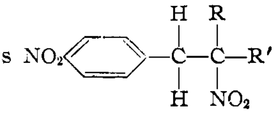
[9] Shechter, Doctoral Thesis, Purdue University, 1946.

[10] Since a primary nitro paraffin contains more than one replaceable hydrogen, a 500% excess of the nitro alkane was used in such cases to diminish the formation of polyalkylated products. When a secondary nitro paraffin was used, a 10% excess of the nitro alkane was usually employed.

[11] The condensation using nitrocyclopentane was heated to reflux and then cooled since further heating produced tars.

TABLE I

p-NITROBENZYL DERIVATIVES OF THE NITRO PARAFFINS

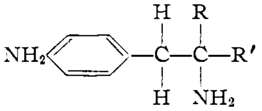


Derivative of	Yield, %	M. p., °C.	Formula	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Nitrogen Calcd.	Nitrogen Found
Nitroethane,[a] R = H, R′ = CH_3	24.4	51–52	$C_9H_{10}O_4N_2$						
1-Nitropropane, R = H, R′ = C_2H_5[b]	50.5	64–65	$C_{10}H_{12}O_4N_2$					12.50	12.40
2-Nitropropane, R = CH_3, R′ = CH_3	52.9	65–66	$C_{10}H_{12}O_4N_2$	53.57	53.84	5.36	5.45	12.50	12.43
1-Nitrobutane, R = H, R′ = C_3H_7	37.5	44–46	$C_{11}H_{14}O_4N_2$	55.46	55.72	5.88	6.09	11.76	11.67
2-Nitrobutane, R = CH_3, R′ = C_2H_5	39.8	58–60	$C_{11}H_{14}O_4N_2$	55.46	55.60	5.88	5.62	11.76	11.50
Nitrocyclopentane, RR′ = cyclopentyl	58.9	89–90	$C_{12}H_{14}O_4N_2$	57.60	57.77	5.60	5.72	11.20	11.26
Nitrocyclohexane, RR′ = cyclohexyl	62.3	98–100	$C_{13}H_{16}O_4N_2$	59.09	58.82	6.06	6.00	10.51	10.48

[a] This compound was first prepared and identified by Hoover.[7] [b] This compound was prepared by Dunning[6] and by Hoover.[7]

TABLE II

DIAMINES FROM *p*-NITROBENZYL DERIVATIVES,



Derivative of	Yield, %	B. p., °C.	B. p., Mm.	M. p., °C.	$n^{20}D$	Formula	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Nitrogen Calcd.	Nitrogen Found
Nitroethane,[a] R = H, R′ = CH_3	70.1	114	1.5	....	1.5742	$C_9H_{14}N_2$						
1-Nitropropane, R = H, R′ = C_2H_5	74.4	110	1	....	1.5642	$C_{10}H_{16}N_2$					17.07	17.00
2-Nitropropane, R = CH_3, R′ = CH_3	93.3	...	...	84–85	....	$C_{10}H_{16}N_2$	73.17	72.93	9.76	9.88	17.07	16.98
1-Nitrobutane, R = H, R′ = C_3H_7	82.5	143	3	....	1.5533	$C_{11}H_{18}N_2$					15.73	15.32
2-Nitrobutane, R = CH_3, R′ = C_2H_5	50.9	128	1.5	....	1.5600	$C_{11}H_{18}N_2$	74.16	74.02	10.11	10.22	15.73	15.90
Nitrocyclopentane, RR′ = cyclopentyl	65.9	125	3	....	1.5808	$C_{12}H_{18}N_2$					14.74	14.88
Nitrocyclohexane, RR′ = cyclohexyl	86.5	...	...	98–100	....	$C_{13}H_{20}N_2$	76.47	76.43	9.80	9.74	13.73	13.80

[a] This compound was first prepared by Hoover[7].

Summary

A series of dinitro compounds has been prepared by the reaction of the sodium salts of primary and secondary nitro paraffins with *p*-nitrobenzyl chloride. These dinitro compounds have been reduced to diamines by high pressure catalytic hydrogenation.

LAFAYETTE, INDIANA RECEIVED JANUARY 20, 1949

[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY OF MICHIGAN STATE COLLEGE]

The Apparent Molal Volume of Strontium Chloride in Ethanol–Water Mixtures

BY RICHARD LOUIS BATEMAN

Measurements made in this Laboratory[1] have shown that the conductance curves (equivalent conductance as a function of solvent composition) for strontium chloride in ethanol–water mixtures give points of inflection at about 60% ethanol in the solvent. This may be attributed to simultaneous changes in the viscosity and dielectric constant of the solvent as well as to changes in the degree of solvation of the ions of the electrolyte as the composition of the solvent is varied. When solvation of the ions of a salt occurs, the solvent molecules of the ion–solvent complex may be assumed to be more closely packed than in the pure solvent.[2] This packing effect should influence the molal volume of the salt; the greater the packing the smaller the molal volume. Thus the molal volume of the salt should be a measure of the size of the ion–solvent complex. The present work was undertaken to determine the influence of solvent composition and solute concentration on solution density and apparent molal volume of strontium chloride in various ethanol–water mixtures at 25°. No previous work has been reported on the apparent molal volume of strontium chloride in ethanol–water mixtures.

Experimental Part

Preparation of Materials.—J. T. Baker C. P. strontium chloride heptahydrate was recrystallized once above and once below 61.34° by the method of Richards and Yngve[3] and oven dried to constant weight.

Ethyl alcohol was freed of amines by treating each liter of stock 95% alcohol with a solution containing 20 ml. of sulfuric acid and 20 ml. of water and then distilling. Al-

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[1] Bateman and Ewing, THIS JOURNAL, **70**, 2137 (1948).

[2] Longsworth and MacInnes, *J. Phys. Chem.*, **43**, 239 (1939).

[3] Richards and Yngve, THIS JOURNAL, **40**, 91 (1918).