g. The ambient temperature was 26°. The *n*-butyllithium solution contained, in addition to *n*-butyllithium, 2.8% heavy mineral oil and less than 9% *n*-octane. Thus, the density of this solution at 26° was 0.697 ± 0.001.

Shelf-life of n-butyllithium solutions in n-heptane. Two solutions of *n*-butyllithium in *n*-heptane were prepared and placed in screw-topped cans (sealed with electrical tape) for shelf-life tests. Can No. 1 (1 quart capacity) contained 340 ml. of 0.639 molar *n*-butyllithium solution, while can No. 2 (1 gallon capacity) contained 1750 ml. of 2.05 molar *n*-butyllithium solution. The data given in Table VIII indicate stability as determined by periodic removal of aliquots from each of the cans (under argon) and analysis of these by hydrolysis and titration with standard acid.

TABLE VIII

RESULTS OF STABILITY TESTS

Can No.	Date of Analysis	Size of Aliquot Taken, Ml.	Concentration of Solution, Molarity	% Change in Molarity from Date of Preparation
1	2/26/58[a]	5	0.639	0
	3/19/58[b]	5	0.620	−3.1
	4/10/58	2	0.615	−3.8
2	3/13/58[a]	2	2.050	0
	4/3/58	2	2.075	+1.2
	6/9/58	2	2.069	+0.9

[a] Date of preparation of these solutions. [b] Screw cap tightened as much as possible and resealed with fresh electrical tape after this aliquot was taken. The old electrical tape had been extensively attacked by the solvent.

Pyrophoricity of n-butyllithium solutions in n-heptane. (A) *Small scale.* A small amount (approx. 1 ml.) of 2 molar *n*-butyllithium in *n*-heptane was placed on a 2-inch-diameter watch glass and allowed to evaporate to dryness. The dry sample did not ignite spontaneously, but formed a white crust. This crust did not react vigorously with water. Another 1-ml. portion of the *n*-heptane solution was placed on a watch glass and a few drops of water added to it. Heat was evolved with some fuming and loss of solvent, but no ignition of the material occurred.

(B) *Large scale.* Two 25-ml. portions of the 2-molar *n*-butyllithium solution were placed in 600-ml. beakers. After standing for 10 minutes, 10 drops of water was added to one of the beakers and 25 ml. of water to the other. A hard white crust formed in both cases with accompanying vigorous frothing in the latter case. In neither case was there spontaneous ignition.

MINNEAPOLIS, MINN.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

The Effect of Triethylamine on the Decomposition of Amylsodium[1]

AVERY A. MORTON AND FRANK K. WARD

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The decomposition of amylsodium appears to be more a cascade of metalations, eliminations of sodium hydride and polymerization than a splitting into simple fragments. Triethylamine hastens these changes but is not itself metalated or cleaved.

Previous work[2] showed that certain halide salts and alkoxides accelerated the decomposition of amylsodium. Presumably these salts were associated or coordinated with the organosodium salt. The present paper reports that triethylamine, a strong coordinating agent, accelerates the decomposition of amylsodium without being metalated or cleaved itself. To a large extent, however, this decomposition (and probably the previous ones[2] also) was largely a metalation of pentene and other unsaturated hydrocarbon units, accompanied by elimination of sodium hydride and polymerization. So much do these secondary processes prevail that any study of the primary dissociation of the organosodium salt into simple fragments is difficult.

$$C_5H_{11}Cl + 2Na \longrightarrow C_5H_{11}Na + NaCl \qquad (1)$$

The decomposition of amylsodium, prepared by equation 1, was observed at room temperature during 2 years and at 0°, 50° and 80° for shorter times, mostly 3 hr. and not exceeding 10 hr. For analysis, a preparation or an aliquot thereof was carbonated. Thereby sodium hydride became sodium formate. This action was quantitative when very small quantities were used, but this fact was not known until later stages of the work. Consequently the data for formic acid and sodium hydroxide in the tables are not complete. Amylsodium was also converted to sodium caproate and sodium butylmalonate, the latter by a secondary reaction[3,4] which was difficult to suppress, even at −72°, because the thickness of the reaction mixture prevented good contact with carbon dioxide. Pentenylsodium became a mixture of sodium hexenoates. In addition, there was formed the sodium salt of a tarry carboxylic acid, the ultimate analysis of which approached one carboxyl group for each five carbon atoms and approximately five hydrogen atoms. Metallic sodium did not react

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(1) This work was performed as part of a research project sponsored by the National Science Foundation.

(2) A. A. Morton and E. F. Cluff, *J. Am. Chem. Soc.*, **75**, 134 (1953).

(3) A. A. Morton, J. B. Davidson, and H. A. Newey, *J. Am. Chem. Soc.*, **64**, 2240 (1942).

(4) H. Gilman and H. A. Pacewitz, *J. Am. Chem. Soc.*, **62**, 1301 (1940).

with carbon dioxide but subsequently became sodium hydroxide by hydrolysis. The total carboxylates and hydroxide were determined by conductometric titration. Extraction of the aqueous layer with pentane removed caproic and hexenoic acids. Ether withdrew butylmalonic acid. The highly soluble formic acid was identified by Duclaux values. The tarry carboxylic acid precipitated with the initial addition of acid, but then redissolved and was finally recovered after the ether extraction by salting and extracting with special organic solvents such as *t*-butyl alcohol. No attention was given this material until the later stages of the work.

Equation 2 represents the initial formation of pentene followed by

$$C_5H_{11}Na \longrightarrow NaH + C_5H_{10} \longrightarrow C_5H_{11}Na + C_5H_{12} \qquad (2)$$

metalation to give pentenylsodium. The conversion to tar is shown overall by equation 3.

$$4C_5H_{11}Na \longrightarrow \underset{\left\lfloor \xrightarrow{CO_2} \text{polymer carboxylate} \right.}{[C_5H_5Na]} + 3C_5H_{12} + 3NaH \qquad (3)$$

Table I gives the results for the two-year experiment, in which the changes were slow enough to be followed easily. The most noteworthy features were (a) the nearly constant values maintained for the total carboxylates (column 3) and (b) the absence of appreciable hexenoic acid during the first six months as shown by the near sameness of the refractive index in column 6 during that period. Table II shows the effect of three equivalents of triethylamine. Within 3 hr. the amine had caused 18% more decomposition at 0° and 54% more at 50°. At 80° the decomposition in the presence of the amine was 90% complete in ten minutes as compared with 60% in 3 hr. in its absence.

TABLE I

DECOMPOSITION OF AMYLSODIUM AT ROOM TEMPERATURE

		Yield of Sodium Carboxylates				
				Extracted		
Time, Months	Na Metal, %	Titr.,[a] %	Total,[b] %	Pentane,[c] %	n_D^{25}	Ether,[d] %
0	5	95	92	89	1.4150	3
1			75	64	1.4151	11
2	5	95	51	40	1.4149	11
3	5	95	45	26	1.4150	19
4	5	95	32	11	1.4151	21
5			26	6	1.4153	20
6	5	95	26	6	1.4155	21
7	5	95	27	6	1.4270	21
9			26	8	1.4369	18
24			26	6	1.4372	20

[a] This column records the total carboxyl groups as determined by conductometric titration. [b] This column shows the sum of caproic, butylmalonic and hexenoic acids. All acids except formic and tarry acids were extracted readily. [c] This column represents caproic and hexenoic acids. [d] Butylmalonic acid is removed by ether.

TABLE II

EFFECT OF THREE EQUIVALENTS[a] OF TRIETHYLAMINE ON THE DECOMPOSITION OF AMYLSODIUM

			Extractable Carboxylates[c]	
Temp.	Time, Hrs.	Total Carb.[b] with Amine, %	No Amine, %	With Amine, %
0	0		85–92	
0	2	95–96	88	71–77
0	4		88	65–67
0	6			60–65
0	8			54
0	10			55
50	3	95–96	83–86	20–41
80	$^1/_6$	90–96		9–11
80	3	94	35–38	3–8

[a] Equivalents of triethylamine per organosodium reagent. [b] This column represents the sum of all carboxylic acids as determined by conductometric titration. [c] These columns represent the sum of the caproic, butylmalonic, and hexenoic acids which have been extracted by pentane and ether.

The tarry acid formed according to Equation 3 probably accounts for a large share of the reaction, although the actual amount isolated was low. It was not measured until the end of the work when the search for nitrogen-containing organic material led to combustion analyses. Then its importance was realized. The estimated final weight was about 5% of the amyl chloride used, and the composition approximated a singly carboxylated amyl fragment which had lost over half of its hydrogen atoms. Theoretically this tar accounted for about 40% of the amyl chloride. The second largest organic reaction product was the 26% (see Table I) of hexenoic acid and a malonic acid. About 5% of the amyl chloride must have been consumed in a Wurtz preparation of decane with some formation of pentane and pentene.[5] The remaining 21% might have been primary decomposition to sodium hydride and pentene.

This material balance is only approximate, but shows that metalation was the predominant reaction, amounting to more than 66%. The excess of pentane over pentene in the initial stages of pyrolysis[6] is accordingly understandable, because this decomposition is more metalation than a dissociation to simple fragments. Other sodium salts have behaved similarly. For instance, ethane was obtained before ethylene in the pyrolysis of ethylsodium,[7] cyclopropane was obtained without appreciable, if any, cyclopropene from the decom-

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(5) A. A. Morton and G. M. Richardson, *J. Am. Chem. Soc.*, **62**, 123 (1940).

(6) A. A. Morton and E. J. Lanpher, *J. Org. Chem.*, **20**, 839 (1955); **21**, 93 (1956).

(7) W. H. Carothers and D. D. Coffman, *J. Am. Chem. Soc.*, **51**, 588 (1929).

position of cyclopropylsodium,[8] and benzene, unaccompanied by biphenyl or other volatile products, was collected from the pyrolysis of phenylpotassium.[9]

The change of amylsodium to tar took place apparently with great ease, probably because each succeeding step was metallated more easily than the previous one. This rapid cascade of reactions, so typical of many processes[10] with organoalkali metal reagents, accounts nicely for the fact that an early step in the process, pentenylsodium, was not demonstrated to be present in the decompositions at room temperature until after 7 months (see Table I, column 6) when most of the amylsodium had been consumed and the drive toward the final product of decomposition had largely ceased. This absence of appreciable quantity of intermediate product is in general accord with an earlier study[11], where small amounts only of impure dicarboxylic were obtained from a decomposition which was not allowed to reach the tarry condition.

Three equivalents of triethylamine accelerated the decomposition, but more caused no further increase. (See Table III.) Therefore its effect is not reasonably attributed to increased solubility of the reagent (actually no appreciable solution of reagent was observed visually), or else the amount would have increased continually. The amine was not metallated or cleaved because no acid or tar which contained nitrogen, and no diethyl amine, were found. The prime role of the amine seems to have been coordination. In an earlier paper[6] coordination of reactants about the cation was described as one of the factors which caused bond stretching in an early phase of chemical reaction and for several years such coordination has been assumed[12] to be important in the reactions of these reagents.

TABLE III

EFFECT OF THE AMOUNT OF TRIETHYLAMINE ON THE DECOMPOSITION OF AMYLSODIUM AT 0° DURING 2 HR.

Et_3N Mole Equiv.	No. of Tests	Yield of Carboxylic Acids Total Extr., %	Pent. Sol., %	Ether Sol., %
0	1	88	85	3
1	1	77	44	33
3	4	71–77	45–30	26–47
4	3	69–77	49–51	20–26
5	2	72	50–47	22.25
6	1	69	42	27
7	1	70	44	26
9	1	70	49	21
10	1	69	49	20

Special attention is called to the fact, mentioned also in earlier work,[2] that during the decomposition at 80° the metallic sodium agglomerated into large balls which occluded amylsodium and the products of decomposition. When the balls were cut open and carbonated and those products were added to the others, the total amount of sodium metal (see Table II) was the same as in the other experiments. Hence no appreciable amount of sodium metal formed during decomposition, contrary to an earlier supposition.[2] The analytical methods used in this work, however, do not exclude the possibility that a tiny amount of atomic sodium (formed as a consequence of dissociation to amyl and atomic sodium[2,6] as in equation 4 and of failure of the sodium radical to disproportionate with the amyl radical to give pentene and sodium hydride) could have deposited upon the particles of metallic sodium left over because of the failure of the preparation by Equation 1 to be quantitative. Only a tiny

$$C_5H_{11}Na \longrightarrow [C_5H_{11}\cdot + \cdot Na] \longrightarrow C_5H_{10} + NaH \quad (4)$$

amount of the atomic sodium is needed to coat the tiny sodium particles. In this connection it is possibly significant that this agglomeration has not occurred in ordinary metalations at 80°, although approximately the same amount of metallic sodium, left over from the preparation of amylsodium, was present in such cases. In metalations, however, there is present a large quantity of hydrocarbon to which the atomic sodium is shifted rather rapidly and the new salt thus formed is thermally relatively stable.

EXPERIMENTAL

Decomposition of amylsodium during two years. Amylsodium was prepared from 0.5 mol. of amyl chloride and 1 g. atom of sodium in heptane in the manner regularly employed in this laboratory.[13,14] After the preparation was completed, the reaction mixture was transferred to a nitrogen-filled bottle and stoppered with a cork covered with a glyptal cement. Three such preparations were made and stored in three separate bottles. From one bottle aliquots were removed for 7 consecutive months for analysis. Each time the bottle was well shaken by hand and a sample was removed by forcing the liquid upward into a pipette by nitrogen pressure. The other two preparations were carbonated entirely after 9 and 24 months, respectively.

Each aliquot was carbonated by forcing the mixture onto solid carbon dioxide. For this operation to be quantitative with respect to sodium hydride, no more than 60 meq. of that salt should be present. Roughly that amount was present in one-eighth of the ordinary preparation of amyl-

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(9) A. A. Morton and E. J. Lanpher, *J. Org. Chem.*, **23**, 1639 (1958).

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(13) A. A. Morton, F. D. Marsh, R. D. Coombs, A. L. Lyons, S. E. Penner, H. E. Ramsden, V. B. Baker, E. L. Little, Jr., and R. L. Letsinger, *J. Am. Chem. Soc.*, **72**, 3785 (1950).

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sodium. Approximately 24 hr. later, 300 ml. of distilled water was added to the carbonated product. After the heptane and aqueous layers were clear, the hydrocarbon layer was extracted twice with 50 ml. of water and the aqueous portion was extracted twice with 200 ml. of ethyl ether. Then the combined aqueous portions were made up to 500 ml. A 2-ml. aliquot was titrated conductometrically against $0.1N$ hydrochloric acid with a Serfass direct reading MHO-OHM model conductance bridge[15] and a dip conductance cell having a constant of 0.98. An input current of 1000 cycles per sec. was used. The solvent was a mixture of 200 ml. of denatured alcohol and 150 ml. of distilled water. A control test of a mixture of 1.77 meq. of caproic acid and 1.83 meq. of sodium hydroxide gave 1.78 meq. of sodium caproate.

The remainder of the aqueous solution was acidified with sulfuric acid and extracted first with three 150-ml. portions of pentane and next with three 150-ml. portions of ether. The extracts were dried with anhydrous calcium sulfate, filtered and diluted to 500 ml. A 5-ml. aliquot was removed and titrated to a phenolphthalein endpoint in order to determine the carboxylic acid in the respective combined extracts.

The pentane extract was evaporated and the caproic or hexenoic acid was removed by distillation through a 35-mm. column of the Podbielniak type. They did not need careful fractionation. Only caproic acid appeared during the first 6 months (see Table I); hexenoic acid was almost the sole product from the later stages of the decomposition. Caproic acid was identified by its boiling point, 50°/1 mm. to 80°/4 mm., neutralization equivalent equal to 116 (calculated 116), refractive index of n_D^{25} 1.4151 (recorded[16] 1.4149), its amide derivative which melted at 99–100° (recorded[17] 101°), and its failure to decolorize bromine. The hexenoic acids (mostly 3-hexenoic) decolorized bromine in carbon tetrachloride and showed strong infrared absorption at 1640 and 965 cm.$^{-1}$, moderate at 990 cm.$^{-1}$, in accord with data published by Bellamy.[18] The boiling point was 80°/4 mm. and the neutralization equivalent was 112.5 (calculated 114). The refractive index was n_D^{25} 1.4369, which agreed with a value, 1.4375, found previously[13] in this laboratory.

The ether extract, after evaporation, yielded butylmalonic acid, which melted at 100–101° (recorded[19] 101.5°) and showed no depression when mixed with an authentic sample. It was further identified by the neutralization equivalent of 80 (calculated 80) and the melting point of its amide derivative 197–199° (recorded[20] 200°). After 9 months (see Table I) this extract contained not only butylmalonic acid but also some unsaturated (to bromine) product as might be expected. Infrared absorption showed strong absorption bands at 1640 and 965 cm.$^{-1}$, typical[18] for unsaturated acids. After numerous precipitations tiny amounts of acids which melted at 144°, 152°, and 183° were recovered, each well above the value for butylmalonic acid. No attempt was made to characterize them.

The tarry acid was soluble in common organic solvents. Neither the acid nor its methyl ester (made from methanol with acid catalyst) distilled when heated to 250°/1 mm. The neutralization equivalent was 155° ± 10 depending on the sample and its solubility during titration. A carbon-hydrogen analysis showed an oxygen percentage by difference of 35.12, equivalent to more than one carboxyl per five carbon atoms. The percentages of carbon and hydrogen were 59.3 and 5.6 respectively, equivalent after deduction for carboxyl to an atom ratio of hydrogen to carbon of 1.17. At that ratio the tar could be derived from an acetylene system. Davis[21] has found some evidence for acetylene type compounds from the decomposition of amylsodium.

The aqueous layer remaining after extraction with ether was steam distilled until about 50% of the original volume was collected. Two drops of this distillate was analyzed by the chromotropic acid color test described by Feigl.[22] The test varied from weak to strong depending upon the amount of formic acid which was present. The remainder of the distillate was fractionally distilled and 150 ml. of the fraction boiling at 100° was analyzed for formic acid by Duclaux numbers[17] (found: 3.90, 4.36, 4.51; recorded[17] 3.95, 4.40, 4.55). The remaining portion of the 150-ml. fraction was made alkaline and evaporated to a small volume. It was then reduced with magnesium powder and acid. The resulting formaldehyde yielded a dimethone derivative which melted at 187–189° in accord with Horning's[23] result (191°).

The residue from the original distillation of the aqueous portion was tested for oxalic acid by the method described by Feigl.[22] No aniline blue color was obtained.

Effect of time and temperature on the decomposition of amylsodium. The amylsodium was prepared as described in the previous section, but the stirring at 10,000 rpm. was continued for the times and temperatures specified in Table II. The separations and identifications of the products were essentially the same as already described.

Decomposition in the presence of triethylamine. The triethylamine obtained from Eastman Kodak Company was distilled and the fraction collected from 88.5° to 89.5° (recorded[24] 89.4°) was dried for several months over potassium hydroxide. The refractive index was n_D^{25} 1.3989 (recorded[25] n_D^{20} 1.4003). Later this material was shown by polymerization tests[26] to contain a trace of water, possibly 0.05%, but this small amount would not reduce the quantity of sodium reagent appreciably. The tests for the usual products of decomposition were as described in a previous section. In addition, tests were carried out for compounds which might contain nitrogen, such as diethylamine from cleavage, amino carboxylic acids from metalation, and nitrogen-containing tar.

The hydrocarbon layers obtained after carbonation and hydrolysis were fractionated through a four-foot, one-inch diameter column packed with $^3/_{32}$-inch single-turned helices. The fraction boiling from 40° to 70°, which should have contained any diethylamine, was treated with hydrochloric acid gas but no diethylamine hydrochloride was obtained. The aqueous layer, after extraction of the carboxylic acids with pentane and ether, was made alkaline and extracted with three 150-ml. portions of ether. The ether extract was dried over anhydrous calcium sulfate and treated with hydrochloric acid gas. No diethylamine hydrochloride separated. In control tests a mixture of diethylaminesodium and amylsodium was carbonated. Subsequent distillation of the

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TABLE IV

EFFECT OF TRIETHYLAMINE UPON THE FORMATION OF TAR

	Without Amine		With Amine
Preparation			
Temp.	Room	80	80
Time, hr.	[3.5][a]	3	3
Analyses			
C, %	59.32	52.70	63.46[b]
H, %	5.56	6.13	5.65
O,[c] %	35.12	31.17	30.89
Atoms or groups			
C	3.48	3.43	4.48
H	4.06	5.18	4.85
CO_2H	1	1	1
H[d]/C	1.17	1.51	1.08
CO_2H/5C[d]	1.44	1.45	1.12

[a] Time in months. This tar was dissolved in methyl ethyl ketone, treated with decolorizing carbon, precipitated, redissolved and reprecipitated in an attempt to separate a pure compound. [b] A combustion analysis for nitrogen showed none present. [c] Oxygen by difference. [d] For these ratios the hydrogen and carbon attached to the carboxyl group are deducted from the total atoms of hydrogen or carbon, respectively.

hydrocarbon fraction and of the aqueous portion by the above described methods yielded diethyl amine hydrochloride in both fractions.

After the butylmalonic acid was extracted with ether, the acidic aqueous layer was salted and extracted successively with *t*-butyl alcohol, methyl ethyl ketone, and ethyl acetate, which should remove some or all of any aminocarboxylic acid, had any such material formed by one of a variety of methods which might be assumed to have occurred. The tarry residues, obtained by evaporation of the solvent, in each case showed no nitrogen when tested by a sodium fusion–Prussian blue test. In another case the tarry residues were burned in the customary ultimate analysis for nitrogen, but no such gas was collected.

Table IV shows a comparison of the tarry carboxylic acids prepared with and without the amine. The products are essentially the same except for the fact that the action seemed to have been carried further by the amine.

Attempts were also made to repeat the observation recorded in an earlier paper[27] that some nitrogen-containing carboxylic acid was obtained. The conclusion was that traces of triethylamine were difficult to remove and had been codistilled with the acid.

Acknowledgments. The authors are indebted to Dr. Nagy for the combustion analyses and to Professor Nelson for the infrared measurements.

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[CONTRIBUTION FROM THE SCHOOL OF PHARMACY, DUQUESNE UNIVERSITY]

The Rhodium-Catalyzed Hydrogenation of Ethyl-5,6-benzocoumarin-3-carboxylate[1]

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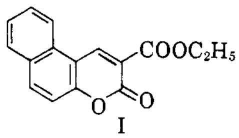
Room temperature, low pressure hydrogenation of ethyl 5,6-benzocoumarin-3-carboxylate (I) employing rhodium (5%) on alumina as the catalyst afforded a decalin derivative, ethyl β-(α-decalyl)isobutyrate (II). The structure of (II) was elucidated by the preparation of the amide and acid derivatives and by an unambiguous synthesis starting with malonic ester.

Since rhodium (5%) on alumina was shown to be effective in the hydrogenation of such aromatic systems as pyridine[2] and arylphosphonic acids,[3] it was thought feasible to use this catalyst in the hydrogenation of ethyl 5,6-benzocoumarin-3-carboxylate (I), in connection with the synthesis of potential oxytocics. It has been shown[4] that the W-1 Raney nickel catalyzed hydrogenation of I yielded a decalin derivative, but only at 2900 pounds per square inch and at 140°; at this temperature, extensive hydrogenolysis of the lactone and ester occurred.



I

When a mixture consisting of a one to one- and-one-half ratio of I to rhodium (5%) on alumina was hydrogenated for thirty-nine hours at room temperature and at a hydrogen pressure of 55 pounds per square inch, an oil was obtained. The ultraviolet spectrum of the oily product showed no absorption indicating that aromaticity had been destroyed. An infrared spectrum of the compound revealed a strong band at 1735 cm.$^{-1}$, suggestive

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(1) Abstracted from a thesis submitted by O. LeRoy Salerni to the faculty of Duquesne University in partial fulfillment of the requirements for the degree of Master of Science, August 1959.

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