The following constants of the purified valerolactone were determined: b. p., 206–207°; 125° (60 mm.) 78° (4 mm.) n_D^{25}, 1.4301; d^{25}, 1.04608. It is miscible with ethyl alcohol, water and ether, in all proportions.

Summary

By substituting metallic sodium for sodium amalgam in the reduction of levulinic acid, a quicker and more convenient method for the preparation of *n*-valerolactone was devised. The latter was highly purified and a few of its physical constants were determined.

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SIDE-CHAIN OXIDATIONS BY MEANS OF NITRO COMPOUNDS

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Introduction

The oxidation of a side chain by means of a nitro compound presents a new type of double decomposition in which each of the reacting organic substances yields a product, or products, of value. Thus, if it were possible to oxidize the side chain of an aromatic hydrocarbon, such as toluene, with an aromatic nitro compound, such as nitrobenzene, the possible products would be benzyl alcohol, benzaldehyde or benzoic acid on the one hand and azoxybenzene, azobenzene, hydrazobenzene or aniline on the other. If nuclear substitution products of toluene and nitrobenzene were used, corresponding derivatives would be anticipated. The products formed and the amount of each would depend, in part, on the acidity or alkalinity of the reacting medium.

Few instances of the employment of nitro compounds as oxidizing agents are recorded in the literature. Such use has been made of nitrobenzene in the manufacture of fuchsin (magenta),[1] and in the Skraup synthesis. Anthranilic acid is formed by an intramolecular rearrangement of *o*-nitrotoluene when heated with alkali.[2]

The general problem, as considered in this paper, relates to the conditions most favorable for the aggressive action of nitro compounds as extramolecular oxidizing agents for side chains.

Experimental Part

Pure toluene was treated with nitrobenzene, first in an acid, then in an alkaline solution, with and without catalysts. There was no indication

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[1] Brüning, *Ber.*, **6**, 25, 1072 (1873). Coupier, *Ber.*, **6**, 423 (1873).

[2] Ullmann, "Enzyklopadie der technischen Chemie," Urban u. Schwarzenberg, **1915**, vol. 2, p. 332.

of oxidation in any case. Benzyl alcohol was successfully oxidized by nitrobenzene in an alkaline solution (Table I). Similar results were obtained when *o*-nitrotoluene was used with benzyl alcohol (Table II). The oxidations of benzyl chloride and bromide were tried with little or no success. The failure was due to the slow hydrolysis of the benzyl halides. Negative results were obtained when *o*-nitrotoluene and nitrobenzene were heated in an alkaline solution; also, *p*-nitrotoluene and nitrobenzene failed to react under similar conditions. When *m*-dinitrobenzene was heated with benzyl alcohol in an alkaline solution, ammonia was evolved and the resultant product was a charred mass. When picric acid, benzyl alcohol and sodium hydroxide were mixed, the reaction proceeded with explosive violence without the application of heat.

Procedure

Each experiment involved placing 10 g. of the side-chain compound, varied amounts of sulfuric acid or sodium hydroxide, and a slight excess of the calculated amount of the nitro compound in a flask, equipped with an air-cooled reflux condenser, and maintaining the mixture at the boiling temperature for a known time. The heated mass was then poured into cold water and suitable tests were made for benzoic acid, azo compounds, etc. The flasks containing alkaline reaction mixtures were set on a false bottom, above water, in an autoclave and heated at 138–140° for four hours.

The products were subjected to steam distillation until crystals of azobenzene appeared in the condenser. The distillate was acidified, extracted with ether and the extract carefully distilled from a previously weighed flask until the ether and dissolved water were removed. The weight of this residue was taken as unchanged nitro compound. The acid residue from the ether extract was tested for aniline by the isonitrile reaction. The residue from the steam distillation was cooled to 10–15°, allowed to stand for an hour and filtered. The azobenzene, collected on

TABLE I

RESULTS OBTAINED WITH BENZYL ALCOHOL AND NITROBENZENE

Benzyl alcohol, 10 g.; nitrobenzene, 12 g.; autoclave temperature, 138–140°; time, 4 hours.

Expt.	NaOH, g.	H_2O, cc.	Distilled oil, cc.	Azobenzene, g.	Benzoic acid, g.	Benzoic acid, %
1	10	..	2	9.5	9.8	86.8
2	5	..	1.5	8.0	9.55	84.6
3	10	10	...	7.0	7.44	65.9
4	5	5	2	7.6	7.45	66.0
5	3	..	3	8.5	10.5	93.0
6[a]	10	..	...	3.7	5.3	47.5
7[a]	10	10	...	3.4	4.0	35.0
8[a]	10	..	...	3.4	4.2	37.0

[a] Five g. of nitrobenzene was used in Expts. 6, 7 and 8.

TABLE II

RESULTS OBTAINED WITH *o*-NITROTOLUENE AND BENZYL ALCOHOL

Benzyl alcohol, 10 g.; *o*-nitrotoluene, 13 g.; autoclave temperature, 138–140°; time, 4 hours.

Expt.	NaOH, g.	H_2O, cc.	Distilled oil, cc.	Azo-toluene, g.	Benzoic acid, g.	Benzoic acid, %
1	10	..	3.6	9.0	8.54	73.68
2	5	..	9	3.0	6.2	55.05
3	10	10	5	7.5	7.87	70.00
4	5	5	3	8.5	8.7	77.07
5	5	..	8	4.5	6.87	60.86

the paper, was dried in the air and weighed. The filtrate was acidified with hydrochloric acid, allowed to stand until cold and then filtered. The weight of the air-dried residue was taken as benzoic acid. The filtrate from the benzoic acid was measured and from its volume the amount of dissolved benzoic acid was calculated. The total of this and the weight of the air-dried residue was taken as the yield of benzoic acid.

The study is to be extended to the action of nitro compounds as oxidizing agents with the several types of nuclear substitutions of toluene and xylene.

Summary

1. Benzyl alcohol can be oxidized to benzoic acid by nitrobenzene or *o*-nitrotoluene in a strongly alkaline solution. At the same time, the corresponding azo compound is formed.

2. Nitrobenzene gave more nearly the calculated yields of benzoic acid and azo compound than did *o*-nitrotoluene.

3. Picric acid and *m*-dinitrobenzene oxidize benzyl alcohol to a charred mass. The former reacts with explosive violence.

4. Toluene, benzyl chloride and benzyl bromide are not oxidized by nitrobenzene or by *o*-nitrotoluene under the described conditions.

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