ing forty-three minutes while a 0.05% (1:2000) solution anesthetizes for six minutes. *n*-Amyl sulfate does not alter the intraocular tension of the rabbit's eye when used in 1% concentrations.

Summary

A series of new β-alkylamino-α,α-dimethylethanols has been prepared.

From these alcohols, as well as two β-alkylamino-α,α-diethylethanols, by combination with *p*-nitrobenzoyl chloride and reduction, there has been prepared a series of new esters.

A pharmacological study of one ester shows it to have interesting surface anesthetic properties.

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[A CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE GOODYEAR TIRE & RUBBER CO.]

Nickel as a Catalyst for the Hydrogenation of Aromatic Halogen Compounds

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The catalytic hydrogenation of *o*-nitrochlorobenzene over nickel was first attempted by Sabatier and Mailhe[1] who, however, obtained aniline hydrochloride as a result of a combined hydrogenation and dehalogenation. Furthermore, Sabatier and Espel[2] found that small amounts of halogen compounds did not interfere with the vapor phase reduction of benzene provided that some nickel remained in catalytically active form after a portion had been converted to nickel halide in removing the impurity. The simultaneous hydrogenation and dehalogenation of organic compounds has been effected by several workers[3] using platinum and palladium catalysts, and certain others have effected hydrogenation without the removal of halogen. Ellis[4] describes the preparation of a reduced nickel catalyst suitable for the production of chlorinated aromatic amines from the corresponding nitro compounds. Strangely, very little has appeared in the recent literature concerning the use of nickel for the hydrogenation of halogen compounds. The present paper attempts to demonstrate that the hydrogenation of these compounds is a general reaction which is applicable in an efficient and economical process.

The success of this conversion depends upon the choice of a stable halide, the use of a temperature below that at which dehalogenation occurs, and the use of a catalyst with sufficient mass of metal. These conditions have been met in the hydrogenation of aromatic halogen compounds at temperatures below 150° with Raney[5] nickel.

The substituents reducible below 150° which may be attached to the halogenated aromatic nucleus include the olefinic, acetylenic, nitro, nitroso, cyano, oximino, azido, azo, and carbonyl groups. Anils and hydro-amides may also be treated. It has not been possible to hydrogenate chlorobenzene to chlorocyclohexane, for at the temperature required to saturate the benzenoid ring halogen was removed giving rise to benzene in small amounts. Benzyl chloride gave some diphenylethane under similar conditions. In the aliphatic series 1-chloropropene, ω-chlorostyrene, *sym*-dichloroethylene, and tetrachloroethylene resisted saturation of the olefin bond.

The accompanying table gives the names of hydrogen acceptors and reaction products with physical properties and yields for fourteen different halogen compounds illustrating the behavior of several types. Most of the products were distilled from the reaction mixture. Others were obtained in crystalline form as solid product or hydrochloride derivative. All products were identified by the formation of known characteristic derivatives or by analysis.

The relative strength of attachment of chlorine, bromine, and iodine to the aromatic nucleus was demonstrated in the reduction of the halogenated nitrobenzenes. *p*-Chloronitrobenzene gave rise to *p*-chloroaniline even at 150° in nearly quantitative yield. *p*-Bromonitrobenzene was not quite so stable, but still the predominant product was *p*-bromaniline. *o*-Iodonitrobenzene was largely dehalogenated during reduction to aniline, only a small amount of *o*-iodoaniline being isolated from

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(1) Sabatier and Mailhe, *Compt. rend.*, **138**, 245 (1904).

(2) Sabatier and Espel, *Bull. soc. chim.*, **15**, 778 (1914).

(3) For a complete résumé of the prior work in hydrogenation of organic halogen compounds, see Ellis, "Hydrogenation of Organic Substances," 3d. ed., D. Van Nostrand Co., Inc., New York, N. Y., 1930.

(4) Page 259 of Reference 3.

(5) Murray Raney, U. S. Patent 1,628,190, May 10, 1927.

TABLE I

Hydrogen acceptor	Product	B. p.		Yield, %
		°C.	Mm.	
o-Chloronitrobenzene	*o*-Chloroaniline[a]	95–100	8	96.5
m-Chloronitrobenzene	*m*-Chloroaniline[b]	95–100	9	90.3
p-Chloronitrobenzene	*p*-Chloroaniline[c]	100–110	8	97.0
p-Bromonitrobenzene	*p*-Bromoaniline[d]	M. p. 60		83.0
o-Iodonitrobenzene	*o*-Iodoaniline[e]	M. p. 52		23.0
2,5-Dichloronitrobenzene	2,5-Dichloroaniline[f]	120–125	10	97.0
2,4-Dinitrochlorobenzene	*m*-Phenylenediamine[g]	135–140	5	91.0
o-Chlorobenzaldazine	*o*-Chlorobenzylamine[h]	95–100	9	81.0
o-Chlorobenzalaniline	*o*-Chlorobenzylaniline[i]	.....		65.5
Benzal-2,5-dichloroanil	Benzyl-2,5-dichloroaniline[j]	M. p. 44–45		91.0
o-Chlorobenzaldehyde and excess ammonia	*o*-Chlorobenzylamine[h]	90–95	8	87.5
p-Bromobenzophenone	*p*-Bromobenzhydrol	M. p. 61–62		72.0
p-Bromobenzophenone oxime	*p*-Bromobenzhydrylamine[k]	M. p. 126		88.5
p-Chlorobenzonitrile	*p*-Chlorobenzylamine[l]	98–102	10	64.0
	Di-*p*-chlorobenzylamine[m]	.....		21.0

[a] Hydrochloride, m. p. 230–235°. [b] Benzoyl deriv., m. p. 118–119°. [c] Benzoyl deriv., m. p. 187–188°. [d] Benzoyl deriv., m. p. 201–202°. [e] Acetyl deriv., m. p. 105–107°. [f] Hydrochloride, m. p. 190–191°. [g] Benzoyl deriv., m. p. 237–238°. [h] Benzoyl deriv., m. p. 115–116°. [i] Isolated as hydrochloride, m. p. 185–186°. [j] *Anal.* Calcd. for $C_{13}H_{11}NCl_2$: N, 5.55; Cl, 28.2. Found: N, 5.6; Cl, 27.7. [k] *Anal.* Calcd. for $C_{13}H_{12}NBr$: N, 5.34; Br, 30.5. Found: N, 5.49; Br, 29.6. [l] Hydrochloride, m. p. 238–240°. [m] Isolated as hydrochloride, m. p. 286–288°.

the reaction mixture. Dinitrochlorobenzene lost chlorine to give *m*-phenylenediamine on reduction, even when the reaction temperature was maintained below 40°. On the other hand, the presence of two chlorine atoms in dichloronitrobenzene did not interfere at all in the conversion to dichloroaniline and similarly benzal-2,5-dichloroanil was reduced to benzyl-2,5-dichloroaniline.

When operating with a readily reducible compound such as *p*-chloronitrobenzene a single portion of catalyst has been used in six successive reductions with only slight diminution in activity as judged by reaction time and temperature. In addition, several catalysts which were no longer sufficiently active for more difficult hydrogenations served very well in these simpler conversions.

Experimental

Apparatus and Catalysts.—The shaking autoclave in which these reactions were carried out had a capacity of 900 ml. and was similar in design to those described by Adkins.[6] The reactants were placed directly in the steel autoclave, no liners of copper or glass being employed. The nickel catalyst was prepared from Raney alloy according to the method of Covert and Adkins.[7]

Manipulation.—All hydrogenations were run in ethanol solution, although other solvents which are compatible with reducible compound, product, and water may also be used. When the hydrogenations were attempted in aqueous suspension, the reaction stopped far short of completion. In general, 5% of catalyst based on the weight of the reducible compound was used, although amounts as low as 2% may be used with accompanying slower reaction rate. Temperature was maintained below 150°, and preferably below 125°. Hydrogen pressures as low as 20 atm. were satisfactory in these hydrogenations, but the reaction rate was quite slow. With pressures of 100 atm. or more the reaction was very vigorous and much heat was evolved.

The following description of an experiment in the hydrogenation of *p*-chloronitrobenzene is quite typical. A mixture of 300 g. of *p*-chloronitrobenzene (tech.), 400 ml. of alcohol, and 15 g. of Raney nickel was charged into the autoclave under 100 atm. hydrogen pressure. The autoclave was shaken and slowly heated above room temperature. At 50° absorption of hydrogen as judged by drop in gage pressure was quite rapid and external heating was discontinued. When the pressure had fallen to 20 atm. more hydrogen was admitted from the storage cylinder. After twenty-three minutes the theoretical amount of hydrogen had been absorbed at a maximum temperature of 100°. The cooled reaction mixture, after removal from the autoclave, was filtered from the catalyst and distilled to give 236 g. (97%) *p*-chloroaniline, b. p. 100–110° (8 mm.). The recovered catalyst could be used repeatedly in subsequent hydrogenations.

Summary

The hydrogenation of certain readily reducible groups attached to a halogenated aromatic nucleus has been accomplished with nickel catalyst. These halogenated compounds behave just as do their unhalogenated analogs in regard to time, temperature, and completeness of hydrogenation.

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[6] Adkins, *Ind. Eng. Chem., Anal. Ed.*, **4**, 342 (1932).

[7] Covert and Adkins, THIS JOURNAL, **54**, 4116 (1932).