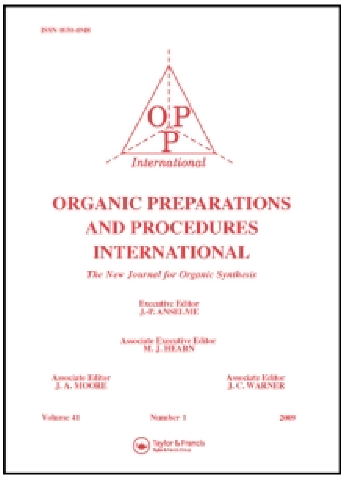

Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

HYDROGENOLYSIS OF ARYL HALIDES IN THE PRESENCE OF RANEY NICKEL IN ALKALINE MEDIUM

A. J. De Koning[a]
[a] University of Botswana, Lesotho, AFRICA

To cite this Article De Koning, A. J.(1975) 'HYDROGENOLYSIS OF ARYL HALIDES IN THE PRESENCE OF RANEY NICKEL IN ALKALINE MEDIUM', Organic Preparations and Procedures International, 7: 1, 31 — 34

To link to this Article: DOI: 10.1080/00304947509356811

URL: http://dx.doi.org/10.1080/00304947509356811

ORGANIC PREPARATIONS AND PROCEDURES INT. 7(1), 31-34 (1975)

HYDROGENOLYSIS OF ARYL HALIDES IN THE PRESENCE OF RANEY NICKEL IN ALKALINE MEDIUM

A. J. de Koning

University of Botswana, Lesotho and Swaziland
Roma, Lesotho, AFRICA

Hydrogenolysis of alkyl and aryl halides under the influence of catalysts such as Pd and Raney Ni has been mentioned by several workers as part of specific syntheses.[1-3] It appears however, that the reaction is relatively unknown; this may well account for the fact that in some reports, lithium aluminium hydride (LAH) in tetrahydrofuran - a much more cumbersome procedure - is recommended for the hydrogenolysis of aryl halides.[4,5] The present report draws attention to this remarkably simple method for the replacement of organically bound halogen by hydrogen. The method can be used for synthetic purposes and for the accurate determination of halogen linked to carbon.

Hydrogenolysis of fluoro-, chloro-, bromo- and iodobenzene in a 0.2 M solution of KOH in ethanol at room temperature and atmospheric pressure in the presence of Raney Ni released the halogen atom quantitatively. The rate of the reaction depended on certain experimental conditions such as the rate of shaking, the amount and activity of the catalyst and the temperature. However, under standardized conditions the following rates were obtained: fluoro 0.8; chloro 1.0;

bromo 1.9; iodo 3.2. These rates clearly reflect the different carbon to halogen bond strengths. It was essential to have alkaline conditions throughout the reaction and two equivalents of alkali were always used for each halogen present. At room temperature, the reaction was complete within one hour and titration of the halide ion according to the Volhard method gave excellent results (see Table). The presence of more than one halogen atom, of an acetylamino group or a carboxyl group in the benzene ring decreased the rate of hydrogenolysis; however, even in hexachlorobenzene, all the chlorine atoms could be readily replaced by hydrogen.

TABLE. - Hydrogenolysis Rates of Aryl Halides[a]

Aryl Halide	Rel. Rate	% Halide Calcd.	% Halide Found	% Yield Product[c]
Chlorobenzene	1.0	31.50	31.8	--
Fluorobenzene	0.8	---	--	--
Bromobenzene	1.9	50.90	50.7	--
Iodobenzene	3.2	62.21	61.1	--
p-Dichlorobenzene	0.9	48.24	47.6	--
p-Dibromobenzene	1.4	67.73	68.7	--
Hexachlorobenzene	---	74.69	74.3	--
o-Chloroacetanilide	0.6	20.90	20.7	69
o-Bromoacetanilide	1.1	37.33	37.4	77
p-Chloroacetanilide	0.4	20.90	20.9	72
p-Bromoacetanilide	0.9	37.33	37.1	69
o-Chlorobenzoic acid	0.9	22.64	22.8	65
3,5-Di-*t*-butyl-2,4-dichloroacetanilide	---	11.24[b]	11.3	79

---

[a] At 18°, relative to chlorobenzene

[b] One chlorine atom only

[c] Pure product

The reaction is subject to steric hindrance. It was impossible to replace a chlorine atom situated between two t-butyl groups, e.g., hydrogenolysis of 3,5-di-t-butyl-2,4-dichloroacetanilide removed only the chlorine atom in the 2-position and produced in excellent yield 3,5-di-t-butyl-4-chloroacetanilide. The chlorine atom in between the t-butyl groups could not be replaced even at 50°. In contrast, hydrogenation of a nitro group situated between two t-butyl groups is possible under similar conditions.[6] The hydrogenolyses described above may be increased to preparative scale.

EXPERIMENTAL

The aryl halides were of A.R. grade and were redistilled or recrystallized before use. Raney Ni was prepared as described by Pavlic and Adkins.[7] The preparation of 3,5-di-t-butyl-2,4-dichloroacetanilide will be described elsewhere.

General Procedure. - A simple hydrogenation apparatus was constructed consisting of a 100 ml gas burette, a 100 ml hydrogenation flask with detachable side arm and shaking device (see Figure). The H_2 was purified by passage through

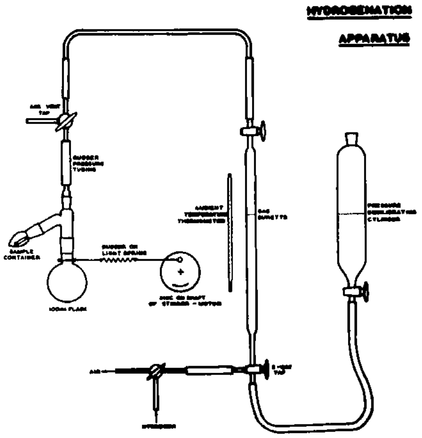

Figure 1

an aqueous solution of $KMnO_4$, then conc. H_2SO_4 and then ethanol. About 1 millimole of substance was weighed into a glass capsule and dropped into 10 ml 0.2 M solution of KOH in ethanol in the hydrogenation flask. The Raney Ni (wet) was weighed (700 mg) into a glass capsule and put into the side arm of the flask. The flask was connected to the burette, filled with H_2 and the shaking was started. After equilibration of the system, the burette was read and the catalyst was added to the flask. The H_2 uptake was read at intervals of 2-5 min. and when no more H_2 was taken up, the flask was disconnected and the catalyst filtered. After washing of the catalyst with distilled water, the halide ion was determined in the acidified (HNO_3) filtrate by the Volhard method. The rate of hydrogenolysis was determined by plotting the H_2 uptake versus time and calculating the tangent of the angle formed by the curve and the abscissa at the origin.

REFERENCES

1. T. G. Halsall, E. R. H. Jones and G. D. Meakins, J. Chem. Soc., 2862 (1952).
2. W. R. Boehme, J. Am. Chem. Soc., 80, 4740 (1958).
3. W. Rundel, Chem. Ber., 96, 636 (1963).
4. H. C. Brown and S. Krishnamurthy, J. Org. Chem., 34, 3918 (1969).
5. P. O. I. Virtanen and P. Jaakkola, Tetrahedron Lett., 1223 (1969).
6. J. Burgers, M. A. Hoefnagel, P. E. Verkade, H. Visser and B. M. Wepster, Rec. Trav. Chim., 77, 491 (1958).
7. A. A. Pavlic and H. Adkins, J. Am. Chem. Soc., 68, 1471 (1946).

(Received October 22, 1974; in revised form December 31, 1974)