

REDUCTION OF AROMATIC HALIDES WITH LITHIUM ALUMINUM HYDRIDE

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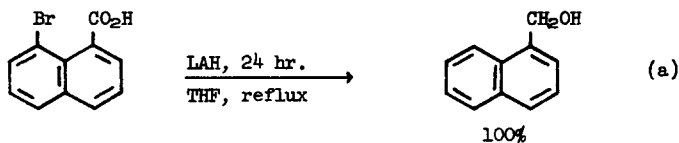
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Only a few reductions of aromatic halides with lithium aluminum hydride have been reported. For example, three hour reflux of *p*-bromotoluene in tetrahydrofuran with a mixture of lithium aluminum hydride and lithium hydride (1) yields 14% toluene; *o*-chloriodobenzene gives 40% chlorobenzene (2) after one-half hour reflux in tetrahydrofuran; a 51% yield of 2,3,5,6-tetrafluorotrifluoromethylbenzene is obtained from pentafluorotrifluoromethylbenzene (3) after eighty-five hour reflux in ether; and for certain halonitrobenzenes iodo and -- when activated -- bromo reduction accompanies the reduction of the nitro group (4).

Prompted by reaction (a) we investigated several aromatic halides in



order to elucidate the structural features and reaction conditions that might facilitate such reductions. Table I summarizes pertinent data.

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TABLE I

Reduction of Aromatic Halides with Lithium Aluminum Hydride

<u>Compound</u>	<u>Time (hr.)</u>	<u>Solvent^a</u>	<u>% Halide_b Reduced</u>	<u>% Acid Recovered</u>
1. <u>o</u> -Bromotoluene	24	Et_2O	4	
2. <u>o</u> -Bromotoluene	24	THF	13	
3. <u>o</u> -Chlorobenzoic acid	24	THF	3 ^c	
4. <u>m</u> -Chlorobenzoic acid	24	THF	0 ^c	
5. <u>o</u> -Bromobenzoic acid	24	Et_2O	19 ^c	
6. <u>o</u> -Bromobenzoic acid	24	THF	100	
7. <u>m</u> -Bromobenzoic acid	24	Et_2O	0 ^c	
8. <u>m</u> -Bromobenzoic acid	24	THF	63 ^c	
9. <u>p</u> -Bromobenzoic acid	24	THF	68 ^c	
10. <u>o</u> -Iodobenzoic acid	24	Et_2O	100	
11. <u>o</u> -Iodobenzoic acid	24	THF	100	
12. <u>m</u> -Iodobenzoic acid	24	Et_2O	73 ^c	
13. <u>m</u> -Iodobenzoic acid	24	THF	100	
14. <u>p</u> -Iodobenzoic acid	24	Et_2O	70 ^c	
15. <u>p</u> -Iodobenzoic acid	24	THF	100	
16. 1-Bromonaphthalene	24	Et_2O	6	
17. 1-Bromonaphthalene	24	THF	49	
18. 2-Bromonaphthalene	24	THF	21	
19. 8-Bromo-1-methylnaphthalene	24	Et_2O	11	
20. 8-Bromo-1-methylnaphthalene	24	THF	46	
21. 8-Bromo-1-naphthylcarbinol	24	Et_2O	19	
22. 8-Bromo-1-naphthylcarbinol	1	THF	36	
23. 8-Bromo-1-naphthylcarbinol	8	THF	97	
24. 8-Bromo-1-naphthoic acid	3	Et_2O	27 ^c	59

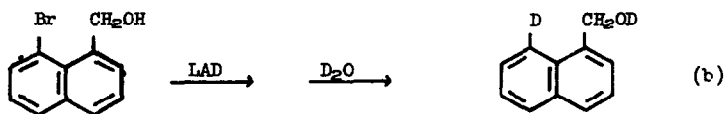
TABLE I (CONT.)

Compound	Time (hr.)	Solvent ^a	% Halide Reduced ^b	% Acid Recovered
25. 8-Bromo-1-naphthoic acid	24	Et_2O	64 ^c	36
26. 8-Bromo-1-naphthoic acid	76	Et_2O	99 ^c	
27. 8-Bromo-1-naphthoic acid	24	THF^d	69 ^c	16
28. 8-Bromo-1-naphthoic acid	24	THF	100	
29. Methyl 8-Bromo-1-naphthoate	24	Et_2O	60 ^c	
30. 8-Bromo-1-bromomethyl-naphthalene	1	Et_2O	5 ^e	

^aReductions were carried out at reflux temperatures. ^bPercent values accurate to $\pm 5\%$, were determined by n.m.r. and in several cases by v.p.c. ^cThe remaining percent is halocarbinal. In entries 24, 25 and 27 these percentages are 73, 36 and 31. ^dCarried out at room temperature. ^eThe remaining 95% is 8-Bromo-1-methylnaphthalene.

Contrary to current views, many of these reductions occur with such ease that they become competitive with the reduction of carboxyl groups (entries 24, 25 and 27.) As evidenced by entries 25, 27, 28, the more extensive reduction in tetrahydrofuran than in ether arises mainly from differences in reaction temperature.

The overall reaction mechanism is nucleophilic substitution without aryne intermediacy, as evidenced by (b). In addition to halogen reactivity (iodo >



bromo > chloro) and to activation of halide by electron withdrawing groups, two structural features affect the reaction rate:

(1) Increase in ground state steric interactions between halogen and neighboring groups. Such interactions increase reduction (compare entries 17

