The Reaction of Lithium Aluminum Hydride with Aromatic Halides[1]

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ortho-Substituted bromo- and iodobenzenes and 8-substituted 1-bromonaphthalenes are readily reduced with lithium aluminum hydride in refluxing ether when the substituents contain reactive functional groups. Their reduction at higher temperatures is quite rapid. Unsubstituted or unactivated aromatic iodides are quantitatively reduced in diglyme at 100° and moderately reduced in refluxing tetrahydrofuran or ether. Unactivated bromides are reduced very slowly in diglyme at 100°, while the corresponding chlorides resist reduction. In diglyme at 100° anisoles with *ortho* substituents containing reactive functional groups are readily converted into phenols.

The difference in reactivity between aryl and alkyl halides toward lithium aluminum hydride is well documented.[2] Although the reduction of many aliphatic halides is a synthetically useful reaction, that of the aromatic halides is largely unexplored. A few examples of such reductions have been reported. For example, a 3-hr reflux of *p*-bromotoluene in tetrahydrofuran with a mixture of lithium aluminum hydride and lithium hydride yielded 14% toluene;[3] *o*-chloroiodobenzene gave 40% chlorobenzene after 0.5-hr reflux in tetrahydrofuran;[4] a 51% yield of 2,3,5,6-tetrafluorotrifluoromethylbenzene was obtained from pentafluorotrifluoromethylbenzene after an 85-hr reflux in ether;[5] for certain halonitrobenzenes iodo and, when activated, bromo reduction accompanied the reduction of the nitro group;[6] and 4,4′-diodo-5-5′-dimethyl-2,2′-dinitrobiphenyl was deiodinated with excess lithium aluminum hydride in refluxing ether to yield 43% of 2,9-dimethylbenzo[*c*]cinnoline.[7]

The facile reduction of 8-bromo-1-naphthoic acid to 1-naphthylcarbinol[8] has prompted us to investigate the reductions of several aromatic halides in order to establish the reaction conditions and elucidate the structural features that might facilitate such reductions.

Results and Discussion

In Table I we have summarized the results of the reductions of various aromatic halides with lithium aluminum hydride. The expected halogen reactivity, iodo > bromo > chloro, is clearly evidenced from the reductions in diglyme, at 100°. Unactivated iodides are quantitatively reduced, the bromides are reduced to a smaller extent, and the corresponding chlorides resist reduction.

TABLE I

LITHIUM ALUMINUM HYDRIDE REDUCTIONS[a] OF SELECTED AROMATIC HALIDES

Compd (no.)	Halogen-reduced product, %		
	Ether, 35°	THF, 65°	Diglyme, 100°
8-Bromo-1-naphthoic acid (**1**)	40, 23	58, 26	...[b]
8-Bromo-1-naphthoic acid (**2**)	100, 0[c]	100, 0[d]	...
Methyl 8-bromo-1-naphthoate (**3**)	60, 40	96, 4	...
8-Bromo-1-naphthylcarbinol (**4**)	19	99 (97, 36)[e]	...
8-Bromo-1-methylnaphthalene (**5**)	11	46	100
1-Bromonaphthalene (**6**)	6	39	61
8-Bromo-1-naphthylcarbinyl chloride (**7**)	5, 73[f]	...	...
1-Chloronaphthalene (**8**)	...	...	28
2-Bromonaphthalene (**9**)	...	21	...
1-Iodonaphthalene (**10**)	14	72	100
2-Iodonaphthalene (**11**)	19	75	100
o-Chlorobenzotrifluoride (**12**)	...	...	27
p-Chlorobenzotrifluoride (**13**)	...	...	27
o-Bromobenzotrifluoride (**14**)	...	59	98
p-Bromobenzotrifluoride (**15**)	...	40	91
o-Iodobenzotrifluoride (**16**)	62	78	100
p-Iodobenzotrifluoride (**17**)	30	71	99
p-Chlorotoluene (**18**)	...	...	0
o-Bromotoluene (**19**)	...	7	41
p-Bromotoluene (**20**)	...	7	28
o-Iodotoluene (**21**)	6	67	92
p-Iodotoluene (**22**)	9	75	82
2-Iodo-*m*-xylene (**23**)	7	61	92
Chlorobenzene (**24**)	...	...	4[g]
Bromobenzene (**25**)	...	...	23
Iodobenzene (**26**)	...	...	88
o-Bromophenol (**27**)	...	...	14[h]
p-Bromophenol (**28**)	...	...	18[h]
o-Iodophenol (**29**)	...	51[h]	100[h]
p-Iodophenol (**30**)	...	46[h]	92[h]

[a] Reductions were carried out with 1.0 mole of lithium aluminum hydride per mole of aromatic halide for 24 hr. When two reduction products are possible, the per cent yield of bromine cleaved product is given first. [b] The leaders indicate that the reaction was not studied under these conditions. [c] By using 2.0 moles of lithium aluminum hydride per mole of acid and a 76-hr reaction period. [d] By using 2.0 moles of lithium aluminum hydride per mole of acid. [e] Yields from 8- and 1-hr reactions, respectively. [f] From a 4-hr reaction. [g] The reaction time was 48 hr. [h] A concentration of 1.25 mole of lithium aluminum hydride per mole of compound was used.

Several reductions occur with such ease that they become competitive with the reduction of the carbonyl group. For example, the reduction of 8-bromo-1-naphthoic acid in ether produced a 2:1 mixture (entry 1) of 1-naphthylcarbinol and 8-bromo-1-naphthylcarbinol. Reduction of the carbonyl group, however, precedes bromine cleavage, as shown by the data summarized in Table II. The concentration of 8-bromo-1-naphthylcarbinol is greatest early in the reaction and the ratio of 8-bromo-1-naphthylcarbinol to 1-naphthylcarbinol decreases as the reaction proceeds. Furthermore, when the recovered acid was esterified with diazomethane and the resulting ester

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[1] Taken from the Ph.D. Thesis of R. L. Shone, Michigan State University, East Lansing, Mich., 1965.

[2] See N. G. Gaylord, "Reduction with Complex Metal Hydrides," Interscience Publishers, Inc., New York, N. Y., 1956, pp 889–924.

[3] J. E. Johnson, R. H. Blizzard, and H. W. Carhart, *J. Am. Chem. Soc.*, **70**, 3664 (1948).

[4] L. W. Trevoy and W. G. Brown, *ibid.*, **71**, 1675 (1949).

[5] D. J. Alsop, J. Burdon, and J. C. Tatlow, *J. Chem. Soc.*, 1801 (1962).

[6] J. F. Corbett and P. F. Holt, *ibid.*, 2385 (1963).

[7] R. S. W. Braithwaite, P. F. Holt, and A. N. Hughes, *ibid.*, 4073 (1958).

[8] G. J. Karabatsos, R. L. Shone, and S. E. Scheppele, *Tetrahedron Letters*, No. 31, 2113 (1964).

TABLE II

EFFECT OF REACTION TIME ON THE REDUCTION[a] OF 8-BROMO-1-NAPHTHOIC ACID

Reacn time, hr	Recovered acid, %	Reduced product, %	8-Bromo-1-naphthylcarbinol/ 1-naphthylcarbinol
1	78	22	4.5/1
3	59	41	2.7/1
8	36	64	0.56/1
76	0	100[b]	<1/200

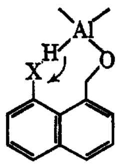
[a] The reduction was carried out in refluxing ether with 1.0 mole of lithium aluminum hydride per mole of acid. [b] Two moles of lithium aluminum hydride were used per mole of acid.

was vapor phase chromatographed, no methyl 1-naphthoate was detected.

In addition to halogen reactivity, *i.e.*, iodo > bromo > chloro, and to activation of the halide by electron-withdrawing groups, two additional structural features apparently facilitate these reductions: (a) steric effects and (b) the presence of groups capable of forming alkoxides with lithium aluminum hydride.

Steric interactions between substituents in *peri*-substituted naphthalenes are well known. For example, the ground-state strain energies of 1,8-dimethylnaphthalene and 1-methylnaphthalene have been estimated to be 7.6 and 1.6 kcal/mole, respectively.[9] Partial relief, therefore, of these steric interactions in the conversion of the trigonal into the tetrahedral carbon in going from the ground state to the transition state would explain the ease of reduction of 1-bromo-8-substituted naphthalenes (compare entries **5** *vs.* **6** and **6** *vs.* **9** in Table I).

The remarkably facile reduction of 1-bromonaphthalenes when the *peri* substituent contains groups capable of forming aluminum alkoxides is undoubtedly due partly to intramolecular reduction as in I. Such intramolecular reductions have been postulated[10] to



I

account for the differences in the yields of dehalogenated alcohols obtained from the lithium aluminum hydride reductions of C_2 through C_5 ω-chloroaliphatic acids. The data summarized in Table III are consonant with this suggestion. For example, the yields of dehalogenated product are consistently greater for *o*-halobenzoic acids than for the *meta* and *para* isomers. These yield differences are too great to be the result of steric effects only (compare entries **19** and **20** in Table I with entries **5** and **7** in Table III).

Another factor that apparently facilitates these reductions is intermolecular and intramolecular catalyses by complexation between the aluminum acids and the halogens. To an intermolecular catalysis we ascribe the results summarized in Table IV. Addition of methanol increases the yield of dehalogenated product, despite the fact that such an addition would increase the concentration of the alkoxyaluminohydrides that are weaker reducing agents than lithium aluminum hydride.[11-13] Such acid catalysis of carbon–halogen bond cleavage also offers a plausible explanation for the fact that halo acids always yield more dehalogenated alcohol than do the corresponding halo alcohols (see ref 9 and compare entries **1** *vs.* **4** in Table I and **5** *vs.* **11** in Table III). Since carboxyl group reduction precedes halogen cleavage, the increase in Lewis acid strength[14] of the aluminum compounds as a result of their greater alkoxy content leads to greater yields of dehalogenated product from the acid than from the alcohol.

TABLE III

LITHIUM ALUMINUM HYDRIDE REDUCTION[a] OF HALOBENZOIC ACIDS

Acid (no.)	Dehalogenated benzyl alcohol, % Ether, 25°	THF, 65°	Diglyme, 100°
p-Fluorobenzoic (**1**)	...[b]	0	...
o-Chlorobenzoic (**2**)	...	3	13
m-Chlorobenzoic (**3**)	...	0	...
p-Chlorobenzoic (**4**)	...	0	...
o-Bromobenzoic (**5**)	21 (18)[c]	100 (36)	...
m-Bromobenzoic (**6**)	5 (0)	63 (28)	...
p-Bromobenzoic (**7**)	2 (0)	68 (27)	...
o-Iodobenzoic (**8**)	100 (26)	100	...
m-Iodobenzoic (**9**)	65 (23)	100	...
p-Iodobenzoic (**10**)	63 (17)	100	...
o-Bromobenzyl alcohol (**11**)	... (4)	... (20)	... (80)

[a] Reductions were carried out with 2.0 moles of lithium aluminum hydride per mole of acid for 24 hr. In all cases the reduction of the carboxyl group was complete. [b] The leaders indicate that the reaction was not studied under these conditions. [c] All figures in parentheses refer to yields obtained from reductions using 1.0 mole of lithium aluminum hydride per mole of acid.

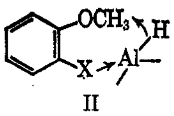
TABLE IV

EFFECT OF METHANOL ON THE REDUCTION[a] OF AROMATIC BROMIDES WITH LITHIUM ALUMINUM HYDRIDE

Compd (no.)	Solvent	$MeOH/LiAlH_4$ (mole/mole)	Debrominated product, %
8-Bromo-1-naphthylcarbinol (**1**)	Ether	0	19
8-Bromo-1-naphthylcarbinol (**2**)	Ether	0.5	36
8-Bromo-1-naphthylcarbinol (**3**)	Ether	2.0	77
p-Bromotoluene (**4**)	THF	0	7
p-Bromotoluene (**5**)	THF	2.0	59

[a] Reductions were carried out with 1.0 mole of lithium aluminum hydride per mole of substrate at solvent reflux temperature for 24 hr.

To an intramolecular Lewis acid catalysis by complexation we ascribe the results summarized in Table V. Whereas *p*-bromo- and *p*-iodoanisole gave insignificant amounts of phenol, *o*-iodo- and *o*-bromoanisole gave 60 and 23% of phenolic products, respectively. An intramolecular reduction, as pictured in II, offers the best rationale for these results. The presence of halophenols and the slow reactivity of phenol itself suggest that carbon–oxygen cleavage precedes carbon–halogen cleavage. Further support for the intramolecular



II

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[9] J. Packer, J. Vaughn, and E. Wong, *J. Am. Chem. Soc.*, **80**, 905 (1958).

[10] E. L. Eliel and J. T. Traxler, *ibid.*, **78**, 4049 (1956).

[11] H. C. Brown and C. J. Shoaf, *ibid.*, **86**, 1079 (1964).

[12] H. C. Brown and R. F. MacFarlin, *ibid.*, **78**, 252 (1956).

[13] H. C. Brown and B. C. Subba Rao, *ibid.*, **80**, 5377 (1958).

[14] H. C. Brown and R. F. MacFarlin, *ibid.*, **80**, 5372 (1958).

path is provided by a comparison of products from the reduction of *o*-methoxybenzyl alcohol and *o*-methylanisole. Whereas the former undergoes 59% carbon–oxygen cleavage, the latter is reduced to the same extent as anisole.

TABLE V
REDUCTION OF HALOANISOLES WITH LITHIUM ALUMINUM HYDRIDE[a]

Haloanisole, (no.)	Recovered starting materials, %	Product yield, %		
		Anisole	Halophenol	Phenol
o-Iodoanisole (1)	0	40	3	57
o-Bromoanisole (2)	18	58	9	14
p-Iodoanisole (3)	9	91	0	0
p-Bromoanisole (4)	62	35	2	1
Anisole (5)	96	[b]	. . .	4
o-Methoxybenzyl alcohol (6)	41	. . .	. . .	59
o-Methylanisole (7)	96	. . .	. . .	4

[a] All reductions were carried out with 1.0 mole of lithium aluminum hydride per mole of substrate for 24 hr in diglyme at 100°. [b] The leaders indicate that the reaction was not studied under these conditions.

The preparative usefulness of the reduction of aromatic halides with lithium aluminum hydride does not equal the analogous aryltin hydride reductions. Although yields from lithium aluminum hydride reductions in diglyme at 100° are equal to or better than those resulting from triphenyltin hydride reductions[15] at 94°, the latter reagent may be used at temperatures as high as 154°. Significantly higher yields from unreactive halides are then obtained. However, the ready availability of lithium aluminum deuteride allows the specific introduction of deuterium into an aromatic nucleus. For example, treatment of *p*-iodotoluene with lithium aluminum deuteride in diglyme at 100° for 24 hr gave *p*-deuteriotoluene in near quantitative yield. Treatment of 8-bromo-1-naphthylcarbinol with lithium aluminum deuteride in tetrahydrofuran also gave quantitative yields of 8-deuterio-1-naphthylcarbinol.

Experimental Section

Materials.—Commercially available aromatic halides were used without purification. The preparation of 8-bromo-1-substituted naphthalenes from 8-bromo-1-iodonaphthalene was carried out according to established procedures.[16] Ether, tetrahydrofuran, and diglyme were dried by distillation from lithium aluminum hydride just prior to use. Diglyme was distilled at reduced pressure.[17]

Procedure.—The following general procedure was used for the reductions. Lithium aluminum hydride, 0.36 g (10 mmoles), was added to 25 ml of dry solvent in a 50-ml single-necked, round-bottomed flask that was fitted with a condenser and drying tube. The aromatic halide (10 mmoles) was added to the hydride slurry and the resulting mixture was refluxed or heated at constant temperature for 24 hr. After reaction, the unreacted hydride was quenched by careful dropwise addition of water. Next, 30 ml of 10% sulfuric acid was added followed by extraction with three 75-ml portions of ether. The ether extract was washed with 25 ml of saturated sodium bicarbonate solution and four 50-ml portions of water, dried over anhydrous magnesium sulfate, and evaporated.

Product Analysis.—Reaction product mixtures were analyzed for reduced aromatic hydrocarbon and aromatic halide by nuclear magnetic resonance or vapor phase chromatography. Aromatic halides with proton-containing functional groups were analyzed by vapor phase chromatography on an Aerograph A-90-P. All peaks were identified by comparison of retention times with known standards. In a number of instances product mixtures were analyzed by both techniques and the results were in agreement. The reported per cent yields are accurate to ±5%.

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(15) D. H. Lorenz, P. Shapiro, A. Stern, and E. I. Becker, *J. Org. Chem.*, **28**, 2332 (1963).

(16) L. F. Fieser and A. M. Seligman, *J. Am. Chem. Soc.*, **61**, 136 (1939).

(17) For a report of an explosive decomposition of lithium aluminum hydride from diglyme distillation at atmospheric pressure, see R. H. Watson, *Chem. Ind.* (London), 665 (1964).

The Synthesis of Triptindan

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The title compound (**11**),[1] a symmetrical tribenzo derivative of tricyclo[3.3.3.$0^{1,5}$]undecane, has been synthesized by a route involving acid cyclization of a substituted dibenzylindanone. The chemical and spectral properties of compounds related to **11** are described and the spectral properties of **11** are discussed in relation to the possibility of nonbonded π orbital interactions.

As a result of our interest in highly symmetrical compounds,[2-4] particularly in tricyclic systems of the [$n.n.n.0^{1,\,n+2}$] type,[3-7] and because a relatively simple route was available, we undertook the synthesis of **11**, a tribenzo derivative of tricyclo[3.3.3.$0^{1,5}$]undecane. A feature of **11** of particular interest is that its ring system, like that of triptycene,[8] incorporates a substituted triphenylmethane into a rigid arrangement such that some overlap between the isolated π-electron systems may be possible. We hoped that our synthetic scheme might produce triptindans with substituents suitable for assessing such "homoconjugative" interactions.

The synthetic route involves a double acid-catalyzed cyclization of the dibenzylindanone **3** (Chart I). This material should theoretically be obtainable by a double alkylation of 1-indanone with a benzyl halide; however,

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(1) P. D. Bartlett, M. J. Ryan, and S. G. Cohen, *J. Am. Chem. Soc.*, **64**, 2649 (1942), foonote 1.

(2) H. O. House, R. W. Magin, and H. W. Thompson, *J. Org. Chem.*, **28**, 2403 (1963).

(3) H. W. Thompson, *Tetrahedron Letters*, 6489 (1966).

(4) H. W. Thompson, *J. Org. Chem.*, **32**, 1222 (1967).

(5) R. L. Cargill and J. W. Crawford, *Tetrahedron Letters*, 169 (1967).

(6) L. F. Fieser and J. T. Dunn, *J. Am. Chem. Soc.*, **58**, 1054 (1936).

(7) J. Altman, D. Becker, D. Ginsburg, and H. J. E. Lowenthal, *Tetrahedron Letters*, 757 (1967).

(8) For a recent brief review of triptycene chemistry, see B. H. Klanderman, "Organic Chemical Bulletin," Vol. 37, No. 1, Research Laboratories of the Eastman Kodak Co., Rochester, N. Y., 1965.