Hydrogenolysis of Diaryl and Aryl Alkyl Ketones and Carbinols by Sodium Borohydride and Anhydrous Aluminum(III) Chloride

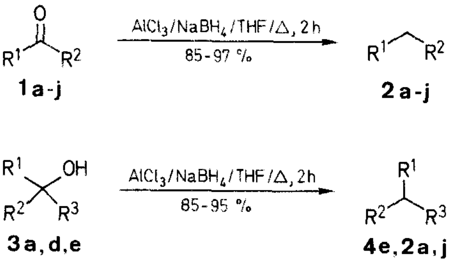
Aoi Ono,* Nobuko Suzuki, Junko Kamimura

Department of Chemistry, Faculty of Education, Niigata University
Niigata, 950-21 Japan

Diaryl ketones such as benzophenone and fluorenone, aryl alkyl ketones such as acetophenone, 4-chloroacetophenone and 4-methylacetophenone, and arylcarbinols such as benzhydrol, triphenylmethanol, and 1-phenylethanol, were effectively hydrogenolyzed to the corresponding hydrocarbons.

Hydrogenolysis of ketones and alcohols to hydrocarbons is an important and valuable procedure in organic synthesis. Hydrogenolysis of ketones to hydrocarbons has been performed by various methods: by triethylsilane/tin(II) chloride,[1] diphenylsilane,[2] sodium borohydride/trifluoroacetic acid,[3,4] lithium aluminum hydride/aluminum(III) chloride,[5,6] triphenylstannane,[7] phosphorus/hydrogen iodide,[8] Clemmensen reduction,[9] and Wolf-Kishner reduction.[10] Further, the hydrogenolysis of alcohols has been performed with sodium borohydride/trifluoroacetic acid[3] and with lithium aluminum hydride-/aluminum(III) chloride.[5] We have now found that sodium borohydride in combination with anhydrous aluminum(III) chloride conveniently reduces diaryl and aryl alkyl ketones as well as diaryl- and arylalkylcarbinols to methylenic hydrocarbons.

The results of the hydrogenolysis of diaryl and aryl alkyl ketones or diaryl- and alkylarylcarbinols by sodium borohydride and anhydrous aluminum(III) chloride in tetrahydrofuran are represented in Tables 1 and 2. As shown in Table 1, acetophenone was satisfactorily hydrogenated to ethylbenzene in 85 % yield, styrene being formed as a minor product. We also found that the hydrogenation of styrene with the system sodium borohydride/anhydrous aluminum(III) chloride affords ethylbenzene in 97 % yield. Both the hydrogenation and the dehydration of 1-phenylethanol were examined.



1-Phenylethanol was hydrogenolyzed to ethylbenzene (90 %) by the system and 1-phenylethanol was dehydrated to styrene (75 %) by anhydrous aluminum(III) chloride in tetrahydrofuran. The results show that, in part, acetophenone is reduced to 1-phenylethanol, that 1-phenylethanol is dehydrated to styrene, and that styrene is subsequently reduced to ethylbenzene. This should be compared with the generally accepted hydrogenolysis mechanism according to which acetophenone is reduced to 1-phenylethanol which then forms a complex with aluminum chloride and the resultant carbenium ion is reduced to ethylbenzene. On the other hand, the same system in diglyme afforded organoboranes with olefins.[11] Further, 1-phenylethanol has been reported to be dehydrated to styrene when distilled in the presence of sodium hydroxide at 140–170°.[12] This dehydration may proceed *via* hydrogen abstraction by hydroxide anion at the elevated distillation temperature. Nystrom et al.[5] published the hydrogenolysis of ketones and alcohols by lithium aluminum hydride/aluminum chloride; they obtained ethylbenzene (50 %) from acetophenone but did not report the production of styrene.

4-Methylacetophenone, 4-chloroacetophenone, 4-aminoacetophenone, propiophenone, and 1-tetralone were hydrogenolyzed to 4-methylethylbenzene (90 %), 4-chloroethylbenzene (95 %), 4-ethylaniline (94 %), propylbenzene (90 %), and tetraline (97 %), respectively, by our method. On the other hand, Nystrom et al.[5] obtained 4-methylethylbenzene from 4-methylacetophenone in only 19 % yield and propylbenzene from propiophenone in 24 % yield. As presented in Table 1, aryl alkyl ketones and alkylarylcarbinols were hydrogenolyzed to hydrocarbons in satisfactory yields, and benzophenone, 4-chlorobenzophenone, 4-bromobenzophenone, 4-methylbenzophenone, and fluorenone were hydrogenolyzed even in high yields to 4-chlorodiphenylmethane, 4-bromodiphenylmethane, 4-methyldiphenylmethane, diphenylmethane, and fluorene, respectively. In addition, benzhydrol and triphenylmethanol were also hydrogenolyzed to diphenylmethane (93 %) and triphenylmethane (95 %), respectively. As mentioned above, diaryl

Table 1. Hydrogenolysis of Aryl Alkyl Ketones **1** and Alkylarylcarbinols **3** by Sodium Borohydride/Aluminum(III) Chloride

Substrate (mmol)		R^1	R^2	R^3	$NaBH_4$ (mmol)	Product	Yield[a] (%)	b.p. (°C/Torr)	
								found	reported
1a	(4.2)	C_6H_5	CH_3	–	18.0	**2a**	85 (90)	36–37/20	38.6/20[13]
						styrene	(5)		
3a	(4.0)	C_6H_5	CH_3	H	18.0	**2a**	85 (90)	36–37/20	38.6/20[13]
						3a	(5)		
						styrene	(5)		
3a	(4.0)	C_6H_5	CH_3	H	–	**3a**	(25)		
						styrene	(75)	101/100	101.3/100[13]
styrene	(4.8)	C_6H_5	CH_3	–	18.0	**2a**	92 (97)	36–37/20	38.6/20[13]
						styrene	(3)		
1b	(3.7)	C_6H_5	C_2H_5	–	18.0	**2b**	90 (93)	92–93/100	94/100[13]
						3b	(7)		
1c	(3.7)	$4\text{-}CH_3C_6H_4$	CH_3	–	18.0	**2c**	90 (95)	81–82/60	83.2/60[13]
						3c	(5)		
1d	(3.2)	$4\text{-}ClC_6H_4$	CH_3	–	18.0	**2d**	95	91/40	91.8/40[13]
1e	(3.6)	$4\text{-}NH_2C_6H_4$	CH_3	–	18.0	**2e**	94	134–135/60	136/60[13]
1f	(3.4)	(1-tetralone)			18.0	**2f** (tetralin)	97	120/59	121.3/60[13]

[a] Yield of isolated product (GLC yields in brackets).

Table 2. Hydrogenolysis of Diaryl Ketones **1** or Carbinols **3** by Sodium Borohydride/Aluminum(III) Chloride

Substrate (mmol)		R^1	R^2	R^3	$NaBH_4$ (mmol)	Product	Yield[a] (%)	m.p. (°C) or b.p. (°C/Torr)	
								found	reported
1g	(2.3)	$4\text{-}ClC_6H_4$	C_6H_5	–	13.2	**2g**	95	b.p. 148–149/8	b.p. 147–148/8[14]
1h	(2.5)	$4\text{-}BrC_6H_4$	C_6H_5	–	13.2	**2h**	94	b.p. 102–104/0.1	b.p. 102–105/0.1[4]
1i	(2.5)	$4\text{-}CH_3C_6H_4$	C_6H_5	–	13.2	**2i**	92	b.p. 68–70/0.24	b.p. 110/1[4]
1j	(2.7)	C_6H_5	C_6H_5	–	13.2	**2j**	95	m.p. 23–24	m.p. 24–25[15]
1k	(2.7)	(fluorenone)			18.0	**2k** (fluorene)	96	m.p. 111–112	m.p. 113[13]
3d	(2.7)	C_6H_5	C_6H_5	H	13.2	**2j**	93	m.p. 23–24	m.p. 24–25[15]
3e	(2.0)	C_6H_5	C_6H_5	C_6H_5	18.0	**4e**	95	m.p. 92–93	m.p. 93–4[13]
1j[b]	(2.7)	C_6H_5	C_6H_5	–	13.2	**2j**	94	m.p. 23–24	m.p. 24–25[15]

[a] Yield of isolated product.

[b] Reaction performed in acetonitrile.

ketones or diarylmethanols were satisfactorily hydrogenolyzed to the corresponding diarylmethanes. Further, it was found that the hydrogenolysis system used efficiently hydrogenates arylalkenes.

In the hydrogenolysis reaction, the solvent tetrahydrofuran forms a complex with aluminum chloride and thus gives a viscous solid-like material. This viscous material is soluble in water so that the reaction mixture is easy to handle when water is added. For sodium borohydride, the use of a nitrogen atmosphere is not necessary.

The present convenient hydrogenolysis procedure has hitherto not been published.

Hydrogenolysis of Benzophenone (1j); Typical Procedure:
A mixture of benzophenone (0.5 g, 2.7 mmol), $NaBH_4$ (0.5 g, 13.2 mmol), and anhydrous $AlCl_3$ (1 g, 7.4 mmol) in THF (25 mL) is heated under reflux for 2 h. The mixture is then cooled, H_2O (~ 10 mL) is added to give two clear phases, and the whole mixture is extracted with EtOAc (4 × 50 mL). The extract is dried ($CaCl_2$) and distilled under reduced pressure to give diphenylmethane; yield: 0.43 g (93%); b.p. 155–156°C.

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