Tetrahedron. Vol. 29, pp. 3807 to 3810 Pergamon Press 1973 Printed in Great Britain

THE REACTION OF PHENALENONE WITH ALUMINUM HYDRIDES

R. M. PAGNI* and C. R. WATSON, JR.
Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37916

(*Received in the USA* 30 *January* 1973; *Received in the UK for publication* 2 *August* 1973)

Abstract—Phenalenone **8** was reduced in refluxing ether with a series of aluminum hydrides. The product distribution in each reduction could be explained by initial 1,2- and 1,12-addition of hydride. Using the mixed chloraluminum hydrides, a high yield synthesis of phanalene **10** was discovered.

INTRODUCTION

The nature and distribution of products obtained by reducing α,β-unsaturated aldehydes and ketones with metal hydrides depend critically on the reaction conditions as well as the type of hydride used. Cinnamaldehyde **1**, for example, affords 3-phenyl-1-propanol **2** on reduction with LAH at 25° and cinnamyl alcohol **3** at − 10°.[1] On the other hand, when **1** is reduced with aluminum hydride, only **3** is formed.[2]

$$\begin{tikzcd} \underset{\mathbf{1}}{C_6H_5CH{=}CHCHO} \arrow[r, "LAH", "25^\circ"'] \arrow[dr, "LAH", "-10^\circ"'] & \underset{\mathbf{2}}{C_6H_5CH_2CH_2CH_2OH} & \\ & \underset{\mathbf{3}}{C_6H_5CH{=}CHCH_2OH} & \mathbf{1} \arrow[l, "AlH_3"'] \end{tikzcd} \qquad (1)$$

In addition to the 1,2-addition of hydride, as seen in the previous examples, many enones undergo 1,4-addition as well. Brown has shown[3] that cyclopentenol **5** and cyclopentanone **6** are formed on reduction of cyclopentenone **4** with LAH. When **4** is reduced with aluminum hydride, however, cyclopentanol **7** is produced in addition to **5** and **6**. All of these products can be explained on the basis of initial 1,2- and 1,4-addition of hydride. The different product distributions from the two reactions (Eq 2) are reasonable, because different hydrides ought to have different propensities for 1,2- and 1,4-addition as well as secondary reduction.

Phenalenone **8** is unique among α,β-unsaturated ketones with respect to hydride reduction. First of all, it can *a priori* undergo, besides the expected 1,2- and 1,4-addition, a 1,12-addition of hydride (Scheme 1).† Secondly, the 1,12-addition is remarkable because it involves hydride attack on an aromatic ring.

Phenalene **10**, one of the products expected from the 1,2-addition of hydride, is a molecule of considerable interest;[4-6] however, much of its potential has not been realized as a result of its synthetic inaccessibility.[6,7] A simple, high yield synthesis of **10** has been developed which should greatly facilitate the study of its chemistry.

RESULTS AND DISCUSSION

The commercially available and synthetically accessible[8] ketone, phenalenone **8**, was reduced with LAH in refluxing ether as described in the Experimental. The NMR of the reaction mixture indicated the formation of three new compounds which were isolated and characterized as **10**[7,9] 1-hydroxyphenalane **11**,[7] and 9-hydroxyphenalene **15** (Experimental). The distribution of these products, which accounted for all of the NMR peaks, is given in Table 1.

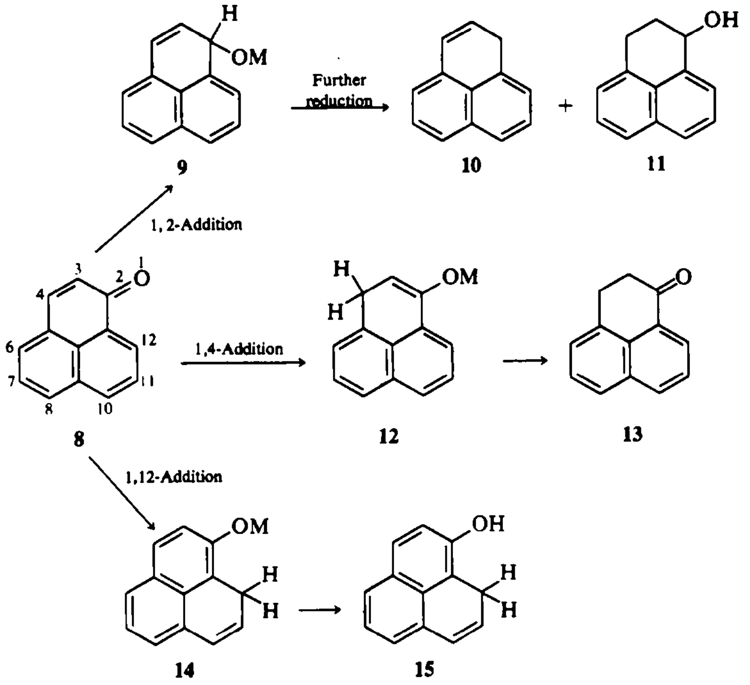
Scheme 1 illustrates how **10** and **11** arise from the secondary reduction of the intermediate **9** which is formed by the 1,2-addition of hydride to **8**. This is in contrast to **15** which is formed by a 1,12-hydride ad-

4 **5** **6** **7** (2)

Hydride		*Product distribution*	
LAH	85%	15%	0%
AlH$_3$	83·8%	8·7%	7·5%

---

†The numbering of phenalenone in Scheme 1 represents the position of a given carbon atom relative to the oxygen atom. It does not represent the IUPAC numbering for this compound.



SCHEME 1. M—Aluminum species whose nature depends on the hydride reducing agent used.

dition to **8**. The product of 1,4-addition, phenalanone **13**, was definitely not present in the initial reaction mixture.* Thus all of the products are accounted for by a combination of 1,2- and 1,12-addition.

The 14% yield of **10** obtained by LAH reduction was increased dramatically to 50% when the reduction was carried out with AlH_3.[10] In this case the only product in addition to **10** was **15** (Table 1). When the reduction was carried out using the mixed chloroaluminum hydrides, H_2AlCl and $HAlCl_2$,[10] the yield of **10** could be increased to 75% with **13** as the only other product.

Thus a facile synthesis of **10** approaching 75% yield is now available using readily obtainable materials. It should be noted, as a word of caution, that **10** is quite susceptible to air-oxidation and that this problem is accelerated when the compound is adsorbed on the silica gel column used in separating it from the other products. Furthermore, the purity of the LAH and $AlCl_3$ used to generate the reducing hydride reagents markedly affected the yields of the products. The best yields of phenalene were obtained when freshly opened bottles of LAH and $AlCl_3$ were used.

One point of mechanistic consideration should be noted. By looking carefully at the data in Table 1, it is quite evident that most, if not all, of the products arise by a combination of 1,2 and 1,12-addition of hydride with little, if any, by 1,4-addition. This phenomenon is easy to explain. Phenalenone **8** is extremely basic[6] and forms very stable complexes with Lewis acids.[6] If the hydride reduction occurs from a complex formed by the CO oxygen of **8** and the metal hydride, the 1,2- and 1,12-addition would be geometrically feasible (structures **16a** and **16b** as shown for the reduction of **8** with AlH_3) and the 1,4-addition would not (structure **16c**).

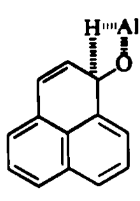
Table 1. Reduction of phenalenone **8** with metal hydrides[a]

Mole ratio $AlCl_3$:LAH	Reactant[c]	Relative percentage of products[b] **10**	**11**	**13**	**15**
0	LAH	14	19	0	67
0·29	AlH_3	50	0	0	50
2·1	$H_2AlCl + HAlCl_2$	75	0	25[d]	0
4·3	$HAlCl_2 + AlCl_3$	75	0	25[d]	0

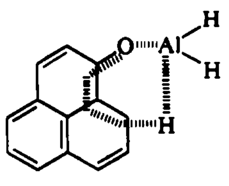
[a] All of the reactions were performed in refluxing ether by a procedure described in the experimental section. [b] The product distributions were calculated by NMR peak areas of the initial product mixtures. [c] Aluminum hydride compositions were calculated from the data of Ref 10. [d] Phenalanone **13** likely arose by isomerization of **15** (Experimental).

---

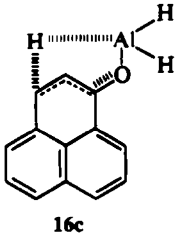
*After column chromatography, this compound is observed; it apparently arises by isomerization of 9-hydroxyphenalene.



16a



16b



16c

EXPERIMENAL

General procedure. Phenalenone was prepared by the procedure of Lewis and Topsom.[8] The hydride reductions were all run in refluxing ether, phenalenone being introduced into the reaction by ether-extraction from a Soxlet extractor. Aluminum hydride and the mixed aluminum hydrides were prepared by known procedures.[10,11] The reactions were worked up in the standard manner. Products were separated by column chromatography either on Davison silica gel (Mesh 60–200) or Merck alumina (Mesh 80–200). NMR spectra were run in CCl_4 or $CDCl_3$ with TMS as internal standard on a Varian A-60 spectrometer. M.ps were taken on a Thomas-Hoover Capillary m.p. apparatus and are uncorrected.

LAH reduction of phenalenone and characterization of 1-hydroxyphenalane. The orange oil obtained from the reduction of phenalenone (1·19 g; 6·61 mmol) with LAH (0·59 g; 15·0 mmol) gave a product distribution shown in Table 1. The oil was chromatographed on a 2 × 50 cm column slurry packed with silica gel in 5% ether-ligroine. Elution was with 675 ml ligroine, 250 ml of 2%, 250 ml of 5%, 250 ml of 10%, 250 ml of 20%, and 1·01 ml of 30% ether-ligroine; 125-ml fractions were collected. Fractions 2–5 contained phenalene, (104 mg; 0·61 mmol, 9%)[7,9] m.p. 83–84° (lit.[7] 85°). Fractions 14–15 contained 234 mg of 9-hydroxyphenalene, and fractions 16–21 contained 750 mg of a mixture of 9-hydroxyphenalene and 1-hydroxyphenalane.

The material in fractions 16–21 was rechromatographed on a 2 × 50 cm column slurry packed with silica gel in 5% ether-ligroine. The column was eluted with 500 ml of 5%, 500 ml of 10%, 1·0 l. of 20%, and 1·5 l. of 30% ether-ligroine. Fractions 10–17 contained 353 mg of a mixture composed of 68% 9-hydroxyphenalene and 32% phenalanone (NMR). Fractions 20–23 comprised 73 mg of essentially pure 1-hydroxyphenalane. Fractions 24–33 weighed 245 mg and consisted of a mixture of 18% 1-hydroxyphenalane and 82% phenalenone.

The 1-hydroxyphenalane from fraction 20–23 was sublimed (20 mm, 150°) and recryst (cyclohexane-ether) to constant m.p., 84–85° (lit.[7] m.p. 85°). This material was identical in every respect to authentic material (undepressed mmp, NMR).

Aluminum hydride reduction of phenalenone and characterization of 9-hydroxyphenalene. The crude oil obtained from the reduction of phenalenone (5·0 g; 28 mmol) with aluminum hydride, prepared from the reaction of LAH (1·1 g; 29 mmol) and $AlCl_3$ (1·1 g; 8·3 mmol), afforded the product distribution (NMR) shown in Table 1. The oil was dissolved in 200 ml of 5% KOH, which was then ether-extracted. The ether was dried ($MgSO_4$) and removed *in vacuo*. The neutral material still contained appreciable amounts of 9-hydroxyphenalene. The basic layer was acidified with 10% HCl until acidic (Hydrion paper) and the organic material extracted into ether. The organic phase was dried ($MgSO_4$) and removed under reduced pressure yielding 1·13 g of a dark red solid, m.p. 110–111°. The solid on recryst from ether-ligroine had m.p. 111–112°.

The NMR of 9-hydroxyphenalene in CCl_4 showed peaks at δ 3·58 br s (2H, methylene), 5·90 and 6·04 half of AB q each line split into triplet (1H, vinyl adjacent to naphthalene ring, J_{23} = 10·0 Hz, J_{13} = 2·0 Hz), 6·45 and 6·65 half of AB q each line split into triplet (1H, vinyl adjacent to methylene, J_{23} = 10·0 Hz, J_{12} = 4·0 Hz), 6·68–7·51 m (5H, naphthalene), 5·91 s (1H, OH); IR ($CHCl_3$): 3560 cm^{-1}.

(Found: C, 85·89; H, 5·53. Calcd for $C_{13}H_{10}O$: C, 85·69; H, 5·53%).

A soln of 9-hydroxyphenalene (1·3 g; 6·2 mmol) and quinone (0·67 g; 6·2 mmol) in 50 ml toluene was refluxed under N_2 for 90 min. On cooling to room temp, the toluene was diluted with an equal volume of ether, extracted twice with 250 ml of 10% KOHaq and once with H_2O. The organic phase was dried ($MgSO_4$) and removed *in vacuo*. This afforded 0·96 g of an orange solid, m.p. 138–140°. The solid was chromatographed on a 2 × 50 cm alumina column; 250-ml fractions were collected. Elution was with 250 ml of ligroine, 250 ml of 5%, 250 ml of 10%, 250 ml of 20%, 250 ml of 30%, and 1·5 l. of 50% ether-ligroine. Fractions 7–11 contained 0·78 g of a yellow solid, m.p. 149–153°, which was sublimed (150°, 0·25 mm) and recryst (cyclohexane-ether) to a constant m.p. of 154–155° (lit.[8] 154·5–155°). The 0·73 g (4·1 mmol, 66%) of phenalenone was identical in every regard to authentic material (undepressed mmp, NMR).

The acid-catalyzed isomerization of 9-hydroxyphenalene. An 80-mg sample comprising 70% 9-hydroxyphenalene and 30% phenalanone was dissolved in 0·3 ml $CDCl_3$ containing traces of DCl. The isomerization to phenalanone was followed by NMR as a function of time. The following results were obtained: t = 0 h, 70% 9-hydroxyphenalene and 30% phenalanone; t = 43 h, 58% 9-hydroxyphenalene and 42% phenalanone; t = 144 h, 25% 9-hydroxyphenalene and 75% phenalanone. The sample was kept at ambient temp; no other products were observed.

The mixed aluminum hydride reductions of phenaleneone. The product distribution (NMR) from the reduction of phenalenone (2·00 g; 11·1 mmol) with LAH (0·702 g; 18·5 mmol) and $AlCl_3$ (5·254 g; 39·44 mmol) is shown on line three of Table 1. The crude product was chromatographed on a 2 × 45 cm column slurry packed with silica gel in 3% of ether-ligroine; 250-ml fractions were collected. The column was eluted with 1·25 l. of ligroine, 250 ml of 2%, 250 ml of 4%, 250 ml of 8%, 250 ml of 16%, 750 ml of 30%, and 750 ml of 50% ether-ligroine. Fractions 2–5 afforded phenalene (1·13 g; 6·81 mmol, 61%) and fraction 10 contained phenalanone (0·153 g; 2·91 mmol, 26%).

The reduction of phenalenone (2·01 g; 11·1 mmol) with LAH (1·40 g; 36·9 mmol) and $AlCl_3$ (21·0 g; 158 mmol) gave an identical product distribution (NMR, see Table 1, line four) as the previous reduction. Chromatography on silica gel gave phenalene (1·23 g; 7·41 mmol, 67%) and phenalanone (491 mg; 2·70 mmol, 24%).

Isomerization of 9-hydroxyphenalene with mixed aluminum hydrides. A soln of 9-hydroxyphenalene (390 mg; 2·14 mmol) in 10 ml ether was added to a mixture of LAH (630 mg; 16·6 mmol) and $AlCl_3$ (5·88 g; 44·3 mmol) in 750 ml ether. The mixture was refluxed for 1 h. The usual workup afforded a yellow oil consisting of 20% 9-hydroxyphenalene and 80% phenalanone (NMR).

Acknowledgements—The authors wish to thank the Research Corporation and the Petroleum Research Fund of the American Chemical Society for support of this work.

REFERENCES

[1] F. A. Hochstein and W. G. Brown, *J. Am. Chem. Soc.* **70**, 3484 (1948)
[2] M. J. Jorgenson, *Tetrahedron Letters* 559 (1962)
[3] H. C. Brown and H. M. Hess, *J. Org. Chem.* **34**, 2206 (1969)
[4] R. M. Pagni and C. R. Watson, *Tetrahedron Letters* 59 (1973)
[5] I. Murata and K. Nakasuji, *Ibid.* 47 (1973)
[6] D. H. Reid, *Quart. Rev.* **19**, 274 (1965)
[7] V. Boekelheide and C. E. Larrabee, *J. Am. Chem. Soc.* **72**, 1245 (1950)
[8] I. K. Lewis and R. D. Topsom, *Aust. J. Chem.* **18**, 923 (1965)
[9] H. Prinzbach, V. Freudenberg, and V. Scheideggar, *Helv. Chem. Acta* **50**, 1087 (1967)
[10] E. C. Ashby and J. Prather, *J. Am. Chem. Soc.* **88**, 729 (1966)
[11] L. F. Fieser and M. Fieser, *Reagents for Organic Synthesis* p. 595. Wiley (1967)