expected acetal and 2,4-dibromo-3-pentanone in about a 1:1 ratio, with a trace of unreacted alcohol. A 3-g portion of the product was separated by using an alumina column and low-boiling petroleum ether to give 1.2 g (40%) of the pure acetal: bp 70–72 °C (6.5 torr); NMR ($CDCl_3$) δ 0.7–1.1 (t, 12 H, J = 5.0 Hz, 4 CH_3), 1.2–1.7 (p, 8 H, J = 5.0 Hz, 4 CH_2), 3.2–3.6 (p, 2 H, J = 5.0 Hz, 2 OCH), 4.65 (s, 2 H, OCH_2O). There was also obtained 1.4 g (47%) of the pure 2,4-dibromo-3-pentanone: bp 54–55 °C (2 torr); NMR ($CDCl_3$) δ 1.7–1.9 (d, 6 H, J = 5.0 Hz, 2 CH_3), 4.8–5.15 (q, 2 H, J = 5.0 Hz, 2 CHBr); IR (neat), 1720 cm^{-1} (C=O).[13]

Reaction of Alcohols with Me_2S–Br_2. The dimethylsulfonium dibromide was prepared by slow addition of a solution of molecular bromine (51 mL, 1.0 mol) in dichloromethane (50 mL) to a magnetically stirred solution of Me_2SO (200 mL, 3.80 mol) in dichloromethane (80 mL) at 0 °C. The yellow solid which had formed 1 h after complete addition of the bromine solution was quickly filtered and washed with dichloromethane (200 mL). The yellow solid liberated bromine on contact with a metal spatula or on prolonged exposure to air. A 25-g sample (~0.1 mol) of the slightly wet compound was added to a magnetically stirred solution of 2-methylpropanol (14.8 g, 0.20 mol) in dichloromethane (150 mL) in an open round-bottomed flask, and stirring was continued for 16 h at room temperature. The reaction mixture was poured into 200 mL of aqueous bicarbonate, and the organic layer was separated, washed with water, dried (Na_2SO_4), and evaporated to leave 10.4 g of a light yellow oil (65% crude yield). Distillation at 50–51 °C under vacuum (5 torr) gave a clear product (9.8 g, 61%) whose NMR and IR spectra were identical with those of the product obtained when 2-methylpropanol was treated according to procedure A: NMR ($CDCl_3$) δ 0.90 (d, 12 H, J = 5.0 Hz, 4 CH_3), 1.40–2.15 (m, 2 H, 2 CH), 3.21 (d, 4 H, J = 5.0 Hz, 2 CH_2), 4.55 (s, 2 H, OCH_2O); IR (neat) 2900–2960, 1450, 1370, 1350 cm^{-1}. This procedure gave a lower yield of the acetal than via procedure A. This is attributed to the fact that the complex which forms between Me_2S–Br_2 and the alcohol is not very soluble in CH_2Cl_2.

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Registry No. 1 (R = Pr), 505-84-0; 1 (R = Bu), 2568-90-3; 1 (R = *i*-Bu), 2568-91-4; 1 (R = $CH_3(CH_2)_7$), 16849-79-9; 1 (R = $(CH_3CH_2)_2CH$), 73728-32-2; 1 (R = cyclopentyl), 73728-33-3; 1 (R = cyclohexyl), 1453-21-0; **3**, 815-60-1; **4**, 50450-21-0; 1-propanol, 71-23-8; 1-butanol, 71-36-3; 2-methylpropanol, 78-83-1; 1-octanol, 111-87-5; 3-pentanol, 584-02-1; cyclopentanol, 96-41-3; cyclohexanol, 108-93-0; Me_2SO, 67-68-5; Br_2, 7726-95-6.

(13) An identical sample of the dibromo ketone was prepared by brominating 3-pentanone with 2 equiv of bromine in acetic acid. D. P. Evans and J. R. Young, *J. Chem. Soc.*, 1310 (1954).

Preparation of Site Specifically Deuterated 7,12-Dimethylbenz[*a*]anthracene Derivatives: Mechanism of Hydrogenolysis of Aryl Halides with Lithium Aluminum Hydride

Srinivas R. Adapa, Younus M. Sheikh, Ronald W. Hart, and Donald T. Witiak*

Department of Medicinal Chemistry, College of Pharmacy, and Department of Radiology, College of Medicine, The Ohio State University, Columbus, Ohio 43210

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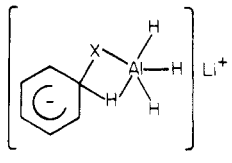
Hydrogenolysis of aromatic halides by LAH is known to proceed in excellent yield.[1] In general, the reactivity of aryl halides is in the order I > Br > Cl > F. Electron-donating groups in the para position decrease the rate of reaction whereas electron-withdrawing groups increase the rate of reaction.[1,2] Additionally, steric compression owing to bulky substituents in the ortho position is known to increase the rate of hydrogenolysis.[1,2] As expected, rates of hydrogenolysis are dependent upon the nature of the solvent and the reaction temperature.[1,2] A minimum of 2 mol of LAH per mole of aryl halide is required for an optimum reaction rate. In light of these observations, hydrogenolysis of aryl halides is thought to proceed either by direct hydride displacement of the halogen[2,3] or by four-membered transition state **1**.[2] It was concluded that bond breaking must be involved in the rate-determining step.[1,2]

Table I. Hydrogenolysis of Aryl Bromides

compd	reagent	% ^2H	% H
2	$LiAl^2H_4/^2H_2O$	100[a]	
	$LiAl^2H_4/H_2O$	23 ± 1[a]	77 ± 1
	$LiAlH_4/^2H_2O$	58 ± 1[a]	42 ± 1
5	$LiAl^2H_4/^2H_2O$	100[b]	
	$LiAl^2H_4/H_2O$	23 ± 1[b]	77 ± 1
	$LiAlH_4/^2H_2O$	58 ± 1[b]	42 ± 1

[a] Site-specific labeling at the 5 position. [b] Site-specific labeling at the 9 position.



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In connection with our program on chemical carcinogenesis, we required a number of site specifically deuterated and tritiated 7,12-dimethylbenz[*a*]anthracene (DMBA) derivatives.[4] Hydrogenolysis of 5-bromo-7,12-dimethylbenz[*a*]anthracene (**2**) in refluxing THF for 24 h resulted in site-specific labeling and furnished [5-^2H]-7,12-dimethylbenz[*a*]anthracene (**3b**). However, the extent of ^2H incorporation was dependent upon the method of reaction workup (Table I). Only when LA^2H followed by ^2H_2O workup was employed was 100% deuterium incorporated. Similar results were obtained by hydrogenolysis of 9-bromoanthracene (**5**) (Table I).

Differences in ^2H-incorporation upon hydrogenolysis of **2** with LA^2H/H_2O (**3b**, 23%) vs. $LAH/^2H_2O$ (**3b**, 58%) suggest that the major portion of the reaction proceeds via the intermediates **4a–d** and **6a–c**. Solvolysis of presumed intermediate **4a**, **4b**, or **4c** would be expected to yield **6a**, **6b**, or **6c**, respectively. In **6a–c**, hydride or deuteride transfer could result either from the HO (or ^2HO) function bonded directly to Al. Furthermore, the reaction likely is complicated by isotope effects.

In contrast to the hydrogenolysis of aryl halides **2** and **5**, LA^2H reduction of 7-(chloromethyl)-12-methylbenz-

(1) G. J. Karabatsos, R. L. Shone, and S. E. Scheppele, *Tetrahedron Lett.*, 2113 (1964); G. J. Karabatsos and R. L. Shone, *J. Org. Chem.*, 33, 619 (1968).

(2) H. C. Brown and S. Krishnamurthy, *J. Org. Chem.*, 34, 3918 (1969).

(3) Aromatic halides have been shown to incorporate deuterium at the site of halogen substitution (see ref 1); site-specific deuteration to furnish **3b** on hydrogenolysis with $LiAl^2H_4$ of **2** was established by detailed 90-MHz NMR analysis; site-specific incorporation of deuterium at C-5 upon hydrogenolysis of **2** was indicated by NMR analysis [DMBA (**3a**), δ 8.0 (d, C-6, 1 H, J = 9.6 Hz, 8.4 (m, aromatic, 3 H) vs. [5-^2H]-DMBA (**3b**), δ 8.0 (s, C-6, 1 H), 8.4 (m, aromatic, 3 H)]. For preliminary results on deuteration of DMBA also see M. Muschik and J. E. Tomaszewski, Abstract No. ORGN 109, National American Chemical Society Meeting, Miami, FL, September 1978.

(4) 7-(Chloromethyl)-DMBA derivatives **7a-d** were prepared by the reaction of anhydrous HCl in ethyl acetate with the corresponding 7,12-dihydro-7,12-dimethyl-7,12-dihydroxybenz[*a*]anthracenes synthesized in these laboratories. M. S. Newman, J. M. Khanna, K. Kanakarajan, and S. Kumar, *J. Org. Chem.*, 43, 2553 (1978).

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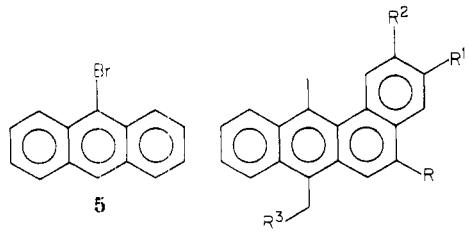

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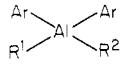
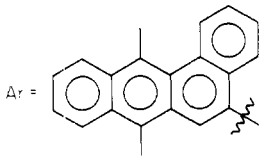
2, R = Br; $R^1 = R^2 = R^3 = H$
3a, R = $R^1 = R^2 = R^3 = H$
3b, R = ^2H; $R^1 = R^2 = R^3 = H$
4a, R = AlH_3^-; $R^1 = R^2 = R^3 = H$
4b, R = $Al^2H_3^-$; $R^1 = R^2 = R^3 = H$
6a, R = Al(H)(O^2H); $R^1 = R^2 = R^3 = H$
6b, R = Al(^2H)(OH); $R^1 = R^2 = R^3 = H$
7a, R = $R^1 = H$; $R^2 = F$; $R^3 = Cl$
7b, R = $R^2 = H$; $R^1 = F$; $R^3 = Cl$
7c, R = F; $R^1 = R^2 = H$; $R^3 = Cl$
7d, R = $R^2 = H$; $R^1 = OCH_3$; $R^3 = Cl$



4c, $R^1 = R^2 = H$
6c, $R^1 = OH(^2HO)$; $R^2 = H$
4d, $R^1 = H$; $R^2 = AR$



[a]anthracenes **7a–d** afforded site specifically monodeuterated compounds at the 7-methyl position. The reaction was insensitive to workup conditions, likely owing to direct displacement of halogen or reduction of an intermediate benzyl carbonium ion.

It thus appears that hydrogenolysis with $LiAlH_4$ of aryl halides proceeds via organoaluminums in addition to proposed four-membered cyclic transition-state intermediates. On the other hand, benzylic chlorides undergo hydrogenolysis exclusively by direct displacement of halogen by hydride.

Experimental Section

All melting points are uncorrected and were determined on a Thomas-Hoover capillary melting point apparatus. Ultraviolet and infrared spectra were recorded on Beckman UV-5260 and IR-4230 instruments. ^1H NMR spectra were determined on a Varian A-60A or Brucker 90-MHz instrument. 5-Bromo-7,12-dimethylbenz[a]anthracene (**2**) and 2-fluoro- (**7a**), 3-fluoro- (**7b**), 5-fluoro- (**7c**), and 3-methoxy- (**7d**) 7-(chloromethyl)-12-methylbenz[a]anthracene were prepared by known methods. Mass spectra were run with a Hewlett-Packard Model 5985 system. The quantity of site specifically introduced deuterium in DMBA was determined by mass spectrometry and nuclear magnetic resonance (90 MHz).

Hydrogenolysis of Aryl Halides (2 and 5). $LiAlH_4$ or $LiAl^2H_4$ (140 mg, 40 μmol) was suspended in dry THF (5.0 mL) and refluxed for 5 min. 5-Br-DMBA (13.3 mg, 40 μmol) in THF (3.0 mL) was added, and the mixture was refluxed for 24 h and cooled to room temperature. The excess $LiAlH_4$ or $LiAl^2H_4$ was decomposed by addition of either H_2O or ^2H_2O. Ether (20 mL) was added and the mixture vigorously stirred. The ether layer was separated, dried over sodium sulfate, and evaporated, furnishing crude DMBA (or deuterated DMBA). Subsequent purification by TLC (silica gel) and high-pressure liquid chromatography over Whatman Partisil PXS 10/25 ODS column (length = 25 cm; diameter = 4.6 mm) furnished pure samples which were analyzed for deuterium incorporation by mass spectrometry and 90-MHz NMR.

Hydrogenolysis of 7-(Chloromethyl)-12-methylbenz[a]anthracene Derivatives 7a to 7d. To a vigorously stirred suspension of $LiAl^2H_4$ (2 mmol) in ether (150 mL) under N_2 was added dropwise a solution of the respective 7-chloromethyl derivative (1 mmol) in dry THF (10 mL). After 1 h the excess $LiAl^2H_4$ was destroyed by addition of saturated ammonium chloride solution. The ether layer was dried over sodium sulfate and evaporated, furnishing a yellow gum which on subsequent column chromatography over silica gel (hexane–benzene, 1:1) furnished pure 7-methyl-deuterated DMBA derivatives characterized by examination of their NMR spectra.

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Registry No. 2, 34698-71-0; **3b**, 73873-01-5; **5**, 1564-64-3; **7a**, 73873-02-6; **7d**, 66240-01-5.

Mechanisms of Decomposition of the Ene Adducts of Some 1,3-Cyclohexadienes to Benzene or Tetralin and Dihydroenophile

Barry M. Jacobson,* Daniela Gerhard, Cynthia Jackson, and Joan Smallwood

Department of Chemistry, Barnard College, New York, New York 10027

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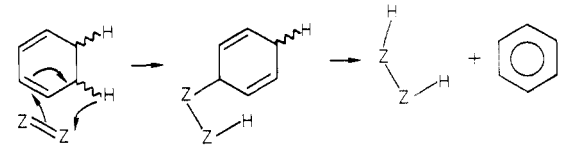
The Alder ene reaction can usually be run under mild conditions, especially when more active enophiles are used.[1] By contrast, it is unusual for either the reverse process[1,2] (retro-ene reaction) or other thermal breakdown of an ene adduct to occur at temperatures much below 200 °C, though there are some exceptions to this, e.g., the concerted decarboxylations of β-oxo acids and related compounds.[3,4] A common factor to several isolated reports of other ene adduct decompositions that occurred at moderate temperatures was a 1,3-cyclohexadiene structure for the adduct precursor.[5] As the decompositions in these cases usually resulted in aromatization and resemble the facile tetracanoethylene (TCNE) or quinone-mediated aromatizations of 1,4-cyclohexadienes,[6] it is not completely surprising that decomposition should occur, (see eq 1 for the overall



(1)

(1) H. M. R. Hoffman, *Angew. Chem., Int. Ed. Engl.*, **8**, 556 (1969).
(2) (a) R. T. Arnold and P. Veeravagu, *J. Am. Chem. Soc.*, **82**, 5411 (1960); (b) H. Kwart, J. Slutsky, and S. F. Sarner, *ibid.*, **95**, 5242 (1973).
(3) (a) F. H. Westheimer and W. A. Jones, *J. Am. Chem. Soc.* **63**, 3283 (1941); (b) J. A. King, *ibid.*, **69**, 2738 (1947).
(4) (a) The ene reaction of SO_2 and alkenes to give allylic sulfinic acid also appears to be readily reversible[4b] as is that of *N*-sulfinyl sulfonamides to give allylic sulfinamides.[4c] A few other ene reactions are also reversible at moderate temperatures,[1,2a] but there is no particular pattern to these. (b) D. Masilamni and M. M. Rogic, *J. Am. Chem. Soc.*, **100**, 4634 (1978); (c) J. Hori, S. P. Singer, and K. B. Sharpless, *J. Org. Chem.*, **43**, 1456 (1978).
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(6) For TCNE: B. M. Jacobson, *J. Am. Chem. Soc.*, **102**, 886 (1980), and references therein. For quinones: P. Müller, *Helv. Chim. Acta.*, **56**, 1243 (1973), and references therein.

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