A New Intermediate in the Reduction of Chromic Acid by Hydrogen Peroxide

Sir:

We wish to report the isolation of a new intermediate formed during the reduction of chromic acid by hydrogen peroxide. When conducted in perchloric acid, the final products of this reaction are oxygen and the hexaaquochromium(III) ion. During the preparation of chromium(III) perchlorate by this method, we observed that the deep blue perchromate formed upon mixing the reagents is not the only intermediate formed during the reaction. After its disappearance the solution turns green; the green color may persist for hours (at room temperature) and finally change to the grayish-blue color of the hexaaquo ion.

Ion-exchange chromatography was used to isolate the green intermediate. It turned out to be a highly charged cation which formed a green ring above the gray ring of the hexaaquo ion, and was eluted by perchloric acid at a much slower rate than the latter. The highest yields were obtained when the reaction was carried out in strong acid (2 to 4 *M* perchloric acid).

In order to minimize decomposition of the complex, all operations were carried out at $-4°$. An excess of chromic acid was used, so as to avoid free peroxide which tends to form bubbles on the ion-exchange column (cooled by circulating brine). A cation-exchange resin of low cross-linking was used (Dowex 50X2 100–200 mesh). The hexaaquo ion was easily eluted with 2 *M* perchloric acid, which also served to rinse the column (lower acid concentration was avoided in order to prevent freezing). The green band of the complex was eluted with 4 *M* acid. The chromium content of the solution was determined spectrophotometrically after oxidation with alkaline hydrogen peroxide at 372 mμ.[1] The absorption spectra of the complex has two maxima in the visible region, at 434 mμ (ϵ 381) and at 625 mμ (ϵ 414), and two in the ultraviolet region, at 230 and 268 mμ.

The band at 625 mμ was used to follow the decomposition of the complex. The rate of decomposition depends only slightly on acidity in the range investigated: at 26.5° the first-order rate constants are 1.23×10^{-4}, 1.24×10^{-4}, 1.45×10^{-4}, and 1.58×10^{-4} sec^{-1} at 4, 1, 0.4, and 0.2 *M* acid, respectively. The rate constant was measured at four different temperatures (in 4 *M* acid) and found to be 4.4×10^{-4}, 2.5×10^{-4}, 1.24×10^{-4}, and 0.34×10^{-4} sec^{-1} at 36.5, 31.5, 26.5, and 16.5°, respectively. The rate constant at $-4°$ was estimated to be 1.43×10^{-6} sec^{-1} ($t_{1/2}$ = 134 hr); *i.e.*, decomposition of the complex during its preparation and analytical determination is negligible.

The green complex is a strong oxidizing agent; iodide is oxidized to iodine, ferrous to ferric ion, etc. The number of oxidizing equivalents per chromium atom was determined by two independent analytical methods: (a) iodometrically, by addition of KI and titrating the liberated iodine with thiosulfate (the result of eight titrations was 1.48 ± 0.04 equiv per chromium atom); and (b) spectrophotometrically, by addition of excess NaOH and measuring the chromate formed by self-oxidation at 372 mμ (the result of 12 determinations was that 50.6 ± 2.6% of the total chromium was oxidized; *i.e.*, there are 1.518 oxidizing equiv per chromium atom).

The decomposition products of the complex ion are the hexaaquochromic ion and chromic acid. The high charge of the complex (revealed by its strong affinity to the ion-exchange resin) supports a polynuclear structure. A structure that accounts for the properties described here is

$$[(H_2O)_5Cr—O—O—Cr(H_2O)_5]^{5+}$$

which is similar to the well-known cobalt ammine

$$[(NH_3)_5Co—O—O—Co(NH_3)_5]^{5+}$$

Other structures are not excluded and further work is required to establish the correct structure.

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(1) G. W. Haupt, *J. Res. Natl. Bur. Std.*, **48**, 414 (1952).

The Chemistry of Alane. XI.[1] A New Complex Lithium Aluminum Hydride, Li_3AlH_6[2]

Sir:

Although many alane derivatives are known, until now the metal aluminum hydrides, such as $LiAlH_4$, and quaternary ammonium aluminohydrides, R_4NAlH_4,[3] have been the only compounds containing only one group III-B element, in which more than three hydrogens were bonded to one aluminum. We now wish to report the first synthesis of a complex lithium aluminum hydride with a hydrogen-to-aluminum ratio greater than 4, lithium hexahydroalanate, Li_3AlH_6.

A solution of 0.10 mole of *n*-butyllithium in 60 ml of hexane was added to a solution of 0.20 mole of lithium tetrahydroalanate ($LiAlH_4$) in 150 ml of diethyl ether. A white precipitate formed immediately on addition of the reagents and the mixture was stirred for 30 min at room temperature. The white, microcrystalline solid (2.30 g) was isolated by filtration, washed thoroughly with anhydrous *n*-hexane and anhydrous diethyl ether, and dried *in vacuo* at room temperature. *Anal.* Calcd for Li_3AlH_6: Li, 38.66; Al, 50.11; H, 11.23; Li:Al:H, 3:1:6. Found: Li, 37.68; Al, 50.29; H, 11.12; C, 0.46; Cl, 0.75; Li:Al:H, 2.9:1:5.9.

That the new hydride was not a mixture of LiH and $LiAlH_4$ was demonstrated by its density which was greater than that of either LiH or $LiAlH_4$ (1.13 g/cc *vs.* 0.915 g/cc for $LiAlH_4$ and 0.775 g/cc for LiH); by thermal and hydrolytic stabilities better than those of LiH and $LiAlH_4$; by a chemical reactivity considerably lower than that of LiH or $LiAlH_4$; and by a unique powder X-ray diffraction pattern. The infrared spectrum of Li_3AlH_6 (KBr pellet) showed only a broad absorption centered at 1720 cm^{-1}.

Lithium hexahydroalanate decomposes without melting or subliming above 210° and, so far, no solvent has been found for it. It decomposes in air without ignition

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(1) Paper X: R. Ehrlich and A. R. Young, II, *J. Inorg. Nucl. Chem.*, in press.

(2) This work was sponsored by ARPA under Order No. 24-62 and was monitored by the Air Force Systems Command, Research and Technology Division, Rocket Propulsion Laboratory, Edwards Air Force Base, Calif., under Contract AF04(611)-7046.

(3) R. Ehrlich, A. R. Young, II, and D. D. Perry, *Inorg. Chem.*, **4**, 758 (1965).

and is hydrolyzed readily and completely with water. It does not react with dimethyl sulfoxide, dimethylformamide, nitrobenzene, ethyl acetate, methyl ethyl ketone, 1-propanol, or *n*-butylamine. It reacts quickly and completely, producing quantitative hydrogen evolution, with an excess of propionic acid, hydrazine, and ethylenediamine, and slowly with oleic acid, nitromethane, and 1,1-dimethylhydrazine. Both toluene diisocyanate and hexamethylene diisocyanate react with Li_3AlH_6 to produce resinous solids which are stable in water suspension but hydrolyze with gas evolution when benzene or diethyl ether is added to the suspension. Heating Li_3AlH_6 at 100° *in vacuo* causes only 2.48% decomposition (based on hydrogen evolution) in a 24-hr period compared to 47.4% for $LiAlH_4$.

The powder X-ray diffraction pattern (Table I) was indexed on the basis of one rhombohedral unit cell, indicating a single phase, and the calculated density was 1.26 g/cc.[4] There was no evidence of the presence of either LiH or $LiAlH_4$. It is interesting that the crystals of Li_3AlH_6 are rhombohedral since the common hexafluoroalanates, such as cryolite (Na_3AlF_6), are monoclinic at low temperatures and cubic at high temperatures.[5]

Table I. Powder X-Ray Diffraction Pattern of Li_3AlH_6[a]

d, A	I/I_0[b]	*d*, A	I/I_0	*d*, A	I/I_0
4.06	vs	2.028	mw	1.333	w
3.96	vs	1.972	mw	1.316	w
3.29	vvw	1.805	m	1.277	w
3.18	vw	1.774	ms	1.250	w
2.825	s	1.646	vw	1.218	w
2.555	m	1.530	ms	1.158	w
2.500	w	1.507	m	1.122	w
2.340	vw	1.480	m	1.115	w
2.318	vs	1.411	w	1.102	w
2.260	m	1.347	w	1.088	w

[a] Cu Kα radiation with a Debye–Scherrer camera with a radius of 5.73 cm. [b] s, strong; m, medium; w, weak; v, very.

Lithium hexahydroalanate can also be prepared by the reaction of (1) *n*-BuLi and $LiAlH_4$ in *n*-hexane, (2) C_6H_5Li and $LiAlH_4$ in diethyl ether or benzene, (3) $LiAl(CH_3)_3H$ and $LiAlH_4$ in diethyl ether (only trace yields), (4) *n*-BuLi and $Et_3N \cdot AlH_3$ in benzene,[6] (5) $LiAlH_4 \cdot NEt_3$ and LiH in benzene,[7] (6) $LiAlH_4 \cdot NEt_3$ and diethyl ether,[8] and (7) $LiAlH_4 \cdot NEt_3$ and $LiAlH_4$ in benzene.

At the present time there is no definite proof to support a stoichiometric equation for the preparation of Li_3AlH_6. We believe that the over-all reaction is that shown in eq 1. The decomposition of alkyllithium reagents to give LiH and an olefin has been well documented. In the case of *n*-BuLi, butene-1 and LiH can be obtained almost quantitatively.[9] A trace of butene-1 was isolated from the vapors immediately above one reaction of $LiAlH_4$ and BuLi carried out in a closed system at atmospheric pressure. The failure to isolate the olefin is to be expected in a system in which is present not only a known catalyst for 1-olefin polymerization (BuLi) but also a metal hydride ($LiAlH_4$) known to add across a double bond of an olefin.

$$LiAlH_4 + 2C_4H_9Li \longrightarrow Li_3AlH_6 + 2C_4H_8 \qquad (1)$$

During an attempt to obtain a mass balance for the preparation of Li_3AlH_6, the ether–hexane filtrate of one reaction was worked up to isolate the by-products. Both $LiAlH_4$ and $LiAlBu_4$ were identified by their infrared spectra, quantitative hydrolyses, and X-ray diffraction patterns. But also isolated was an unresolvable mixture of lithium butylaluminum hydrides (infrared spectrum and quantitative hydrolysis) in which the Li:Al ratio was greater than 1, and a small quantity of a viscous oil which showed only hydrocarbon absorptions in the infrared and contained no aluminum.

Thus, a probable scheme for the reaction is a stepwise addition of LiH to $LiAlH_4$ (eq 2 and 3) with concurrent side reactions of the intermediate products, such as those shown in eq 4–6. The great insolubility of Li_3AlH_6 probably prevents its further reaction with *n*-BuLi. The side reactions also would help to explain why an excess of $LiAlH_4$ is beneficial in the preparation of Li_3AlH_6.

$$LiAlH_4 + C_4H_9Li \longrightarrow Li_2AlH_5 + C_4H_8 \qquad (2)$$

$$Li_2AlH_5 + C_4H_9Li \longrightarrow Li_3AlH_6 + C_4H_8 \qquad (3)$$

$$LiAlH_4 + xC_4H_8 \longrightarrow LiAlH_{4-x}Bu_x \qquad (4)$$

$$Li_2AlH_5 + xC_4H_8 \longrightarrow Li_2AlH_{5-x}Bu_x \qquad (5)$$

$$xC_4H_8 + C_4H_9Li \longrightarrow \text{polymer} \qquad (6)$$

Support of the idea that the LiH necessary to form Li_3AlH_6, in the reaction of *n*-BuLi and $LiAlH_4$, came from the *n*-BuLi was obtained when $LiAlD_4$ was allowed to react with *n*-BuLi. The product isolated was $Li_3AlD_4H_2$. *Anal.* Calcd Li, 35.99; Al, 46.64; D:H, 2.00. Found: Li, 35.69; Al, 45.44; D:H, 2.01.

No proof has yet been obtained as to whether the LiH abstraction from *n*-BuLi involves an α or a β elimination. Indications are that it is a β elimination since the reaction of MeLi and $LiAlH_4$ did not give Li_3AlH_6, but only methylated derivatives of this complex hydride and those only in reactions with equimolar quantities of reagents or with an excess of $LiAlH_4$.[10] Interestingly, some of these methylated compounds ($Li_3AlH_{6-x}Me_x$) possessed the same X-ray diffraction pattern as Li_3AlH_6 up to a carbon content of about 28% which corresponds to that found in $Li_3AlH_4Me_2$.

One attempt was made to prepare a mixed alkali metal hexahydroalanate by using $NaAlH_4$ and *n*-BuLi. The reaction was run in *n*-hexane in the same manner as the reaction of $LiAlH_4$ and *n*-BuLi except

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[4] The diffraction pattern was obtained and indexed by Professor Benjamin Post, Polytechnic Institute of Brooklyn.

[5] *Cf.* E. G. Steward and H. P. Rooksby, *Acta Cryst.*, **6**, 49 (1953); G. J. Landon and A. R. Ubbelohde, *Proc. Roy. Soc.* (London), **A240**, 160 (1957).

[6] Equimolar quantities of reagents or excess *n*-BuLi gave a mixture of $LiAlH_4$ and Li_3AlH_6 (3:1). Excess $Et_3N \cdot AlH_3$ gave only $LiAlH_4$, in agreement with the results of J. K. Ruff, *J. Am. Chem. Soc.*, **83**, 1798 (1961).

[7] $LiAlH_4 \cdot NEt_3$, which is the subject of another paper to be published, is a compound with properties different from those of $LiAlH_4$. It reacts readily with commercial grade LiH while $LiAlH_4$ does not.

[8] F. M. Peters, *Can. J. Chem.*, **42**, 1755 (1964), has reported that the reaction of $LiAlH_4$ and NMe_3 in Et_2O gave insoluble materials with high Li:Al and H:Al ratios (2.5 and 4.5, respectively).

[9] *Cf.* G. E. Coates, "Organometallic Compounds," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1960, p 19, 20.

[10] G. D. Barbaras, C. Dillard, A. E. Finholt, T. Wartik, K. E. Wilzbach, and H. I. Schlesinger, *J. Am. Chem. Soc.*, 73, 4585 (1951), reported that the reaction of MeLi and $LiAlH_4$ in Et_2O (unspecified stoichiometry) gave LiH. No LiH was found in our studies in a series of reactions where the mole ratio of MeLi:$LiAlH_4$ was varied from 10:1 to 1:2.

that tetrahydrofuran was used as the extractant for unreacted $NaAlH_4$. However, the analyses were inconclusive.

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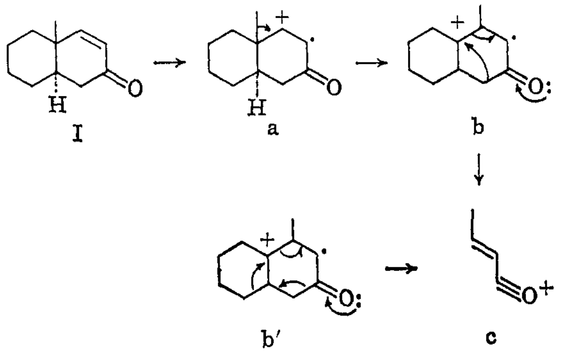
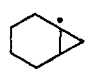
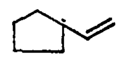
Mass Spectrometry in Structural and Stereochemical Problems. CIII.[1] Electron Impact Induced Methyl Migration in Some 2-Arylidene-1-decalones[2]

Sir:

Increasing attention is being paid to the electron impact induced rearrangement of substituents other than hydrogen in mass spectrometric fragmentation reactions. This is due to the intrinsic mechanistic interest that such rearrangements possess and the possible limitation that their occurrence may impose on the use of the "element mapping" technique.[3] One such rearrangement is typified by the elimination of stable neutral fragments such as formaldehyde, carbon monoxide, carbon dioxide, and diimide from the nonterminal portion of some linear molecules.[4] Another type is represented by authentic 1,2 migrations, which have been of particular concern to us because of their potential for comparison with carbonium ion rearrangements and for an evaluation of the hitherto unexamined field of relative migratory aptitudes in mass spectrometry. Such a methyl migration has recently been described[5] in *trans*-Δ^3-10-methyl-2-octalone (I) and related compounds, which give rise to an abundant ion which may be depicted as c.

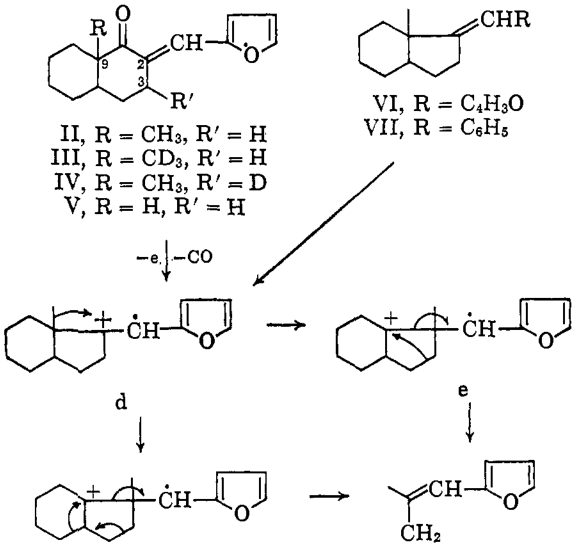



i


ii

We describe now a second example of such a methyl migration, which in spite of the structural dissimilarity of the starting compounds (I *vs.* II) seems to be mechanistically identical with the octalone rearrangement (a → c).[5] The base peak in the mass spectrum of *trans*-2-furfurylidene-9-methyl-1-decalone (II)[6] as well as in the analogous steroid ketones occurs at *m/e* 121 and by high-resolution mass spectrometry was shown to correspond to $C_8H_9O^+$. This peak is shifted to *m/e* 124 in the 9-d_3 analog III and to *m/e* 122 in the 3-d_1 derviative IV,[7] while it occurs at *m/e* 107 in the unmethylated precursor V. Appropriate mass shifts were encountered in the benzylidene (*m/e* 131), *p*-chlorobenzylidene (*m/e* 165/167), and *p*-methylbenzylidene (*m/e* 145) derivatives, and no significant change was observed in the mass spectrum of the *cis* isomer of II.

These results are only compatible with the assumption that the intense $C_8H_9O^+$ ion (*m/e* 121) of II retained the furfurylidene moiety together with carbon atoms 2 and 3 as well as the angular methyl group. We formulate its genesis through initial loss of carbon monoxide to species d,[8] followed by concerted methyl migration and subsequent bond cleavages (e or e') to the resonance-stabilized ion f (*m/e* 121). It should


II, R = CH_3, R' = H
III, R = CD_3, R' = H
IV, R = CH_3, R' = D
V, R = H, R' = H

VI, R = C_4H_3O
VII, R = C_6H_5

d
e
e'
f

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[1] Paper CII: P. Potier, C. Kan, J. Le Men, M.-M. Janot, H. Budzikiewicz, and C. Djerassi, *Bull. Soc. Chim. France*, in press.

[2] Financial support (Grants No. CA-07195 and AM-04257) from the National Institutes of Health of the U. S. Public Health Service is gratefully acknowledged.

[3] K. Biemann, *Pure Appl. Chem.*, **9**, 95 (1964); K. Biemann, P. Bommer, and D. M. Desiderio, *Tetrahedron Letters*, 1725 (1964).

[4] For recent examples see P. Brown, C. Djerassi, G. Schroll, H. J. Jakobsen, and S.-O. Lawesson, *J. Am. Chem. Soc.*, **87**, 4559 (1965); J. H. Bowie, R. Grigg, D. H. Williams, S.-O. Lawesson, and G. Schroll, *Chem. Commun.*, 403 (1965); A. Bhati, R. A. W. Johnstone, and B. J. Millard, *J. Chem. Soc.*, in press.

[5] F. Komitsky, Jr., J. E. Gurst, and C. Djerassi, *J. Am. Chem. Soc.*, **87**, 1398 (1965). In this paper we postulated conversion of b to c, which implies the elimination of the cyclopropyl radical i. Dr. W. J. Richter (Hoffman-LaRoche, Basel) has pointed out to us that a series of 1,2 cleavages as indicated in b' are equally feasible, the principal difference being the nature of the expelled radical (ii). Experiments are under way in our laboratory which may differentiate between these two subtle but important alternatives.

[6] W. S. Johnson, B. Bannister, and R. Pappo, *ibid.*, **78**, 6331 (1956). We are indebted to Professor Johnson for supplying us with starting materials for the d_3-labeled substrates, which were obtained by substituting methyl-d_3 iodide in the appropriate methylation steps in the decalone and steroid series.

[7] This substance was prepared by lithium aluminum deuteride reduction of (+)-*trans*-1-methoxy-9-methyl-$\Delta^{1,6}$-3-hexalone, followed by acid cleavage to *trans*-9-methyl-$\Delta^{2,6}$-1-decalone-3-d_1, catalytic hydrogenation of the two double bonds, and finally condensation with furfuraldehyde.

[8] The M − 28 peak at *m/e* 216 amounts to 40% of the intensity of the base peak (f, *m/e* 121) and by high-resolution mass spectrometry was shown to correspond to the expulsion of carbon monoxide rather than of ethylene. No metastable peaks were encountered in this work to substantiate the postulated intermediacy of the M − CO species in the formation of ion f, nor were any observed which would correspond to the direct production of f from the molecular ion.