Hydrogen Absorption and Hydrogen Exchange Reactions in Solution by 1:2 Electron Donor–Acceptor Complexes of Anthracene with Various Alkali Metals

Sir:

We have studied the heterogeneous[1] and homogeneous mechanisms of hydrogen activation by some electron donor–acceptor (EDA) complexes of aromatic compounds and alkali metals, and found that anthracene-dianion complexes in solution catalyzed both hydrogen absorption and hydrogen exchange to a different extent, depending upon the alkali metal cations.

The 1:2 anthracene–alkali metal complexes (An^{2-}-$2M^+$; M = Li, Na, K, and Rb) were prepared by a reaction between anthracene (10^{-5}–10^{-2} mol) and each alkali metal in 80 cm³ of dry THF (tetrahydrofuran) or DME (dimethoxyethane), in a manner similar to that described previously.[2] Formation of the stoichiometric complexes was confirmed by their electronic spectra. The solution of the complex was introduced into a 270-cm³ reaction vessel through a glass filter to remove the unreacted metal. When D_2 (23 cm) was placed in the solution of the complex (*ca.* 6 × 10^{-2} *M*) and the solution was stirred strongly a considerable amount of deuterium was absorbed in the temperature range from 0 to 50°, and at the same time the gaseous deuterium became diluted with the hydrogen of the complex molecule.

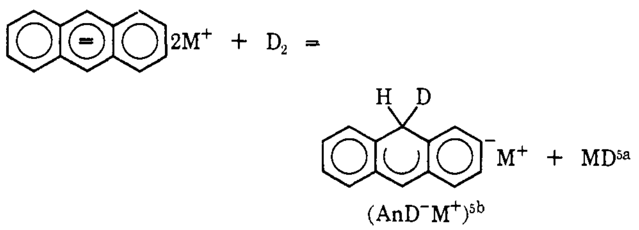
Table I

Complex (5 × 10^{-3} mol)	Solvent (80 cm³)	Hydrogen absorption: V_{D_2ads},[a] cm³/hr at 27°	Hydrogen absorption: *E*, kcal/mol	Hydrogen exchange: V_{HD},[a] cm³/hr at 27°	Hydrogen exchange: *E*, kcal/mol
An^{2-}–Li^+	THF	6.8	10.8	0.05	
	DME	6.3	11.0	0.03	
An^{2-}–$2Na^+$	THF	5.7	11.0	0.12	10.5
	DME	4.2	11.4	0.08	
An^{2-}–$2K^+$	DME	<0.01		2.40	12.0
An^{2-}–$2Rb^+$	DME	<0.01		1.35	12.8
AnH^-–Li^+	THF	<0.01		0.07	
AnH^-–Na^+	THF	<0.01		0.08	9.8
AnH^-–Na^+–NaH[c]	THF	<0		0.08	9.8

[a] V_{D_2ads} and V_{HD} denote the initial rates of D_2 uptake and of HD formation in the D_2–HZ exchange reaction, respectively. [b] It was found that the isotope effect of hydrogen absorption in the THF solution of An^{2-}–$2Na^+$ at 27° was V_{H_2ads}/V_{D_2ads} = 1.8. [c] After complete H_2 adsorption by 5 × 10^{-3} mol of An^{2-}–$2Na^+$ solution, a 1:1 mixture of AnH^-–Na^+ and NaH could be obtained, into which D_2 was admitted at 27°.

The initial rates of D_2 absorption in various complex solutions and those of HD formation in the D_2–HZ (HZ = An^{2-}–$2M^+$) exchange reaction are given in Table I. The principal points to note are that the hydrogen absorption took place in An^{2-}–$2Li^+$ or An^{2-}-$2Na^+$ solutions more vigorously than in An^{2-}–$2K^+$ or An^{2-}–$2Rb^+$ solutions at room temperature, whereas the hydrogen exchange reaction proceeded at higher rates in An^{2-}–$2K^+$ or An^{2-}–$2Rb^+$ solutions than in An^{2-}-$2Na^+$ or An^{2-}–$2Li^+$ solution.

When hydrogen was absorbed[3] by a solution of the complexes of Na or Li, a 1:1 mixture of 9-monohydroanthracenium-anion complex (AnD^-M^+) and metal hydride was produced according to the stoichiometry[4]



where M = Li or Na. HD formation resulted mainly from slow hydrogen exchange between D_2 and the AnD^-M^+ which was produced by hydrogen absorption. In Table I, data for hydrogen exchange over AnH^-Na^+ or AnH^-Li^+ solution are given, where AnH^-M^+ was prepared independently by the reaction between An^{2-}-$2M^+$ and AnH_2 (9,10-dihydroanthracene) in THF or DME. As is also shown in Table I, the presence of NaH did not enhance the hydrogen exchange reaction between AnH^-Na^+ and D_2.

On the other hand, the hydrogen exchange reaction proceeded between D_2 and the hydrogen of An^{2-}–$2K^+$ or An^{2-}–$2Rb^+$ without a detectable amount of hydrogen absorption, that is *via* the reversible formation of a monohydro-anion complex.[6] The hydrogens attached to the 9 and 10 carbon atoms in anthracene were the ones involved in the D_2–HZ exchange reaction (by mass and nmr spectrometry[7]).

These results suggested that hydrogen absorption and hydrogen exchange reactions in various An^{2-}–$2M^+$ solutions take place as shown in the equations below.

The remarkable activity of An^{2-}–$2K^+$ and An^{2-}–$2Rb^+$ toward hydrogen exchange reactions in solution is attributed to the strong reversibility of monohydro-anion

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(1) M. Ichikawa, M. Soma, T. Onishi, and K. Tamaru, *Trans. Faraday Soc.*, **63**, 997, 1215, 2012 (1967); *J. Phys. Chem.*, **70**, 2069, 3020 (1966); **73**, 1174 (1969); *J. Amer. Chem. Soc.*, **91**, 6050 (1969).

(2) M. Ichikawa, M. Soma, T. Onishi, and K. Tamaru, *Trans. Faraday Soc.*, **66**, 976, 981 (1970).

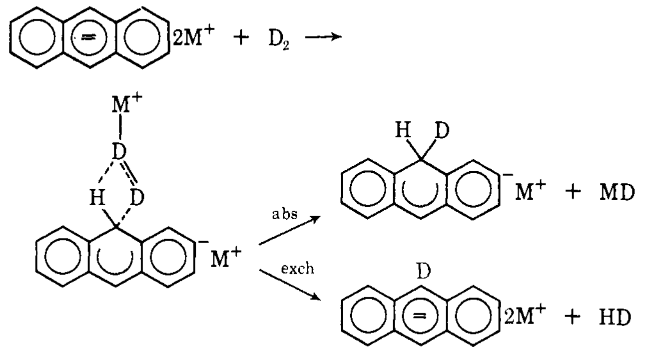
(3) At saturation, 5 × 10^{-3} mol of An^{2-}–$2Na^+$ (or An^-–$2Li^+$) solution absorbed 4.8 × 10^{-3} mol of D_2, and the complex was completely converted to 9-monohydroanthraceniumsodium (432 mμ) and 2.4 × 10^{-3} mol of NaD.

(4) A similar mechanism for hydrogen dissociation processes was proposed by S. Bank, *et al.*, in the solution of naphthalene⁻ sodium⁺: S. Bank, T. A. Lois, and M. C. Prislopski, *J. Amer. Chem. Soc.*, **91**, 5407 (1969).

(5) (a) The amount of metal hydride was measured by the D content in the hydrogen gas obtained from hydrolysis of the resultant product by H_2O after the solvent was thoroughly removed. (b) The 9-monohydro species was identified by peaks at 370 (AnD^-Li^+) and 432 mμ (AnD^-Na^+) in the electronic spectra. After D_2 absorption, the product 9-monohydroanthraceniumsodium was quenched by H_2O, and monodeuterated 9,10-dihydroanthracene was detected by nmr and mass spectroscopy.

(6) We found that hydrogen gas was rapidly evolved and the anthracene-dianion complex was regenerated when KH was mixed at room temperature with the AnH^-–K^+ solution which was prepared independently in DME.

(7) After deuteration the complexes (An^{2-}–$2K^+$ and An^{2-}–$2Rb^+$) were oxidized to anthracene by dry oxygen gas at 25°.



complex formation, relative to the formation of complexes of Na and Li.

Similar different behavior of the different alkali metals was observed in other EDA complexes such as naphthalene, phenanthrene, and pyrene.

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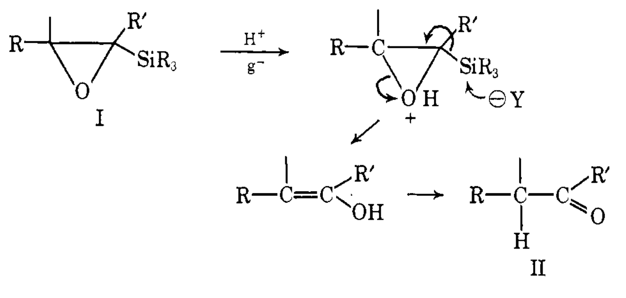
A New Synthesis of Aldehydes *via* Vinylsilanes

Sir:

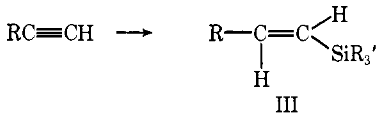
We describe a new synthesis leading to aldehydes (and ketones).

The synthesis was designed on the assumption that the well-known propensity of suitably substituted organosilanes toward β elimination[1] should result in the transformation of epoxysilanes into carbonyl compounds, as shown in I → II. This has now been shown to be the case.

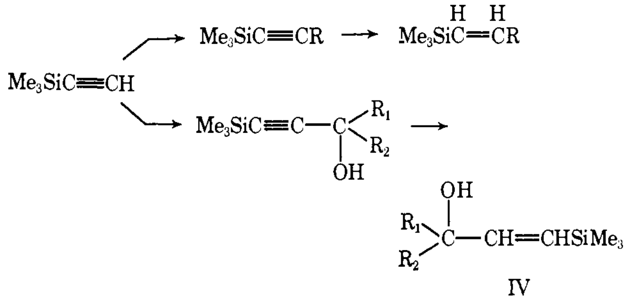


Epoxysilanes (*cf.* I) have been described previously.[2] They are easily made by epoxidation of the corresponding ethylene derivatives which can themselves be prepared easily (when R′ = H),[3] either by the addition of trialkysilanes to terminal acetylenes in the presence of chloroplatinic acid[4] (Scheme I), or by the alkylation of organometallic derivatives of the easily available trimethylsilylacetylene[5] followed by semihydrogenation (Scheme II).

Scheme I

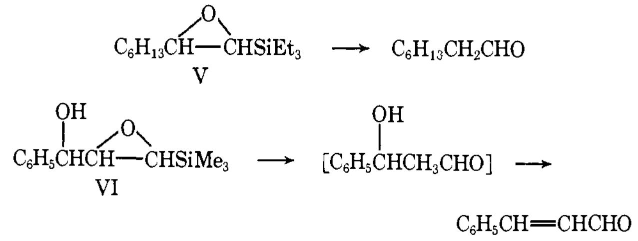


Scheme II



The complete sequence is illustrated by the transformation of 1-octyne to octanal and of benzaldehyde to cinnamaldehyde. Addition of triethylsilane (100% excess) to 1-octyne (100°, 5 hr, 2 drops of 10% H_2PtCl_6 under N_2) gave a 90% yield of *trans*-1-octenyltriethylsilane (III, R = C_6H_{13}; R′ = C_2H_5): bp 128–132° (6 mm); λ_{max}^{film} 6.18, 8.1, 9.85, 12.8, and 13.6–13.9 μ; δ (neat) 0.3–1 (m, 18 H) 2.2 (m, 2 H), 5.55 (d, J = 18 Hz, 1 H), 6.13 (d of t, J_1 = 18 Hz, J_2 = 6 Hz, 1 H). Epoxidation with *m*-chloroperbenzoic acid in methylene chloride at room temperature overnight gave the corresponding epoxide V: bp 98° (0.8 mm); λ_{max}^{film} 8.05, 9.85, and 13.5–13.9 μ; δ (CCl_4) 0.3–1 (m, 18 H), 1.88 (d, J = 4 Hz, 1 H), 2.7 (broad d, J = 4 Hz, 1 H). Treatment of the epoxide with 2,4-dinitrophenylhydrazine reagent gave a 65% yield of the 2,4-dinitrophenylhydrazone of octanal, mp 105.5–106° (lit.[6] 106°).

Treatment of the epoxysilane with a solution of 1 ml of sulfuric acid in 10 ml of methanol at 90° for 10 min, followed by work-up, gave a 60% yield of octanal as its dimethyl acetal: λ_{max}^{film} 8.8, 9.2–9.5, and 10.4 μ; δ (CCl_4) 3.2 (s, 6 H), 4.25 (t, J = 5 Hz, 1 H), 0.9 (broad s, 3 H), and 1.35 (broad s, 12 H). Hydrolysis with aqueous acetic acid again gave octanal.



Similarly, 1-(3-hydroxy-3-phenylpropenyl)trimethylsilane (IV, R_1 = C_6H_5; R_2 = H) was prepared by the reaction of the chloromagnesium salt of trimethylethynylsilane with benzaldehyde in ether (6-hr heating), followed by semihydrogenation in ethyl acetate with 10% palladium/charcoal, in the presence of some pyridine. The resulting mixture of olefins (largely cis)

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(1) L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill, New York, N. Y., 1965. *Cf.* F. C. Whitmore, L. H. Sommer, J. Gold, and R. E. Van Strien, *J. Amer. Chem. Soc.*, **69**, 1551 (1947).

(2) *Inter alia*, J. J. Eisch and J. T. Trainor, *J. Org. Chem.*, 28, 478 (1963); H. Sakurai, N. Hayashi, and M. Kumeda, *J. Organometal. Chem.*, 18, 351 (1969).

(3) The synthesis and use of vinylsilanes where R′ = CH_3 (leading to methyl ketones) are reported in G. Stork and E. Colvin, *J. Amer. Chem. Soc.*, in press.

(4) *Cf.* R. A. Benkeser, M. L. Burrous, L. E. Nelson, and J. V. Swisher, *ibid.*, **83**, 4385 (1961).

(5) L. Q. Minh, J. C. Billiotte, and P. Cadiot, *C. R. Acad. Sci.*, **251**, 730 (1960); *cf.* R. West and L. C. Quass, *J. Organometal. Chem.*, **18**, 351 (1969).

(6) C. F. H. Allen, *J. Amer. Chem. Soc.*, **52**, 2955 (1930).