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NEW TYPES OF HYDRIDE TRANSFER*

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THE interpretation of organic reaction mechanisms often involves hydride[1-3] transfer, but this hydride transfer has seldom been proved experimentally.[4] As the hydride ion is usually transferred to a carbonium ion, the presence of which is not easily established, it is difficult to prove experimentally that hydride transfer has actually taken place. Stable carbonium ions may be formed from cycloheptatriene or triphenylmethyl carbonium salts.[5] The conversion of tropylium ion to cycloheptatriene by the addition of a hydride ion would, therefore, be an unequivocal hydride transfer reaction.

We have established that tropylium ion readily removes a hydride ion from lithium aluminium hydride, sodium borohydride or di-isobutyl-aluminium hydride with the formation of cycloheptatriene.

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* Translated by A.L. Pumpiansky, Moscow.

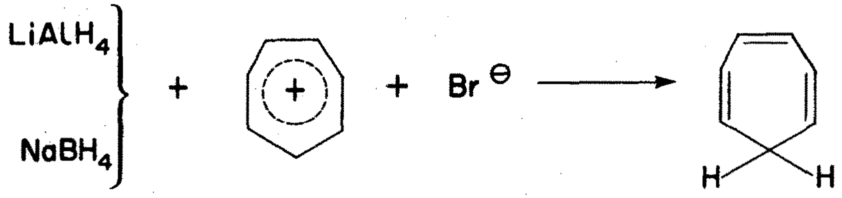
[1] E.K. Alexander, Principles of Ionic Organic Reactions pp. 167-170. N.Y.L. (1950).

[2] K.D. Nenitsesku, Ucpekhi Khim. 26, 399 (1957).

[3] N.C. Deno, H.J. Peterson and G.S. Saines, Chem. Rev. 60, 7 (1960).

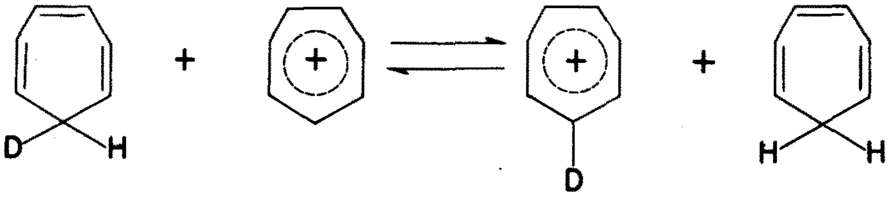
[4a] P.D. Bartlett, F.E. Condon and A. Schneider, J. Amer. Chem. Soc. 66, 1531 (1944); [b] P.D. Bartlett and J.D. McCollum, Ibid. 78, 1441 (1956).

[5] J. Dauben, F.A. Gadecki, K.M. Harmon and D.J. Pearson, J. Amer. Chem. Soc. 79, 4557 (1957).



Similarly, the reaction between a tropylium salt and triethyl tin $(C_2H_5)_3SnH$ of triethyl silane $(C_2H_5)_3SiH$ results in the formation of cycloheptatriene Alcohols may also be used as hydride donors. The action of benzyl alcohol on tropylium bromide results in the formation of cycloheptatriene and benzaldehyde. We have found this reaction to have the kinetic isotopic effect. The low value of the kinetic isotopic effect shows that the rate determining step of this reaction is the hydride transfer.

Of special interest is the hydride transfer reaction using cycloheptatriene as donor. This compound readily releases a hydride ion by the action of electrophilic reagents such as PCl_5,$AlCl_3$, conc H_2SO_4 and $(C_6H_5)_3C^+$ with the formation of tropylium ion.[5,6] Further, a reversible hydride transfer may take place between cycloheptatriene and tropylium.[7]



The hydride exchange reaction between monodeuteriocycloheptatriene and tropylium ion was studied in acetic acid, methanol, ethanol and nitromethane solutions, equilibrium being reached at 20° in less than 6 hours. In Table 1 the kinetic data of this reaction in glacial acetic acid are listed. The

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[6] D.N. Kursanov and M.E. Volpin, Dokl. Akad. Nauk SSSR **113**, 339 (1957).

[7] Z.N. Parnes, M.E. Volpin and D.N. Kursanov, Izv. Akad. Nauk SSSR, Otdel. khim. nauk (1960).

reaction was run at 10,15,20 and 30°, the hydrogen exchange rate being 0.010, 0.015, 0.023 and 0.044 respectively. The activation energy proved to be 14.3 kc.

TABLE 1

Hydride Exchange Rate between Cycloheptatriene-d* and Tropylium Bromide in Glacial Acetic Acid**

Temp. (°C)	Time (min)	Deuterium*** in tropylium salts (at.%)	Reaction rate (g mole/l.min)
30	10	0.95	0.046
	15	1.23	0.043
	20	1.95	0.056
20	10	0.58	0.026
	20	0.99	0.027
	30	1.22	0.020
	40	1.46	0.019
	50	1.89	0.022
15	15	0.50	0.015
	30	0.98	0.016
	45	1.31	0.015
10	20	0.54	0.012
	40	0.92	0.012
	60	1.51	0.010
	80	1.46	0.010
	100	1.72	0.010

* Deuterium concentration: 7.7 at. %.
** Concentration of each component: 0.44 g mole/l.
*** Equilibrium deuterium concentration: 3.9 at. %.

Hydrogen exchange reaction rates were calculated in terms of the formula $Rt = -\frac{(A)\,(B)}{(A)+(B)}\ln(1-F)$[8]

This hydrogen exchange cannot result from proton hydrogen exchange as the tropylium ion does not undergo hydrogen exchange even with very strong

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[8] A.C. Wahl (Editor), Radioactivity Applied to Chemistry. N.Y.L. (1951).

proton donors such as D_2SO_4 and DBr + $AlBr_3$.[9] Further, it cannot be suggested that the reaction gives rise to kinetically independent hydride ions as it takes place in media involving labile protons including acids without molecular hydrogen being evolved. The reaction may proceed via an activated complex in which the hydrogen ion is removed from the cycloheptatriene molecule and transferred to the tropylium ion. The hydrogen exchange reactions previously investigated involved a reversible transfer of proton. The exchange reaction between cycloheptatriene-d and tropylium is, therefore, the first instance of a reversible hydride transfer.

It has recently been shown[10] that the tropylium ion is capable of removing a hydride ion from ditropyl ether with the formation of tropone and cycloheptatriene.* Thus by making use of the stable tropylium ion as a hydride acceptor, we have succeded in establishing hydride transfer in a number of reactions as well as the reversible hydride transfer.

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* To prepare tropone from ditropyl ether it is advantageous to use benzaldehyde as acceptor of hydride ions, one molecule of ditropyl ether giving two tropone molecules.

[9] M.E. Volpin, K.J. Zdanova, D.N. Kursanov, V.N. Setkina and A.J. Shatenshtein, Izv. Akad. Nauk SSSR, Otdel. khim. nauk 754 (1959).

[10] A.P. Ter Borg, R. van Helden, A.F. Bickel, W. Renold and A.S. Dreiding, Helv. Chim. Acta 43, 457 (1960); M.E. Volpin, Z.N. Parnes and D.M. Kursanov, Izv. Akad. Nauk SSSR, Otdel. khim. nauk (1960).