Tetrahedron Letters No. 23, pp. 2079-2082, 1971. Pergamon Press. Printed in Great Britain.

A TWO-STEP HYDRIDE SHIFT TO ARYL CARBONIUM IONS

M. Ballester, J. Riera-Figueras, J. Castañer and A. Rodríguez-Siurana

Instituto de Química de Barcelona, Patronato "Juan de la Cierva"

Zona Universitaria, Barcelona 17

(Received in UK 29 April 1971; accepted in UK for publication 5 May 1971)

A typical reaction of carbonium ions is the hydride shift from hydrocarbons.[1,2] Mechanisms have been suggested where the shift is regarded as a one-step process.[3,4,5]

The authors now wish to report that perchlorodiphenylcarbonium (I) hexachloroantimonate reacts with cycloheptatriene to give α$\underline{H}$-undecachlorodiphenylmethane (II) and tropylium (III) hexachloroantimonate, as expected.

$$\underset{\text{(I)}}{(C_6Cl_5)_2\overset{+}{C}Cl} + C_7H_8 \longrightarrow \underset{\text{(II)}}{(C_6Cl_5)_2CHCl} + \underset{\text{(III)}}{(C_7H_7)^+}$$

However, under the same reaction conditions, perchlorotriphenylcarbonium (IV) hexachloroantimonate[6] immediately gives perchlorotriphenylmethyl (PTM) radical[7,8] and III hexachloroantimonate.*

---

* Suggested over-all stoichiometry:

$$4\ (C_6Cl_5)_3\overset{+}{C} + SbCl_6^- + 3\ SH = 4\ (C_6Cl_5)_3\overset{\bullet}{C} + SbCl_3 + 3\ S^+ + 3\ HCl.$$

While antimonium pentachloride is an oxidizing species, it has been found that under the conditions of the reactions here described the hexachloroantimonate ion is not.

$$\underset{\text{(IV)}}{(C_6Cl_5)_3\overset{+}{C}} + C_7H_8 \longrightarrow \underset{\text{(PTM)}}{(C_6Cl_5)_3\overset{\bullet}{C}} + \underset{\text{(III)}}{(C_7H_7)^+}$$

These results strongly suggest a two-step hydride shift: The first step being an electron-transfer process, and the second a hydrogen-atom shift.

$$(C_6Cl_5)_2\overset{+}{C}R + SH \xrightarrow{\text{step 1}} (C_6Cl_5)_2\overset{\bullet}{C}R + (SH)^{+\bullet}$$

$$(C_6Cl_5)_2\overset{\bullet}{C}R + (SH)^{+\bullet} \xrightarrow{\text{step 2}} (C_6Cl_5)_2CHR + S^+$$

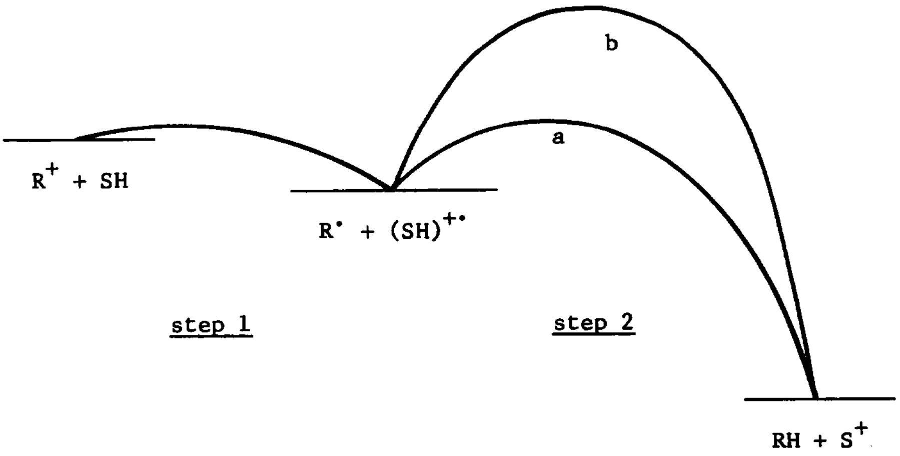
It has been shown that while PTM,[7,8] its cation[6] and its anion[7,8,9] are very active in electron-transfer processes, their inertness in bond formation reactions is, however, remarkable. PTM withstands even highly reactive chemical species. Such stability is traced to steric shielding of the central (*alpha*) carbon atom by three benzene rings and three pairs of *ortho* chlorines.

Therefore, it is reasonable to assume that a high energy barrier between $[R^\bullet + (SH)^{+\bullet}]$ and $[RH + S^+]$, as shown schematically in Fig. 1 (path b), prevents IV from proceeding through step 2.

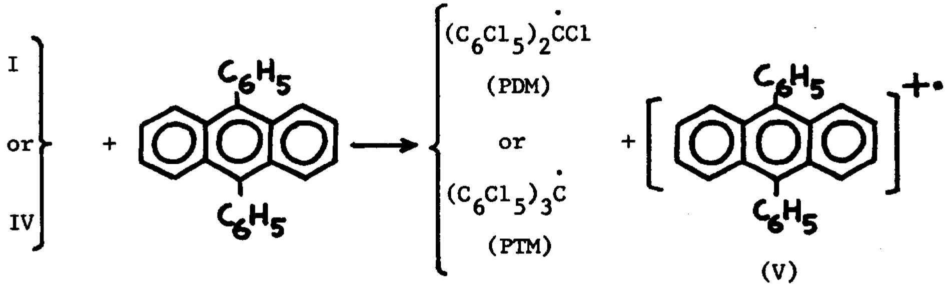
The reaction with I is practically instantaneous. When it is run in an epr spectrometer a small, disappearing amount of perchlorodiphenylmethyl (PDM) radical[7,8,10] is detected. Possibly, because of a "cage effect", most of the $SH^{+\bullet}$ reacts immediately with the PDM through step 2. However, a small fraction of the $SH^{+\bullet}$ decomposes with counter-ion $SbCl_6^-$ leaving, therefore, an equivalent amount of unreacted PDM.

From both the epr data, and the first-order II-giving decay rate of PDM in cycloheptatriene, it is estimated that about 6% of this radical does not react through step 2.

FIGURE 1



In connection with the preceding results, reactions of 9,10-diphenylanthracene (a purely aromatic hydrocarbon which cannot release hydrogen as in step 2) have been performed with I and with IV. In both cases the corresponding radicals have been isolated along with cation-radical V hexachloroantimonate.



Step 1 in perchloroaryl carbonium ions is allowed because the ionization potential I of the perchloroaryl radicals is high on account of the chloro groups.[*]

---

[*] The effect of the chlorines in the pentachlorophenyl group is about equivalent to that of two nitro groups.[11,12] One nitro group in benzyl radical raises I from 7.7 to 8.6 ev.[13]

Consequently, the observed electron transfers are energetically-allowed inter-molecular transitions from one bonding orbital of the donor* to a lower lying non-bonding orbital of the carbonium ion.

These and related results will be reported in full detail in forthcoming papers.

Acknowledgements The authors thank the Aerospace Research Laboratories, Wright-Patterson AFB (Ohio, USA), for the Contract F-61052-67-C-0065 granted through the European Office of Aerospace Research, USAF, in support of this research, and their scientist, Dr. L. Spialter, for his valuable assistance.

References

1) C. D. Nenitzescu in G. A. Olah and P. von R. Schleyer's "Carbonium Ions", vol. II (1970), Wiley-Interscience, pages 463-520.
2) N. C. Deno, H. J. Peterson and G. S. Saines, *Chem. Rev.*, **60**, 7 (1960).
3) P. D. Bartlett, F. E. Condon and A. Schneider, *J. Amer. Chem. Soc.*, **66**, 1531 (1944).
4) N. C. Deno, G. Saines and M. Spangler, *J. Amer. Chem. Soc.*, **84**, 3295 (1962).
5) E. S. Lewis and M. C. R. Symons, *Quart. Rev.*, **12**, 230 (1958).
6) M. Ballester, J. Riera-Figueras and A. Rodríguez-Siurana, *Tetrahedron Letters*, **1970**, 3615.
7) M. Ballester, *Pure and Appl. Chem.*, **15**, 123 (1967).
8) M. Ballester, J. Castañer, J. Riera-Figueras, C. Badía and J. M. Monsó, *J. Amer. Chem. Soc.*, in press.
9) M. Ballester and G. de la Fuente, *Tetrahedron Letters*, **1970**, 4509.
10) M. Ballester and J. Riera-Figueras, *J. Amer. Chem. Soc.*, **86**, 4505 (1964).
11) G. Huett and S. I. Miller, *J. Amer. Chem. Soc.*, **83**, 408 (1961).
12) P. J. Bray and R. G. Barnes, *J. Chem. Phys.*, **27**, 551 (1957).
13) A. G. Harrison, P. Kebarle and F. P. Lossing, *J. Amer. Chem. Soc.*, **83**, 777 (1961).
14) V. I. Vedeneyev, L. V. Gurvich, V. N. Kondratyev, V. A. Medvedev and Y. L. Frankevich, "Bond Energies and Electron Affinities", Edward Arnold, London (1966), page 158.

---

* Cycloheptatriene: **I**, 8.5 ev.[14]