Tetrahedron Letters No.1, pp. 27-32, 1968. Pergamon Press Ltd. Printed in Great Britain.

PROTOLYSIS OF TRANS-2-CHLOROVINYL MERCURIC CHLORIDE IN DIMETHYL SULPHOXIDE SOLUTION

P. J. Banney, William Kitching and Peter R. Wells
Department of Chemistry, University of Queensland,
Brisbane, 4000 Australia

(Received in UK 19 September 1967)

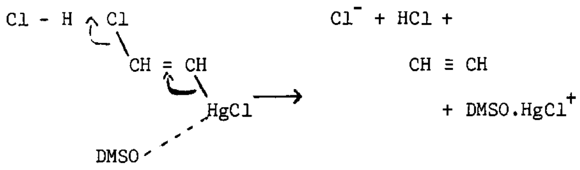
There are several reported examples of S_E1 reactions of organo-metallic substrates which on further examination have for various reasons proved to be erroneous (cf. 1,2). Another example, the reaction of trans-2-chlorovinyl mercuric chloride with hydrogen chloride in dimethyl sulphoxide solution now can be added to this list.

The observation, reported by Beletskaya, Karpov, Moskalenko and Reutov (3), that this substrate is converted to vinyl chloride by a relatively rapid ($t_{\frac{1}{2}}$ = 540 sec. at 30°C) first order process independent of acid concentration, was in our view most surprising. The mercurial is prepared by reaction of acetylene with mercuric chloride in 6N hydrochloric acid solution (4) and appears to be as stable in dimethyl sulphoxide containing water as in other partially aqueous solutions.

We have attempted to follow the protolysis reaction both by titration of the acid consumed and by mercurimetric titration of the change in chloride concentration. The latter method, employed in the previous work (3), was found by us to be rather unsatisfactory for typical reaction mixtures due to difficulties in end-point observation. Over a period of three days we find no significant change in acidity nor in chloride concentration.

Examination of the p.m.r. spectrum of trans-2-chlorovinyl mercury chloride in acidified dimethyl sulphoxide solutions reveals, however, that the substrate does in fact disappear in this system fairly rapidly at a rate strongly dependent upon acid concentration.

The product of this reaction has been identified as acetylene, and we consider the process to be a reversal of the formation reaction brought about by co-ordination of the solvent to the mercury atom,



$$\mathrm{DMSO.HgCl^{+} + Cl^{-} \rightleftharpoons DMSO + HgCl_2}$$

Other agents, such as cyanide and thiocyanate ions, which co-ordinate strongly to mercury, also will effect this reversal. (5).

The protolysis of this substrate in dioxane solution was also examined by p.m.r. spectroscopy and it was found to be converted to vinyl chloride at about the same rate as that reported (3) for its second order (S_E2) reaction in this solvent ($k = 2 \times 10^{-4} M^{-1} sec^{-1}$ at $40^{o}C$). Figure Ia represents the spectrum at 60 Mc/s of an equimolar mixture of trans-2-chlorovinyl mercuric chloride (3.82τ), with satellites arising from $^{199}Hg-^{1}H$ coupling, and hydrogen chloride (3.61τ) in dioxane solution. Figure Ib is the same solution after 3 days at room temperature. The acid and substrate resonances are now indistinguishable and the spectrum of vinyl chloride, represented in figure Ic, is clearly visible. Spectrum Ib is particularly important since it shows that had vinyl chloride been formed in the dimethylsulphoxide reaction it could hardly have been overlooked.

Both the S_E2 and the supposed S_E1 deuterolysis of 2-chlorovinyl

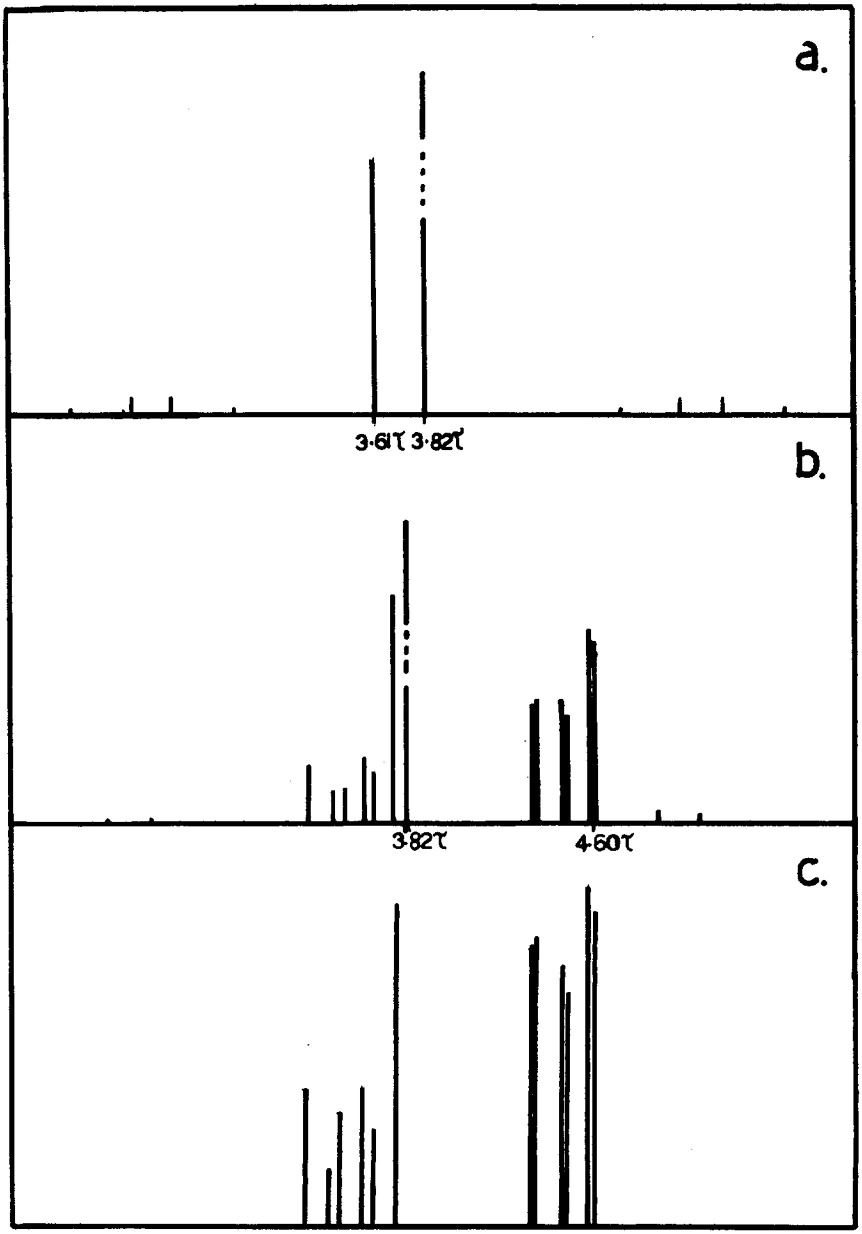


FIG. 1.

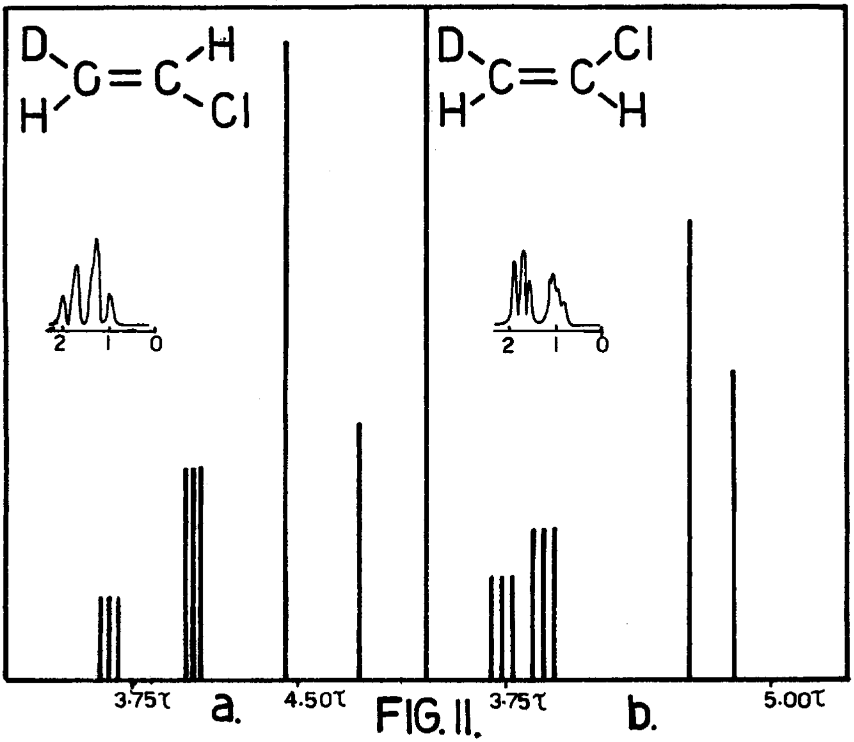


FIG. II.

mercuric chloride are reported (3) to be stereospecific in that trans and cis-2d-vinyl chloride are obtained from the trans and cis isomers, respectively, of the mercurial. The calculated p.m.r. spectra (40 Mc/s) including H-D coupling of the 2d-vinyl chlorides based upon the results of Whipple, Stewart, Reddy and Goldstein (6) are given in Figures IIa and b.

The inserts in these figures are reproductions of the reported spectra of the deuterolysis products (3). Agreement between the observed and calculated spectra of trans-2d-vinyl chloride is satisfactory, but the observed spectrum assigned to cis-2d-vinyl chloride does not correspond with expectation. The only way that we have found to account for the observed spectrum is to assume that in this case the low field direction is to the right of the spectrum and that a mixture of 2/3 cis and 1/3 trans-2d-vinyl chloride is under examination. This, at-first-sight unlikely explanation is consistent with our previous report (7) that "pure" cis-2-chlorovinyl mercury chloride (m.p. 76-77°C) prepared following as closely as possible the procedure of Friedlina and Nogina (8) contains at least 25% of the trans-isomer.

A corollary of this report is that the iodine cleavage of this chlorovinyl mercurial, which was reported (9) to proceed at roughly the same rate as the protolysis, also appears to be incorrect. We have now turned our attention towards reactions of α-carbalkoxybenzyl mercury substrates (10) which appear to remain the only credible examples of S_E1 reactions of organo-mercurials.

REFERENCES

1. F. R. Jensen and D. Heyman, J.Am.Chem.Soc., **88**, 3438 (1966).
2. B. F. Hegarty, W. Kitching and P. R. Wells, J.Am.Chem.Soc., **89**, 4816 (1967).
3. I. P. Beletskaya, V. I. Karpov, V. A. Moskalenko and O. A. Reutov, Dokl.Akad.Nauk S.S.S.R., **162** 86 (1965).

4. A. N. Nesmeyanov and R. K. Freidlina, Izvest.Akad.Nauk S.S.S.R. Otdel Khim. Nauk, 105 (1945).

5. D. Seyferth, Progress in Inorganic Chemistry, 3, 249 (1961).

6. E. B. Whipple, W. E. Stewart, G. S. Reddy and J. H. Goldstein, J.Chem.Phys., 34, 2136 (1961).

7. P. R. Wells and W. Kitching, Aust.J.Chem., 17, 1204 (1964).

8. R. K. Freidlina and O. Nogina, Izvest.Akad.Nauk. S.S.S.R., Otdel Khim.Nauk., 150 (1945).

9. I. P. Beletskays, V. I. Karpov and O. A. Reutov, Dokl.Akad.Nauk. S.S.S.R., 161, 586 (1965).

10. E. D. Hughes, C. K. Ingold and R. M.G. Roberts, J.Chem.Soc., 3900 (1964).