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REINVESTIGATION OF THE REACTION OF TRANS-ß-CHLOROVINYLMERCURYCHLORIDE WITH HYDROGEN CHLORIDE IN DIMETHYLSULFOXIDE

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In recent work (1) reaction of trans-ß-chlorovinylmercurychloride (CVMC) with HCl in dimethylsulfoxide (DMSO) was asserted to result not in vinyl chloride as shown in our study (2) but in acetylene. We have therefor reinvestigated this reaction by PMR. The PMR spectra were taken on JNM-4H-100 and JNM-C-60H Model Spectrometers. Trans-ß-CVMC was prepared by a previously reported method (3).

We have established that results reported in (1) are incorrect and associated with improper refining of the solvent.

It was firstly shown that under preparative conditions (high concentrations of reactants, heating, DMSO purified by the ordinary procedure (4)) this reaction results in near quantitative yield of vinyl chloride.

In our believe, this result is principally essential since namely such conditions are meant when the regular conduction of employing organic reactions takes place.

Our kinetic study was carried out at considerably lower concentrations when both the reaction rate and course may be exceptionally sensitive to any negligible impurities in the solvent. Therefor DMSO was thoroughly purified by zonic fusion with subsequent distillation over calcium hydride in an argon atmosphere. The chromatogram of DMSO obtained is shown in Fig. 1.

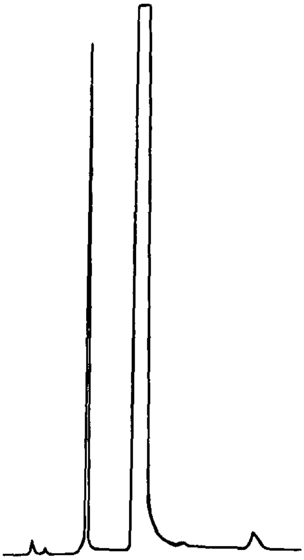

Fig. I. Chromatogram of DMSO

Use was made of a chromatograph with flame-ionization detector l=1.49 m, ϕ = 4 mm and carbowax (M = 6000, 15% on C-545 "80-100 mesh"). Analysis was carried out with temperature programming from 60 to 190°, R_h = 30°/min, $t_{evapor.}$= 120°, $t_{detector}$ 190°, rate of gas carrier (He) was 25 ml/min. Quantitative analysis was performed using tridecane as internal reference. The DMSO was of 99.98% grade purity. In the DMSO thus purified, no reaction was observed for 1 day at 0.1 M concentration of reactants*. At the 2M concentrations, however, the reaction product was exclusively vinyl chloride and its spectrum was then registered (Fig. 2). These experiments were multiply reproduced.

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* Reaction mixture becomes dark and the spectrum disappears at further standing (perhaps owing to the polymerization of vinyl chloride and some other side reactions). The PMR spectra sometimes (but not usually) indicate some quantity of acetic aldehyde.

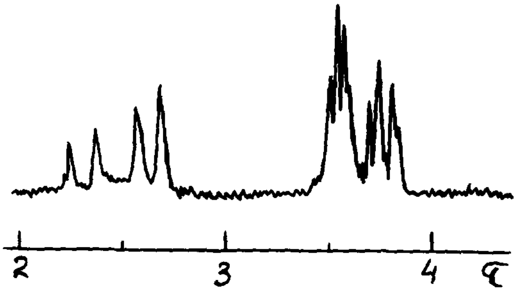

Fig.2. PMR spectrum of vinyl chloride forming in the reaction mixture at the concentration of reactants 2M

Rate of protodemercuration reaction being very slow seems hence responsible for the absence of any interaction during 24 hours at low concentrations of reactants and in DMSO thoroughly purified. But our earlier study employing DMSO (prepared by oxidation of dimethylsulfide with hydrogen peroxide) without special refining showed rapid formation of vinyl chloride. This shows that the reaction discussed may be considerably stimulated by impurities in the DMSO. It can be not excluded either that the presence of such impurities as catalysts may promote a reaction between DMSO and HCl. Thus, the effect displayed by increase in concentration of reactants may be not only a response to kinetic dependencies but also to an increase in content of impurities*.

Thus the reaction of trans-ß-CVMC with HCl in DMSO is by no means a regular acidic cleavage, involving the C-Hg bond.

We assume finally that it is the insufficiently dried DMSO that led to the results reported in (1). Dissociation of HCl should increase in the presence of a small quantity of moisture. This results in the Cl → Hg coordination of organomercury compound generating ions and ionic pairs and in sponsoring the elimination process as well. Indeed addition of very small quanti-

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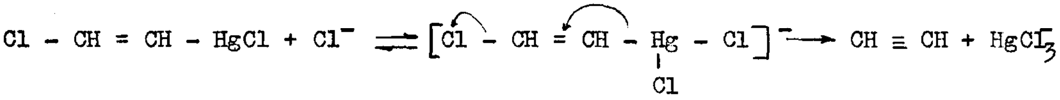
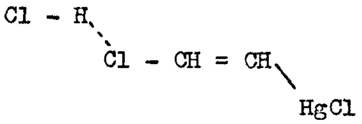
* Notice should be made, however, that quality of employed DMSO effects the reaction rate considerably. In some portions of DMSO, subjected to thorough refining, even the concentration of 0.01 produces vinyl chloride at sufficiently high rate.

ties of water to the reaction mixture in DMSO causes instanteneous formation of acetylene*. (A singlet at 4.6 similar to that of the an acetylene solution in DMSO shows up in the PMR spectrum). In the anhydrous DMSO solution, this reaction is stimulated by chloride ions (addition of LiCl). There is no doubt that the elimination reaction in the last case proceeds via the chloride ion complexation by mercury:



$$\mathrm{Cl-CH=CH-HgCl + Cl^-} \rightleftharpoons \left[\mathrm{Cl-CH=CH-\underset{\underset{\displaystyle Cl}{|}}{Hg}-Cl}\right]^- \longrightarrow \mathrm{CH\equiv CH + HgCl_3^-}$$

This makes unlikely the mechanism of elimination advanced in (1) according to which HCl may attack the ß-chlorine atom



The authors of (1) assert that elimination rate increases with increasing HCl concentration. This result is not in disagreement with the mechanism that we have proposed.

Thus, we believe that conclusions drawn in (1) are erroneous**.

LITERATURE

1. P.J. Banney, W. Kitching and P.R. Wells, Tetrahedron Letters, 1, 27 (1968).
2. I.P. Beletskaya, V.I. Karpov and O.A. Reutov. Dokl. Akad. Nauk SSSR, 162, 86 (1965).
3. L.G. Makarova and A.N. Nesmeyanov, "Methods of Elemenorganic Chemistry", Mercury. "Nauka" Publ. House, Moscow, 1965, p. 295.
4. W.W. Epstein and F.W. Sweat, Chem. Rev., 67, 247 (1967).

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* It should be noted, however, that addition of H_2O to the DMSO solution of the Biginelli compound in the absence of HCl does not cause acetylene formation.

** According to the authors of (1) the aim of their work was to prove that no reactions may ever follow the S_E1 mechanism, and the assertion is strangely ascribed to us that the S_E1 mechanism involves not ionic pairs but free ions.