## Infra-red Spectroscopic Evidence on the Structure of Isomerized Dimethylaminoethoxy-methylphosphoryl Fluoride LENNART LARSSON

Research Institute of National Defence, Dept. 1, Sundbyberg 4, Sweden

It was found by Tammelin 1 that, when dimethylaminoethoxy - methyl - phosphoryl fluoride is stored at room temperature, the liquid is transformed in a few days into a solid compound with the same per cent composition as the initial liquid. In contrast to the liquid isomer, the solid one is not easily hydrolyzed in alkaline solutions but is in acid solutions and apparently yields the same products of hydrolysis as

with the rearrangement proposed above.

Another conceivable rearrangement analogous to that described by Fukuto and Stafford 2 for the isomerization of diethoxy-

to occur. This observation is not consistent

diethylaminoethoxy-thionophosphate the thiolo-isomer is that the liquid is transformed to an ethylene-immonium salt (II) or to the more stable piperazinium salt (III).

It was thus of interest to make an infrared spectroscopic study of the rearranged product to elucidate its structure. As appears from Fig. 1, the infra-red spectrum of the solid isomer (1) shows mainly the same pattern as that of the quaternized derivative of the liquid compound, methyl-fluoro-phosphorylcholine iodide (2), with two fundamental exceptions: in the spectra of the solid isomer the strong absorption band at 11.79  $\mu$  (848 cm<sup>-1</sup>), assigned to the

the liquid compound. Moreover, the solid isomer gives no Schönemann reaction whereas the liquid one does. On the basis of these results Tammelin has postulated the following rearrangement for dimethylaminoethoxy-methyl-phosphoryl fluoride (I).

isopropoxy-methyl-phosphoryl When fluoride (Sarin) was mixed with triethylamine in mole ratio 1:1, no reaction seemed

vibration of the P-F bond 3, is absent and at  $13.52 \mu$  (740 cm<sup>-1</sup>) a band appears which can probably be attributed to the vibration of a P-N bond 3. The spectrum of the solid isomer adheres closely also to that of ethoxy-methyl-phosphorylcholine iodide (3) with the exception of the absorption band at 13.52  $\mu$  mentioned above. The absorption bands at about 3  $\mu$  and 6  $\mu$  in all the

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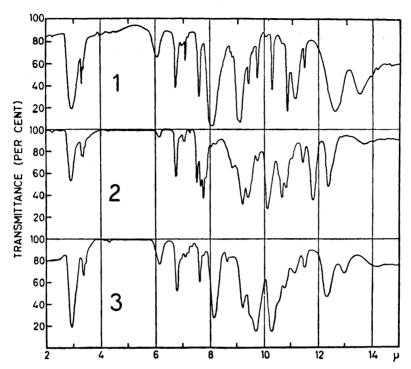


Fig. 1. The infra-red spectra of the solid isomer of dimethyl-aminoethoxy-methyl-phosphoryl fluoride (1) and the iodides of methyl-fluoro-phosphorylcholine (2) and of ethoxy-methyl-phosphorylcholine (3).

spectra are probably caused by moisture, picked up during the preparation of the potassium bromide disks. The remaining absorption bands agree well with those usually obtained in the infra-red spectra of organic phosphorus compounds. The results obtained from the infra-red measurements are thus entirely in accordance with the structure that Tammelin has suggested for the solid isomer of dimethylaminoethoxy-methyl-phosphoryl fluoride, and they exclude structures like II and III.

It has been shown that thiosulphate ion reacts with ethylene-immonium ion <sup>5</sup>. From a study, performed in the same manner as described by Fukuto and Stafford <sup>2</sup>, it has been found that the solid isomer does not react with thiosulphate ion indicating that there is no immonium ion present in the solid isomer. This result is a further argument against structure II.

Experimental. The compounds studied were synthesized by Tammelin 1,4 at this institute. The infra-red spectra were recorded by means

of a Perkin-Elmer spectrometer, Model 21, equipped with a rock salt prism, and the following settings were used: Resolution 927; response 2:1170; gain 6; suppression 3; speed about 1  $\mu$ /min; scale 5 cm/ $\mu$ . The potassium bromide disk technique was employed, and 1 mg of sample was mechanically ground together with 300 mg of potassium bromide.

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