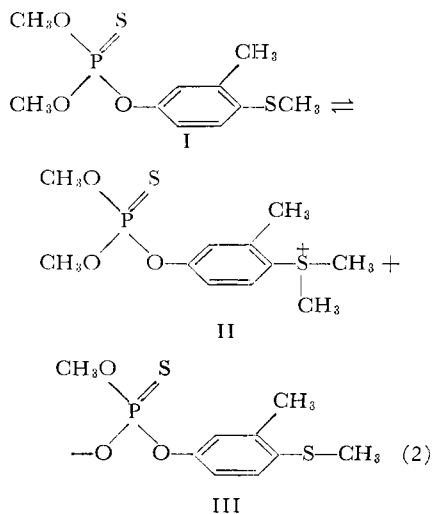


CH₃ and SCH₃ on the aromatic ring. Since in the heating experiments peak *E* remained constant and peak *D* increased in size relative to the other peaks, the more labile SCH₃ moiety is assigned peak *D*, and more stable CH₃, assigned peak *E*.

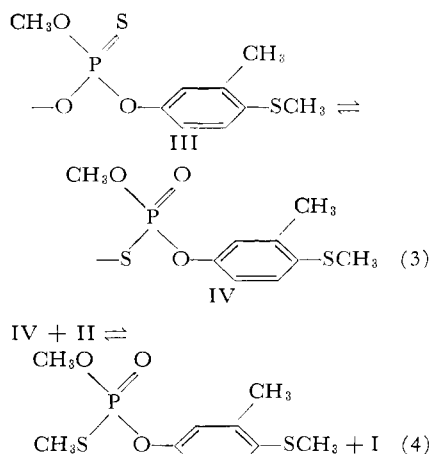
At 60° C., Baytex appears to be quite stable, and no change in the proton spectrum was observed even after 164 hours. Heating for 1 hour at 100° C. resulted in a slight change in the high field peaks (*D* and *E*)—peak *D* becoming slightly higher than *E*; no further change was noted after 2.5 hours. At 135° C., the first change, observable after 15 minutes, was also a slight increase in peak *D*. *D* continued to grow for another 30 minutes, then remained steady until the total heating period was 4.5 hours. At 45 minutes, the origin of a new peak (*F*) could be detected at low attenuation. *F* increased in size until it was about 1/8 the height of the *B-C* doublet after 1 3/4 hours and remained at this size until after 4 1/2 hours, when it began to increase further.

The H¹ spectrum of Baytex after being heated for 4 1/2 hours at 135° C. is given in Figure 1. The increase in peak *D* and the formation of the new peak *F* is clearly evident. The spectrum is surprisingly "clean" at this point and remained so even after 5 1/2 hours, except for slight increases in peaks *D* and *F*. Because of the heightening in peak *D*, this resonance was assigned the —SCH₃ moiety, and the increase is probably due to an intermolecular reaction in which the sulfonium ion is formed.



An intramolecular mechanism is possible but unlikely because of the low probability of a cyclic transition state. Intermolecular alkylations of thioethers of type depicted in equation 2 are well known and have been described by Heath (4) for *O,O*-dimethyl *O*-(2-ethylthio)ethyl phosphorothioate.

Because of the nearness of peak *F* to the phenyl-SCH₃ resonance (*D-F* separation about equal to the *B-C* doublet), *F* is probably due to the formation of the PSCH₃ moiety. Support for this belief is found in the P³¹ spectrum where a considerable quantity of the *S*-methyl isomer was indicated. The initial increase in peak *D* and subsequent formation of peak *F* would indicate that the isomerization may be proceeding through the sulfonium ion. The establishment of an equilibrium between the thionate and thiolate forms of the intermediate anion in equation 2 and subsequent methylation of the thiolate form by the sulfonium ion would lead to the *S*-methyl isomer.



This reaction is similar to that between metal salts of *O,O*-diethyl phosphorothioic acid and an alkyl halide which invariably results in the *S*-alkyl ester. The mechanism suggested here is analogous to that proposed by Hilgetag *et al.* (5) for the catalytic isomerization of *O,O,O*-trimethyl phosphorothioate by dimethyl sulfide. Evidence of decomposition appeared in the H¹ spectrum of 5 1/2 hours at 135° C. The aryl proton peak *A* became a doublet, probably due to a fission of the P—O—aryl linkage. A slight shoulder appeared on the low field side of peak *C* and became equal to *C* in 5 1/2 hours and larger than *C* in 6 1/2 hours. The splitting of *C* might

be caused by a slight change in the chemical shift in the POCH₃ resonance due to gross changes in the rest of the molecule such as fission of the P—O—aryl bond. Furthermore, the *B-C* doublet began to decrease until it was smaller than the aryl proton peak *A* at 6 1/2 hours. A concurrent increase in the viscosity of the liquid sample caused decided loss in the resolution of the spectrum, with complete loss at 7 1/2 hours. The increase in viscosity plus the loss of methoxy proton resonance would indicate that polymerization was taking place, probably in the same manner as that suggested for methyl parathion (6) and *O,O,O*-trimethyl phosphorothioate (5).

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Correction

The Metabolism of Dimethoate by Vertebrate Tissues

In this article by Tetsuo Uchida, W. C. Dauterman, and R. D. O'Brien [*J. Agr. Food Chem.* **12**, 48 (1964)], the guinea pigs were incorrectly identified. They should be described as male guinea pigs.