flexion from the twin will nearly coincide with the -(h+l)kl reflexion from the main crystal and will appear as a satellite, displaced by 0.057  $la^*$  from the main reflexion. The apparent "absences" follow from the space group absences. This interpretation accounts successfully not only for the positions but also for the intensities of the observed subsidiary reflexions 3.

The arguments for the existence of two distinct molecular forms in the crystal are seriously weakened by rejecting the space group  $P2_1$  in favour of  $P2_1/a$ . In the higher space group, the 4 molecules in the unit cell are symmetry related and hence identical or enantiomorphic, at least in a statistical sense. The existence of two distinct forms is only possible if the crystal structure is disordered, and there seems to be no compelling evidence for this.

Dr. Sörum has informed me that he agrees with my interpretation of the subsidiary reflexions, and has undertaken to re-examine the crystal structure. I am grateful to him for helpful correspondence concerning this problem.

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## The Stability of 1,1-Dibromoacetone

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1,1-Dibromoacetone can be prepared according to Hughes, Watson and Yates in about 30 % yield by bromination of bromoacetone 1. It is found that a sample of this compound kept at room temperature undergoes rearrangement, while a sample kept in the dark in a refrigerator for 2 months is only little affected.

Rearranged samples were analyzed by NMR-techniques and the following compounds identified: monobromoacetone, 1,1-dibromoacetone, 1,3-dibromoacetone and 1,1,3-tribromoacetone. The relative amounts of the different products were determined.

Two samples were studied. One sample (A) was kept in a light place for 50 days and the percentages of the different products found are given in Table 1.

In order to ascertain if the rearrangement was catalyzed by light, a sample of 1,1-dibromoacetone (B) was kept in the dark at room temperature for 13 and for 20 days. The compositions after these times were determined and are given in Table 1.

The occurrence of monobromoacetone and 1,1,3-tribromoacetone indicates that the rearrangement is intermolecular, but no details of the mechanism are known. Bromoketones are known to undergo a halogen rearrangement, and in these examples the rearrangements were found to be catalyzed by free hydrogen bromide; see Ref. <sup>2</sup> where references are collected.

It is interesting to note that the rearrangement of 1,1-dibromoacetone gives products with one more and one less bromine atom, as in the rearrangement of 3-bromo- to 5-bromolaevulic acid.

Although no equilibrium is reached and the results are preliminary, one can notice that the main product of the rearrangement is the symmetrical dibromoketone. The amount of monobromoacetone appears to be constant during the procedure.

The author has started to study this rearrangement in more detail, particularly with regard to its mechanism and kinetics, and the results will be published elsewhere.

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Table 1.

|                    | $\mathrm{CH_{3}COCHBr_{2}}$ | $\mathrm{CH_3COCH_2Br}$ | $\mathrm{CH_2BrCOCH_2Br}$ | $\mathrm{CH_{2}BrCOCHBr_{2}}$ |
|--------------------|-----------------------------|-------------------------|---------------------------|-------------------------------|
| Sample A (50 days) | 6                           | 21                      | 68                        | 6                             |
| Sample B (13 days) | <b>42</b>                   | 18                      | 26                        | 14                            |
| Sample B (20 days) | 33                          | 21                      | 33                        | 14                            |