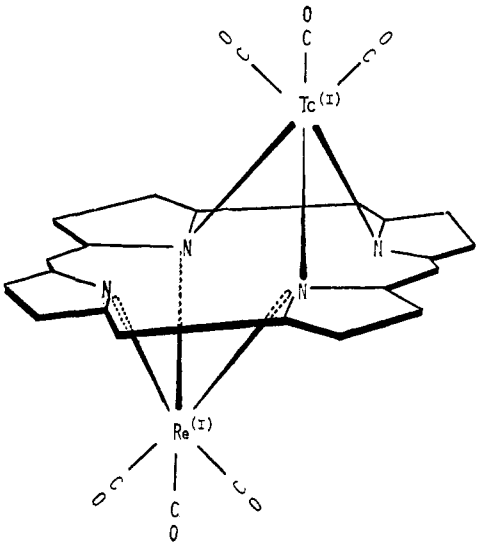

Figure 2. Schematic picture of $(OC)_3TcMPRe(CO)_3$ (I); the alkyl substituents on the porphine ring are left out of the figure for clarity.

structures identical with that of IV were proposed for II[1] and III.[7] For the same reason, the structure shown in Figure 2 is proposed for I.

Acknowledgment. This research project was supported in part by both the National Science Foundation under Grant no. GP-28685 and the Office of Naval Research.

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Received May 21, 1973

Indole Alkaloid Rearrangements in Acetic Acid

Sir:

Scott and Qureshi in 1968[1] claimed the conversion of (−)-tabersonine into (±)-catharanthine (12% yield) and (±)-pseudocatharanthine (28%), and of (+)-stemmadenine into (±)-tabersonine (12%), (±)-catharanthine (9%), and (±)-pseudocatharanthine (16%) *in refluxing glacial acetic acid* over periods ranging from 16 to 72 hr; even after extensive exchange of experimental information with the above authors we were unable to reproduce these results, indeed we failed to observe even traces of the rearrangement products claimed. With reluctance, we eventually felt obliged to publish our findings,[2] more recently with full experimental details.[3,4] One simple example of a result which could not be affected by experimental factors such as added boiling chips, external bath temperature, etc., is our observation that, on a 500-mg scale, catharanthine survives to the extent of less than 1% in refluxing acetic acid after 12 hr,[3] and that on a 5-mg scale it ceases to be detectable by tlc even after only 30 min; this makes the isolation of the order of 10% of (±)-catharanthine[1] under such conditions difficult to understand.

We wish to state quite simply that none of the experimental work now described in preliminary form by Scott and Wei[5a,c,d] contradicts our findings; there is mention of general factors on which the success of the original rearrangements apparently depends, but these factors are not quantified,[5a] and we still await the full experimental details of the original work of Scott and Qureshi.[1]

It must be pointed out that the only reaction in acetic acid described in the four papers is that of (−)-tabersonine, from which only the isolation of allocatharanthine is now reported,[5c] in keeping with our own observations[2,4] and not with those of Scott and Qureshi.[1] The remaining reactions[5a,c,d] are carried out under *completely different* conditions (four on silica at 150° and one in methanol) and in any case on *none* of the original compounds studied by us (stemmadenine, tabersonine, and catharanthine). We wish to refrain from commenting on this new work.

The substance referred to by Scott as the "levorotatory preparation to which they allude as pseudocatharanthine" was prepared as described by Gorman *et al.*,[6] except that it was not crystallized, and was fully characterized spectrally;[3] the fact that the recrystallized material handled by Scott is fully racemic is not surprising, as the ~10% excess of one of the enantiomers in the total material would not be expected to cocrystallize. Our ~90% racemic pseudocatharanthine was not used at all by us as a reference compound in the sense indicated by Scott[5b] for the simple reason that pseudocatharanthine, whether partially or fully racemic, never turned up in the reactions of stemmadenine and tabersonine; Scott's criticisms are thus void.

Scott states that "the manipulation of microgram quantities in biomimetic experiments is an art which, in our experience, has oft-times required several hundred trials before declaring a negative result";[5b] whatever this statement may mean, it has no relevance to our work, which was carried out on the larger scale of 5–20 mg, with the exception of the preparative experiments, which approached the gram scale.

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Direct Observation of Oxaphosphetanes from Typical Wittig Reactions

Sir:

Nonstabilized phosphorus ylides attack simple ketones or aldehydes at −70° to form 1:1 adducts which decompose into triphenylphosphine oxide and olefins above 0°. This sequence of events is traditionally explained by assuming that a betaine such as **1** or its