Monthly
Ecumenical
Letters from
Laboratories
Of
N-M-R

No. 1

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L aboratories
O f
N-M-R

Introduction

This is No. 1 of a proposed monthly letter designed to expedite the exchange of information and ideas among laboratories engaged in research on the application of N-M-R to problems in organic chemistry. We hope that you will be interested in receiving this letter and in being a regular contributor to its contents. We feel that the effectiveness with which its purpose is accomplished depends directly on the informality and small size of the undertaking; to this end we suggest that distribution be limited to those who contribute with some regularity. It is understood that appearance of material in this letter will be construed in no way to constitute official publication. Material appearing in this letter is to be solely for the readers' personal use, and quotation of results is to be made only by direct arrangement with the originators of the work.

Subject Matter

We hope that you will feel free to submit any material whatsoever, whether complete or fragmentary. Data already in hand is, of course, welcome. Among subjects which you might consider appropriate are:

(1) Reproductions of spectra or parts of spectra.

(2) Measurements and calculations on same.

(3) Theoretical considerations and interpretations.

(4) Novel experimental methods and techniques.

(5) Complete or partial mysteries.

(6) Comments on material appearing in earlier letters.

(7) Requests for help in locating sources of odd or rare compounds.

We intend to exercise no editorial function, but will simply assemble and reproduce sufficient copies of what is submitted to furnish the contributors with one copy each.

Practical Considerations

The reproductions of submitted material will be made by the Xerox process, which requires only that (1) material be submitted in an 8 1/2" x 11" format with a 1 1/2" left-hand margin, and (2) no blue ink be used - heavy black lines and writing are best. As this is essentially a photographic process, the originals of any material submitted can be returned, and actual spectra pasted to 8 1/2" x 11" paper, etc., will produce quite well.

We would like to suggest further that (1) the contributors use a minimum number of pages to present their material adequately, and (2) an identification of the origin of the submitted material appear on each page.

Material received by B. Shapiro by the 25th of each month will be included in the next letter, which will be sent out as soon as compilation, reproduction, collation and mailing can be completed.

It is with considerable trepidation that we approach the subject of standardization of spectra. Nevertheless we are compelled to settle on some convention so that submitted spectra and measurements will be readily interpretable by all participants without resort to an IBM 704, witchcraft or much tedious arithmetic.

After considering the numerous systems which have been used in the literature and discussed and suggested at various meetings, public and private, we have come to the conclusion that the best scheme for reporting chemical shifts is a combination of that suggested by Reilly et al and that suggested by Tiers. The system we suggest is as follows:

(A) Both an internal and an external reference should be used.

(B) The internal reference of choice is tetramethylsilane (obtainable from either Anderson Laboratories, Inc., Weston, Michigan, or Peninsular ChemResearch Inc., 1103 N.W. Fifth Avenue, P.O. Box 3597, Gainesville, Fla.).

(C) The position of tetramethylsilane as an internal reference is assigned the chemical shift number, $\delta = +10.00$.

(D) Chemical shifts will be quoted in parts per million (ppm), increasing positive values of δ corresponding to resonances occurring at increasing applied magnetic fields (i.e. to increasing shieldings).

This is a rather arbitrary set of rules, and some amplification and explanation is probably in order. Firstly, to define terms: by internal reference, we mean a substance added directly to the sample whose spectrum is being taken, so that the spectrum is actually recorded on a liquid mixture; by an external reference, we mean a substance whose spectrum is recorded simultaneously with that of the sample, but which is not physically mixed with it -- perhaps contained in a sealed capillary added to the N-M-R sample tube, or contained in an annular space in a specially constructed cell.

We suggest running the chemical shift scale from the internal reference, because this usually gives a more nearly consistent scale of chemical shifts than external referencing. It is not perfect, however, and no satisfactory theory has as yet been developed which would allow one to correct exactly for specific solvent effects. It is not outside the realm of possibility that such a theory will be developed, and it seems quite possible that the deduction of and/or the application of such a theory may be based on a knowledge of absolute (i.e. externally referenced) line positions. For this reason, it would seem highly desirable that both internal and external reference substances be used in standardizing N-M-R spectra. Whatever practice is followed, it is clear that the spectra will have the greater potential value the more completely are the conditions described under which they are obtained. For example, as a minimum requirement, the following should also be specified:

(1) R.F. oscillator frequency

(2) Solute and internal reference concentrations

(3) Details of source + preparation of sample (e.g. whether or not dried, distilled, degassed, etc.)

(4) Temperature of the sample

(5) Any unusual conditions

We are very much looking forward to hearing from you. We hope for your contributions, but will also welcome any comments, criticisms, or suggestions on the operation of this newsletter. Appended is the current mailing list for this letter -- if you have any suggestions for additions (or deletions!?), we will be happy to receive them.

A. A. Bothner-By

B. L. Shapiro

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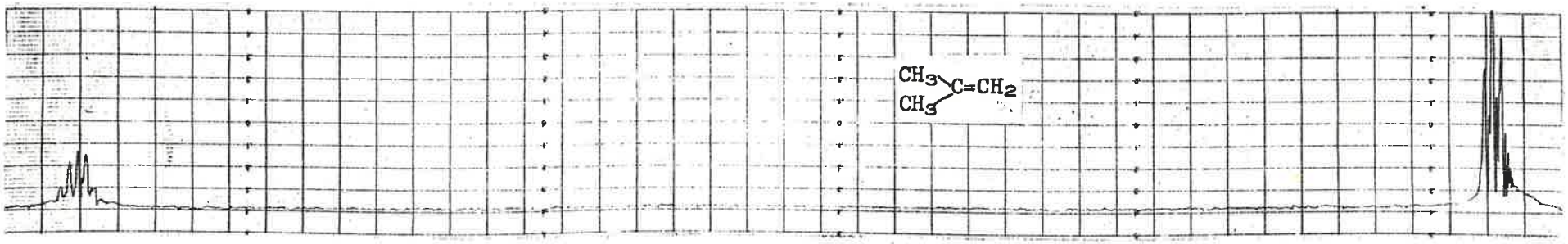

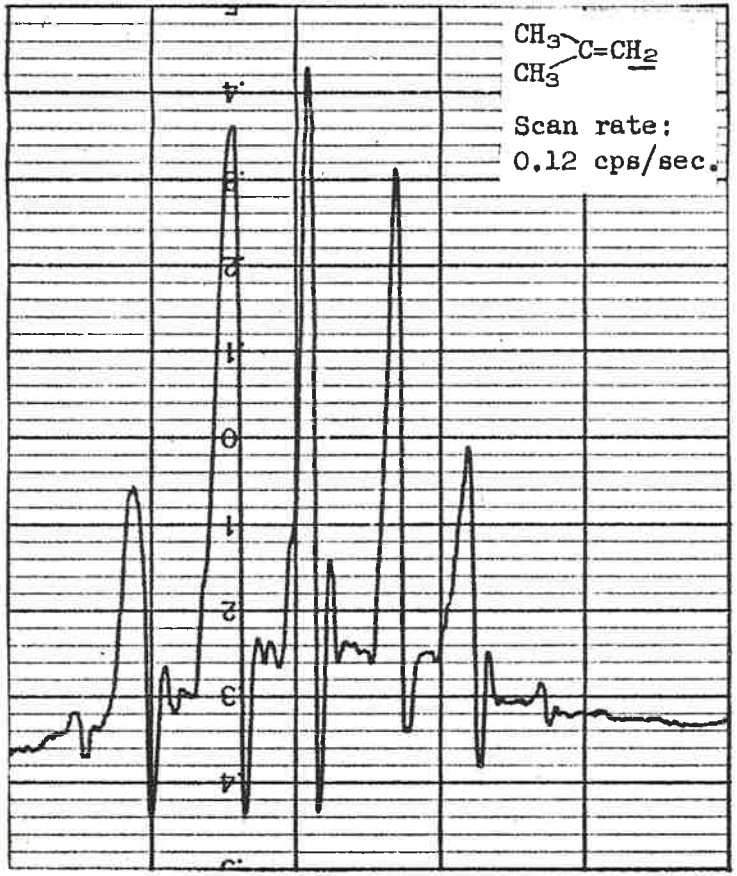

Isobutylene

CH_3
CH_3 $C=CH_2$

Neat, degassed

See data on following page.

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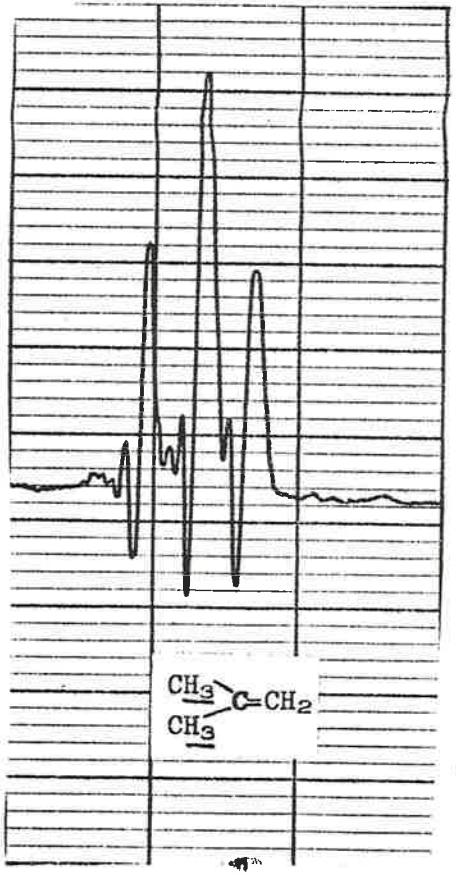

Isobutylene $CH_3>C=CH_2$ CH_3

(Phillips Petroleum Co. Pure Grade)

CCl_4 solution: $Me_2C = CH_2$ 10%

Me_4Si 1%

External reference: $CHCl_3$

Both the sample solution and the $CHCl_3$ capillary were degassed.

Resonances observed at 60 mc.

Temperature: 24°C.

$\delta_{Me} = 8{\cdot}30 \pm 0{\cdot}01$

$\delta_{CH_2} = 5{\cdot}40 \pm 0{\cdot}01$

The external $CHCl_3$ resonance signal appears at 7·42 ppm from the line of Me_4Si.

$\delta_{Me}-\delta_{CH_2} = 2{\cdot}90$ In the neat liquid, the Me-CH_2 separation is 2.96 ppm.

$J = 1{\cdot}20 \pm 0{\cdot}03$ cps. (apparently, the same for cis and trans hydrogens.)

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13 October 1958

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