

## NOTE.

*Infra-red Spectrum and Structural Diagnosis: Substituted Carbazoles.* By R. E. RICHARDS.

THIS note describes an example, not only of the value to the organic chemist of infra-red measurements in structural diagnosis, but also of an experimental method developed in this laboratory for measuring the spectra of very small amounts of material. A sample was received for examination which had been formed by degradation of a substance of which the structure was not completely known. The specimen was a crystalline solid, only 1.5 mg. being available, and was suspected to be a mixture of carbazole and one or more of its methyl derivatives. It was required to determine which methyl derivatives were present and approximately in what proportions.

The experimental method had been mentioned by early workers (see also Thompson, *J.*, 1944, 191), but had not been widely used until it was developed in this laboratory in connection with recent studies on penicillin.

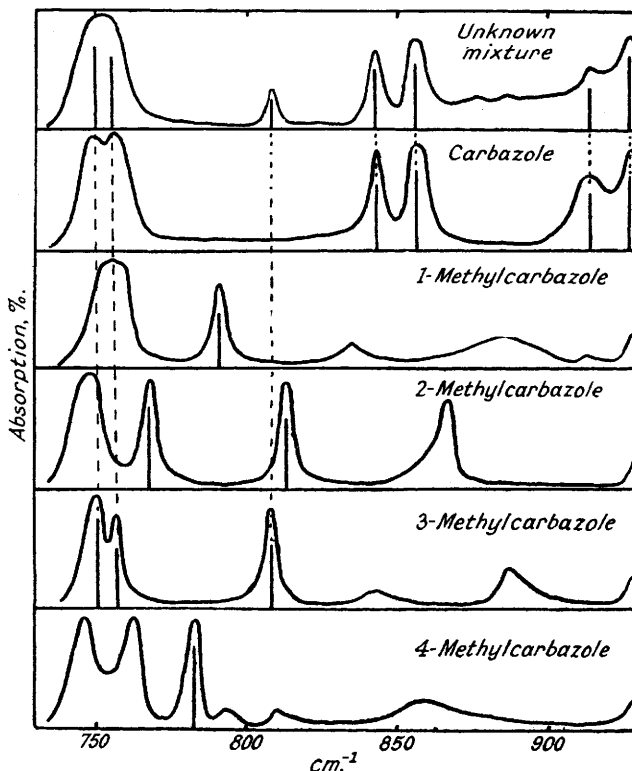
The specimen is ground to a very fine powder in a small glass or agate mortar. A suitable glass mortar can easily be made by rounding off a short piece of narrow glass tubing, and a piece of well-fitting glass rod with rounded end is used as the pestle; a small quantity of dry medicinal paraffin is then added to the powder, and the whole is ground to a smooth paste. This is transferred to a rock-salt plate, about  $1.5 \times 0.5$  cm. in area, and another similar plate is placed on top. With the aid of a small spatula it is possible to prepare the specimen as a long narrow film between the plates, and almost any desired thickness can be obtained by appropriate manipulation, although it is obviously impossible to obtain an exact measure of the thickness of the absorbing layer. No clamping device or spacing washer is necessary, since the surface tension of the oil is sufficient to hold the plates together. The plates are placed on a flat platform so that the film lies exactly at a sharply focused image of the source of radiation, which is usually a Nernst filament. The sample, when thus prepared, causes very little scattering of the infra-red radiation, and a good spectrum can be obtained. The paraffin has strong absorption bands at about 720, 1375, 1460, 2850, 2925  $\text{cm.}^{-1}$ , but in all other regions of the spectrum it shows no appreciable absorption except in very thick layers. When the spectrum has been measured, a large proportion of the sample can be recovered by extraction with a suitable solvent or by washing away the paraffin with a solvent which does not dissolve the specimen.

This method is often preferable to the alternative procedure of measuring the spectrum in solution; it is very simple, quick, and requires little of the sample. If it is desired to study such a small quantity of a specimen in solution, arrangements must be made to recover it from the solution in the absorption cell, and this requires a rather elaborate technique. This may, however, be essential, since more than one solvent must be used in order to cover the whole range of the infra-red spectrum, no single solvent being available which is completely transparent over the whole spectral range 1–14  $\mu$ . Such difficulties imply that in many cases the measurements in solution are impossible. In some circumstances it is useful to study the whole range of the spectrum of the solid as above, then to recover the sample, and to study some particularly interesting region in a suitable solvent which is transparent in that particular range.

The spectrometer used in this problem was a single-beam recording instrument, using a rock-salt prism (Whiffen and Thompson, *J.*, 1945, 268).

*Results.*—The figure shows the spectrum, over the range 730–930  $\text{cm.}^{-1}$ , of the unknown mixture,

together with the spectra of pure samples of carbazole and 1-, 2-, 3-, and 4-methylcarbazoles, obtained by the same method. Key bands are emphasised by the vertical lines. The presence of carbazole in the mixture is confirmed by the complete correspondence between the bands in the pure specimen and similar bands in the mixture. The complete absence of bands at either 790 or 782  $\text{cm}^{-1}$  indicates the absence of 1- and 4-methylcarbazoles, whereas the band in the mixture at 808  $\text{cm}^{-1}$  exactly corresponds to the strong key band of 3-methylcarbazole at this frequency—its weaker band at 886  $\text{cm}^{-1}$  is lost between the strong bands of carbazole itself at 856 and 915  $\text{cm}^{-1}$ . The strong key bands of 2-methylcarbazole lie rather close to those of 3-methylcarbazole and make it impossible to establish the complete absence of the former, although if it is present, it can only be in very small amounts, for not a trace of the band at



767  $\text{cm}^{-1}$  appears in the mixture, and the band at 808  $\text{cm}^{-1}$  is not broadened noticeably towards 813  $\text{cm}^{-1}$ . It was therefore concluded that the unknown mixture contained mostly carbazole and 3-methylcarbazole. Comparison of the original spectrum with mixtures made from the pure materials shows that the unknown mixture contained between 5% and 12% of 3-methylcarbazole. A closer estimate of the relative proportions was not justifiable owing to the unknown differences in thickness and homogeneity of the different solid samples studied, but if larger amounts of material were available, solutions could be made up and compared with solutions of either the pure components or known match mixtures, so as to obtain a far more exact quantitative estimate.

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