Acknowledgment.—The author thanks Dr. T. H. Coffield for helpful discussions throughout the course of this work.

A Chart of Ultraviolet Absorption Maxima of Semicarbazones

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Received September 11, 1963

A Colthup-type chart of the principal ultraviolet absorption maximum in the spectra in chloroform of several hundred 2,4-dinitrophenylhydrazones[1] suggested some possible utility in a similar analysis of the spectra of the other major carbonyl derivative, the semicarbazone. The source of data was again the three published volumes of "Organic Electronic Spectral Data"[2] supplemented by a rather unproductive search of *Chemical Abstracts* for 1960–1962. (Though many such spectra must have been published in those years, they appear to have been too widely scattered for indexing under general headings in Abstracts.)

A total of over 400 distinct semicarbazone spectra, nearly all of them in ethanol as solvent, were found. A frequency plot of the raw data for the entire group showed the largest numbers of entries in the 224–230- and 260–272-mμ regions, these corresponding to saturated and α,β-unsaturated carbonyl derivatives, respectively. In indexing the entries for the chart of Fig. 1 about 270 compounds were used, the remainder either lacking an identifiable structure or falling outside the classes of the index.

It is well-known that semicarbazone spectra are characterized by a moderately large bathochromic shift and an increase in molar absorptivity as compared to the parent carbonyl compounds.[3,4] A fairly regular increase in λ_{max} with the number of double bonds conjugated with the carbonyl and a corresponding rise in log ϵ also are noted generally.

As compared to either the carbonyl compounds or the 2,4-dinitrophenylhydrazones, however, the semicarbazones appear strikingly insensitive to most minor structural influences on their spectra. For example, aldehyde semicarbazones seldom differ enough from those of ketones to warrant separate chart entries, and the substitution of alkyl groups in α,β-unsaturated carbonyl compounds (*cf.* Woodward's rules) has an inappreciable effect on the semicarbazone spectra.

The only important structural effects are found in acetylcyclohexenes, methyl alkenyl ketones, and a few related compounds where the semicarbazones absorb at somewhat shorter wave lengths than other α,β-unsaturated systems (*cf.* Dorfman[5] for some explanatory notes on these), and in *o*-alkylacetophenones and a few highly alkylated cyclohexene derivatives where steric hindrance appears to account for decreased λ_{max} and log ϵ. An outstanding anomaly is the higher cycloalkenones whose semicarbazones absorb at 215 and 230 mμ,[6] well below the usual region for α,β-unsaturated compounds.

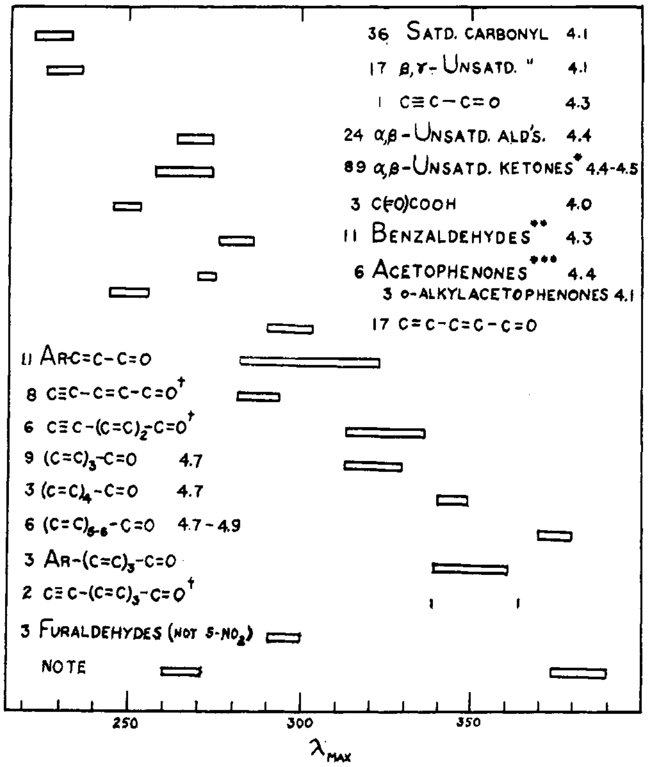

Fig. 1.—Principal maxima in the ultraviolet spectra of semicarbazones. Number of compounds in each class is given at left, and approximate log ϵ at right (when scatter of data is small); *, acetylcyclohexenes with λ_{max} near 260 mμ; **, salicylaldehyde falls below this indicated range for other benzaldehydes; ***, and higher homologs; $^+$, includes some compounds with triple bond position interchanged with one of the double bonds. (Note that this last group consists of ten 5-nitro-2-furylcarbonyl compounds, each having two maxima.)

For classification purposes in Fig. 1 compounds with isolated multiple bonds or other functions have all been grouped under the saturated carbonyl heading.

Acknowledgment.—This work was partially supported by a grant (CA-05607) from the National Cancer Institute of the Public Health Service. The author is also grateful to Pamela Ferguson for her help in processing the data.

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Structure of Ylangene

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Received October 21, 1963

The structure of ylangene previously has not been proposed, although it had been isolated from many

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