was removed by distillation and 60 ml. of water added. Extraction of the basic solution with ether afforded an almost quantitative yield of III, which after several recrystallizations from a 1:3 mixture of benzene and low boiling (b.p. 30–60°) petroleum ether had m.p. 77–79° (lit.[6] m.p. 65°).

Anal. Calcd. for $C_{10}H_9NO$: C, 75.50; H, 5.70; N, 8.80. Found: C, 75.76; H, 5.77; N, 8.63.

Benzoic acid was obtained upon acidification of the alkaline solution remaining.

The phenylurethane derivative of III was obtained as a white crystalline solid from carbon tetrachloride, m.p. 148–150°.

Anal. Calcd. for $C_{17}H_{14}N_2O_2$: C, 73.37; H, 5.07; N, 10.07. Found: C, 73.22; H, 5.29; N, 9.76.

Conversion of 1-Isoquinolylcarbinol (III) to 1-Methylisoquinoline.—A 2.0-g. portion of III was reduced[7] to 1-methylisoquinoline (0.51 g., 28.2%). This was characterized as its picrate, which after recrystallization from ethanol had m.p. 231–232° (lit.[10] m.p. 230–232°), and as its methiodide, which after recrystallization had m.p. 207–208° (lit.[10] m.p. 208°).

Hydrochloride of 2-Quinolylcarbinyl Benzoate (II).—This compound was prepared from 10.4 g. (0.04 mole) of 1-benzoyl-1,2-dihydroquinaldonitrile[11] in exactly the same manner as described above for the hydrochloride of I; 8.5 g. (72.1%) was obtained. Recrystallization from ethanol gave m.p. 107–109°.

Anal. Calcd. for $C_{17}H_{14}NClO_2$: C, 68.15; H, 4.79; N, 4.67; Cl, 11.83. Found: C, 67.78; H, 5.01; N, 4.48; Cl, 10.72.

2-Quinolylcarbinol (IV).—This compound was obtained in almost quantitative yield from the saponification of 4.0 g. (0.013 mole) of the hydrochloride of II in a manner analogous to that described above for III. Recrystallization from a 1:3 mixture of benzene and low boiling petroleum ether gave m.p. 65–67° (lit.[12] m.p. 66–68°).

The phenylurethane derivative of IV had m.p. 127–129° (lit.[12] m.p. 128–130°).

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The Preparation of Formic Benzoic Anhydride

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Although formic acetic anhydride may be prepared readily,[2] examination of the literature revealed no references to formic benzoic anhydride (I).

Formic benzoic anhydride has been prepared by the action of benzoyl chloride on a twofold excess of sodium formate in diethylene glycol dimethyl ether (DMC) or tetrahydrofuran (THF). The infrared spectrum of I in carbon tetrachloride solution showed carbonyl bands at 1785 and 1755 cm.$^{-1}$, in addition to strong bands at 1045 and 1020 cm.$^{-1}$. The proposed structure was confirmed by the neutralization equivalent of a hydrolyzed sample and by elemental analysis, although a slightly high value for carbon was obtained (presumably due to decomposition of I before analysis of the sample could be made). Reaction of I with aniline afforded both formanilide and benzoic acid in good yields. The formation of formanilide rather than benzoic acid anilide is analogous to the behavior of formic acetic anhydride.[2]

Although a small amount of I was isolated by distillation, there was extensive thermal decomposition. To obtain larger amounts of material, the reaction (in THF) was allowed to go almost to completion and was filtered from sodium chloride and unchanged sodium formate while there was still a small amount of benzoyl chloride present. The reaction could be followed conveniently by infrared. In this manner, formic benzoic anhydride, contaminated with small amounts of both benzoic acid (decomposition product of I) and benzoyl chloride, was obtained after removal of solvent.

If the reaction of sodium formate with benzoyl chloride was allowed to go to completion, formic benzoic anhydride was found to decompose in the reaction mixture to benzoic acid with the evolution of a gas (probably carbon monoxide). The infrared spectra of samples removed periodically throughout the reaction showed that this decomposition did not begin until essentially all of the benzoyl chloride had reacted. This suggests the possibility that small amounts of sodium formate dissolved in the reaction medium are catalyzing the observed decomposition.

Experimental[3]

Preparation of Formic Benzoic Anhydride.—To a stirred suspension of 80 g. (1.178 moles) of pulverized sodium formate in 100 ml. of dry DMC was added 82.8 g. (0.589 mole) of benzoyl chloride over a period of 65 min. (internal temperature 8–9°). After addition was complete, the mixture was stirred for 2.7 hr. at 9–15° and filtered under nitrogen. The infrared spectrum of the colorless filtrate showed bands at 1785, 1755, 1045, and 1020 cm.$^{-1}$, which were assigned to formic benzoic anhydride. There was no benzoic acid carbonyl, and it appeared that most of the benzoyl chloride had reacted. After the solution had stood overnight at room temperature, infrared analysis indicated that no decomposition had taken place. An aliquot of the above filtrate was distilled through a micro Vigreux column to yield 10.15 g. of formic benzoic anhydride, b.p. 64.5° (0.45 mm.)–69° (0.60 mm.). There was a white crystalline residue of 6.51 g., the infrared spectrum of which showed a strong benzoic acid carbonyl at 1695 cm.$^{-1}$. Infrared analysis showed the distillate to contain formic benzoic anhydride contaminated with a small amount of benzoic acid. Formic benzoic anhydride was purified by placing a small amount of the distillate in a sublimation apparatus and distilling the liquid at room temperature and high vacuum onto a cold finger cooled with ice–water. A sample of this purified material was hydrolyzed with water and a neutralization equivalent was obtained on the liberated acids.

Anal. Calcd. for $C_8H_6O_3$: C, 64.0; H, 4.03; neut. equiv., 75.06. Found: C, 64.8; H, 4.29; neut. equiv., 75.2

When a similar reaction mixture was not filtered from excess sodium formate but was stirred for 19.3 hr. at 19–37° after the completion of the benzoyl chloride addition, the infrared spectrum of the mixture showed a benzoic acid carbonyl at 1695 cm.$^{-1}$ and no trace of formic benzoic anhydride.

In THF, 100 hr. was required for the reaction of sodium formate (0.589 mole) with 0.294 mole of benzoyl chloride to go almost to completion. The temperature was varied from 0 to 53°, and the reaction was followed carefully by observing the disappearance of the 876-cm.$^{-1}$ band of benzoyl chloride in the infrared. The formic benzoic anhydride obtained after dilution of the reaction mixture with pentane, filtration, and removal of solvent from the filtrate was contaminated with only small amounts of benzoic acid and benzoyl chloride.

The reaction of I with aniline in ether solution afforded a 65.5% yield of formanilide, m.p. 43–49° (m.p. 47–50° after recrystn.), and a 74.5% yield of benzoic acid, m.p. 120–122°. Formanilide and benzoic acid were identified by their infrared spectra and by mixture melting points with authentic samples.

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[2] C. W. Huffman, *J. Org. Chem.*, **23**, 727 (1958), and references quoted therein.

[3] Melting points and boiling points are uncorrected. The infrared spectra were recorded on a Perkin-Elmer Infracord spectrophotometer.

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A Chart of Ultraviolet Absorption Maxima of Semicarbazones

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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.

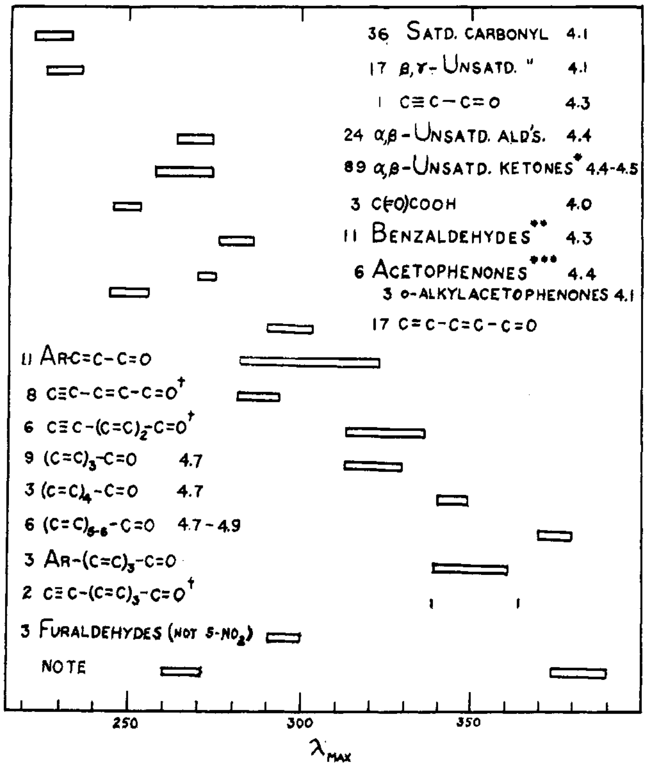

Fig. 1.—Principal maxima in the ultraviolet spectra of semicarbazones. Number of compounds in each class is given at left, and approximate log ϵ at right (when scatter of data is small); *, acetylcyclohexenes with λ_{max} near 260 mμ; **, salicylaldehyde falls below this indicated range for other benzaldehydes; ***, 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.

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Structure of Ylangene

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

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