Odor and the Organic Chemist

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TO MANY organic chemists and particularly to students of organic chemistry, odor consciousness has been limited to isolated chemicals possessing to a high degree some particularly disagreeable and obnoxious characteristics. The mercaptans, scatol, the amines, etc., have been widely advertised as powerful disturbers of the olfactory sense. Little if any attempt, however, has been made to make the student aware of association of chemicals and odor. Indeed, odor has been looked upon as more or less of an anomalous or purely incidental property of organic substances.

To realize the importance of odor it may be quite needless to mention the fact that a few billion dollars are expended annually in the United States alone on the purchase of cosmetic preparations whose successful sale often hinges on their odor appeal. Every ounce of soap, skin cream, sachet, hair preparation, bath preparation, household insecticide, furniture polish, shoe polish, kitchen "deodorizer," to list only a few, contains a small percentage of a mixture of chemicals whose sole claim for such application resides in the fact that they have odors.

The art of recognizing, identifying, classifying, and choosing chemicals on the basis of odor has been put almost exclusively in the hands of a comparatively few highly specialized men known as perfumers. Some of these perfumers have but a limited knowledge of organic chemistry and its method of procedure. And yet, from experience alone they are able to distinguish hundreds of hydrocarbons, alcohols, aldehydes, esters, etc., or types, not by what we know as "scientific methods," but by smelling them!

It must first be emphasized that odor is as much a property of a chemical as is color, melting point, density, etc. The fact that a pure chemical is odorless is often as important as that it possesses a distinctive and powerful aroma. Unfortunately the sense of smell lacks the precision attained by less subjective means of determining attributes of chemicals. Perhaps the future will perfect a method of accurately and objectively describing odors and their intensities.

The resourceful and imaginative scientific worker does not forego the opportunity of accepting and capitalizing on any clues concerning the nature of the material he may be investigating. During his research on carotene and vitamin A, Paul Karrer recognized the presence of ionone by its odor only. This shortened the work of establishing the structure and hastened the ultimate synthesis of this vital accessory food factor. How fortunate it was that the ionones had been synthesized some 40 years before by Tiemann who had interested himself in the perfume of the violet!

Another giant of organic chemistry, Leopold Ruzicka, through his keen appreciation of the phenomena of odors, showed us that our notions about the size of ring structures and stability had to be revised when he disclosed the 15 and 17 carbon atom rings of muscone and civetone. Even one of the sterols, he claims, has a musk odor. On the other hand, Ruzicka, working with Staudinger on the chemistry of pyrethrin, failed to mention the powerful odor of dihydrojasmone although he later claims to have discovered its perfume value.

During the preparation of organic chemicals the chemist should be forever on the alert for odors, foreign or novel, which may help him to identify impurities or indicate the presence of some new compound. Time and effort may be conserved if the chemist can recognize odors which may immediately indicate the direction of his subsequent research on purification and isolation. How many chemicals are buried in the masses of scientific literature, awaiting a deserved place in the roster of perfume chemicals? The situation is as unfortunate as when the chemist reads an article on a dye, to find everything explained in detail, but no mention made of color.

What odors are of interest to a perfumer, I venture to say, is almost impossible for a chemist to predict. The good perfumer has often startled us by his choices. What shall we say of the alkyl substituted quinolines and the indols, the alpha alkyl substituted cinnamic aldehydes, trichlormethyl phenyl carbinyl acetate, the macrocyclic esters, diphenyl methane, octinoic acid methyl ester, etc., to mention a few of the purely synthetic chemicals he has utilized? There also arises the question of how to describe the odors of new chemicals. Even when by good fortune the odor of a new substance is reminiscent of that of a flower, such as a rose, violet, or lily, the problem is still only half solved. What remains to be said involves nuances, and at this point the difficulties of language seem almost insurmountable. The perfumer uses such terms as sweet, woody, powdery, green, leafy, musty, harsh, earthy, tarry, etc., and by a casual consideration of these terms it is clear that they are highly inadequate adjectives because they are not precise. The word "sweet," for example, means for all of us the well-defined sense of taste of cane sugar; but the sugars are odorless, and we must now learn to think of vanillin as having a sweet odor. The pure taste sensation stimulated by vanillin is that of bitterness. To say that geraniol is sweeter than citronellol or phenylethyl alcohol sweeter than phenylpropyl alcohol, a new concept must be learned. But this qualitative distinction of the so-called sweetness exists to a large extent in the imagination of the perfumer. What I mean to infer is not that the perfumer cannot detect these subtle differences in the odor of chemicals, but rather that his choice of describing them is subjective, arbitrary, and inadequate. "Woody" may conjure the odor of cedar to some, poplar to others, and birch to still others. Surely the "leafy" odor of peppermint, geranium, hedge, and hemlock does not convey a single general sensation to the nose. These are awkward words, but they are the best we know and possess at least some value.

At the moment, accurate descriptions are impossible, but we must to the best of our ability translate our odor impressions to our fellow chemists. Certainly there is less harm done by inadequately describing an odor than by omitting to mention it at all. For the sake of simplicity it is best to do this by reference to well-known substances or odor complexes. This is at least practical because we are familiar with the floral and flavor complexes and because the types of perfume chemicals are legion.

For reference substances the author recommends the commonly known and generally experienced odors which, when used as the prototypes, have at least the possiblity of being recognized by all of us. These substances would include the flower, spice, fruit, animal, and vegetable odors, kerosene, turpentine, gasoline, naphthalene, camphor, cedar (pencil), tar, nitrobenzene (shoe polish), amyl acetate (banana oil), pine, butter, etc. For instance we might immediately think of rose, hyacinth, lily, gardenia, lilac as floral odors; apple, pear, peach, orange, lemon, and pineapple as fruit odors; spearmint, peppermint, wintergreen, cinnamon, clove, dill, anise, or vanilla as spice odors; raspberry, currant, and blackberry as berry odors; bitter almond as a nut odor. The reference substances may be clarified in further detail by listing the known ingredients which compose the original complex, as follows:

Rose—geraniol, citronellol, phenyl alcohol
Lemon—citral, limonene
Wintergreen—methyl salicylate

It is important and informative to indicate whether a chemical possesses an agreeable or disagreeable odor and also to attempt to estimate its intensity quantitatively. A chemical may be very powerful in odor, or weak, or lasting, or evanescent. The persistence or volatility of a chemical in relation to its odor may often be predicted on the basis of such physical properties as its vapor pressure or boiling point. Odor intensity seems to be to a large extent a physiological phenomenon associated with some chemical reaction occurring at the locus of the olfactory stimulation.

The chemist should be made aware of and practice the qualitative sort of distillation at atmospheric pressure which is universally employed by the perfumer. The distillation equipment of the perfumer consists simply of a container of so-called smelling blotters. With this simple apparatus he has become highly skilled and proficient. He places a few milligrams of a perfume or chemical, or a dilute solution of them, in some solvent such as alcohol, on the end of a smelling-blotter and wafts it under his nose. He tries to recognize the constitutents as they evaporate from the blotter. In the case of a chemical the odor should remain constant from the first moment to the last, when it has just escaped in the form of vapor from the blotter. Traces of odoriferous impurities are often readily detected by this method when all others fail. In some cases a blotter must be studied for a week or more.

It may be of some interest to the chemist who has synthesized a new chemical and found it pleasantly odoriferous to mail a very small sample to some perfume manufacturing company for inspection. The perfumer will welcome a prospective, novel, and useful odor and will attempt to analyze its aroma value for the chemist. Such cooperation may be of mutual benefit to the perfumer and the organic chemist.

Perhaps I should add here a note of caution for the organic chemist. Because he is in most cases unfamiliar with the perfume value of the chemicals available to the perfumer, the chemist may find results occasionally discouraging by the rejection of many or most of the odors which he considers unusual or intriguing. For example, isoamyl salicylate finds a wide application in many of the cheaper types of perfumes. Let us imagine that the *n*-hexyl ester had never been prepared. Some chemist, having produced it for the first time, finds its odor pleasant and suggestive and hopefully submits a sample to the perfumer. The latter agrees that the odor is pleasant but so similar in character to that of isoamyl salicylate that the extra cost of the *n*-hexyl ester is not justified.