the material of 26,000–30,000 molecular weight will be published.[6]

[6] Supported by a grant No. C-2290 from the National Cancer Institute, National Institutes of Health. The prolactin used in this work was a gift from the Endocrinology Study Section, National Institutes of Health.

DEPARTMENT OF PHYSIOLOGICAL CHEMISTRY
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RECEIVED MAY 29, 1958

ABSENCE OF HYPERCONJUGATIVE EFFECTS ON THE STRUCTURE OF MALONONITRILE[1]

Sir:

Microwave studies of derivatives of acetonitrile and methylacetylene suggest[2] that the length of a carbon–carbon single bond adjacent to a triple bond never deviates significantly from an average value just over 1.46 Å. Several different hypotheses have been used to explain, for each compound separately, the shortening of the bond relative to the standard value, 1.54 Å. In acetonitrile, a major part of the bond shortening has been attributed to π-bonding arising through hyperconjugation. To test this assumption, we have studied the structure of malononitrile, $CH_2(CN)_2$. Consideration of the possible valence-bond structures shows that each C–C bond here should have appreciably less double-bond character than in acetonitrile, and hence should be appreciably longer.

We have measured about two hundred frequencies in the microwave rotational spectrum of gaseous malononitrile, and assigned fifteen of these to low-J transitions. The rotational constants are

$$a = 20{,}882.35 \text{ mc.}$$
$$b = 2{,}942.15 \text{ mc.}$$
$$c = 2{,}616.75 \text{ mc.}$$

The structural parameters which we feel best fit the data are

$$r(\text{C—H}) = 1.09 \text{ Å. (assumed)}$$
$$r(\text{C}\equiv\text{N}) = 1.158 \text{ Å. (assumed)}$$
$$r(\text{C—C}) = 1.460 \text{ Å.}$$
$$\angle \text{H—C—H} = 105°39'$$
$$\angle \text{C—C—C} = 113°39'$$

An unambiguous structure determination will be possible when we complete work on malononitrile-d_2. It seems certain that the correct C–C distance is again very nearly 1.46 Å. Taken with the data on related molecules, this makes it appear very unlikely that π-bonding arising through hyperconjugation is a major factor in fixing bond lengths.

According to the principle of parsimony, one should seek a common explanation for the essentially constant single-bond distances in all these molecules. We suggest that the bond contraction is principally attributable to the change from sp^3 to sp hybridization at one end of the bond. It has been supposed[3] that such a hybridization change decreases the covalent radius of carbon by 0.04 Å., just accounting for the difference between the C–H distances in ethane and acetylene. We suggest that C–C distances are much more sensitive to hybridization changes than C–H distances, so that sp carbon has a smaller covalent radius *toward carbon* than *toward hydrogen.* The radius toward halogens is apparently still smaller, as evidenced by the even larger differences between C–X distances in the methyl halides and the haloacetylenes or cyanogen halides.[4] The variability of the covalent radius may be due to the fact that the hybridization change must alter the *repulsive* as well as the attractive forces associated with the bond. The repulsive forces should be particularly sensitive to the size and electron distribution in the atom bonded to the sp carbon.

We feel that these results call for a searching reexamination of the common assumption that variations in C–C bond lengths are primarily determined by bond-order changes, and that they may be used as unequivocal evidence for bond-order changes due to resonance.

[1] Supported by the Purdue Research Foundation acting under contract AT-(11-1)-164 with the Atomic Energy Commission.

[2] W. Zeil and J. P. Pfrommer, *Z. Elektrochem.*, **61**, 938 (1957), and references given there.

[3] C. A. Coulson, "Valence," Oxford University Press, London, 1952, pp. 206, 310.

[4] W. Gordy, W. V. Smith and R. F. Trambarulo, "Microwave Spectroscopy," John Wiley and Sons, New York, N. Y., 1953, p. 371.

DEPARTMENT OF CHEMISTRY
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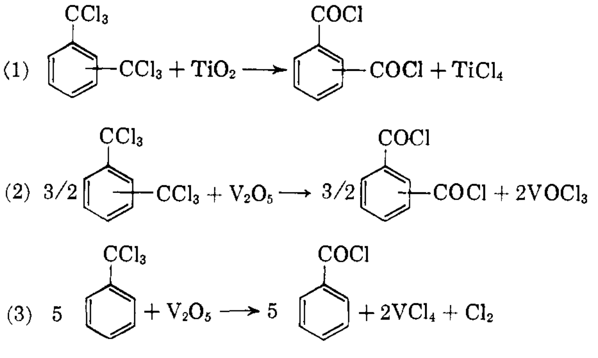
SIMULTANEOUS SYNTHESIS OF AROMATIC ACID CHLORIDES AND METAL CHLORIDES

Sir:

A new simultaneous synthesis of aromatic acid chlorides and metal chlorides from trichloromethylated aromatic compounds and metal oxides has been discovered. The method of preparation is simple and consists of heating the reactants in the proportions as shown in equations 1, 2 and 3.



Metal oxides such as TiO_2 and V_2O_5 give the best yields of both the aromatic acid chloride and the metal chloride. Other oxides such as those of arsenic, antimony and zirconium are operable but give lower yields of the aromatic acid chloride. Aromatic compounds containing mono- or bis-(trichloromethyl) groups, which are obtained readily by the side-chain chlorination of the corresponding hydrocarbon, work equally well. With the mono-(trichloromethyl) compounds, monoacid