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

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

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

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 re-examination 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.

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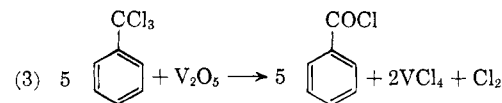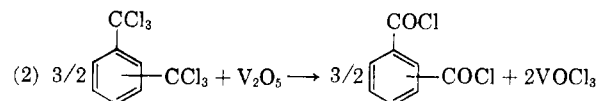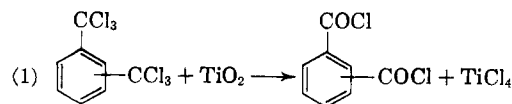
Metal oxides such as TiO_2 and V_2O_5 give the best yields of both the aromatic acid chloride and the metal chloride. Other oxides such as those of arsenic, antimony and zirconium are operable but give lower yields of the aromatic acid chloride. Aromatic compounds containing mono- or bis-(trichloromethyl)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

chlorides are obtained and with the bis-(trichloromethyl) compounds, diacid chlorides such as terephthalyl or isophthalyl chloride are obtained.

The reaction is carried out by heating a stoichiometric mixture of the reactants to 200–300°. A vigorous reaction occurs and the volatile metal chloride or oxychloride is distilled from the reaction mixture. Vacuum distillation of the residue gives an excellent yield of the acid chloride. For example, 313 g. (1 mole) or 1,3-bis-(trichloromethyl)-benzene and 82 g. of TiO_2 (1.02 mole) are added to a suitable reaction vessel equipped with an efficient stirrer and a fractionating column. The reactants are heated rapidly to about 270° with continuous agitation. During this heating period, there is a slight evolution of HCl gas. When the reaction vessel reaches 220°, $TiCl_4$ begins to distill indicating that the reaction has begun. The distillation of $TiCl_4$ becomes quite rapid when the temperature of the reaction mixture reaches 270°. Completion of the reaction is indicated by a marked rise in the temperature of the charge and a rise of the vapor temperature in the column At this point, the pressure in the system is reduced and isophthalyl chloride is distilled at a pressure of 15 mm. and a temperature of 145°. The distilled isophthalyl chloride solidifies to a crystalline solid melting in the range 39–40° (reported[1] m.p. 41°). The yield of $TiCl_4$, which on redistillation boiled at 135–136°, (reported[2] b.p. 135–136°) is 95% and the yield of isophthalyl chloride is 85%.

Acknowledgment.—The assistance of Dr. R. B. Hand of the Pigments Department of E. I. du Pont de Nemours & Co. is gratefully acknowledged.

(1) J. Schreder, *Ber.*, **7**, 708 (1874).

(2) Georg Brauer, "Handbuch der präparativen anorganischer Chemie," Ferdinand Enke, Stuttgart, Germany, 1954, pp. 894–897.

POLYCHEMICALS DEPARTMENT
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## THE ABSOLUTE CONFIGURATION OF SOME INDOLE ALKALOIDS[1]

Sir:

We wish to report the first chemical determination of the absolute configuration of non-cinchona indole alkaloids. It was accomplished by the conversion of ajmalicine (I), corynantheine (II) and cinchonamine (III) into common intermediates.
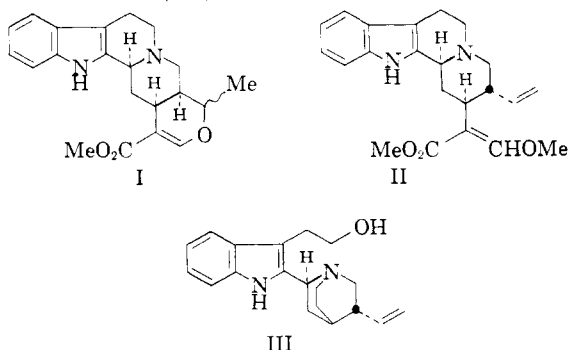

I

II

III

An alcoholic alkali treatment of ajmalicine[2] (I), followed by short heating with aqueous acid, led to the hemiacetal IV, m.p. 226–228° (Found for $C_{19}H_{24}O_2N_2$: C, 72.65; H, 7.85; N, 8.95), which on Wolff–Kishner reduction yielded the alcohol V, m.p. 200–201° (Found for $C_{19}H_{26}ON_2$: C, 76.62; H, 9.12; N, 9.82). Oppenauer oxidation of the latter gave the ketone VIa, m.p. 225–227° (found for $C_{19}H_{24}ON_2$: C, 76.98; H, 8.35), which could be converted by Wolff–Kishner reduction to dihydrocorynantheane[3] (VIb), identical in m.p. 189°, m.m.p. 188–189°, $[\alpha]_D$ −94° (pyridine) and infrared spectrum with an authentic specimen.

IV   V   VIa, R = $COCH_3$
                       b, R = Et
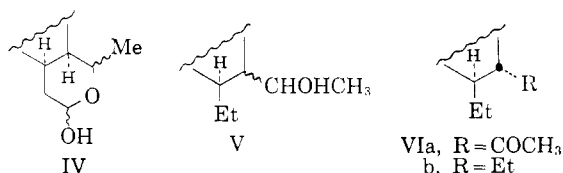
Tosylation of dihydrocinchonamine[4] in pyridine solution led to the quaternary chloride VII, m.p. 320–321°. Silver tosylate treatment of the latter yielded the quaternary tosylate VII, identical in m.p. 313–315° (dec.), m.m.p. 315° (dec.), $[\alpha]_D$ −69.5 (90% methanol) and infrared spectrum with the compound obtained from the tosylation and dimethylformamide refluxing of dihydrocorynantheol.[5]

VII
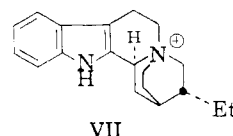
In view of the recent conversion of dihydrocinchonidine into dihydrocinchonamine[6] and the known absolute configuration of the cinchona bases,[7] *the above data constitute the first chemical tie-up between the two great classes of alkaloids, the cinchona and yohimbé bases, they prove the absolute configuration of ajmalicine and corynantheine to be as indicated in I and II, respectively, and they point up again the unique C(15)-H α-orientation of the indole bases.*[8] The biogenetic significance of these results will be reported in the full publication.[9,10]

DEPARTMENT OF CHEMISTRY
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AMES, IOWA   N. V. BRINGI

(2) E. Wenkert and D. K. Roychaudhuri, THIS JOURNAL, **80**, 1613 (1958).

(3) M.-M. Janot, R. Goutarel and V. Prelog, *Helv. Chim. Acta*, **34**, 1207 (1951).

(4) R. Goutarel, M.-M. Janot, V. Prelog and W. I. Taylor, *ibid.*, **33**, 150 (1950).

(5) C. Vamvacas, W. v. Philipsborn, E. Schlittler, H. Schmid and P. Karrer, *ibid.*, **40**, 1793 (1957).

(6) E. Ochiai and M. Ishikawa, *Pharm. Bull.* (Japan), **5**, 498 (1957).

(7) V. Prelog and E. Zalán, *Helv. Chim. Acta*, **27**, 545 (1944).

(8) *Cf.* E. Wenkert, E. W. Robb and N. V. Bringi, THIS JOURNAL, **79**, 6570 (1957).

(9) A novel theory of alkaloid biogenesis, able to interpret the above and other yet puzzling structural features of alkaloids, was first enunciated by the senior author in lectures before a chemistry colloquium at Northwestern University and the Organic Discussion Group, New York Section, A.C.S., on February 14 and 17, 1958, respectively.

(10) The authors are most grateful to Drs. Hochstein, Lucas, Raymond-Hamet and Schlittler for generous gifts of alkaloids and to the Institute of Atomic Research, Ames, Iowa, and Dr. Kniseley for the infrared spectra.