

(II, R = O=, no 1,2-unsaturation), m.p. 254–255°, $[\alpha]^{23D} +36^\circ$, $\lambda_{\max}^{\text{CHCl}_3}$ 2.75, 5.90 and 6.18 μ , $\lambda_{\max}^{\text{EtOH}}$ 234 (22,900), 274 (6500) and 325 $m\mu$ (5300), (found for $\text{C}_{17}\text{H}_{19}\text{NO}_5$: C, 64.42; H, 5.96), and oxoapohaemanthidine, (III, R = O=), m.p. 142–145°, $[\alpha]^{24D} +230^\circ$, $\lambda_{\max}^{\text{CHCl}_3}$ 5.88 and 6.20 μ , $\lambda_{\max}^{\text{EtOH}}$ 236 (24,200), 276 (6000) and 322 $m\mu$ (5000), (found for $\text{C}_{16}\text{H}_{13}\text{NO}_4$: C, 67.89; H, 4.53), respectively. These oxidation products represent three compounds of proven structure which, for theoretical reasons, should possess the properties of amino ketones rather than lactams.⁸ Preliminary evidence supporting this view includes the positions of the infrared carbonyl maxima, the ultraviolet spectra and the facile reduction in methanol of each oxo compound to the respective starting alcohol by sodium borohydride.

(8) Cf. the reported synthesis of 2-quinuclidone, L. N. Yakhontov and M. V. Rubtsov, *Zhur. Obshchei Khim.*, **27**, 72 (1957); *C.A.*, **51**, 12085b (1957).

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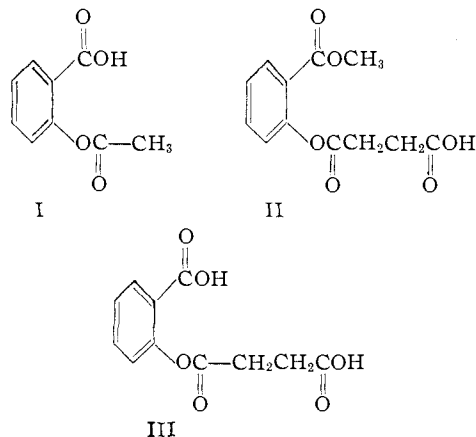
RECEIVED APRIL 2, 1958

INTRAMOLECULAR BIFUNCTIONAL CATALYSIS OF ESTER HYDROLYSIS

Sir:

It has been demonstrated previously that the solvolysis of phenyl esters is powerfully catalyzed by suitably spaced neighboring ionized carboxyl groups.^{1,2,3} Such reactions should be further accelerated, if the ester carries a second substituent which will stabilize the transition state, *e.g.*, by hydrogen bonding or by ion pair formation. The principle is similar to the "bifunctional catalysis" of Swain and Brown⁴ except that all three functional groups form part of a single molecule.

We have tested this assumption by comparing the pH dependence of the solvolysis rate of com-



(1) J. D. Chanley, E. M. Gindler and H. Sobotka, *THIS JOURNAL*, **74**, 4347 (1952).

(2) (a) H. Morawetz and P. E. Zimmering, *J. Phys. Chem.*, **58**, 753 (1954). (b) P. E. Zimmering, E. W. Westhead, Jr., and H. Morawetz, *Biochim. Biophys. Acta*, **25**, 376 (1957).

(3) E. R. Garrett, *THIS JOURNAL*, **79**, 3401 (1957).

(4) C. G. Swain and J. F. Brown, Jr., *ibid.*, **74**, 2538 (1952).

pounds I, II, and III. The results obtained in aqueous solution at 25° are plotted in Fig. 1 and show that I and II hydrolyze in the pH range 3–9

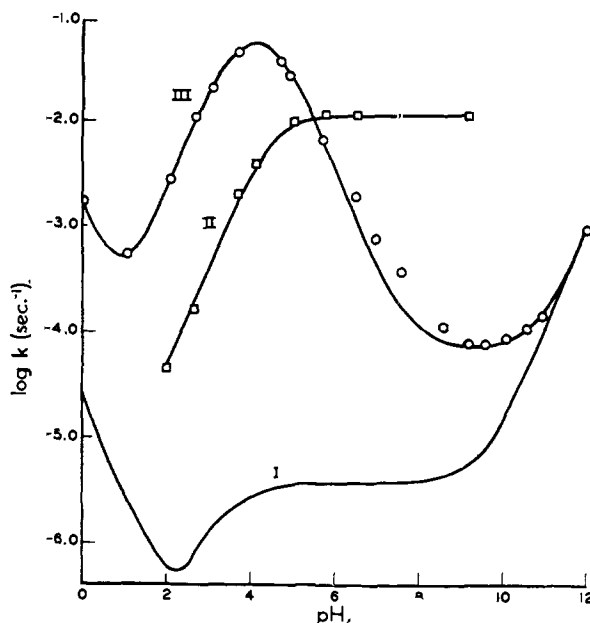
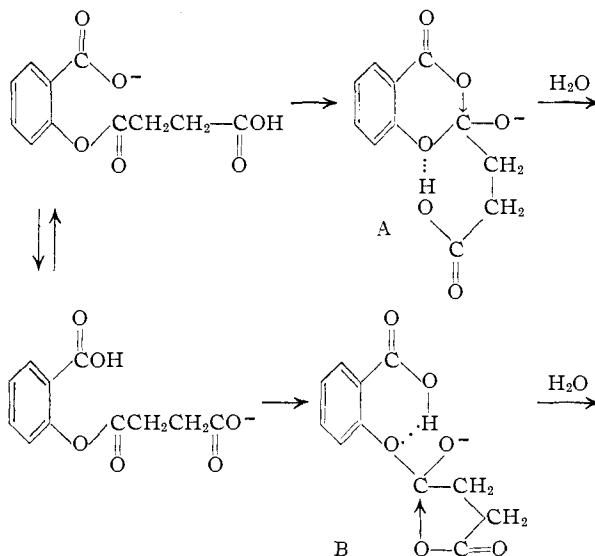


Fig. 1.—Hydrolysis rate constants at 25°; data for compound I from reference 3.

at rates proportional to their carboxyl ionization, while III hydrolyzes at a rate corresponding to the concentration of the singly ionized species, assuming $pK = 3.62$ and 4.5 for the salicylic and succinic carboxyls, respectively. Two pathways are pos-



sible and no distinction may be made between them from kinetic data. If the reaction proceeds exclusively through A, this intermediate would decompose 24,000 times as fast as ionized I which has the carboxylate in the same position but lacks the second, un-ionized, carboxyl. Conversely, if the reaction proceeds through B, this intermediate is 66 times as reactive as ionized II.

Intramolecular catalysis by neighboring functional groups, such as observed with compound

III, is of interest because of its analogy to the high reactivity of enzyme-substrate complexes.^{2b,5,6}

Acknowledgment.—This research was supported by the U. S. Army Office of Ordnance Research. Helpful discussions with Dr. J. F. Brown, Jr., and Professors M. L. Bender, C. G. Swain and F. H. Westheimer are gratefully acknowledged.

(5) H. Morawetz and E. W. Westhead, Jr., *J. Polymer Sci.*, **16**, 273 (1955).

(6) M. L. Bender, *THIS JOURNAL*, **79**, 1258 (1957).

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RECEIVED APRIL 4, 1958

A NEW CRYSTALLINE MODIFICATION OF BORON

Sir:

We have found that the product of the pyrolytic decomposition of BI_3 on a surface heated at 800–1000° contains a crystalline modification of boron different from any hitherto reported. Substrates of tantalum, tungsten or boron nitride yield the same results. Above 1500° the new modification transforms to the rhombohedral form of boron recently reported by Sands and Hoard.¹ The new modification is stable to twenty-four hours heating at 1100° or below, but a similar heating at 1200° produces a few new lines in the X-ray diffraction pattern which match the strong lines of the high temperature form.

The new modification appears in the product prepared at 1000° as a red sandy, red glassy, or red microcrystalline material. These forms may be recovered from the total deposit by leaching with warm concentrated nitric acid. Clear red crystals about 0.25 mm. long have been collected from the product. These, when examined by X-ray emission, show about 0.04 weight per cent. iodine but no other impurities of $Z = 13$ or larger in concentration greater than 0.001% (the limit of detection for the amount of sample available). The carbon content was determined by vacuum fusion analysis to be 0.003%. The density of the crystalline material was determined to be 2.46 g./cc. as opposed to 2.33 g./cc. for normal boron.

A preliminary crystal structure determination has been made from the isolated red crystals. The structure is rhombohedral, space group $R\bar{3}m$, with $a = 5.06$ Å. and $\alpha = 58^\circ 4'$. The experimental density yields 12.0 for the number of atoms in the rhombohedral unit cell; they are in 2 sets of the special positions 6(h) with $x = 0.01$, $z = -0.35$, and $x' = 0.23$, $z' = -0.37$. The structure may be described as composed of units of nearly regular icosahedra in a slightly deformed cubic close-packing. There are two kinds of bonds between boron atoms of neighboring icosahedra. One-half of the atoms in an icosahedron are bound by conventional single bonds to atoms of other icosahedra. The other kind of binding consists of equilateral triangles formed by boron atoms from three icosahedra.

This new boron structure is essentially the same

(1) D. E. Sands and J. L. Hoard, *THIS JOURNAL*, **79**, 5582 (1957).

as the boron framework in boron carbide, B_4C .^{2,3} There is the significant difference, however, that omission of the chains of three carbon atoms from the octahedral holes results in the closer approach of icosahedra and the formation of the new triangular boron bonds to replace the 3 bonds to 3 icosahedra formed by an end carbon of the three-carbon chains. The other bonds between icosahedra are the same in the two structures. Details of the preparation, properties, and structure will be published separately.

(2) H. K. Clark and J. L. Hoard, *ibid.*, **65**, 2115 (1943).

(3) G. Zhdanov and N. Sevastjanov, *J. Phys. Chem. U.R.S.S.*, **17**, 326 (1943); *Compt. Rend. Acad. Sci. U.R.S.S.*, **32**, 432 (1941).

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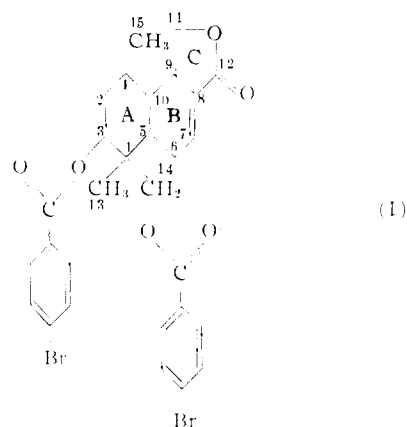
L. V. McCARTY
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RECEIVED MARCH 28, 1958

MOLECULAR STRUCTURE AND STEREOCHEMISTRY OF AN IRESIN DIESTER

Sir:

Three-dimensional analysis of 1432 independent X-ray diffraction maxima from single crystals of the *p*-bromobenzoate diester of the sesquiterpenoid, iresin,^{1,2,3} has yielded a complete molecular structure (I). Rings A and B are fused *trans* and



the angular methyl group is attached to C-10. Ring A has the chair form, and Rings B and C are nearly coplanar except for atom C-5. In agreement with chemical evidence (ref. 3, footnote 26), the OH group on C-3, the carbon atom bearing the primary hydroxyl function, and the 5–6 bond are all *cis*. Our results also provide an independent proof of all structural features of iresin except for the hydrogen atom positions.

The crystals are monoclinic with space group $P2_1$ and cell parameters $a = 28.75$, $b = 7.41$, $c = 6.40$ Å and $\beta = 92^\circ$. The observed density of 1.526 g. cm.⁻³ gives a molecular weight of 627 in agreement with the expected value of 632 for the diester. Three-dimensional Patterson, Fourier and difference syntheses plus nine cycles of least squares

(1) C. Djerassi, P. Sengupta, J. Herran and F. Walls, *THIS JOURNAL*, **76**, 2966 (1954).

(2) C. Djerassi, W. Rittell, A. L. Nussbaum, F. W. Donovan and J. Herran, *ibid.*, **76**, 6410 (1954).

(3) C. Djerassi and W. Rittell, *ibid.*, **79**, 3528 (1957).