bered ring. The facts that in III the tertiary hydroxyl and the methoxyl cannot be beta to the secondary hydroxyl, and that IX does not react with periodate, severely limit the possible arrangements of the three oxygen functions on the ring in III. The conversion of IX to perhydrobenzofuran derivatives, the structure of one of which is established by synthesis,[17] indicates the correctness of structures IX, III and II.

[17] D. D. Chapman, *et al.*, This Journal, **82**, 1009 (1960).

[18] Abbott Laboratories Fellow, 1957–1958.

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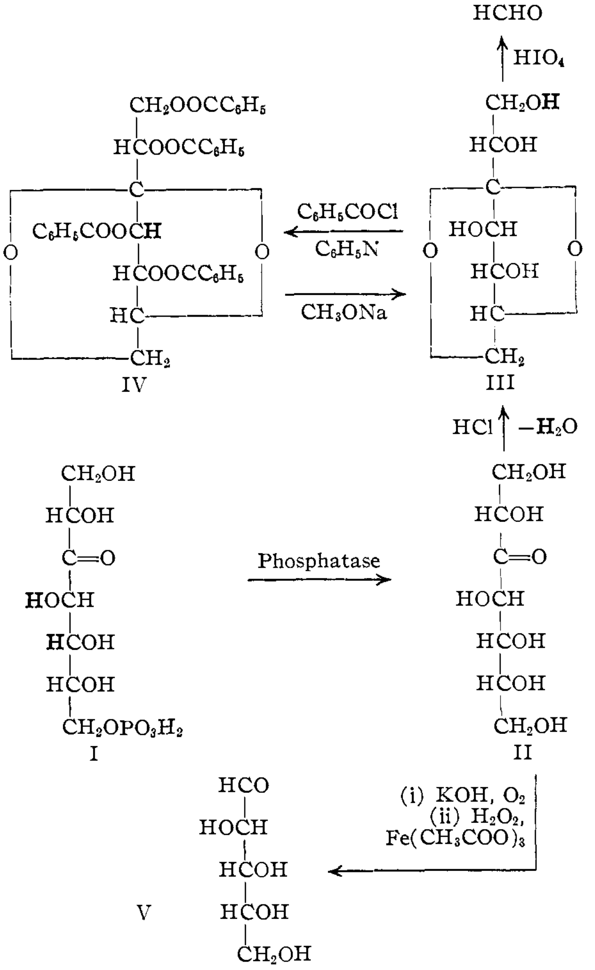
3-KETO-D-ARABOHEPTOSE PHOSPHATE: PROPOSED STRUCTURE FOR A NEW HEPTULOSE PHOSPHATE[1]

Sir:

In a previous communication,[2] we reported the isolation of a new heptulose phosphate from a digest of rat liver supernatant plus glucose 6-phosphate (G6P) as well as some properties of the heptulose, its phosphate, anhydride and anhydride tetrabenzoate. Evidence supporting its structure as 3-keto-D-*arabo*heptose phosphate (I) is now presented.

Phosphatase ("polidase") hydrolysis of I (free of other sugar phosphates) yielded the free sugar II which exhibits positive color reactions for ketose (resorcinol HCl; naphthoresorcinol-HCl and α-naphthylamine phosphoric acid) and for ketoheptose by the orcinol trichloroacetic acid reagent. II was degraded first by alkali oxidation[3] and then by ferric acetate–H_2O_2[4] to a pentose V. This was identified as arabinose by circular paper chromatography in two separate solvent systems[5] and by its crystalline diphenylhydrazone (2 mg.) m.p. 202.5°. The mixed melting point with authentic D-arabinose diphenylhydrazone (m.p. 202.5°) was not depressed. Acid treatment[6] of II yielded an anhydride III which was converted to the pure crystalline tetrabenzoate derivative[2] IV. Debenzoylation of IV (3 mg.) with sodium methoxide reagent produced III, which was oxidized with periodate to yield an equimolar amount of formaldehyde.[7] Gluco- and mannoheptulose[8] exhibited a rate of migration on paper different from II in butanol–pyridine–water (6:4:3).



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Received December 28, 1959

[1] Supported by research grants (P-106, P-107) from the American Cancer Society, Inc., New York, and (C-3213) from the National Cancer Institute, National Institutes of Health, Bethesda, Md.

[2] H.-G. Sie, V. N. Nigam and W. H. Fishman, This Journal, **81**, 6083 (1959).

[3] N. K. Richtmyer, R. M. Mann and C. S. Hudson, *ibid.*, **61**, 343 (1939).

[4] H. G. Fletcher, Jr., H. D. Diehl and C. S. Hudson, *ibid.*, **72**, 4246 (1950).

[5] Acetone:butanol:water (7:2:1) and butanol:pyridine:water (6:4:3) separate ribose and arabinose completely in six hours. The pentose consistently occupied the arabinose position. The conditions of degradation were ones which yield ribose only from sedoheptulose[8] and this fact was confirmed in this laboratory with both solvent systems.

[6] H.-G. Sie, V. N. Nigam and W. H. Fishman, *J. Biol. Chem.*, **234**, 1955 (1959).

[7] D. A. McFadyen, *ibid.*, **158**, 107 (1945).

[8] We thank Dr. H. S. Isbell, National Bureau of Standards, Washington, D. C., for making these reference sugars available to us.

NOVEL THERMAL REARRANGEMENTS ACCOMPANYING ACETATE PYROLYSIS IN SMALL RING SYSTEMS

Sir:

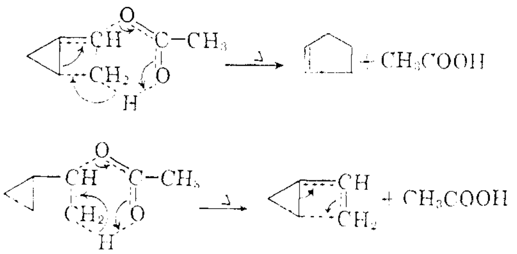
Pursuant to the preparation and the polymerization of vinylcycloalkanes, the acetate pyrolysis procedure[1,2] was applied to esters of secondary alcohols bearing an alpha carbocyclic group. We wish to report the discovery that the principal product from the pyrolysis of 1-cyclopropylethyl acetate was *cyclopentene* and that from 1-cyclobutylethyl acetate was *cyclohexene*. The pyrolysis of 1-cyclopentylethyl acetate proceeded in the reported manner[3] while the pyrolysis of 3-cyclohexenylmethyl acetate yielded 4-methylenecyclohexene, 60%, toluene, 24%, and methylenecyclohexene, 3%.

[1] C. G. Overberger and D. Tanner, This Journal, **77**, 369 (1955).

[2] W. J. Bailey and W. F. Hale, *ibid.*, 647 (1959), and previous references.

[3] J. R. van der Bij and E. C. Kooijman, *Rec. trav. chim.*, **71**, 837 (1952).

Thermally induced rearrangements have been found for the pyrolysis of medium ring cycloalkyl acetates,[4] the pyrolysis of cyclononyl acetate yielding mainly 1,8-nonadiene.[5] Our results are not an extension of these proposed transannular rearrangements. Elimination of the elements of acetic acid from 1-cycloalkylethyl acetates probably occur in the established fashion.[1,2] The rearrangement by ring expansion common to 3 and 4 membered carbocyclic systems can be concerted, similar to the preparation of 1,3-butadiene from cyclobutyl S-methyl xanthate[6] or else proceed through an intermediate vinylcycloalkane or result from a combination of these two choices. In this case, evidence is presented that the latter process accounts for a major portion of the reaction.



1-Cyclopropylethyl acetate, boiling at 139–140° (755 mm.), $n^{25}\text{D}$ 1.4140, C, 65.71, H, 9.67, was pyrolyzed[1] at 510°; and a mixture of 6 olefins, as evidenced by G.P.C.,[7] 87% was obtained. Fractionation yielded cyclopentene, boiling at 44° (755 mm.), 69%, $n^{25}\text{D}$ 1.4202, (lit. boiling at 41–42° (760 mm.), $n^{25}\text{D}$ 1.4190).[8] 1,4-Pentadiene, 10%, vinylcyclopropane, 12%, and isoprene, trace amount, were similarly identified, in all cases a comparison with known samples was made for positive identification.

A thermal isomerization of vinylcyclopropane was responsible, at least in part, for the formation of cyclopentene. Vinylcyclopropane in acetic acid was pyrolyzed under identical conditions and 40% of this material was converted to cyclopentene, 95%, and 1,4-pentadiene, 5%.

1-Cyclobutylethyl acetate, boiling at 157–159° (755 mm.), $n^{25}\text{D}$ 1.4230, was pyrolyzed[1] at 500°; and a five-component mixture boiling at 50–82° (755 mm.), 80%, was obtained. Fractionation yielded crude cyclohexene boiling at 80–84° (755 mm.), 65%, $n^{25}\text{D}$ 1.4410, (lit. boiling at 82–84° (760 mm.), $n^{25}\text{D}$ 1.4435).[9]

1-Cyclopentylethyl acetate[3] boiling at 91–92° (38 mm.), $n^{25}\text{D}$ 1.4332, was pyrolyzed[1] at 520° and a mixture of olefins was obtained, 76%. The major isomer, vinylcyclopentane, boiled at 98.8–99° (755 mm.), 74%, $n^{25}\text{D}$ 1.4336, (lit. boiling at 100.3° (760 mm.), 70%, $n^{20}\text{D}$ 1.4367)[3]. Ethylidenecyclopentane boiled at 111–112° (755 mm.), 24%, $n^{25}\text{D}$ 1.4470, (lit. boiling at 112.6° (760 mm.), 10%, $n^{20}\text{D}$ 1.4490).[3]

This research was supported by the United States Air Force under Contract No. AF 33(616)-5253, monitored by the Materials Laboratory, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio.

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RECEIVED OCTOBER 31, 1959

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(4) A. T. Blomquist and P. R. Taussig, THIS JOURNAL, **77**, 6399 (1955).

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(6) J. D. Roberts and C. W. Sauer, *ibid.*, **71**, 3925 (1949).

(7) Gas phase chromatography.

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(9) G. H. Coleman and H. F. Johnstone, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., H. Gilman, Ed., 1941, p. 183.

BISACRYLONITRILE NICKEL BISTRIPHENYLPHOSPHINE[1]

Sir:

In a recent paper[2] the discovery of a new class of highly reactive π-complexes of nickel with α-substituted olefins was described and exemplified for bisacrylonitrile nickel, $Ni(CH_2{=}CH{-}CN)_2$ (I). Due to extensive changes in the vinyl region and the presence of one practically unchanged nitrile band in the infrared spectrum of I[3] a structure was proposed in which the π-electrons of the double bond of the two acrylonitrile molecules were assumed to take part in the bonding, thus leading to the unusual coördination number of two for a zerovalent nickel complex. The nature of bonding between the metal and the olefinic ligand can be understood by applying the view of bonding of ethylene to a transition metal by Dewar[4] and Chatt.[5] Whereas vinylogs with electron donating α-substituents are not suitable as ligands, a sufficient bond stabilization is attained through the introduction of the strongly electronegative nitrile group. The effect of this substituent can be seen in that it lowers the energy levels of the antibonding π*-orbitals of the olefinic double bonds and thus facilitates the back-donation of electrons from the nickel atom. The combined effects of electron-donation to and back-donation from the nickel atom may lead to a rehybridization at the carbon atoms and thus to metal–carbon bonds with partial σ-character. In this respect the conditions of bond formation appear to be similar to a recently prepared bis-tetrafluoroethylene complex of iron carbonyl.[6] A zerovalent nickel complex with the coördination number of two would involve a $3d^{6}4sp$ configuration. A necessary requirement for such an electron distribution would be the possibility of filling the two empty 4 p orbitals with the electron pairs of two additional ligands to produce the stable sp^3 configuration. The catalytic activity of I in part can be attributed to this unusual coördinative unsaturation. So far, however, only a 1:1 triphenylphosphine adduct of I was isolated.[2] The preparation of a bistriphenylphosphine adduct of I now has been successful through reaction of I with excess of triphenylphosphine in diethyl ether in a specially designed apparatus in which all necessary operations were performed under exclusion of of oxygen. After filtration of the reaction solu-

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(1) Paper II on Bisacrylonitrile Nickel and Related Complexes.

(2) G. N. Schrauzer, THIS JOURNAL, **81**, 5310 (1959).

(3) A detailed description of the infrared spectra of I and related complexes in both the NaCl and CsBr region is in preparation.

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