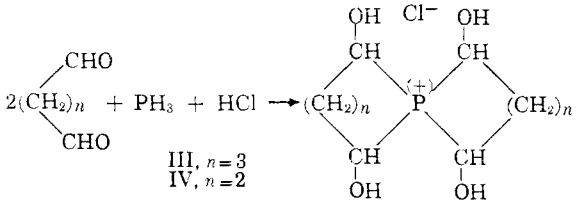
Presumably, these substances are formed rather than the phosphonium derivatives obtained from unbranched aldehydes because of steric hindrance toward further phosphine-aldehyde reaction in the disubstituted intermediates, $(R_1R_2CHOH)_2PH$.

We have also found that the phosphine-aldehyde reaction can be adapted to the preparation of spirophosphonium salts if suitable dialdehydes are employed. The application of this reaction to the preparation of simple heterocycles is obvious. A single spirocyclic phosphonium derivative has



been reported previously and required eleven steps in its preparation.[5] The stereochemical features of the spiranes reported here are interesting, and are being studied further.

The reaction of phosphine with isobutyraldehyde gave a 75% yield of 2,4,6-triisopropyl-1,3-dioxa-5-phosphacyclohexane (I), b.p. 110° (14 mm.), $n^{25}D$ 1.4602. Found: C, 61.82; H, 10.78; P, 13.26. Reaction with 2-ethylhexaldehyde gave a 90% yield of 2,4,6-(3-heptyl)-1,3-dioxa-5-phosphacyclohexane (II), b.p. 149–150° (0.02 mm.), $n^{24}D$ 1.4709. Found: C, 71.87; H, 12.35; P, 7.57. Glutaraldehyde gave a 65% yield of 1,5,7,11-tetrahydroxy-6-phosphazoniaspiro[5.5]undecane chloride (III), m.p. 167–168°. Found: C, 44.51; H, 7.55; Cl, 13.07; P, 11.58. Succinaldehyde[6] gave a 34% yield of 1,4,6,9-tetrahydroxy-5-phosphazoniaspiro[4.4]nonane chloride, m.p. 94–95°. Found: C, 39.49; H, 6.55; Cl, 14.65; P, 12.85; mol. wt., 92.0 (cryoscopic in water). These reactions were carried out by simultaneous addition of the aldehyde[6] and phosphine to a mixture of concentrated hydrochloric acid and tetrahydrofuran at room temperature. The derivatives I and II separated from the reaction mixture as upper phases.

Treatment of I with air in 2-propanol gave 2,4,6-triisopropyl - 1,3 - dioxa - 5 - phosphacyclohexane-5-inoic acid (59%), m.p. 159–160°. Found: C, 54.51; H, 9.44; P, 11.95; neut. equiv., 268.1. Hydrolysis of the acetal linkage in this phosphinic acid gave isobutyraldehyde (92%) and bis-(1-hydroxy-2-methylpropyl)-phosphinic acid (100%), m.p. 168–169°. Found: C, 45.78; H, 9.18; P, 14.73. Reaction of I with *p*-chlorophenylisocyanate in benzene solution catalyzed with triethylamine led to the formation of 5-(*p*-chlorophenylcarbamoyl) - 2,4,6 - triisopropyl - 1,3 - dioxa - 5 - phosphacyclohexane (42%), m.p. 162–163°. Found: C, 58.88; H, 7.89; P, 8.14.

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RECEIVED NOVEMBER 3, 1958

(5) F. A. Hart and F. G. Mann, *J. Chem. Soc.*, 4107 (1955).

(6) Succinaldehyde was added in the form of its acetal, 2,5-diethoxytetrahydrofuran.

MECHANISM OF ETHYLENE POLYMERIZATION WITH VANADIUM CATALYSTS

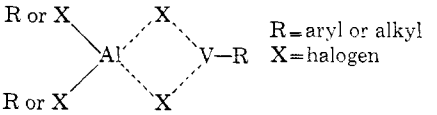
Sir:

In contrast to the usual heterogeneous, low-pressure catalysts, hydrocarbon soluble ethylene polymerization catalysts are formed by mixing aluminum bromide, an organoaluminum compound, and a hydrocarbon soluble vanadium halide. Thus, addition of 0.05 millimole of vanadium tetrachloride to a solution of 3 millimoles aluminum bromide, and 1 millimole of triphenylaluminum (or triisobutylaluminum) in 1 liter of cyclohexane formed a clear, pink solution. The subsequent addition of ethylene at 60° and atmospheric pressure gave 20–25 g. of polyethylene in 30 minutes. This polyethylene is linear (<1 CH_3—/1000 carbons), and highly saturated (<1 C=C/5000 carbons), with a melt index of 0.01.

The inorganic components of the pink solution were extracted into *N* sulfuric acid, and the vanadium was shown to be exclusively divalent by polarographic analysis.[1] In this catalyst the vanadium is reduced completely in less than one minute. By incremental addition of the vanadium halide to a cyclohexane solution, that is *M* in aluminum compounds ($3AlBr_3$ to $1AlR_3$), 0.05–0.1 *M* solutions of the soluble divalent vanadium species can be obtained. These solutions are very stable, retaining catalytic activity after months of storage in the absence of air and moisture.

Significantly, VCl_2 and VBr_2 are not cyclohexane soluble and are not catalysts for the low pressure polymerization of ethylene. Both compounds dissolve in a cyclohexane solution of aluminum bromide, but the resulting solutions are not catalytically active. Addition of an aluminum aryl or alkyl to these solutions provides the initiator and forms the active catalyst.

The solubility of the active catalyst, and of the divalent vanadium halides in an aluminum bromide solution in cyclohexane demonstrates complex formation between the aluminum and vanadium molecules. The active complex probably has the halogen bridged structure



found in the alkyl aluminum halide dimers,[2] and in the complex formed from triethylaluminum and bis-(cyclopentadienyl)-titanium dichloride.[3] Complexes of this type derive their stability from the Lewis acid character of the molecules and should be disrupted by Lewis bases. Addition of diethyl ether to the catalyst solution did, indeed, destroy it and the vanadium was precipitated as vanadium dibromide. Since the vanadium was added to the solution as the chloride (VCl_4) and later isolated as the bromide (VBr_2) the transfer of groups between aluminum and vanadium must take place very readily, and the species which precipitates is the *least soluble* of the possible divalent vanadium compounds.

(1) J. J. Lingane, THIS JOURNAL, **67**, 182 (1945).

(2) L. O. Brockway and N. R. Davidson, *ibid.*, **63**, 3287 (1941).

(3) G. Natta, P. Corradini and I. W. Bassi, *ibid.*, **80**, 755 (1958).

It is unlikely that the aluminum end of the aluminum–vanadium complex is the catalytically active site since this portion is structurally identical to one end of an alkyl aluminum halide dimer, and these compounds are not low pressure polymerization catalysts. The polymer molecule is believed to grow from the vanadium center by a two-step process[4,5] of coördination of the ethylene with a vacant orbital of the vanadium species followed by a rearrangement to give net addition of the V–R bond across the ethylene double bond. The function of the aluminum alkyl is to reduce the vanadium to the divalent state and alkylate it to form the active species (RVX). By formation of a complex, the aluminum bromide (or $RAlX_2$) dissolves the active species, stabilizes it, and prevents further reduction of the vanadium.

(4) D. B. Ludlum, A. W. Anderson and C. E. Ashby, THIS JOURNAL, **80**, 1380 (1958).

(5) W. L. Carrick, W. T. Reichle, R. W. Kluiber, E. F. Bonner, and J. J. Smith, Paper No. 47, Polymer Division, 133rd Meeting of the American Chemical Society, San Francisco, California.

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RECEIVED AUGUST 28, 1958

EFFECTS OF DIAMINES ON THE PROTOPLAST-INFECTING AGENT DERIVED FROM T2 BACTERIOPHAGE

Sir:

Hershey[1] has reported the presence in T2 bacteriophage of two low molecular weight, ninhydrin-positive components derived biosynthetically from arginine, and associated with the deoxyribonucleic acid (DNA) of the virus in the process of infection of cells of *Escherichia coli*. Ames, *et al.*,[2] have identified these two components as putrescine (tetramethylenediamine) and spermidine (H_2N-$(CH_2)_4NH(CH_2)_3NH_2$). We now wish to report that the probable function of these amines is the preservation of the bacteriophage DNA in an infective conformation. The basis for this hypothesis is found in experiments with the protoplast-infecting agent (π)[3] (Table I): (1) heating at 72.5° destroys π very rapidly; (2) certain preparations of π show marked inactivation with dilution in 0.10 or 0.15 *M* NaCl; (3) repeated freezing and thawing of π renders it much more labile to subsequent heat inactivation.

TABLE I

PROTECTIVE EFFECTS OF CADAVERINE

Retention, % of infectivity after treatment	Treatment: Dilution 64-fold	Heat Treatment 72.5°/5 min.	Heat Treatment 67.5°/1.5 min.	Heat treatment 67.5°/1.5 min. after 10 × freezing-thawing In saline	Heat treatment 67.5°/1.5 min. after 10 × freezing-thawing In 0.01 *M* cadaverine
In 0.15 *M* saline	<2.0	<0.04	6.0	0.19	1.6
Same plus 0.01 *M* cadaverine	100	88	85	12	56

(1) A. D. Hershey, *Virology*, **4**, 237 (1957).

(2) B. Ames, D. T. Dubin and S. M. Rosenthal, *Science*, **127**, 814 (1958).

(3) D. Fraser, H. R. Mahler, A. L. Shug and C. A. Thomas, *Proc. Natl. Acad. Sci.*, **43**, 939 (1957).

Certain polymethylene diamines of the general structure H_2N-$(CH_2)n$-NH_2 as well as spermidine protect π against all of these effects to a remarkable degree; maximum protective action is exerted by cadaverine (n = 5). A reasonable model for the cadaverine dihydrochloride molecule (the species present at *p*H 5.5) leads to an N–N distance of 7.30 Å. The distance between phosphate oxygens in the revised DNA structure proposed by Wilkins[4] is 7.65 Å.

All experiments performed at the temperature indicated, in 0.15 *M* NaCl (plus cadaverine where indicated) at a *p*H of 5.5. The π preparation was diluted 1:20 into the incubation tube and samples were withdrawn at 30-second intervals, and diluted 1:20 into chilled 0.15 *M* NaCl kept at 0°. They were then assayed for infectivity in our standard system.[3]

(4) *Cf.* drawing by J. C. Kendrew, and M. F. Perutz, in *Ann. Rev. Biochem.*, **26**, 340 (1957); also R. Langridge, W. E. Seeds, H. R. Wilson, C. W. Hooper, M. H. F. Wilkins and L. D. Hamilton, *J. Biophys. Biochem. Cytol.*, **3**, 767 (1957).

(5) Supported by Grant No. E-1854 from the Institute of Microbiology and Immunology of the National Institutes of Health.

(6) Contribution No. 867.

DEPARTMENT OF BACTERIOLOGY DEAN FRASER[5]
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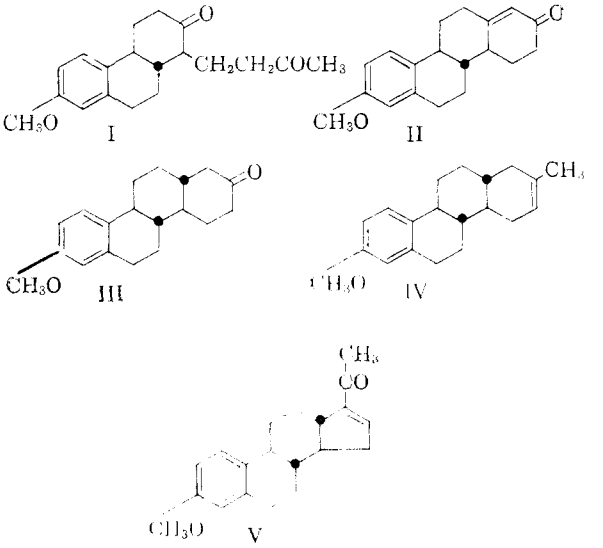
RECEIVED OCT. 22, 1958

SYNTHESIS OF 18,19-DINOR STEROIDS

Sir:

A practicable route from natural steroids to 18,19-dinor steroids, including the estrone, testosterone, progesterone, and desoxycorticosterone analogs, has been achieved and is reported here.

Boric acid-catalyzed rearrangement of estradiol 3-methyl ether[1] followed by ozonolysis of the resulting olefin produced the diketone I, m.p. 119–120°; $[\alpha]D$ +98°; (*Anal.* Found: C, 76.14; H,



(1) Personal communication from Dr. D. A. Taylor of these laboratories.