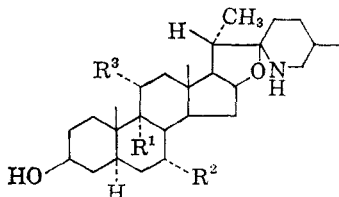


manganese dioxide in chloroform at room temperature. Although the molecular rotation data is suggestive of a 7β configuration (ΔM_D , $+114^\circ$),¹⁰ a definite assignment awaits further study.

In contrast to solasodine, the incubation of tomatidine (VII) ($R^1, R^2, R^3 = H$) with *Helicostylum piriforme* affords a preponderant amount of the diol, $7\alpha,11\alpha$ -dihydroxytomatidine (VIII) ($R^1 = H; R^2, R^3 = OH$) m.p. $266-270^\circ$ dec., $[\alpha]_D^{20} +23^\circ$ (ethanol) (found: C, 72.42; H, 10.43) (yield ca. 20%); a lesser amount of the monohydroxy compound, 7α -hydroxytomatidine (IX) ($R^1, R^3 = H; R^2 = OH$) m.p. $238-242^\circ$ dec., $[\alpha]_D^{20} -3.5^\circ$ (chloroform) (found: C, 75.22; H, 10.68) (yield ca. 5%), and a third component (X) ($R^2, R^3 = H; R^1 = OH$) m.p. $188-191^\circ$ (found: C, 74.50; H, 11.02) (yield ca. 0.5%) to which we tentatively ascribe a 9α -hydroxytomatidine structure. The assignment of a $7\alpha,11\alpha$ -diol formulation to VIII was based on the degradation of VIII into the known allopregnane-3,11,20-trione¹¹ and allopreg-



- VII. ($R^1, R^2, R^3 = H$)
 VIII. ($R^1 = H; R^2, R^3 = OH$)
 IX. ($R^1, R^3 = H; R^2 = OH$)
 X. ($R^2, R^3 = H; R^1 = OH$)

nane-3,7,11,20-tetrone.¹² The 7-hydroxylic function is apparently easily removed during the degradation. The assignment of α -configurations to both the 7- and 11-hydroxyl moieties was based on the conversion of the intermediate 3,7,11-trihydroxy-20-one derivative into $7\alpha,11\alpha$ -dihydroxyallopregnane-3,20-dione, whose structure has been fully elucidated.¹³ The structure of IX was determined by its degradative conversion into the known 3β -acetoxyallopregnane-7,20-dione.¹⁴ Molecular rotation data (ΔM_D , -39°) and the fact that IX only partially acetylates under normal acetylating conditions support the assignment of the 7α -configuration. Compound X acetylates to yield only the 3β -*O,N*-diacetyl derivative. In view of the tertiary nature of the second hydroxyl moiety, reminiscent of its solasodine counterpart, II, the 9α position is tentatively assigned to substance X. The homogeneity of all of the hydroxylated com-

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pounds was tested by paper and gas chromatography.¹⁵

It is of some interest to note that 7α -hydroxylation in the steroids of the C-5 allo series is an unique occurrence. The hydroxylation of these steroidal alkaloids enhances their usefulness as starting material for the preparation of biologically active hormones. The fungus, *Helicostylum piriforme*, is capable of transforming other steroidal alkaloids (e.g., solanidine). Further work along these lines is being pursued.

NATIONAL INSTITUTES OF ARTHRITIS
 AND METABOLIC DISEASES
 NATIONAL INSTITUTES OF HEALTH
 BETHESDA, MD.

Y. SATO
 S. HAYAKAWA¹⁶

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(16) Visiting Scientist, National Institutes of Health.

A New Reaction for Forming Carbon-Phosphorus Bonds

Sir:

We wish to report a new general method for forming carbon-phosphorus bonds by adding phosphorus trichloride to an olefin in the presence of aluminum chloride. The reaction is quite general and has been applied to various types of olefins, including highly branched structures such as trimethylpentene, propylene trimers, tetramers, and hexamers, α -olefins and olefins with centrally located double bonds such as methyl oleate and tricosene.

Previous reports on the formation of carbon-phosphorus bonded compounds from aliphatic olefins are limited to such examples as Kharasch's free radical-catalyzed addition of phosphorus trichloride,¹ the addition of phosphorus pentachloride to primary olefins to yield unsaturated phosphonic acids,² the free radical-catalyzed addition of dialkyl phosphites,^{3,4} or Willstaetter's oxidative phosphorylation.^{5,6}

The reaction is carried out at ordinary temperatures in a solvent such as methylene chloride, using one mole of phosphorus trichloride and one mole of

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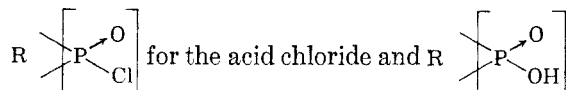
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aluminum chloride per olefinic bond. When a functional group which complexes with aluminum chloride is also present, such as the carboxylate group in methyl oleate, an additional mole of aluminum chloride must be used. The intermediate complex is decomposed with aqueous methanol, and the product is isolated from methylene chloride solution after drying with sodium sulfate.

The reaction products thus obtained contain one atom of phosphorus per (original) double bond; stability to hydrolysis and failure to observe P—O—C bonding in the 10- μ region of the infrared indicate that the phosphorus is bonded directly to carbon. Absorption at 8 μ , however, confirms the presence of the P \rightarrow O group. Loss of unsaturation, indicated by infrared analysis and iodine value determination, suggests that the reaction occurs at the double bond.

The products isolated as described above contain varying amounts of chlorine, up to one chlorine per double bond, depending on the structure of the starting olefin. This chlorine is labile and the chlorides are readily hydrolyzed to monobasic phosphorus-containing acids. Elemental analyses indicate the formula



for the acid. While the exact attachment of the phosphorus to the carbon skeleton has not been established completely at this time, it is apparent that to fulfill the natural valence requirements of phosphorus, the products must be either polymeric, cyclic, or have a P—H bond. The first possibility was eliminated, since ebullioscopic molecular weight determinations of the acid and the methyl ester from 2,4,4-trimethyl-2-pentene indicated monomeric structures with some association. The other possibility, presence of a P—H bond, was eliminated because of the stability of the compound to oxidation with bromine and the absence of supporting NMR and infrared data. A detailed report on the structure of the product obtained from 2,4,4-trimethyl-2-pentene will be the subject of a forthcoming publication.

Some typical examples are given below:

2,4,4-Trimethyl-2-pentene yielded a crystalline material, (I), m.p. 74–75°. [Anal. Calcd. for C₈H₁₆POCl: C, 49.36; H, 8.29; P, 15.92; Cl, 18.22. Found: C, 49.80; H, 8.45; P, 15.90; Cl, 18.20]. The compound (I) is readily hydrolyzed to a monobasic acid (II), m.p. 75–76°. [Anal. Calcd. for C₈H₁₆PO₂H: C, 54.53; H, 9.73; P, 17.58; neut. equiv., 176.2; mol. wt., 176.2. Found: C, 54.89; H, 9.72; P, 16.07; neut. equiv., 176.0; *pK* 2.85; mol. wt. (ebullioscopic in acetone),

302, indicating ca. 50% association.] Reaction of I with sodium methoxide yields the methyl ester, m.p. 35–36°, b.p. 78°/0.7 mm. [Anal. Calcd. for C₈H₁₆PO₂CH₃: sap. equiv., 190.2; mol. wt. 190.2; Found: sap. equiv., 190.6; mol. wt. (ebullioscopic in acetone), 201.] Reaction of II with thionyl chloride regenerates the acid chloride (I).

A commercial nonene (a propylene trimer) gave an oil with the following analysis: Calcd. for C₉H₁₈POCl: P, 14.9; Cl, 17.0. Found: P, 13.9; Cl, 15.3. Hydrolysis yielded a chlorine free acid. (Anal. Calcd. for C₉H₁₈PO₂H: neut. equiv., 190.6; Found: neut. equiv., 210.) Methyl oleate yielded an oil with the following analysis: Calcd. for C₁₉H₃₆PO₂Cl: P, 8.6; Cl, 9.4; sap. equiv., 189; Found: P, 8.3; Cl, 3.6; sap. equiv., 210. The low value for chlorine indicates that extensive hydrolysis of the acid chloride occurs during decomposition of the complex.

The above constitute the first reported examples of the addition of phosphorus trichloride to olefins under ionic conditions and obviously differ from the well known Friedel-Craft reaction between aromatic compounds and phosphorus trichloride. In the latter case, a dibasic acid results on hydrolysis, and the aromatic character of the molecule is not affected; on the other hand, in the reaction with olefins, saturated monobasic acids are formed.

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ARMOUR AND Co.
SOAP RESEARCH DEPARTMENT
1355 WEST 31ST ST.
CHICAGO 9, ILL.

ERIC JUNGERMANN

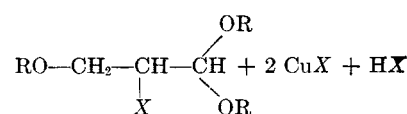
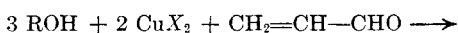
ARMOUR INDUSTRIAL CHEMICAL Co.
RESEARCH LABORATORY
MCCOOK, ILL. JOSEPH J. MCBRIDE, JR.

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Halogenation of Unsaturated Aldehydes with Cupric Halides

Sir:

In the course of another investigation, α,β -unsaturated aldehydes have been found to reduce cupric to cuprous halides in alcoholic media.¹ The reaction provides a convenient route to β -alkoxy- α -haloaldehydes or their acetals.



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