comparison of their spectra and physical properties with authentic samples.

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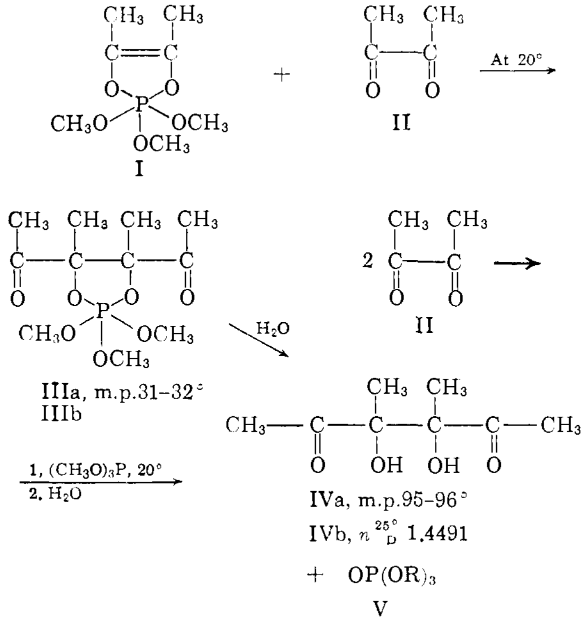
A CYCLIC SATURATED PENTAALKOXYPHOSPHORANE. DIKETOLS *VIA* OXYPHOSPHORANES[1]

Sir:

We have discovered a new property of some *cyclic unsaturated oxyphosphoranes*,[2] such as I, which makes possible a very mild and selective pinacolic reduction of certain aliphatic dicarbonyl compounds to diketols, for instance IV. We have also obtained evidence for the existence of stable *cyclic saturated oxyphosphoranes* of type III, a point which is of interest in connection with the pentacovalency of phosphorus.



I

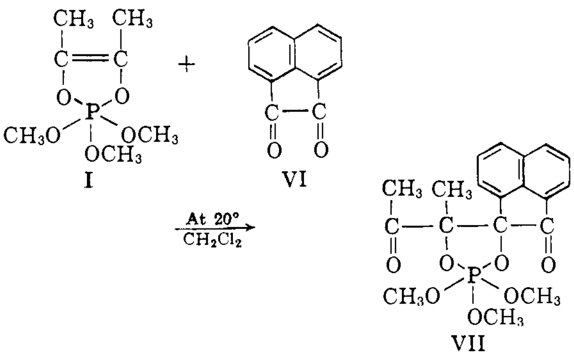
II

IIIa, m.p.31-32°
IIIb

IVa, m.p.95-96°
IVb, $n^{25°}_D$ 1.4491

+ OP(OR)$_3$
V

We wish to report also the preparation of a crystalline adduct, VII, which contains an aliphatic and an aromatic α-diketone in conjunction with a trialkyl phosphite. Adduct VII resembles the 2:1 acenaphthenequinone–trimethyl phosphite adduct recently reported by us.[3]



I

VI

VII

Biacetyl (74 g.) was added dropwise to trimethyl phosphite (135 g.), under nitrogen, with stirring and cooling. The mixture was kept at 60° for 15 min. and then distilled. The colorless 1:1 adduct I was collected at 45–47° (0.5 mm.) and had $n^{25°}_D$ 1.4387, d^{25} 1.166 g./cc.; the yield was quantitative. The *1:1 adduct* I (18.3 g.) and the biacetyl II (22.5 g., 1:3 mole-ratio) were allowed to react at 20° for 48 hours under nitrogen, with stirring. The excess biacetyl was recovered by distillation, and the mixture of diastereomeric 2:1 adducts, IIIA and IIIB (22.7 g., n^{25}_D 1.4470) was collected at 65–75° (*ca.* 0.1 mm.). Redistillation gave a colorless, viscous oil n^{25}_D 1.4471; strong bands at 5.80, 5.82 (shoulder), 9.22–9.30, 9.13 (shoulder) μ in CCl_4; calcd. for $C_{11}H_{21}O_7P$: C, 44.6; H, 7.1; P, 10.4; found: C, 44.6; H, 7.1; P, 10.6. The P^{31} n.m.r. spectrum[4] had a line at +51 ± 2 p.p.m. *vs.* 85% H_3PO_4 as external reference.

The mixture of 2:1 adducts, IIIA and IIIB, (66.8 g.) was dissolved in benzene (350 ml.). Water (*ca.* 12 ml.) was added and a very vigorous reaction was initiated by careful heating. The solution was maintained 1 hour at reflux temperature, and the aqueous layer was separated, saturated with salt and extracted with benzene. The combined benzene solutions gave a mixture of diastereomeric diketols IVA and IVB. One recrystallization from hexane afforded isomer IVA, m.p. 95–96° in 63% yield. Isomer IVB, b.p. 30–32° (0.2 mm.), n^{25}_D 1.4491 was obtained in 25% yield by distillation of the hexane filtrate. Calcd. for $C_8H_{14}O_4$: C, 55.2; H, 8.1. Found for IVA: C, 54.6; H, 8.2; for IVB: C, 55.7; H, 8.2. Both IVA and IVB had bands at 2.9 (OH), 5.88 (CO) and 7.3 and 8.8 (tertiary alcohol) μ (in CCl_4), but the spectra were not identical. Both isomers gave bis-2,4-dinitrophenylhydrazones. Cold, dilute alkali readily cleaved IVA and IVB to mixtures which gave comparable amounts of biacetyl-2,4-dinitrophenylosazone.

The 1:1 adduct I need not be isolated in the preparation of the 2:1 adducts: biacetyl (137.8 g.) was added, dropwise, *to* trimethyl phosphite (49.6 g., 4:1 mole-ratio); and the mixture was stirred for 5 days at 20°. Distillation gave 118.2 g. of the mixture of isomers, IIIA and IIIB, which partly crystallized at 0°. Pentane (35 ml.) was added and the solution kept 48 hr. at 0°. The solution was decanted from the resulting crystals, which were redissolved in pentane (25 ml.). Cooling afforded 53.5 g. (45% yield) of pure oxyphosphorane IIIA, m.p. 30–32°. Analytical sample: m p.

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(1) These investigations are being supported by the Cancer Institute of the National Institutes of Health (Grant CY-4769); the Petroleum Research Fund Administered by the American Chemical Society (Grant 286-A) and the National Science Foundation.

(2) (a) F. Ramirez and N. B. Desai, *J. Am. Chem. Soc.*, **82**, 2652 (1960). (b) The structure suggested for the 1:1 biacetyl-trialkyl phosphite adducts by Kukhtin and Orekhova [*Zhur. Obshchei Khim.*, **30**, 1208 (1960); *J. Gen. Chem., U.S.S.R.*, **30**, 1229 (1960); *C. A.*, **55**, 358i (1961)] is untenable. The *pure* 1:1 biacetyl-trimethylphosphite adduct I lacks a strong carbonyl absorption in the infrared. Furthermore, the pure liquid I, undisturbed by solvent or internal standard, has only *three lines* in the proton n.m.r. spectrum. These are at +3.08, +3.31 and +4.98 p.p.m. to high field of external benzene as reference. Two of these lines are due to the protons of the methoxy groups attached to phosphorus (J = 13 c.p.s.).

(3) F. Ramirez and N. Ramanathan, *J. Org. Chem.*, **26**, 3041 (1961).

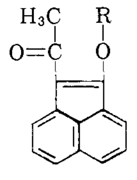
(4) Obtained through the courtesy of Dr. J. Lancaster of the American Cyanamid Company, Stamford Connecticut.

31–32° (pentane); split carbonyl at 5.80 and 5.83μ and the strong band at 9.22–9.30 μ (CCl_4); Found: C, 44.4; H, 7.5; P, 9.8; mol. wt., 297 (calcd. 296). Hydrolysis of crystalline oxyphosphorane IIIA gave crystalline diketol IVA, exclusively (over 95% yield of recrystallized IVA).

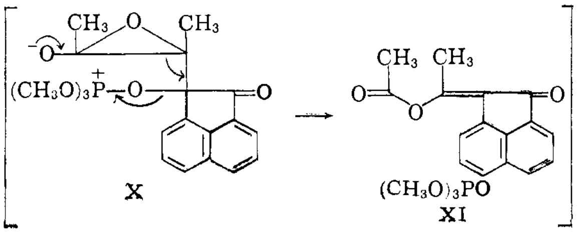
The pentaalkoxyphosphorane structure III is based mainly on a comparison with the unsaturated oxyphosphorane I. (1) The large P^{31} n.m.r. shifts to high field of the phosphoric acid reference (+ 51 for III and + 53 p.p.m. for I) suggest comparatively large shielding of the phosphorus nucleus in III and I, inconsistent with the phosphonium group of open dipolar structures. It should be noted that the dipolar structure of I should show strong carbonyl absorption in the infrared, contrary to our observations[2] with pure 1:1 adduct I. (2) The infrared absorption in the CH_3OP region is very similar in III and I (as well as in VII): there is a very strong and broad band at 9.2–9.35 μ, which is considerably lower than the normal methyl phosphate ester absorption.

The 1:1 adduct I (10.1 g.) and acenaphthenequinone VI (8.7 g.) were allowed to react for 10 hours at 20° in methylene chloride (750 ml.), under nitrogen. The solvent was removed *in vacuo*, the crystalline residue was dissolved in carbon tetrachloride (200 ml.); 0.54 g. of naphthalic anhydride was filtered-off. Evaporation *in vacuo* gave 18 g. of crystalline 2:1 adduct VII. After recrystallization from cyclohexane, VII had m.p. 95–96°; strong bands at 5.76, 5.80 (shoulder), 9.22–9.30 μ (CCl_4). Calcd. for $C_{19}H_{21}O_7P$: C, 58.2; H, 5.4; P, 7.9. Found: C, 58.1; H, 5.0; P, 7.9. VII and III were sensitive to moisture.

When a solution of the 2:1 adduct VII in methanol was heated for 30 minutes, a rearrangement occurred. Three products were isolated: trimethyl phosphate, methyl acetate and 1-acetyl-2-acenaphthenone (75% yield based on acenaphthenequinone VI) written as the probable enol VIII. VIII is yellow, m.p. 112–113° (methanol); bands at 6.05 and 6.20μ (CH_2Cl_2); calcd. for $C_{14}H_{10}O_2$: C, 80.0; H, 4.8; found: C, 79.4; H, 4.9. VIII gives a yellow methyl ether IX (with diazomethane); m.p. 150–151° (methanol); bands at 5.92 and 6.20 μ (CH_2Cl_2); calcd. for $C_{15}H_{12}O_2$: C, 80.3; H, 5.4; found: C, 80.1, H, 5.2. The β-diketone VIII was cleaved to acenaphthenone by dilute alkali.



VIII, R=H
IX, R=CH3



X

XI

A possible mechanism[5] for the rearrangement of the 2:1 adduct VII to an enol-acetate XI, with concomitant *ejection of phosphate ester*, is indicated in formula X. The β-diketone VIII and methyl acetate would result from the enol-acetate XI and methanol by a transesterification.

[5] H. F. von Pechmann, *Ber.*, **21**, 1421 (1888). Our experience with the Zn–H_2SO_4 reduction of biacetyl will be described elsewhere.

[6] Alfred P. Sloan Fellow, 1961–1963.

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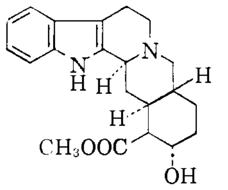
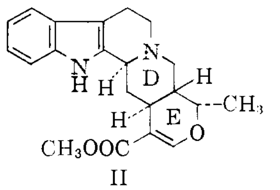
THE CONVERSION OF TETRAHYDRO-β-CARBOLINE ALKALOIDS INTO OXINDOLES. THE STRUCTURES AND PARTIAL SYNTHESES OF MITRAPHYLLINE AND RHYNCOPHYLLINE[1]

Sir:

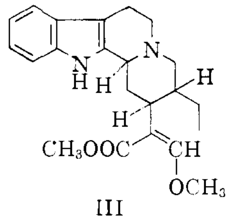
The relationship between indole and oxindole alkaloids often has been discussed.[2]



I



II



III

Conversion of certain oxindole alkaloids into known indole alkaloids or *vice versa* would enable the detailed stereochemistry of the former to be elucidated. We now wish to report the conversion of yohimbine (I) into its oxindole and the preparation of mitraphylline and rhyncophylline from ajmalicine[3] (II) and dihydrocorynantheine (III), respectively.

Yohimbine (I) was transformed into a 50:50 mixture of epimeric C_7 chloroindolenines (γ_{max} 1710 cm.$^{-1}$, 1595 cm.$^{-1}$, no NH; λ_{max} 282 mμ) by the action of tertiary butyl hypochlorite.[4] Meth-

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[1] Presented at the New York, North Jersey Meeting-in-Miniature, New York, January 22, 1962.

[2] (a) B. Witkop, *Bull. Soc. Chim. France*, 423 (1954); (b) E. E. van Tamelen, K. V. Siebrasse and J. B. Hester, *Chem. and Ind.*, 1145, (1956); (c) T. Nozoye, *Chem. Pharm. Bull.*, **6**, 300, (1958); (d) E. Wenkert, J. H. Udelhofen, and N. K. Bhattacharya, *J. Am. Chem. Soc.*, **81**, 3863 (1959).

[3] The conversion of ajmalicine into mitraphylline has also been accomplished by J. Shavel and H. Zinnes, *ibid.*, **84**, 1320 (1962).

[4] W. O. Godtfredson and S. Vangedal, *Acta. Chem. Scand.*, **10**, 1414 (1956), employed this reagent to prepare Δ^3 compounds of the yohimbine class. Only deserpidine yielded a crystalline isolatable chloro compound, which was assigned an incorrect structure. Our observations provide proof of the 7-chloroindolenine structure proposed by J. E. Saxton (R. H. Manske, "The Alkaloids," Vol. VII,