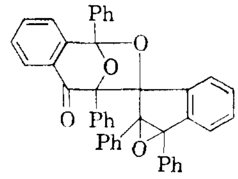
With the structures of IV and, by analogy, III thus established, there was little doubt that the colored species produced on heating of I must be the pyrylium oxide II, and indeed the appearance of a strong new band in the infrared of the colored species at 6.37 $\mu$ (benzene) attributable to an enolate grouping provided strong support for this conclusion. On the other hand, the decolorization reaction could not necessarily be assumed to lead to the regeneration of I, since an irreversible conversion of II to other colorless products could also produce apparent thermochromic behavior. Clarification of this point was provided by the recovery of unchanged I after heating in benzene at 150° under conditions which led to its complete disappearance *via* II when bicyclo[2,2,1]heptadiene was used as solvent. Hence, the rate of disappearance of I is lower than the rate of its conversion to II, and therefore *the pyrylium oxide II must be reconverted to its valence tautomer I.*

In addition to recovered starting material, a dimer was also isolated after heating I in benzene. The new compound reacted readily with a 0.5 *N* solution of hydrochloric acid in moist acetonitrile at 25° to give a monohydrated derivative, $C_{42}H_{30}O_5$. Like I, the dimer was also thermochromic, the same colored species arising as shown by the reaction of the dimer with excess dimethyl acetylenedicarboxylate at 190–200° to give two equivalents (82% yield) of the adduct IV which had previously been isolated from the reaction with I itself. Based on its acid lability, a single infrared carbonyl peak at 5.86 $\mu$, and an ultraviolet spectrum which was very similar to that of III in both peak positions and extinction coefficients, the dimer is tentatively assigned structure VI.



VI

Additional evidence concerning the structure and stereochemistry of this product, and a further elaboration of the chemistry of I and related compounds will be presented in a future publication.

AMERICAN CYANAMID COMPANY
CENTRAL RESEARCH DIVISION EDWIN F. ULLMAN
CHEMICAL RESEARCH DEPARTMENT
STAMFORD, CONNECTICUT J. E. MILKS

RECEIVED MARCH 3, 1962

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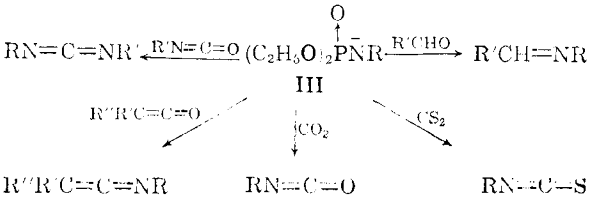
## PHOSPHORAMIDATE ANIONS: THE PREPARATION OF CARBODIIMIDES, KETENIMINES AND ISOTHIOCYANATES

*Sir:*

The investigation of the utility of dialkyl phosphonate carbanions in olefin synthesis[1] prompted examination of their nitrogen analogs in comparable reactions. We have found the behavior of dialkyl phosphoramidate anions (III) toward carbonyl compounds to be similar to phosphinimines[2] (I) and phosphorimidates[3] (II). The anion (III), prepared by reaction of sodium hydride with the phosphoramidate in dimethoxyethane, reacts smoothly with isocyanates, ketones, carbon dioxide, carbon disulfide and aldehydes to form, respectively, carbodiimides, ketenimines, isocyanates, isothiocyanates, and imines. Since (in contrast to I and II) the phosphoramidates are readily available,[4] this synthesis is the basis of convenient laboratory procedures for preparation of unsaturated nitrogen compounds.

$$\underset{\text{I}}{R_3P{=}NR} \qquad \underset{\text{II}}{(RO)_3P{=}NR}$$



The addition of phenyl isocyanate to III (R = $C_6H_{11}$) in 1,2-dimethoxyethane gave, at room temperature, a precipitate of sodium diethyl phosphate and after distillation of the mother liquor, a 60% yield of N-phenyl-N'-cyclohexyl carbodiimide,[5] b.p. 116–120 (0.35 mm.). Its infrared spectrum showed characteristic carbodiimide absorption at 2150 cm.$^{-1}$ [6] Conversion to N-phenyl-N'-cyclohexyl urea[7] was accomplished by stirring with dilute HCl.

Treatment of III (R = $C_6H_{11}$) with phenylethylketene gave a 58% yield of phenylethylketenecyclohexylimine (R = $C_6H_{11}$, R' = $C_2H_5$, R'' = $C_6H_5$), b.p. 122–124° (0.5 mm.) (*Anal.* Calcd. for $C_{16}H_{21}N$: C, 84.53; H, 9.25; N, 6.17. Found: C, 84.36; H, 9.28; N, 5.95). The ketenimine structure was confirmed by its strong absorption at 2000 cm.$^{-1}$.[8] Treatment with dilute HCl gave N-cyclohexyl-$\alpha$-phenylbutyramide. The structure of the amide was confirmed by comparing it to an authentic sample prepared from $\alpha$-phenylbutyryl chloride and cyclohexylamine.

Passage of $CO_2$ through a solution of I (R = $C_6H_{11}$) gave two products, cyclohexyl isocyanate (24%), b.p. 70–71°(15 mm.) and dicyclohexylcarbodiimide (53%), b.p. 100–102° (0.75 mm.). The isocyanate is undoubtedly a precursor of the carbodiimide. Addition of carbon disulfide to III (R = *n*-$C_4H_9$) gave *n*-butyl isothiocyanate (75%), b.p. 169–170°. Finally, the treatment of III (R = $CH_3O$) with benzaldehyde produced *o*-methylbenzaldoxime[9] (82%), b.p. 90° (15 mm.). The structures of these materials were verified by

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(1) W. S. Wadsworth, Jr., and W. D. Emmons, *J. Am. Chem. Soc.*, **83**, 1733 (1961).

(2) H. Staudinger and E. Hauser, *Helvetica Chimica Acta.*, **4**, 861 (1921).

(3) M. I. Kabachnik and V. A. Gelyarov, *Izvest. Akad. Nauk S.S.S.R., Otdel, Khim. Nauk.*, 790 (1956).

(4) Dialkyl phosphoramidates may be prepared by treating a dialkyl phosphorochloridate with a primary amine or more conveniently by treating a dialkyl phosphite with a primary amine and carbon tetrachloride (F. R. Atherton, H. T. Openshaw, and A. R. Todd, *J. Chem. Soc.*, 660 (1945).

(5) H. G. Khorana, *J. Chem. Soc.*, 2081 (1952).

(6) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 267.

(7) A. Skita and H. Rolfes, *Chem. Ber.*, **53**, 1248 (1920).

(8) M. S. Newman, T. Fukunaga and T. Miwa, *J. Am. Chem. Soc.*, **82**, 873 (1960).

(9) K. V. Auwers and B. Ottens, *Chem. Ber.*, **57**, 447 (1924).

comparison of their spectra and physical properties with authentic samples.

ROHM & HAAS COMPANY WILLIAM S. WADSWORTH, JR.
PHILADELPHIA, PENNSYLVANIA WILLIAM D. EMMONS

RECEIVED FEBRUARY 9, 1962

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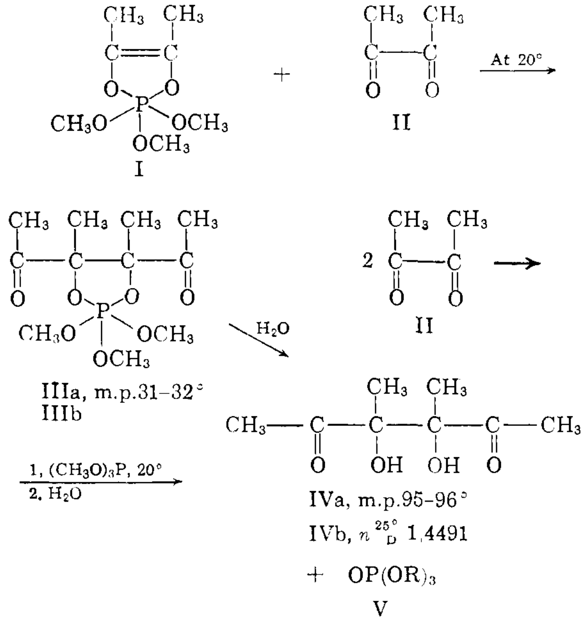
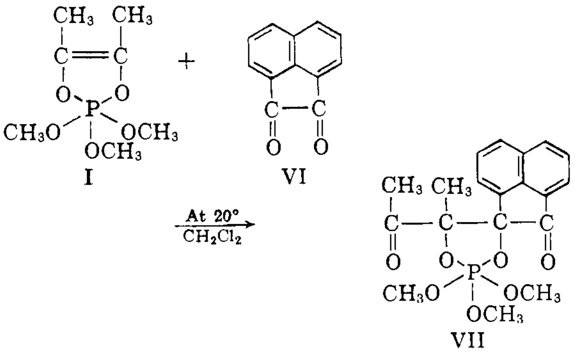
## A CYCLIC SATURATED PENTAALKOXYPHOSPHORANE. DIKETOLS *VIA* OXYPHOSPHORANES[1]

*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.



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



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 $n^{25\circ}_{D}$ 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) $\mu$ 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) $\mu$ (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.