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NUCLEOPHILIC REACTIONS OF TRIVALENT PHOSPHORUS COMPOUNDS. SYNTHESIS OF STABLE DIFLUOROMETHYLENEPHOSPHORANE ANALOGS.*

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Modifications in the phosphorus reactant of Wittig's olefin-forming reaction resulted in the synthesis of mono- and dihalomethylenephosphoranes, (phosphinemethylenes), which were obtained and used as unstable reaction intermediates. The methods of synthesis comprised the reaction of triphenylphosphine with halocarbenes (1) and with tetrahalomethanes (2). The analogous difluoromethylenephosphorane was reported in a brief announcement (3) but subsequent attempts to prepare it have failed (4).** The trapping of difluorocarbene by phosphorus trifluoride was also unsuccessful (6).

Extending our investigation on the reactions of the powerful nucleophiles, hexaalkylphosphorus triamides, $(R_2N)_3P$, (I), from

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* Work done at the Central Research Department, Monsanto Company, St. Louis, Missouri

** The intermediacy of difluoromethylenetriphenylphosphorane was postulated recently in the synthesis of 1,1-difluoroethylenes from aldehydes with the aid of chlorodifluoroacetate and triphenylphosphine (5). These results are in yet unexplained contrast with the failure to obtain difluoroolefins from benzaldehyde and benzophenone via the chlorodifluoromethane or dibromodifluoromethane routes (4).

aldehydes (7) to ketones and esters, we wish to report on their reaction with two trifluoroacetyl compounds. One of these, 2,2,2-trifluoroacetophenone, yielded difluoromethylenephosphorane derivatives in form of isolable and stable reaction products.

The addition of Ia (R = methyl), in equimolar proportion or in excess, to a solution of 2,2,2-trifluoroacetophenone in benzene resulted in an exothermic reaction, which was kept under control (between 20 and 30°) by cooling. Fractionation of the reaction mixture yielded a colorless liquid, (II), b.p. 30-32° at 2.5 m.m., n_D^{25} 1.4220, the analysis of which (C, 37.0; H, 8.8; F, 18.0; N, 20.4; P, 14.9%; mol. wt. 232±10%) indicated a $C_7H_{18}F_2N_3P$ composition (calculated: C, 39.4*; H, 8.5; F, 17.9; N, 19.8; P, 14.5%; mol. wt. 213.2). H^1 n.m.r. (FIG. 1) indicated the presence of only one kind of hydrogen, centered at 2.64 p.p.m. downfield from tetramethylsilane; the spectrum contained a doublet (J = 10.80 c.p.s.) split into triplets (J = 2.86 c.p.s.). P^{31} n.m.r. showed a triplet, δ +65.5 p.p.m. (from 85% H_3PO_4), J = 695 c.p.s., the branches of which were broad, due to unresolved fine splittings (half-width ~ 70 c.p.s.). The F^{19} n.m.r. spectrum was a doublet, δ -25.2 p.p.m. (CF_3COOH), J = 705 c.p.s. (half-width ~ 13 c.p.s.)

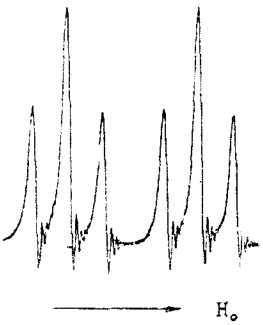


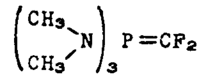
FIG. 1

H^1 n.m.r. spectrum of II.

Standard carbon determinations often yield low values for compounds with C-P bonds (8).

Mass spectometry indicated the following main peaks: 179, 154 (abundant), 139, 135, 110 (abundant), 44 (abundant). Vapor phase chromatography confirmed the high purity of the sample indicated H^1 n.m.r.

The analytical and spectroscopic data thus indicate the difluoromethylenetris(dimethylamino)phosphorane structure for II:



$$\left(\begin{matrix}CH_3\diagdown \\ \quad N \\ CH_3\diagup\end{matrix}\right)_3 P{=}CF_2$$

the assignment of the coupling constants being: J_{PH} = 10.8 c.p.s.: J_{FH} = 2.86 c.p.s., J_{FP} = 695 $\simeq$ J_{PF} = 705 c.p.s. The large positive shift indicates a highly shielded and thus a pentacovalent phosphorus.* The equivalence of the hydrogens requires a symmetrical arrangement of the dimethylamino substituents around the P=C axis. The abundance of peak 154 in the mass spectrum indicates the ready detachment of trimethylamine from II.

The infrared spectrum [$\lambda_{max.}$ of the strongest bands: 2934, 2896, 2858, and 2813 (C-H stretching), 1459 (C-H deformation), 1283 and 1213 (asym. and sym. $=CF_2$ stretching), 1069 (tentatively: P=C stretching), 1001 (C-N stretching), 743 (P-N stretching), 502 cm^{-1}] and the ultraviolet spectrum of II [shoulder at

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* Probably the closest examples of phosphorus nuclei highly shielded by four neighbors and unsaturation can be found in the linear or cyclic "phosphonitrilic halides" (9), e.g. $(NPBr_2)_3$, δ +49.5; $(NPBr_2)_4$, δ +71.8 p.p.m. Disruption of the unsaturation in II would result in an "ylid" or phosphonium structure with a greatly deshielded phosphorus nucleus. In support of this reasoning, the chemical shift of a closely related phosphonium compound, $\{[(CH_3)_2N]_3P\text{-}CCl_2F\}^+Cl^-$, δ -44 p.p.m. (10), is found to be about 110 p.p.m. downfield from II.

227 mµ (ϵ 524), blending into a maximum of a lower wavelength] are consistent with the suggested structure. The absence of strong absorption in the 810-885 cm^{-1} region indicates the absence of P-F bonds.

When I and 2,2,2-trifluoroacetophenone were used in equimolar proportion, the yield of II (distilled) was 60%. The remainder of the material balance was present as a viscous distillation residue, the H^1, F^{19} and P^{31} n.m.r. of which indicated the presence of all three elements by broad maxima.

Hexaethylphosphorus triamide and 2,2,2-trifluoroacetophenone reacted similarly and yielded difluoromethylenetris(diethylamino)-phosphorane, $[(C_2H_5)_2N]_3P{=}CF_2$, III, in 56% yield; (b.p. 54-55° at 0.06 m.m., n_D^{25} 1.4390, $\delta_{P^{31}}$ +58.0 p.p.m., J_{PF} = 677 c.p.s.; (H^1 n.m.r.: δ_{CH_3} -1.06 p.p.m., J_{HH} = 7.0 c.p.s., δ_{CH_2} -2.91 p.p.m., J_{HH} = 7.0, J_{HP} = 15.10, J_{HF} = 1.94 c.p.s.; infrared spectrum similar to that of II).

Preliminary experiments indicate that *pure* II and III do not react on heating with benzaldehyde and o-chlorobenzaldehyde between 20 and 80° for a one hour period.* This behavior and the stability of II and III** are consistent with the "ylene" struc-

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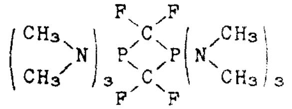
[*] An impure sample of II, however, did react with benzaldehyde at room temperature as indicated by H^1 n.m.r. A description of this reaction will be given in the full paper.

[**] Vapor phase chromatography of an aged sample of II resulted in the isolation of a species (6%), for which, based on the much longer retention time and on the close similarity of its infrared spectrum with that of II, a dimeric structure, IV, is tentatively postulated:



IV

ture indicated for them by P^{31} n.m.r. The chemical shifts of several examined Wittig reagents are downfield from H_3PO_4 and, being very close to those of the corresponding phosphonium salts, they indicate essentially a dipolar, "ylid" structure for these compounds (11) in accordance with requirements of the postulated mechanism (12).

The two new structures, II and III, Seem to be the first examples of pentacovalent phosphorus compounds with an actual phosphorus-carbon double bond (d-p pi overlap). In contrast with the effect of halogens in the reactive dichloro and dibromomethylene Wittig reagents (1,2) the difluoromethylene group in II apparently provides for a marked return of electron density to the phosphorus as sensed by phosphorus n.m.r.* This effective d-p π overlap is probably related to the recently suggested p-π interaction between aromatic rings and fluorinated substituent groups (13).

The reaction of I with ethyl trifluoroacetate, (V), was also investigated. The mildly exothermic reaction apparently took a different course and yielded, depending on the ratio of reactants, products represented by the following equations:

$$I + V \rightleftharpoons [(CH_3)_2N]_2P(OC_2H_5)\ (VI) + CF_3CON(CH_3)_2\ (VII) \qquad (1)$$

$$VI + V \rightleftharpoons [(CH_3)_2N]P(OC_2H_5)_2\ (VIII) + VII \qquad (2)$$

$$VIII + V \rightleftharpoons P(OC_2H_5)_3\ (IX) + VII \qquad (3)$$

The course of the reaction was best followed with P^{31} n.m.r. VI, VIII and IX were identified with the aid of synthetic samp-

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* Repulsion between the electrons of the fluorine and those of the incipient carbanions (resonance extremes of II and III) might well account for the effects observed.

les, which had the following P^{31} resonances: VI, -135.2: VIII, -143.4: IX, -137.1: I, -122.0 p.p.m. The coproduct, VII, was isolated in essentially quantitative yield and identified by matching its properties with those of an authentic specimen (14).

Further data as well as possible mechanistic pathways (one comprising the intermediacy of difluorocarbene in the sequence leading to II and III) will be presented in the full paper.

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