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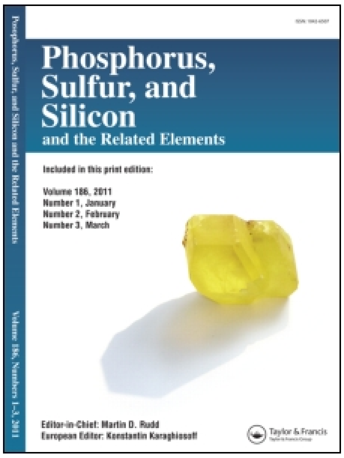

Phosphorus, Sulfur, and Silicon and the Related Elements

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Phosphorus Reagents in Organic Synthesis

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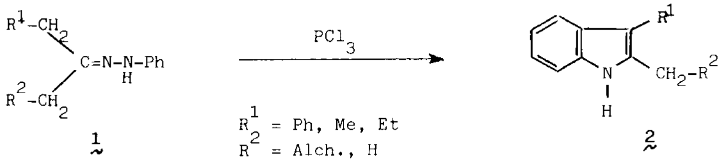
REGIOSELECTIVE INDOLIZATION FROM THE REACTION OF UNSYMMETRICAL ARYLHYDRAZONES WITH PHOSPHORUS TRICHLORIDE.

G. Baccolini, E. Marotta and P.E. Todesco. Istituto Chimica Organica, Università, Viale Risorgimento 4, 40136 Bologna (Italy).

Recently, we reported a new method for the synthesis of 2,3-disubstituted indoles (70-90% yields) from reaction, at room temperature, between ketone arylhydrazones and PCl_3. Now, we describe the results of this indolization reaction when unsymmetrical arylhydrazones such as **1** are used. The reaction proceeds quickly at room temperature and gives the prevalent formation of only one (**2**) of the two possible 2,3-disubstituted indoles. A prediction of the direction of indolization is also possible: a feature not inherent in the classical Fischer indole synthesis.



1

R^1 = Ph, Me, Et
R^2 = Alch., H

2

A possible mechanistic explanation of this reaction will also be discussed.

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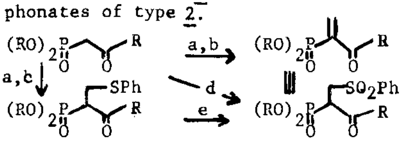
MASKED VINYLPHOSPHONATES - SYNTHESES AND REACTIVITY.

B. CORBEL, Faculté des Sciences, ERA 612, 29283 BREST-CEDEX - FRANCE -

The vinylphosphonates $(RO)_2P(O)C(=CH_2)EWG$ can serve as versatile reagents for molecular designs since they could be used as reagents suitable for coupling carbonyl compounds with nucleophilic compounds in a Michael addition and subsequent Wittig-Horner reaction. A few methods for their preparation have been reported (see Ref.). The yields varied from excellent to poor when they were thermally unstable. This was especially the case for the keto compounds of type **1** and why we decided to investigate the reactivity of masked vinylphosphonates of type **2**.



1

2

a) $(HCHO)_n$,piperidine,MeOH; b)APTS,PhH;
c) PhSH,APTS,PhH; d) $PhSO_2Na$,AcOH;
e) 2[O]

The preparations and the uses of these new α-(dialkylphosphono)β-ketosulfones will be discussed.

Ref. S.PATAI et al.,J.Org.Chem.1960,25,1232;A.N.PUDOVIK et al.,J.Gen.Chem.of URSS 1969, 39,197;W.LEHNERT,Tetrahedron 1974,30,301;M.F.SEMMELHACK et al.,J.Org.Chem.1978,43,1259; J.M.Mc INTOSH et al.,Can.J.Chem.1978,56,226;J.Org.Chem.1978,43,4431;C.H.HEATHCOCK et al., J.Org.Chem.1978,43,1256;T.MINAMI et al.Chem.Lett.1978,285;J.Org.Chem.1982,47,2360; S.M.WEINREB et al.,J.Am.Chem.Soc.1981,103,6387;J.IDE et al.Chem.Lett.1978,401; M.MIKOLAJCZYK et al.Tetrahedron Lett.1981,3097.

A COMPARATIVE INVESTIGATION OF THE CHLORINATION AND/OR CYCLODEHYRATION OF DIOLS WITH TRIPHENYLPHOSPHINE-TETRACHLOROMETHANE-POTASSIUM CARBONATE, TRIPHENYLPHOSPHINE-t-BUTYLHYPOCHLORITE, AND DIETHOXYTRIPHENYLPHOSPHORANE REAGENTS.

Carey N. Barry, Philip L. Robinson, and Slayton A. Evans, Jr., The William Rand Kenan, Jr., Laboratories of Chemistry, The University of North Carolina, Chapel Hill, North Carolina, U.S.A.

The yields of epoxides obtained from the reaction of 1,2-diols with triphenylphosphine (TPP)-tetrachloromethane (CCl_4)-potassium carbonate (K_2CO_3) range from 27-85% depending on the relative concentration of TPP and diol. In the absence of heterogeneous K_2CO_3, reactions of 1,2-diols with TPP-CCl_4 give largely 1,2-chlorohydrins.

The stereochemical implications of TPP-CCl_4 promoted cyclodehydrations have been examined. (S)-1,2-Propanediol and (R)-1,4-pentanediol were converted to the corresponding cyclic ethers with prodominant retention of configuration at the carbinol carbon (76.9 and 87.8% retention of stereochemistry, respectively). By contrast, treatment of (S)-phenyl-1,2-ethanediol with TPP-CCl_4 affords racemic styrene oxide.

The reagent, triphenylphosphine-t-butylhypochlorite (TPP-tBHC), converts 1,4-diols into the corresponding tetrahydrofurans and 1,2-diols into a mixture of the regioisomeric chlorohydrins and epoxides at -78°→25°C. The facility for ether ring formation decreases in the following manner: $3 \approx 5 > 6 > 4 \approx 7$.

Diethoxytriphenylphosphorane, $Ph_3P(OEt)_2$, is extremely useful in converting 1,2-diols to epoxides in essentially neutral media. Simple diols cyclodehydrate to the epoxides in good to excellent yields (65-95%) while sterically hindered diols give epoxides and ketones. The latter arise from 1,2-hydride and 1,2-methyl shifts.

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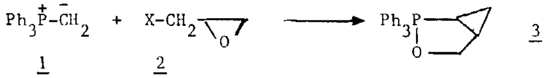
REACTIVITE COMPAREE DE L'EPICHLORHYDRINE ET DE L'EPIBROMHYDRINE VIS A VIS DU METHYLENETRIPHENYLPHOSPHORANE.

Maurice LE CORRE, Alain HERCOUET, Hervé DANIEL - Laboratoire de Synthèse Organique
Avenue du Général Leclerc - 35042 RENNES CEDEX

L'épichlorhydrine se condense avec le méthylènetriphénylphosphorane en donnant l'oxaphospholane 3 (1)



L'épibromhydrine conduit au même résultat mais le marquage au deutérium montre que cette réaction complexe fait intervenir deux mécanismes différents selon la nature de l'halogène : attaque de la fonction époxyde (X = Cl) ou de la fonction halogénure (X = Br).

(1) A. TURCANT et M. LE CORRE, *Tetrahedron Letters*, 1277, 1976.

PREPARATION OF AZIRIDINES FROM AMINOALCOHOLS USING TPP/DIAD

H. Loibner, W. Streicher, and R. Reuschel
SANDOZ Research Institute, A-1235 Vienna, Brunnerstraße 59, Austria

Only few methods are available for the conversion of vicinal aminoalcohols to aziridines. These methods require drastic conditions, which are inconsistent with more complex and sensitive molecules.

We were interested in various aziridines in the carbohydrate field. A new method for the preparation of aziridines is described, which takes place at mild and neutral conditions. Vicinal aminoalcohols or N-acylaminoalcohols on treatment with triphenylphosphine/diisopropylazodicarboxylate (TPP/DIAD) in an inert solvent are converted to aziridines or N-acylaziridines respectively in good yields.

PHOSPHORUS PENTOXIDE IN THE SYNTHESIS OF PURINES, AZAPURINES AND DEAZAPURINES.

Flemming E. Nielsen and Erik B. Pedersen. Department of Chemistry, Odense University, DK-5230 Odense M, Denmark.

The reaction of molten mixtures of P_2O_5, *N*,*N*-dimethylcyclohexylamine and a primary amine hydrochloride with 4-acylamino-1'*H*-imidazole-5-carboxylates in 4:4:4:1 molar ratios resulted in the formation of 1-substituted hypoxanthines. N^6-Aryl-7-methyladenines were prepared from 4-acetylamino-1,2-dimethyl-1*H*-imidazole-5-carbonitriles at 180 °C in analogous reaction mixtures using tributylamine as the tertiary amine component, while the corresponding N7-unsubstituted compounds were obtained from the same starting materials at 240 °C, due to a demethylation reaction. Heating of 5-acetylamino-1*H*-1,2,3-triazole-4-carboxylates with amine hydrochlorides in our reaction mixture afforded the expected 1-substituted-8-azapurin-6-ones along with N^6,1-disubstituted-6-imino-8-azapurines as simple mixtures, easy to separate. N^6-substituted-8-azapurin-6-amines were obtained from analogous 4-carboxamido-1*H*-1,2,3-triazoles. Attempts to use our mixtures as a ring closure reagent for 3-acetylamino-2-chloropyridines resulted in the formation of the intermediate *N*-substituted-*N*'-(2-chloro-3-pyridyl)-acetamidines, which were cyclized to 9-substituted-1-deazapurines in almost quantitative yield in refluxing DMF containing potassium carbonate. The reagent mixture is also useful in the direct conversion of oxo groups in heterocyclic compounds into amino groups. Thus we have prepared *N*,*N*'-disubstituted 2,4-diaminopyrimidines, 2,6-diaminopurines and 4,7-diamino-1*H*-1,2,3-triazolo[4,5-*d*]pyridazines from uracil, xanthine and 4,7-dihydroxy-1*H*-1,2,3-triazolo[4,5-*d*]pyridazine, respectively.

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PYRIDINIUM HEXAFLUOROPHOSPHATE II - A REAGENT FOR THE PREPARATION OF ALKYLAMMONIUM HEXAFLUOROPHOSPHATES.

K.SYED MOHAMED, D.K.PADMA and A.R. VASUDEVA MURTHY (Department of Inorganic and Physical Chemistry Indian Institute of Science, Bangalore 560 012 (India)

The reagent, pyridinium hexafluorophosphate, has been prepared in good yields and high purity by the reaction of pyridinium poly(hydrogen fluoride) and phosphorous pentachloride. On treatment with primary, secondary and tertiary alkyl amines, the corresponding mono, di and trialkylammonium hexafluorophosphates are obtained in good yields and high purity. When quarternary ammonium halides are treated with this reagent in aqueous medium, tetra alkylammonium hexafluorophosphates are obtained. The reactions are represented as follows.
$RNH_2 + C_5H_5NHPF_6 \longrightarrow RNH_3PF_6 + C_5H_5N$ (R = Me, Et, n-Pr, i-Pr, n-Bu, i-Bu, t-Bu, cyclohexyl and benzyl). $R_2NH+C_5H_5NHPF_6 \longrightarrow R_2NH_2PF_6+C_5H_5N$ (R_2 = Me_2, Et_2, n-Pr_2, n-Bu_2, i-Bu_2, n-$amyl_2$, dibenzyl, piperidine, N-methylcyclohexyl, morpholine). $R_3N + C_5H_5NHPF_6 \longrightarrow R_3NHPF_6$
$|R_3 = Me_3, Et_3,$ n-$Pr_3|$ $R_4NX + C_5H_5NHPF_6 \longrightarrow R_4NPF_6 + C_5H_5N$
($R_4 = Me_4, Et_4$; X = Cl or I). The compounds have been characterised by infra-red ^1H NMR spectra and chemical analysis.

N, N-BIS (2OXO-3-OXAZOLIDINYL) PHOSPHORDIAMIDIC CHLORIDE: A NEW STRATEGY FOR THE ESTER FUNCTION PREPARATION.

M. BALLESTER-RODES and A.L. PALOMO-COLL.
Gema S.A. Research Department, Beethoven, 15. Barcelona (21) and Marga Research Center, Muntaner, 212. Barcelona (36), Spain.

The inter and intramolecular reaction of a carboxylic group with an hidroxile by means of the organophosphorus reagent has been successfully used (1,2). Of interest are the 2-oxetidinones (2) and, in the antibiotics of macrolides group (3), the lactone function is relevant. By a mechanistic evaluation of the behaviour of N,N-bis (2-oxo-3-oxazolidinyl) phosphordiamidic chloride reagent, the formation of acyl intermediates is observed; these evolve to give esters by direct reaction with the alcohols or by previous reaction with carboxylate ions giving anhydrides (4) to yield afterwards the esters. The activity and nucleophilic selectivity of the reagent conditionates the one-step synthesis in front to the one-pot procedures. The described results are obtained with several hydroxile functions, and (E) geraniol, (E)/(Z) phytol, α-tocoferol and (E)(E) farnesol derivatives. (2) I. Casinos, R. Mestres. Anales de Química 78C, (3), 364 (1.982). (1) Fieser and Fieser's. Reagents for Organic Synthesis, (1.982). John Wiley Sons, New York 1.982, Vol 10, pág 41. (3) J.S. Glasby. Encyclopaedia of Antibiotics (2ª Edit.) John Wiley Sons, Chichester (1.979). (4) J. Cabré, A. Palomo, A.L. Palomo. Synthesis, 616, (1.981).

THIOXAPHOSPHORANESULFENYL HALIDES
NEW REAGENTS IN ORGANIC PHOSPHORUS-SULFUR CHEMISTRY

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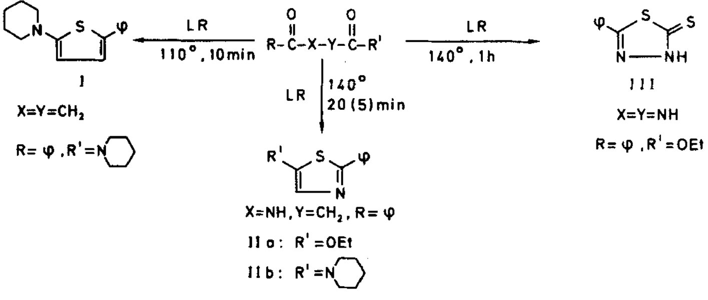
Polish Academy of Sciences, Centre of Molecular and
Macromolecular Studies, Boczna 5, 90-362 Lodz, Poland

Recently we have described a new class of sulfenyl halides namely thioxaphosphoranesulfenyl bromides RR′P(S)SBr 1. They exhibit a pronouced reactivity towards C, N, O, S and P nucleophiles giving access to a variety of novel organophosphorus compounds which are accessible only with difficulties by other methods. Using 1 as a starting material the efficient synthesis of thioxaphosphoranesulfenyl chlorides RR′P(S)SCl was realised. The synthetic and meçhanistic aspects of the bromide 1 in organophosphorus chemistry were discussed. The synthetic applications of these bromides as well as some mechanistic aspects of the reaction will be discussed.

NOVEL METHODS FOR THE PREPARATION OF SUBSTITUTED THIOPHENES, THIAZOLES AND 1,3,4-THIADIAZOLE-2(3H)-THIONES,

P.B.Rasmussen, I.Thomsen, U.Pedersen, B.Yde, T.P.Andersen and S.-O.Lawesson, Department of Organic Chemistry, University of Aarhus, 8000 Aarhus C, Denmark

Bifunctional substrates, such as 4-oxocarboxylic acid derivatives, N-acyl aminoacid derivatives and N-acyl-N′-ethoxycarbonylhydrazines, undergo ringclosure on reaction with 2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane-2,4-disulfide, LR, producing the corresponding thiophenes, I, thiazoles, II, and 1,3,4-thiadiazole-2(3H)-thiones, III, all in yields from 80-100%.



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UTILISATION DES SELS DE SULFONIUM A LA SYNTHESE D'ESTERS DE L'ACIDE PHOSPHORIQUE.

L. Jacob, H. Mestdagh, C. Rolando
Laboratoire de Chimie de l'Ecole Normale Supérieure, 24 rue Lhomond, Paris 5ème

L'utilisation des sels de sulfonium $R^1\ R^2_2S^+,X^-$ permet une synthèse très efficace dans des conditions très douces de triesters mixtes de l'acide phosphorique :

$$(R^3O)_2\ P(O)\ OK\ +\ R^1R^2_2\ S^+,X^-\ \longrightarrow\ (R^3O)_2\ P(O)\ OR_1\ +\ R^2SR^2\ +\ KX$$

rendement > 80%

L'emploi de $Bu_4N^+,\bar{O}P(O)(OH)_2$ permet d'accéder aux phosphates libres $R^1OP(O)(OK)_2$ en particulier aux phosphates terpèniques (R^1= prenyl, geranyl) avec un rendement de l'ordre de 30% sans nécessiter de séparation par chromatographie.

La remarquable catalyse par les sels de cuivre(I) de la substitution nucléophile des sulfoniums allyliques en position γ nous a permis d'accéder aux phosphates allyliques tertiaires correspondants (R^1 = methyl-2 butène-3 yl-2, linalyl).

Enfin le traitement des triesters diméthyliques de l'acide phosphorique par le diméthylsulfure en milieu acide méthanesulfonique permet un débloquage quantitatif et spécifique des méthyles en milieu non aqueux acide :

$$(MeO)_2\ P(O)\ OR^4\ +\ Me_2S\ +\ HX\ \longrightarrow\ (HO)_2\ P(O)\ OR^4\ +\ 2\ Me_3S^+,\ X^-$$

rendement > 75%

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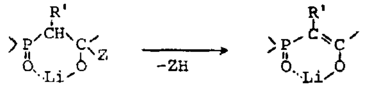
FACTEURS INFLUENCANT LA REACTION DES ESTERS ET AMIDES PRECURSEURS DE CARBONYLES AVEC LES CARBANIONS LITHIENS PHOSPHONATES,

E. Elia Aboujaoude [+], N. Collignon [+], P. Savignac [++], [+]Laboratoire de Chimie Organique I.N.S.C.I.R., BP 08, 76130 Mont Saint Aignan (France), [++]Equipe CNRS-SNPE, 2-8 rue H. Dunant, 94320 Thiais (France)

La fonctionnalisation d'un carbanion lithien issu d'un alkylphosphonate $(RO)_2P(O)CH_2R'$ a fait son apparition en synthèse en 1966 (Corey et Kwiatkowski) ; cette démarche n'a pas cependant connu les débouchés souhaités. Nous nous sommes proposés d'examiner le comportement de ces carbanions vis à vis des précurseurs de carbonyles (esters, amides etc...). L'analyse d'une telle réaction suggère dans sa phase dynamique l'intervention d'un chélate cyclique à six chaînons dont la stabilité est garantie par l'affinité du lithium pour l'oxygène du phosphonyle.



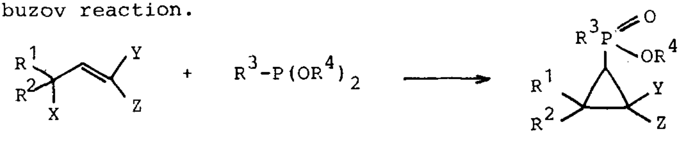
Ce chélate est susceptible de subir une β-élimination dont la facilité dépend de l'aptitude nucléofuge des substituants du carbone en β. Une élimination précoce en libérant l'acide ZH a pour conséquence de régénérer le phosphonate d'origine aux dépens du carbanion. Nous examinons cette réaction avec plusieurs précurseurs : $HCON(R)_2$, HCOOR, $RCON(R)_2$ R-COOR, Ar-COOR, ROCO-COOR etc...

REACTIVITY OF ELECTROPHILIC ALLYL HALIDES TOWARDS TRIVALENT PHOSPHORUS COMPOUNDS

R. Verhé, N. De Kimpe, L. De Buyck, G. Van Heeke, N. Schamp

State University of Gent, Faculty of Agricultural Sciences, Laboratory of Organic Chemistry, Coupure Links 653, B-9000 Gent, Belgium

Reactions of allyl halides substituted with one electronwithdrawing group in γ-position with phosphites gave rise to normal Arbuzov products. On the other hand treatment of allyl halides geminally substituted with two electronwithdrawing groups with trivalent phosphorus nucleophiles provided cyclopropanes formed via a Michael addition and a subsequent intramolecular Arbuzov reaction.



Y; Z = COOR, CN
R^3 = Ph, OR^4
R^4 = alkyl

The influence of the substitution pattern, the nature of the halogen electronwithdrawing group and the p-nucleophile on the reaction rate will be discussed.

SYNTHESES BASED ON DIALKYL PHOSPHITES

G.Borisov K.Troev
Central Laboratory on Polymers
Bulgarian Academy of Sciences, Sofia 1113

The dialkyl phosphites(DAP) are industrially available and comparatively reactive compounds. They are of considerable interest with the view to preparing novel organophosphorus compounds.

Polyfunctional monomers and oligomers with terminal hydroxyl groups are prepared via transesterifying DAP with diols depending on the reaction conditions i.e. mole ratio and temperature.The transesterification of DAP with glycols, 1,3-propanol-2,bis-beta-hydroxyethylpolysulphide, pentaerythrite and others is carried out.

The interaction of DAP with metal salts(mainly bivalent) is examined and new bifunctional phosphorus-containing compounds and oligomers are synthesized.

It is demonstrated that the reaction is a bimolecular one the rate of which depends on the size of the positive charge on the alpha-carbon atom at phosphorus as well as on the strength of the attacking agent. A probable mechanism of the reaction is suggested on the basis of the studies carried out and products isolated.

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THE ENANTIO-DIFFERENTIATING CHIROSPECIFICITY OF SOLID-BOUND CHIRAL PHOSPHINE OXIDES.

Peter Krebser, Hans-Rudolf Marti and Paul Rys

Dept. of Ind. and Eng. Chemistry, Swiss Federal Inst. of Techn. ETH, ETH-Zentrum,
CH-8092 Zurich, Switzerland

Many attempts have been made in the past years to achieve racemate resolution using chromatographic methods. Direct liquid-chromatographic resolutions of enantiomers can be realized either by the use of an optically active packing material or by employing an optically active solvent.

The present study introduces a method for a quantitative determination of the enantio-differentiating behaviour of polystyrene-bound chiral phosphine oxides as solids. This behaviour can be of a kinetic or a thermodynamic nature. The presented method is based on a competitive sorption model which enables the chirospecificity to be studied by analyzing the sorption kinetics and isotherms of the enantiomers of mandelic acid onto polymer-bound chiral phosphine oxides.

The following surprising experimental observation was made: If an insoluble polymer-bound chiral phosphine oxide was added to a racemic solution of mandelic acid, not only the optical rotation of the bulk solution, but also the sign of the rotation changed with time. The presented model offers a detailed explanation for these unusual experimental data.

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