H, 32), 707 (100), 650 (18), 576 (31), 518 (27), 465 (28); HRMS calcd for $C_{49}H_{79}O_5Si_3$ ($M^+ + H$) 830.5157, found 830.5188.

Methyl (6*Z*,10*E*,12*E*,5*S*,14*R*,15*S*)-5,14,15-Trihydroxy-6,10,12-eicosatrien-8-ynoate (44). To a cooled (0 °C) solution of **43** (710 mg, 0.857 mmol) in THF (4.3 mL) under argon in a Nalgene bottle was added HF·pyr complex (0.2 mL). After being stirred at 0 °C for 5 min, the cooling bath was removed and the reaction mixture was allowed to warm to room temperature and stirred for 30 min. This procedure was repeated four additional times until TLC monitoring (silica, 5% ether in petroleum ether and 5% MeOH in CH_2Cl_2) indicated that the reaction was complete. The reaction mixture was then poured into an Erlenmeyer flask, diluted with ether (10 mL), and neutralized (pH paper) by the cautious addition of a saturated aqueous $NaHCO_3$ solution. The phases were separated and the aqueous layer was extracted with ether (4 × 10 mL). The combined organic extract was dried ($MgSO_4$), filtered, and concentrated to provide a yellow oil. Radial preparative chromatography (chromatotron, Harrison Research, silica, 5% MeOH in CH_2Cl_2) gave, in order of elution, δ-lactone **45** (65.5 mg, 23% yield) and triol **44** (162.4 mg, 52% yield). The δ-lactone **45** was quantitatively converted to **44** by being dissolved in methanol (1 mL) and treatment with triethylamine (60 μL) (15 min, 25 °C). **44**: colorless oil that yellows upon exposure to air; R_f 0.24 (silica, 7.5% MeOH in CH_2Cl_2); $[\alpha]^{25}_D$ −30.92° (*c* 0.60, CH_2Cl_2); UV (MeOH) λ_{max} 283 (shoulder), 295, 314 nm; IR (neat) ν_{max} 3390, 3021, 2930, 2858, 1730, 1441, 1072 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 6.60 (dd, *J* = 15.5, 10.9 Hz, 1 H, olefinic), 6.35 (dd, *J* = 15.2, 10.9 Hz, 1 H, olefinic), 5.89 (m, 2 H, olefinic), 5.76 (dd, *J* = 15.5, 2.3 Hz, 1 H, olefinic), 5.69 (dd, *J* = 10.9, 2.3 Hz, 1 H, olefinic), 4.65 (m, 1 H, -C*H*(OH)CH=CH-), 4.17 (dd, *J* = 6.6, 3.4 Hz, 1 H, -C*H*(OH)CH=CH-), 3.70 (m, 1 H, C*H*OH), 3.67 (s, 3 H, $COOCH_3$), 2.39 (m, 2 H, CH_2COOCH_3), 2.25 (br s, 2 H, O*H*), 1.79–1.63 (m, 2 H, -CH_2-), 1.57 (m, 1 H, -CH_2-), 1.49 (m, 1 H, -CH_2-), 1.39 (m, 2 H, -CH_2-), 1.29 (m, 7 H, -CH_2-, O*H*), 0.89 (t, *J* = 6.7 Hz, CH_3); MS *m/e* (rel intensity) 387 ($M + NH_4^+$, 3), 365 ($M^+ + H$, 5), 347 ($M^+ - OH$, 68), 329 (100), 311 (55), 263 (90), 246 (95), 215 (33); HRMS calcd for $C_{21}H_{31}O_4$ ($M^+ - OH$) 347.2222, found 347.2224.

Methyl (6*Z*,8*Z*,10*E*,12*E*,5*S*,14*R*,15*S*)-5,14,15-Trihydroxy-6,8,10,12-eicosatetraenoate (4). The acetylene **44** (31.1 mg, 0.0865 mmol) in CH_2Cl_2 (1.7 mL) was selectively hydrogenated with Lindlar catalyst (Fluka Chemical Co., 9.4 mg, 30% by weight) in the presence of freshly distilled quinoline (CaH_2, 8.5 μL). The reaction mixture was stirred under a hydrogen atmosphere at room temperature for 2.5 h and the reaction was monitored by HPLC as described for compound **3**. The resulting crude product was purified by reverse-phase HPLC (same conditions as above, t_R 16.2 min) to give, after removal of the solvents, **4** (21.6 mg, 69.1% yield). **4**: white, waxy solid; R_f 0.32 (silica, 5% MeOH in CH_2Cl_2); $[\alpha]^{25}_D$ +33.73° (*c* 0.257, CH_2Cl_2); UV (MeOH) λ_{max} 285, 298, 314 nm; IR (CH_2Cl_2) ν_{max} 3390, 3031, 2914, 2835, 1732, 1482, 1392, 1170, 1072, cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 6.70 (dd, *J* = 14.3, 11.9 Hz, 1 H, H-10), 6.53 (t, *J* = 11.4 Hz, 1 H, H-7), 6.39 (dd, *J* = 14.9, 10.9 Hz, 1 H, H-12), 6.28 (m, 2 H, H-8, H-11), 6.11 (t, *J* = 11.2 Hz, 1 H, H-13), 5.50 (t, *J* = 9.6 Hz, 1 H, H-6), 4.63 (m, 1 H, H-5), 4.16 (m, 1 H, H-14), 3.20 (m, 1 H, H-15), 3.67 (s, 3 H, $COOCH_3$), 2.34 (m, 2 H, H-2), 2.02 (s, 1 H, O*H*), 1.94 (s, 1 H, O*H*), 1.77–1.26 (m, 13 H, O*H*, -CH_2-), 0.89 (t, *J* = 6.8 Hz, 1 H, H-20); MS *m/e* (rel intensity) 366 (M^+), 203, 173 (100); HRMS calcd for $C_{21}H_{35}O_5$ ($M^+ + H$) 367.2485, found 367.2489.

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Supplementary Material Available: ^1H NMR and IR spectra of compounds 1–4, 6–9, 11–13, 15, 16, 18, 20–22, 32, 33, 35–37, 39, 41, and 43–45 (27 pages). Ordering information is given on any current masthead page.

Carbenoid Properties of Phosphenium Salts. Synthesis of the First 1-Aza-3-phosphetine Cations

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Further examples of the synthetic utility of phosphenium cations are reported. They react with isocyanides to produce 1-aza-3-phosphetine cations **3a–f** or cyano- and dicyanophosphines **4**, **5**, and **7**, depending on the experimental conditions and on the nature of the substituents of each partner. The transient formation of hitherto unknown cationic phosphacumulenes $R_2P^+{=}C{=}NR'$ in resonance with the nitrilium salts $R_2PC{\equiv}N^+R'$ can explain the formation of this new series of phosphorus heterocycles.

Introduction

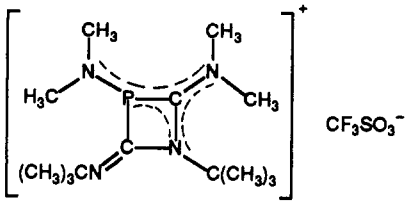
It has been shown that low coordinated phosphorus cationic species, that is, the phosphenium salts R_2P^+, react as carbenoids with alkynes or 1,3- or 1,4-dienes to give the corresponding unsaturated three-, four-, or five-membered rings.[1] They can exhibit carbocation-like behavior toward 1,5-dienes.[2] Due to the fact that they possess a formal positive charge and a sextet of electrons on phosphorus, they can also function as Lewis acids; furthermore, the presence of a lone pair and a vacant π orbital render phosphenium ions excellent ligands[1] (Scheme I).

On the other hand, isocyanides can interact either with nucleophiles or with electrophiles. Moreover, by virtue of their carbenic character, isocyanides react easily with most of the common multiple bonds to give a range of heterocyclic systems often inaccessible by other methods.[3]

(1) Cowley, A. H.; Kemp, R. A. *Chem. Rev.* **1985**, *85*, 367.
(2) Weissman, S. A.; Baxter, S. G.; Arif, A. M.; Cowley, A. H. *J. Chem. Soc., Chem. Commun.* **1986**, 1081.
(3) Moderhack, D. *Synthesis* **1985**, 1083.

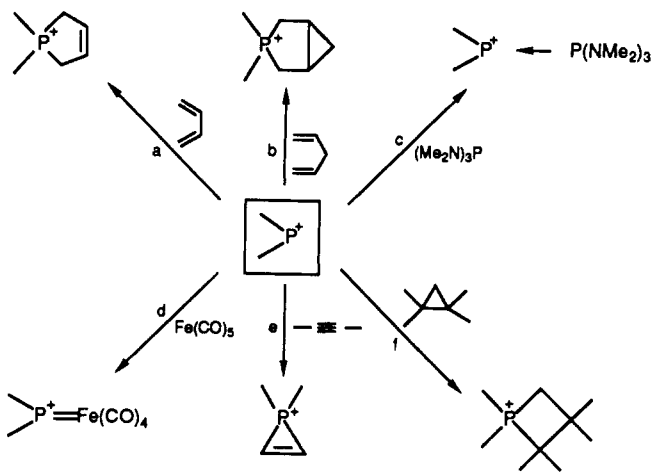
0022-3263/89/1954-5535$01.50/0

Table I. Nuclear Magnetic Resonance Spectral Data of the 1-Aza-3-phosphetine Cation 3a



^{31}P NMR:	^1H NMR			^{13}C NMR		
δ, ppm	δ, ppm	J, Hz		δ, ppm	J, Hz	
	1.35 (s)		tBu	30.8 (d)	$^4J_{CP}$ = 4.2	$C(CH_3)_3$
	1.59 (s)		tBu	32.1 (d)	$^4J_{CP}$ = 5.4	$C(CH_3)_3$
129.4	2.51 (d)	$^3J_{HP} < 2$	$PNCH_3$	36.5 (s)		$CN(CH_3)_2$
	2.82 (d)	$^3J_{HP}$ = 13.2	$PNCH_3$	37.7 (d)	$^2J_{CP}$ = 11	$PN(CH_3)_2$
	2.67 (s)		$CNCH_3$	42.0 (d)	$^2J_{CP}$ = 40.2	$PN(CH_3)_2$
	3.53 (s)		$CNCH_3$	44.6 (s)		$CN(CH_3)_2$
				58.6 (d)	$^3J_{CP}$ = 5.8	$NC(CH_3)_3$
				63.7 (d)	$^3J_{CP}$ = 1.6	$NC(CH_3)_3$
				121.9 (q)	$^1J_{CF}$ = 320.6	$CF_3SO_3^-$
				160.1 (d)	$^1J_{CP}$ = 18.9	PC
				160.92 (d)	$^1J_{CP}$ = 14.3	PC

Scheme I. Some Main Reactions of Phosphenium Salts[a]



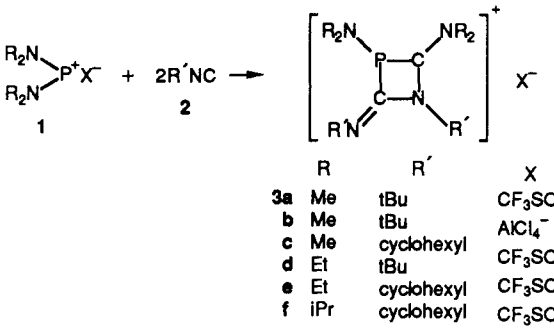
[a] Dienophile[4] (a); electrophilic carbene[5] (b); Lewis acid[6] (c); ligand[7] (d); carbene- or silylene-like reactivity[8] (e); insertion in a C–C bond[9] (f).

These properties of phosphenium salts and isocyanides prompted us to investigate what these species lead to, when they are combined. The versatile behavior of each partner and the lack of theory rationalizing the reactivity of each create difficulty in predicting the orientation of the reaction even if phosphenium ions are expected to react as electrophiles[4,5] and isocyanides as nucleophiles. If they do, still unknown cationic phosphacumulenes $R_2P^+{=}C{=}NR'$ might be formed as well as cyclic adducts and especially unusual three- or four-membered rings derived by formal [1 + 1 + 1] or [1 + 1 + 2] cycloaddition.

Results and Discussion

1-Aza-3-phosphetine Cation Formation. Phosphenium salts 1 (1 equiv) were allowed to react with *tert*-butyl isocyanide or cyclohexyl isocyanide (2 equiv) in dichloromethane at room temperature for 3 h. The first stable cyclic 1-aza-3-phosphetine cations **3a–f** were obtained in excellent yields (Scheme II). Half of the starting phosphenium salt is recovered when 1 equiv of isocyanide is used.

Scheme II



	R	R′	X
3a	Me	tBu	$CF_3SO_3^-$
b	Me	tBu	$AlCl_4^-$
c	Me	cyclohexyl	$CF_3SO_3^-$
d	Et	tBu	$CF_3SO_3^-$
e	Et	cyclohexyl	$CF_3SO_3^-$
f	iPr	cyclohexyl	$CF_3SO_3^-$

The presence of the anions $AlCl_4^-$ or $CF_3SO_3^-$ is proved by NMR. Indeed the anion $AlCl_4^-$ gives a sharp signal at δ 104 ppm in ^{27}Al NMR while the ^{19}F and ^{13}C NMR of $CF_3SO_3^-$ are characteristic for such anionic species (see Experimental Section). In no case did we observe a supplementary coupling constant $^3J_{CP}$ in ^{13}C NMR, which would have resulted from formation of a covalent bond $>POSO_2CF_3$. The insolubility of derivatives **3a–f** in nonpolar solvents confirms their cationic structures.

The structural identification of these compounds was mainly established by NMR spectroscopy. For clarity we shall discuss the NMR spectroscopic parameters of one of these compounds, i.e., **3a** (see Table I).

The ^{31}P chemical shift (+130 ppm) is in agreement with either a $\sigma^3\lambda^3$, a $\sigma^3\lambda^5$, or even a $\sigma^3\lambda^4$ phosphorus atom. Note that Bertrand et al.[10] reported the same ^{31}P chemical shift

(4) Soohoo, C. K.; Baxter, S. G. *J. Am. Chem. Soc.* **1983**, *105*, 7446. Cowley, A. H.; Kemp, R. A.; Lasch, J. G.; Norman, N. C.; Stewart, C. A. *J. Am. Chem. Soc.* **1983**, *105*, 7444.

(5) Cowley, A. H.; Kemp, R. A.; Lasch, J. G.; Norman, C. A.; Stewart, C. A.; Whittlesey, B. R.; Wright, T. C. *Inorg. Chem.* **1986**, *25*, 740. Cowley, A. H.; Stewart, C. A.; Whittlesey, B. R.; Wright, T. C. *Tetrahedron Lett.* **1984**, *25*, 815.

(6) Schultz, C. W.; Parry, R. W. *Inorg. Chem.* **1976**, *15*, 3042. Schmidpeter, A.; Lochschmidt, S. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 253. Schmidpeter, A.; Lochschmidt, S.; Sheldrick, W. S. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 226.

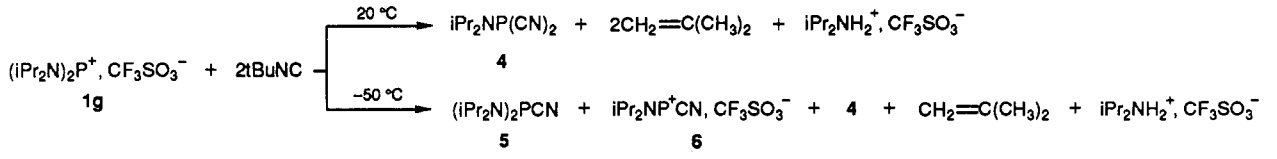
(7) Montemayor, R. G.; Sauer, D. T.; Fleming, S.; Bennett, D. W.; Thomas, M. G.; Parry, R. W. *J. Am. Chem. Soc.* **1978**, *100*, 2232.

(8) Fongers, K. S.; Hogeveen, H.; Kingma, R. F. *Tetrahedron Lett.* **1983**, *24*, 643. Lochschmidt, S.; Mathey, F.; Schmidpeter, A. *Tetrahedron Lett.* **1986**, *27*, 2635. Cowley, A. H.; Stewart, C. A.; Whittlesey, B. R.; Wright, T. C. *Tetrahedron Lett.* **1984**, *25*, 815.

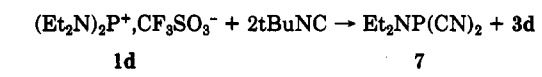
(9) Weissman, S. A.; Baxter, S. G. *Tetrahedron Lett.* **1988**, *29*, 1219.

(10) Igau, A.; Grutzmacher, H.; Baceiredo, A.; Bertrand, G. Private communication.

Scheme III



Scheme IV

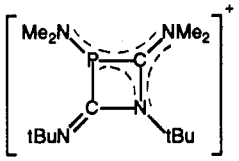


for the linear cation $(iPr_2N)_2P^+{=}C(SiMe_3)_2$.

The cyclic structure does not contain any element of symmetry: all the methyl and *tert*-butyl groups are diastereotopic. Thus the proton NMR spectra show two different signals for the methyl groups of the Me_2N–P fragment [δ = 2.51 (d), $^3J_{HP} < 2$ Hz; δ = 2.82 (d), $^3J_{HP}$ = 13.2 Hz] and for the methyl groups of the Me_2N–C fragment [δ = 2.67 (s), δ = 3.53 (s)]. The geminal CH_3 groups are nonequivalent probably because of hindered rotation around the P–N and C–N bonds due to delocalization along the $Me_2N{=}{-}P{=}{-}C{=}{-}NMe_2$. As expected, no proton–phosphorus coupling constant is detected for the dimethylamino group attached to carbon; moreover, the two *tert*-butyl groups are also nonequivalent.

The ^{13}C NMR spectrum reveals all carbon atoms of the molecule. The relatively low direct C–P coupling constant (14.30 and 18.90 Hz), already observed for neutral four-membered rings,[11] can be pointed out. Lastly, characteristic ν C=N (1670 and 1630 cm^{-1}) are detected by infrared spectroscopy.

To summarize, the spectroscopic data for **3a** allowed us to propose structure A in which the π electrons are delocalized along the three sequences of atoms N_1–P–C_1, P–C_1–N_2, and N_2–C–N_3. Therefore, we can conclude that the ring is probably planar and that the stabilities of **3a** and derivatives **3b–f** seem to be a consequence of charge delocalization.



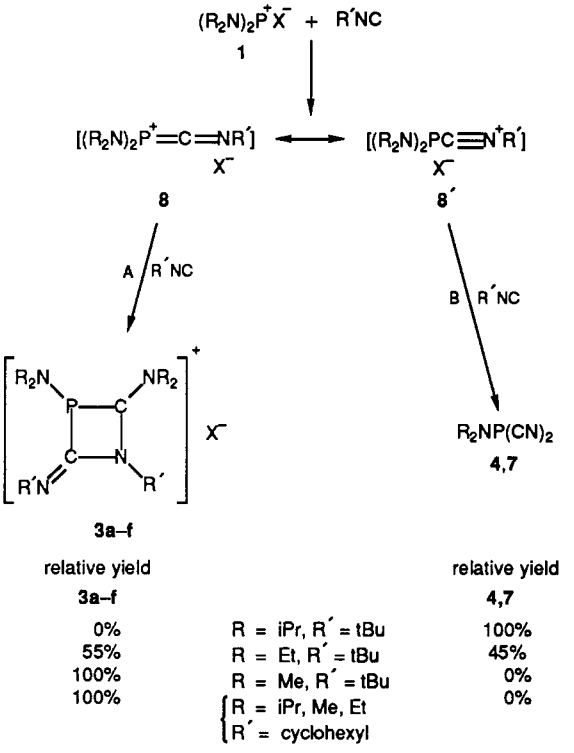
A

Cyano- and Dicyanophosphine Formation. Addition of *tert*-butyl isocyanide (2 equiv) to phosphenium salt **1g** [$(iPr_2N)_2P^+CF_3SO_3^-$, 1 equiv] at room temperature did not lead to the cyclic cation **3g** (R = iPr, R′ = tBu) but to the aminodicyanophosphine **4**, the salt $iPr_2NH_2CF_3SO_3$, and isobutene (Scheme III). The same reaction performed at −50 °C allowed us to isolate the diaminocyanophosphine **5** and the phosphenium cyanide **6** in addition to the three already mentioned products.

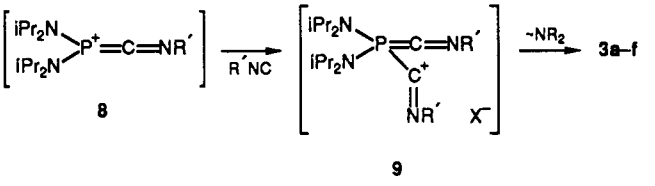
On the other hand, the 1-aza-3-phosphetine cation **3d** and (diethylamino)dicyanophosphine ($Et_2NP(CN)_2$, **7**) were both obtained when the bis(diethylamino)phosphenium salt **1d** (1 equiv) was added to *tert*-butyl isocyanide (2 equiv) (Scheme IV).

Mechanism of Formation of 1-Aza-3-phosphetines 3a–f and Cyano- and Dicyanophosphines 4, 5, and 7.

Scheme V



Scheme VI



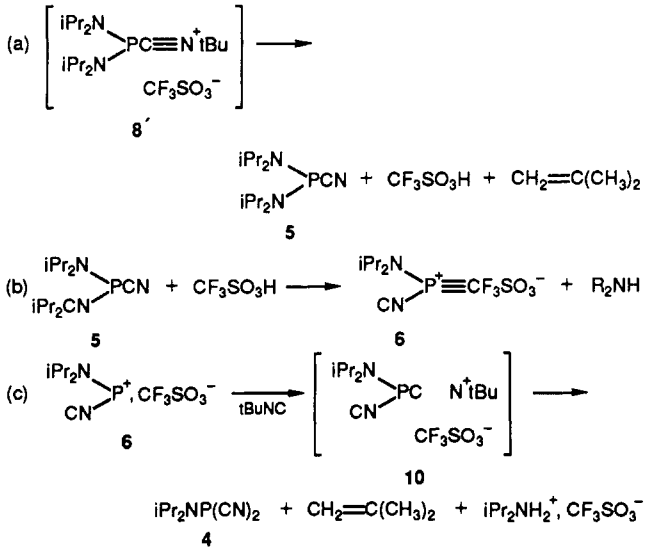
Whatever the nature of the substituents R and R′, the first step of the reaction is probably nucleophilic attack of the isocyanide, which leads to intermediate phosphacumulene cation $(R_2N)_2P^+{=}C{=}NR'$ **8**, which is in resonance with nitrilium salt $(R_2N)_2PC{\equiv}N^+R'$ **8′**. Two competitive reactions then occur: (i) attack of the second equivalent of isocyanide on the electrophilic center $>P^+{=}$ and formation of the cyclic cations **3** (route A, Scheme V) and (ii) elimination of isobutene from **8′** and formation of dicyanophosphines **4** or **7** (route B, Scheme V).

The reaction of phosphenium salts **1** with *tert*-butylisocyanide strongly depends on the nature of the phosphorus substitutents. Indeed, the presence in compound **1f** of two diisopropylamino groups bonded to phosphorus hinders the attack of the second molecule of *tert*-butyl isocyanide, and consequently, elimination of isobutene predominates. The reduced hindrance of the diethylamino groups in **1e** explains why two possible reactions (paths A and B) can occur. The fact that only the cyclic cation **3a** is obtained from **1a** and tBuNC strongly suggests that path A is kinetically favored.

One can postulate that attack of the second equivalent of isocyanide on the electrophilic phosphorus atom of **8**

(11) Becker, G.; Härer, J.; Uhl, G.; Wessely, H. J. *Z. Anorg. Allg. Chem.* **1985**, *520*, 120. Becker, G.; Riffel, H.; Uhl, W.; Wessely, H. J. *Z. Anorg. Allg. Chem.* **1986**, *534*, 31. Appel, R.; Winklaus, V.; Knoch, F. *Chem. Ber.* **1986**, *119*, 2466.

Scheme VII



affords the transient species **9**. Cyclization of **9** followed by 1,2-amino migration from phosphorus to carbon gives rise to the 1-aza-3-phosphetine **3** (Scheme VI).

The mechanism of formation of dicyanophosphine **4** from nitrilium salts **8'** is outlined in Scheme VII and might involve reactions a–c, as follows.

Reaction a: nucleophilic attack of anion $CF_3SO_3^-$ on an acidic proton of the *tert*-butyl group of **8'** which produces triflic acid, isobutene, and bis(diisopropylamino)-cyanophosphine (**5**) (isolated when the reaction is performed at low temperature).

Reaction b: cleavage of a P–N bond of **5** by triflic acid and generation of the cyanophosphenium cation iPr_2NP^+CN (**6**) unambiguously characterized by ^{31}P NMR (δ ^{31}P = +73).[12] Such a P–N bond breaking was also observed by Dahl[13] when tris(dimethylamino)phosphine was treated with triflic acid:

$$(Me_2N)_3P + 2CF_3SO_3H \rightarrow (Me_2N)_2P^+CF_3SO_3^- + H_2NMe_2CF_3SO_3$$

Reaction c: nucleophilic attack of the second equivalent of *tert*-butylisocyanide on iPr_2NP^+CN and formation of (diisopropylamino)dicyanophosphine (**4**) through intermediate **10**.

Such a mechanism is corroborated by two experiments: (i) reaction of compound **5** with tBuNC in the presence of CF_3SO_3H and (ii) addition of tBuNC to the cation iPr_2NP^+CN (**6**). In both cases, the dicyanophosphine **4** is obtained in excellent yield.

Conclusion. Reactions of R_2P^+ with isocyanides afford either the new 1-aza-3-phosphetine cations **3a–f** or unstable cyanophosphenium salts and the corresponding cyano- and dicyanophosphines. The formation of all these species can be rationalized in terms of the transient formation of novel key intermediates: the cationic phosphacumulenes $R_2P^+=C=N-R'$ in resonance with the nitrilium salts $R_2PC\equiv N^+R'$. New examples of the use of phosphenium salts in heterocyclic chemistry are thus proposed.

Experimental Section

All experiments were performed in an atmosphere of dry argon. Dry, oxygen-free solvents were used at all times. ^1H NMR spectra were recorded on a Bruker WM 250 or a Bruker AC80 spectrometer. ^1H chemical shifts are reported in parts per million relative to Me_4Si as internal reference. ^{31}P NMR spectra were obtained on a Bruker WM250 or a Bruker AC80. Downfield shifts are expressed with a positive sign, in parts per million relative to external 85% H_3PO_4. ^{19}F and ^{27}Al chemical shifts are reported in parts per million relative respectively to CF_3CO_2H and $Al(NO_3)_3 \cdot 6H_2O$ as internal reference. Infrared spectra were recorded on a Perkin-Elmer 225 instrument. Mass spectra were obtained on a Varian MAT 3MA instrument.

General Procedure for the Preparation of the 1-Aza-3-phosphetine Cations 3a–c,e,f. A solution of isocyanide (0.01 mol) in dichloromethane (5 mL) was slowly added dropwise at room temperature under argon to a solution of bis(dialkylamino)phosphenium trifluoromethanesulfonate or tetrachloroaluminate[12] in dichloromethane (20 mL). The reaction mixture was stirred for a half-hour, the solvent evaporated, and the brown residue washed with a 9/1 mixture of pentane/dichloromethane (4 × 10 mL) to give **3a–c,e,f** as brown oils.

3a: yield 92%; see Table I. Anal. Calcd for $C_{15}H_{30}F_3N_4O_3PS$: C, 41.47; H, 6.96; N, 12.89; Found: C, 41.22; H, 6.75; N, 12.68.

3b: yield 89%. The NMR parameters are similar to those for **3a**. ^{27}Al NMR ($CDCl_3$): δ 102.3 (s, $AlCl_4^-$) ppm. IR ($CDCl_3$): 1630 (br) (ν C=N) cm^{-1}. Anal. Calcd for $C_{14}H_{30}AlCl_4N_4P$: C, 37.02; H, 6.66; N, 12.33. Found: C, 37.31; H, 6.70; N, 12.25.

3c: yield 90%. ^{31}P NMR ($CDCl_3$): δ 124.2 ppm. ^1H NMR ($CDCl_3$): δ 1.8 (m, CH_2 cycl), 2.70 (m, 6 H, $PNCH_3$), 3.23 (s, 3 H, $CNCH_3$), 3.46 (s, 3 H, $CNCH_3$), 3.60 (m, 2 H, CH cycl) ppm. ^{13}C NMR ($CDCl_3$): δ 24 (m, CH_2 cycl), 32.8 [s, $CN(CH_3)_2$], 34 (m, CH_2 cycl), 35.71 [s, $CN(CH_3)_2$], 38.34 [d, $^2J_{CP}$ = 12.3 Hz, $PN(CH_3)_2$], 42.57 [d, $^2J_{CP}$ = 56.4 Hz, $PN(CH_3)_2$], 66.49 (d, $^3J_{CP}$ = 12 Hz, CH cycl), 70.99 (s, CH cycl), 158.99 (d, $^1J_{CP}$ = 19.6 Hz, PC<), 161.41 (d, $^1J_{CP}$ = 7.5 Hz, PC=N) ppm. ^{19}F NMR ($CDCl_3$): δ –0.2 (s, $CF_3SO_3^-$) ppm. IR ($CDCl_3$): 1645 (ν C=N) cm^{-1}. Anal. Calcd for $C_{19}H_{34}F_3N_4O_3PS$: C, 46.90; H, 7.04; N, 11.51. Found: C, 46.71; H, 7.31; N, 11.19.

3e: yield 80%. ^{31}P NMR ($CDCl_3$): δ 119.0 ppm. ^1H NMR ($CDCl_3$): δ 1.10 (t, $^3J_{HH}$ = 7 Hz, 3 H, CH_3CH_2), 1.20 (t, $^3J_{HH}$ = 7 Hz, 9 H, CH_3CH_2), 1.70 (m, 20 H, CH_2 cycl), 3.50 (m, 8 H, CH_3CH_2), 4.00 (m, 2 H, CH cycl) ppm. ^{13}C NMR ($CDCl_3$): δ 14.60 [s, $CN(CH_2CH_3)_2$], 16.70 [s, $CN(CH_2CH_3)_2$], 15.3 [m, $PN(CH_2CH_3)_2$], 24 (m, CH_2 cycl), 34 (m, CH_2), 44 [m, $PN(CH_2CH_3)_2$], 47.29 [s, $CN(CH_2CH_3)_2$], 48.5 [s, $CN(CH_2CH_3)_2$], 58.78 (d, $^2J_{CP}$ = 5.6 Hz, CH cycl), 66.48 (d, $^2J_{CP}$ = 12.3 Hz, CH cycl), 121.8 (q, $^1J_{CF}$ = 320 Hz, $CF_3SO_3^-$), 159.8 (d, $^1J_{CP}$ = 19.34 Hz, PC<), 162.7 (d, $^1J_{CP}$ = 7.45 Hz, PC=N) ppm. ^{19}F NMR ($CDCl_3$): δ –0.25 (s, $CF_3SO_3^-$) ppm. IR ($CDCl_3$): 1660 (ν C=N) cm^{-1}. Anal. Calcd for $C_{23}H_{42}F_3N_4O_3PS$: C, 50.91; H, 7.80; N, 10.32. Found: C, 50.69; H, 7.61; N, 10.24.

3f: yield 90%. ^{31}P NMR ($CDCl_3$): δ 109.4 ppm. ^1H NMR ($CDCl_3$): δ 1.10 (d, 3 H), 1.22 (d, 3 H), 1.37 (d, 6 H), 1.47 (d, 3 H), 1.50 (d, 6 H), 1.52 (d, 3 H), (6 d, $^3J_{HH}$ = 6.7 Hz, CCH_3), 2 (m, 20 H, CH_2 cycl), 3.41 (m, 2 H, $CHMe_2$), 3.61 (m, 2 H, $CHMe_2$), 3.95 (m, 1 H, CH cycl), 4.50 (m, 1 H, CH cycl) ppm. ^{13}C NMR ($CDCl_3$): δ 21.37 (s, CH_3), 21.74 (s, CH_3), 24.1 (s, CH_3), 24.6 (s, CH_3), 25.34 (s, CH_3), 25.73 (s, CH_3), 33.35, 33.85, 34.7, 35.0 (CH_2 cycl), 47.06 (d, $^2J_{CP}$ = 27.4 Hz, PNCH), 50.75 (d, $^2J_{CP}$ = 11.2 Hz, PNCH), 47.97 (s, =CNCH), 53.5 (s, =CNCH), 60.78 (d, $^3J_{CP}$ = 6.3 Hz, CH cycl), 65.62 (d, $^3J_{CP}$ = 13.7 Hz, CH cycl), 121.5 (q, $^1J_{CF}$ = 321 Hz, $CF_3SO_3^-$), 164.84 (d, $^1J_{CP}$ = 4.43 Hz, PC<), 165.35 (d, $^1J_{CP}$ = 18.54 Hz, PC=N) ppm. ^{19}F NMR ($CDCl_3$): δ –0.22 (s, $CF_3SO_3^-$) ppm. IR ($CDCl_3$) 1660 (ν C=N) cm^{-1}. Anal. Calcd for $C_{27}H_{50}F_3N_4O_3PS$: C, 54.16; H, 8.42; N, 9.36. Found: C, 54.61; H, 8.28; N, 9.27.

Synthesis of the Azaphosphetine Cation 3d and of Dicyano(diethylamino)phosphine (7). A solution of *tert*-butyl isocyanide (0.831 g, 0.01 mol) in dichloromethane (10 mL) was added, dropwise at room temperature, to a solution of bis(diethylamino)phosphenium trifluoromethanesulfonate (1.621 g, 0.005 mol) in dichloromethane (10 mL). The reaction mixture was stirred for 1 h. After evaporation of the solvent under reduced pressure, dicyanophosphine **7**[14] was extracted with 10 mL of a 9/1 pentane/dichloromethane mixture. The residue was dissolved in 2 mL of dichloromethane and maintained at –10 °C for 24 h,

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(13) Dahl, O. *Tetrahedron Lett.* **1982**, *23*, 1493.
(14) Wilkie, C. A.; Parry, R. W. *Inorg. Chem.* **1980**, *19*, 1499.

till all the diethylammonium trichloromethanesulfonate salt precipitated, while the azaphosphetine cation **3d** remained in solution. Evaporation of the solution afforded **3d** as a brown oil.

3d: yield 50%. ^{31}P NMR ($CDCl_3$): δ 132.4 ppm. ^1H NMR ($CDCl_3$): δ 1.00 (t, $^3J_{HH}$ = 7 Hz, 3 H, CH_3CH_2), 1.12 (t, $^3J_{HH}$ = 7 Hz, 9 H, CH_3CH_2), 1.15 [s, 9 H, $C(CH_3)_3$], 1.33 [s, 9 H, $C(CH_3)_3$], 2.6–2.9 (m, 8 H, CH_2CH_3) ppm. ^{13}C NMR ($CDCl_3$): δ 11.34 [s, $CN(CH_2CH_3)_2$], 14.0 [s, $CN(CH_2CH_3)_2$], 14.2 [m, $PN(CH_2CH_3)_2$, 30.2 [d, $^4J_{CP}$ = 4.6 Hz, $NC(CH_3)_2$], 31.3 [d, $^4J_{CP}$ = 6.4 Hz, $=NC(CH_3)_3$], 41.9 [d, $^2J_{CP}$ = 13.1 Hz, $PN(CH_2CH_3)_2$], 43.4 [s, $CN(CH_2CH_3)_2$, 46.9 [s, $CN(CH_2CH_3)_2$], 45.8 [d, $^2J_{CP}$ = 45 Hz, $PN(CH_2CH_3)_2$], 58.65 [d, $^3J_{CP}$ = 6.4 Hz, $>NC(CH_3)_3$], 63.58 [d, $^3J_{CP}$ = 1 Hz, $=NC(CH_3)_3$], 120.83 (q, $^1J_{CF}$ = 319.7 Hz, $CF_3SO_3^-$, 158.59 (d, $^1J_{CP}$ = 14.5 Hz, $PC<$), 160.44 (d, $^1J_{CP}$ = 19.4 Hz, $PC=N$) ppm. ^{19}F NMR ($CDCl_3$): δ −0.25 (s, $CF_3SO_3^-$) ppm. IR ($CDCl_3$): 1670, 1600 (ν C=N) cm^{-1}. Anal. Calcd for $C_{19}H_{38}F_3N_4O_3PS$: C, 46.52; H, 7.81; N, 11.42. Found: C, 46.18; H, 7.71; N, 11.21.

Addition of *tert*-Butyl Isocyanide to Bis(diisopropylamino)phosphenium Trifluoromethanesulfonate. A solution of *tert*-butyl isocyanide (0.831 g, 0.01 mol) in dichloromethane (10 mL) was slowly added at −78 °C to a solution of bis(diisopropylamino)phosphenium trifluoromethanesulfonate (1.900 g, 0.005 mol) in dichloromethane (10 mL). At the end of the addition, the resulting mixture was immediately concentrated to dryness. The residue thus obtained was treated with 4 × 15 mL of pentane. The insoluble portion contained the (diisopropylamino)cyanophosphenium trifluoromethanesulfonate as a brown oil while evaporation of the pentane solution afforded bis(diisopropylamino)cyanophosphine (**5**) as a white powder.

5: yield 50%. ^{31}P NMR ($CDCl_3$): δ 36 ppm. ^1H NMR ($CDCl_3$): δ 1.2 (d, $^3J_{HH}$ = 6.5 Hz, 24 H, CH_3), 3.5 (m, 4 H, C*H*) ppm. IR ($CDCl_3$): 2180 (ν C≡N) cm^{-1}. MS: *m/e* 257 (M^+), 231 (M^+ − CN), 157 (M^+ − NPr^i_2). Anal. Calcd for $C_{13}H_{28}N_3P$: C, 60.67; H, 10.97; N, 16.32. Found: C, 60.58; H, 10.88; N, 16.27.

The same reaction performed at room temperature led after similar workup to (diisopropylamino)dicyanophosphine (**4**) obtained as a white powder.

4: yield 40%. ^{31}P NMR ($CDCl_3$): δ −21 ppm. ^1H NMR ($CDCl_3$): δ 1.23 (d, $^3J_{HH}$ = 7 Hz, 12 H, CH_3), 3.7 (m, 2 H, C*H*) ppm. IR ($CDCl_3$): 2180 (ν C≡N) cm^{-1}. Anal. Calcd for $C_8H_{14}N_3P$: C, 52.45; H, 7.70; N, 22.94. Found: C, 52.41; H, 7.61; N, 22.87.

Reaction of Bis(diisopropylamino)cyanophosphine (5) with tBuNC in the Presence of Triflic Acid. To a solution of bis(diisopropylamino)cyanophosphine (**5**, 1.29 g, 0.005 mol) in dichloromethane (10 mL) were added triflic acid (0.750 g, 0.005 mol) and then a solution of *tert*-butyl isocyanide (0.416 g, 0.005 mol) in dichloromethane at room temperature. After stirring for 2 h, the solvent was evaporated. The resulting oil was dissolved in dichloromethane (2 mL) and maintained at −20 °C overnight. The ammonium salt precipitated while (diisopropylamino)dicyanophosphine (**4**, 60%) remained in solution and was treated as above.

Reaction of (Diisopropylamino)cyanophosphenium Salt 6 with tBuNC. To a solution of (diisopropylamino)cyanophosphenium salt **6**[12] in dichloromethane (1.531 g, 0.005 mol) was added a solution of *tert*-butyl isocyanide (0.416 g, 0.005 mol) in dichloromethane (10 mL) at room temperature. After stirring for 4 h, the solvent was evaporated and the resulting oil treated as above. (Diisopropylamino)dicyanophosphine (**4**) was obtained in 90% yield.

Registry No. **1a**, 122947-19-7; **1b**, 100084-30-8; **1d**, 114706-85-3; **1f**, 114684-87-6; **2a**, 7188-38-7; **2c**, 931-53-3; **3a**, 122947-21-1; **3b**, 123001-74-1; **3c**, 122947-23-3; **3d**, 122947-25-5; **3e**, 122947-27-7; **3f**, 122947-29-9; **4**, 122947-30-2; **5**, 97135-49-4; **6**, 114684-85-4; **7**, 33326-16-8.

Organoaluminum-Induced Opening of the Pyranosidic Ring of Benzyl 2-Deoxy-2-*C*-methylpentopyranosides[1]

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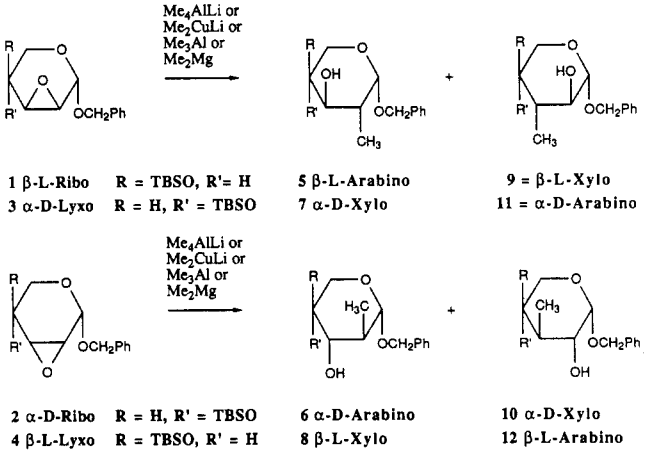
Benzyl 2-deoxy-2-*C*-methylpentopyranosides ring open via attack at the anomeric carbon by the nucleophilic part of organoaluminum reagents (Me_2AlR) to give chiral, partially protected, branched 1,2,3,5-tetrol derivatives **13–32**. The reaction represents a direct chain extension of the glycosides at C-1.

We recently reported that the oxirane rings of certain 2,3-anhydropentopyranosides (**1–4**) were regio- and stereoselectively cleaved by organometallic reagents such as Me_4AlLi, Me_2CuLi, Me_3Al, and Me_2Mg to give the branched carbohydrate derivatives **5–8** or **9–12** (Scheme I).[2] The selectivity was controlled by the proper matching of substrate and reagent. We noticed, however, that a side reaction took place when oxirane **1** was treated with Me_3Al. This reaction has now been further studied.

When **1** was treated with 1.3 equiv of Me_3Al, the deoxymethyl pentosides **5** and **9** were formed in 37% and 11% yield, respectively. Under similar reaction conditions but with 4.0 equiv of Me_3Al, neither **5** nor **9** could be detected. Instead, the major product of this reaction turned out to be a 10:1 diastereomeric mixture of the chain-extended tetrol derivatives **13**/**14**[3] (Scheme II). The primary epoxide opening product, i.e. the aluminum alcoholate of **5**, obviously underwent opening of the pyranosidic ring, since pure **5** when treated with 3.0 equiv of Me_3Al gave the same product mixture (**13**/**14**). Similar results were obtained

Scheme I



(1) Presented in part at the Seventh IUPAC Conference on Organic Synthesis, July 4–7, 1988, in Nancy, France.

(2) Inghardt, T.; Frejd, T.; Magnusson, G. *J. Org. Chem.* **1988**, *53*, 4542.

(3) There are a few examples in the literature of acetal cleavages by trialkylalanes. See: Takano, S.; Ohkawa, T.; Ogasawara, K. *Tetrahedron Lett.* **1988**, *29*, 1823 and references cited therein.

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