Communications to the Editor

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ALLYLIC REARRANGEMENT OF α,β-UNSATURATED KETONE-DIETHYL PHOSPHOROCYANIDATE ADDUCTS

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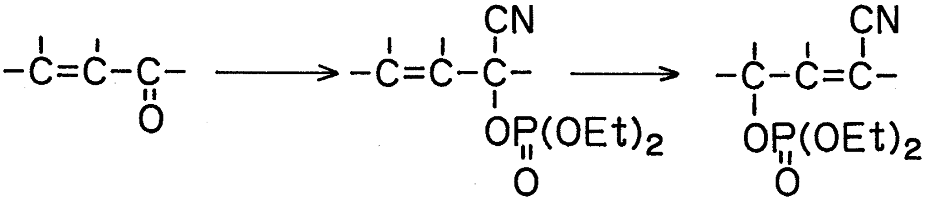
α,β-Unsaturated ketones react with diethyl phosphorocyanidate in the presence of lithium cyanide to give α-diethylphosphonooxy nitriles which are transformed into conjugated allylic phosphates *via* a novel boron trifluoride etherate-catalyzed allylic rearrangement.

KEYWORDS —— diethyl phosphorocyanidate; lithium cyanide; cyanophosphate; α, β -unsaturated ketone; boron trifluoride etherate; allylic rearrangement

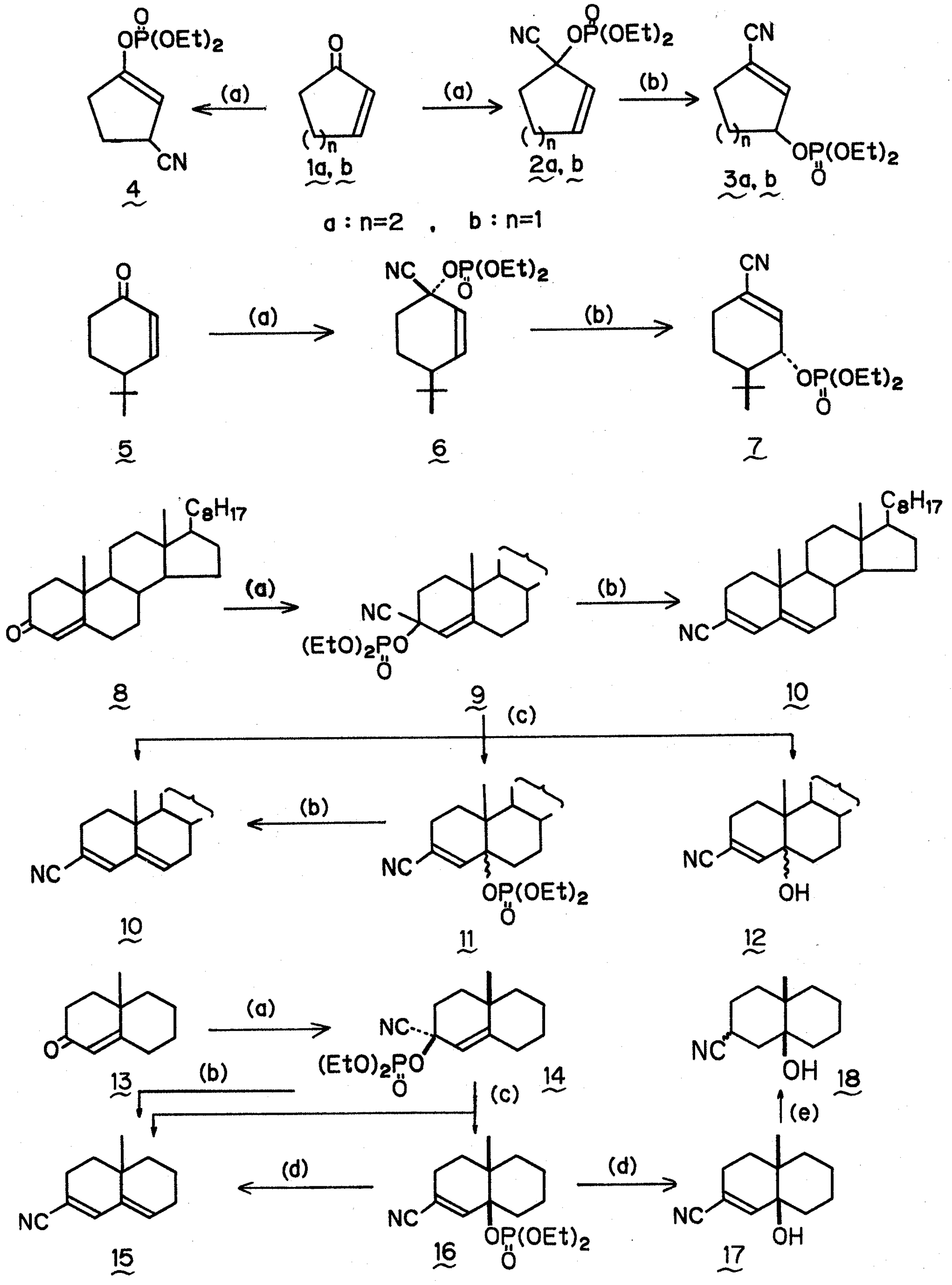
We recently reported that the *p*-benzoquinone-diethyl phosphorocyanidate [DEPC, $(EtO)_2P(O)CN$] adduct, a product of 1,2-addition to enone, was an effective intermediate for the synthesis of some 3-aryl-4-hydroxybenzonitriles.[1] Selective 1,2-addition to enones has also been reported with cyanotrimethylsilane by Evans and co-workers.[2] Conjugate hydrocyanation of α,β -unsaturated carbonyl compounds as a powerful tool in organic synthesis has been extensively studied.[3,4,5] This paper describes a 1,2-addition of DEPC to α, β -unsaturated ketone (A) and a novel boron trifluoride (BF_3) etherate-catalyzed rearrangement of the resulting allylic phosphate B to the isomer C.



A B C

Bartlett and co-worker have demonstrated the bis(acetonitrile)palladium(II)-chloride-catalyzed rearrangement of allylic phosphate in the synthesis of 3-phosphoshikimic acid.[6] However, this rearrangement requires long reaction times up to 7 days at room temperature.

To a solution of DEPC (90 mmol, 14.67 g) and lithium cyanide (LiCN) (90 mmol, 2.97 g) in 45 ml of THF was added 2-cyclohexen-1-one (**1a**, 30 mmol, 2.88 g) at room temperature. The mixture was stirred for 5 min, then the THF was removed by evaporation. The residue was partitioned between water (20 ml) and benzene-ethyl acetate (70 ml). The organic layer was separated, washed (water, brine), dried (Na_2SO_4), and concentrated. The resulting 1,2-adduct **2a** was stirred with BF_3 etherate (3 mmol, 426 mg) in 45 ml of benzene at room temperature for 2 h. After the addition of benzene (50 ml), the reaction mixture was washed (water, brine), dried (Na_2SO_4), and concentrated. Column chromatography of the residue afforded 6.30 g (81%) of 1-cyano-3-diethylphosphonooxy-1-cyclohexene (**3a**).[7] When a solution of **2a**



(a): DEPC / LiCN (b): $BF_3 \cdot Et_2O$ (c): in benzene / Δ

(d): dil. HCl in EtOH (e): 5% Pd-C / H_2

in benzene was refluxed without BF$_3$ etherate, 3a was obtained in 48% yield, thus indicating the effectiveness of BF$_3$ etherate as a catalyst for the allylic rearreangement. In contrast to the behavior of 1a, 2-cyclopenten-1-one (1b) has been found to react with DEPC-LiCN at room temperature to yield the enol phosphate (4)$^{8)}$ in 74% yield. But at -17°C the reaction afforded the 1,2-adduct 2b which was readily converted to 3b in 64% overall yield. Of the stereochemical interest, the 1,2-adduct 6 was derived from 4-t-butyl-2-cyclohexen-1-one (5)$^{9)}$ under the condition described above and was then transformed to 7 as a sole product by treatment with BF$_3$ etherate in 51% yield. The structure of 7 whose diethylphosphonooxy group is in a quasi-equatorial orientation was assigned based on the ^{1}H-NMR analysis.$^{10)}$

Furthermore, cholest-4-en-3-one (8) was treated with DEPC-LiCN in THF at -10°C followed by treatment of the resulting 1,2-adduct (9)$^{11)}$ with BF$_3$ etherate affording the heteroannular-diene nitrile (10)$^{12)}$in 90% yield. When a solution of 9 in benzene was refluxed for 2 h without a catalyst, conjugated allylic phosphate (11, 53%)$^{13)}$ and allyl alcohol (12, 17%)$^{13)}$ as well as diene nitrile (10, 17%) were obtained. Treatment of 11 with BF$_3$ etherate gave 10 in quantitative yield, thus indicating that 11 is a precursor of 10.$^{14)}$ Reaction of 6-methylbicyclo[4.4.0]dec-1-en-3-one (13) with DEPC-LiCN gave the 1,2-adduct 14 [^{1}H-NMR (CDCl$_3$) δ: 1.17 (3H, s, CH$_3$), 5.60 (1H, s, =CH)] as a sole product which was converted to the diene nitrile 15 by treatment with BF$_3$ etherate in 94% yield. Refluxing a benzene solution of 14 for 2 h without catalyst gave a mixture of 15 (50%) and 16 (46%), and the latter gave 15 in quantitative yield when treated with BF$_3$. Hydrolysis of 16 with dil. hydrochloric acid-EtOH gave the allyl alcohol (17) in 21% yield together with 15 in 42% yield. The stereochemistry of 14, 16 and 17 was inferred from comparisons of the ^{1}H- and ^{13}C-NMR spectra of the dihydro derivative (18) of 17 with those of cis- and trans-10-methyl-9-decalol.$^{15)}$

In summary, we have described a novel BF$_3$ etherate-catalyzed allylic rearrangement of α,β-unsaturated ketone cyanophosphates to produce conjugated allylic phosphates, which are useful intermediates for the synthesis of $\alpha,\beta;\gamma,\delta$-unsaturated heteroannular-diene nitriles or β-cyano-α,β-unsaturated ketones.

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7) IR ν_{max}^{liq} cm^{-1} : 2190 (CN), 1260, 960-1020 [P(O)(OEt)$_2$]. ^{1}H-NMR (CDCl$_3$) δ: 4.95 (1H, m, CHOP), 6.65 (1H, bs, =CH).

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8) Compound **4** was be easily differentiated from **3b** by hydrolysis of **4** with dil. hydrochloric acid-EtOH to yield 3-cyanocyclopentanone.

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10) The multiplet [H-C-P(O)$(OEt)_2$, δ 4.93 ppm] changed to the double triplet (J=7, 7, 2.5 Hz) by irradiation at a vinyl proton.

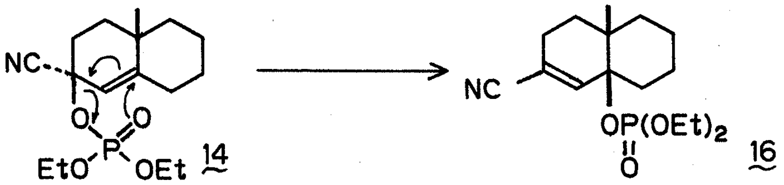
11) The ^{1}H-NMR spectrum of **9** showed a vinyl proton at δ 5.50 ppm as a singlet. Treatment of **9** with 20% NaOH in MeOH at 0°C afforded **8** in 50% yield.

12) The structure was confirmed by the fact that no Diels-Alder adduct with 4-phenyl-1,2,4-triazolin-3,5-dione was formed and by UV [$\lambda_{max}^{cyclohexane}$ nm (ε) : 262 (27,930)] spectral analysis.

13) The stereochemistry has not been determined yet. The ^{1}H-NMR spectrum showed a vinyl proton at δ 6.65 ppm in **11** and 6.63 ppm in **12** as a singlet.

14) Direct formation of the diene-nitrile **10** from **9** is also possible.

15) Catalytic hydrogenation (5% Pd-C) of **17** gave the saturated nitrile (**18**) whose NMR spectra showed angular methyl protons and carbon signals [^{1}H-NMR (CCl_4), δ 0.89 ppm ; ^{13}C-NMR ($CDCl_3$), δ 21.8 ppm] which are more comparable to the data of cis-10-methyl-9-decalol [^{1}H-NMR (CCl_4), δ 0.93 ppm$^{16)}$; ^{13}C-nmr ($CDCl_3$), δ 22.4 ppm$^{17)}$] than those of trans-isomer [^{1}H-NMR (CCl_4), δ 1.02 ppm$^{16)}$; ^{13}C-nmr($CDCl_3$), δ 20.4 ppm$^{17)}$]. The following mechanism explains the stereochemistry of **14** in which the diethylphosphonooxy group should be quasi-equatorial.



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