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Studies on Heterocyclic Analogs of Azulenes. IV.[1] Behavior of 2-Chlorocyclohepta[*b*]pyrrole Derivatives toward Phosphorus Ylide

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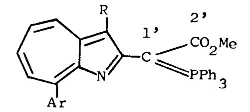
Synopsis. The transylidation reaction of methyl (triphenylphosphoranylidene)acetate with 2-chlorocyclohepta[*b*]pyrrole derivatives has been studied. 3,8-Disubstituted derivatives gave a transylidation product only, whereas 3-substituted derivatives afforded not only a transylidation products but also the compounds formed by the addition of ylide at C-8. ^{13}C NMR spectra of the transylidation products are recorded in part.

The transylidation reaction[2] has been utilized for the preparation of heterocyclic ylides[3] and alkyl- and alkenyl-substituted hetreocycles.[4] The present study was undertaken from our interest[1,5] in the reactivities of 2-chlorocyclohepta[*b*]pyrrole derivatives toward nucleophiles.

The reaction of methyl (triphenylphosphoranylidene)acetate (**5**) with 2-chloro-3-ethoxycarbonyl-8-phenyl- (**1**) and 2-chloro-3-cyano-8-*p*-methoxyphenylcyclohepta[*b*]pyrrole (**2**), respectively, proceeded to give the corresponding phosphoranes (**6**) and (**7**). However, 2-chloro-3-cyanocyclohepta[*b*]pyrrole (**3**), when treated with **5**, gave a complex mixture of products, among which a transylidation product (**8**), 2-chloro-3-cyano-8-methylcyclohepta[*b*]pyrrole (**10**), and 2-chloro-1-cyano-4-(methoxycarbonyl)cyclohepta[1,2,3-*hi*]indolizine (**11**) were characterized. The reaction of 2-chloro-3-(ethoxycarbonyl)cyclohepta[*b*]pyrrole (**4**) with **5** proceeded in a similar way to give a number of compounds besides (**9**). Most of them were obtained in small quantities, too unstable to be identified.

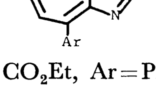
Phosphoranes (**6**—**9**) were characterized by spectral methods. IR spectra of the products show a ν(C=O) absorption at 1650—1615 cm^{-1}, characteristic of the phosphoranes possessing an α-carboxylic ester group,[6] whereas their mass spectra contain abundant ions at *m*/*e* 108, 152, 183, 185, and 262 which are diagnostic of (triphenylphosphoranylidene)acetates.[7] ^{13}C NMR spectra provide a conclusive evidence in favor of the structures (**6**—**9**). The ^{13}C chemical shifts and ^{13}C- ^{31}P couplings for these products (Table 1) were easily assigned by reference to the spectra of the related azaazulenes and data on phosphoranes.[8] We see that there are long-range couplings (J=6—12 Hz) involving ^{31}P nucleus and each of the ring carbons-2 and -3; the structure in which the ylide moiety is attached to C-8 is not compatible with the observations. The phosphoranes are protonated by acid. As an example, UV spectrum of **9**, when determined for a neutral solution, displays absorptions at 272, 309, 354, and 448 nm. However, the spectrum taken in the presence of trifluoroacetic acid (265, 286^{sh}, 345, and 482 nm) resembles that of 1,2-dihydro-3-ethoxycarbonyl-2-[cyano(ethoxycarbonyl)methylene]cyclohepta[*b*]pyrrole.[1] This fact indicates that protonation occurred at the ring nitrogen atom. The spectrum of the neutral solution was also obtained on basification of the acidified solution.

Table 1. Partial ^{13}C chemical shifts and $J_{^{31}P\text{-}^{13}C}$ values of **6**, **8**, **9**

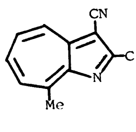


Carbon	6	8	9
1′	129.4(112.3)	131.0(112.3)	131.0(129.4)
2′	168.0(13.4)	166.6(14.6)	168.6(14.6)
2	168.5(6.1)	168.8(7.0)	169.1(12.2)
3	114.7(8.5)	92.2(9.8)	115.2(8.5)
3a	147.5	150.5	146.7
4	129.1	128.8	130.4
5	126.6	126.7	129.5
6	129.8	129.4	130.7
7	129.1	127.6	130.3
8	130.3	132.9	132.6
8a	154.6	157.1	158.1

Compound **10** was identified by a comparison of its melting point with that reported.[9] The NMR spectrum of **11** indicates the presence of a 2,3,8-trisubstituted cyclohepta[*b*]pyrrole ring, whereas its UV spectrum suggests the presence of a chromophore more extended than that of **3**. From these results, together with the presence of additional two sets of one-proton doublets at δ 6.58 and 6.74 (J=8 Hz) in its NMR spectrum, we assigned the structure.



1 $R^1=Cl$, $R^2=CO_2Et$, Ar=Ph
2 $R^1=Cl$, $R^2=CN$, Ar=*p*-$MeOC_6H_4$
3 $R^1=Cl$, $R^2=CN$, Ar=H
4 $R^1=Cl$, $R^2=CO_2Et$, Ar=H
6 $R^1=C(CO_2Me)=PPh_3$, $R^2=CO_2Et$, Ar=Ph
7 $R^1=C(CO_2Me)=PPh_3$, $R^2=CN$, Ar=*p*-$MeOC_6H_4$
8 $R^1=C(CO_2Me)=PPh_3$, $R^2=CN$, Ar=H
9 $R^1=C(CO_2Me)=PPh_3$, $R^2=CO_2Et$, Ar=H



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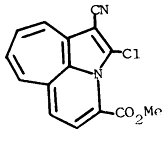

11

It is concluded that the C-6 and C-8 positions of 2-chlorocyclohepta[*b*]pyrroles are reactive toward nucleophiles despite the presence of a good leaving group at the most electron deficient C-2 and reactivities of these three positions depend on the reaction conditions[1] and the nature of nucleophiles.

Experimental

Melting points were uncorrected. IR spectra were recorded for nujol mulls. ^{1}H NMR spectra were obtained with a Varian HA-100 spectrometer at 100 MHz (solvent $CDCl_3$; Me_4Si as internal standard), and ^{13}C NMR spectra with a JEOL FX-100 spectrometer (solvent $CDCl_3$). UV spectra were measured for chloroform solutions. Molecular weights were determined by mass spectrometry with a Hitachi RMU 7 spectrometer. Chromatography was performed on Kiesel gel 60. Yields are based on unrecovered starting material.

*Reaction of **1** with **5**.* A mixture of **1** (1.00 g, 3.21 mmol) and **5** (2.08 g, 6.2 mmol) in xylene (100 ml) was heated under reflux for 5.5 h, and then heated with 10% aqueous sodium carbonate solution (20 ml) for 30 min. Water was added and the mixture was extracted with chloroform, the extracts being dried and evaporated. Chromatography of the residue with chloroform afforded triphenylphosphine oxide (1.12 g). Further elution with chloroform and benzene-ethyl acetate (4:1) gave **6** (0.25 g, 66%), orange prisms (from cyclohexane), mp 183—184 °C, NMR $\delta=1.52$ (3H, t, $J=7$ Hz), 3.43 (3H, s), 4.47 (2H, q, $J=7$ Hz), 6.82 (2H, d, $J=8$ Hz), 6.96—7.48 (15H, m), 7.52—7.80 (6H, m), 8.72—8.90 (1H, dm, $J=8$ Hz); UV_{max} 264 nm (log ε 4.35), 305 (4.30), 365 (3.84), 458 (4.18); IR 1685 (C=O), 1640 cm^{-1} (C=O). Found C, 76.57; H, 5.39; N, 2.05; P, 4.78%. Calcd for $C_{39}H_{32}NO_4P$: C, 76.84; H, 5.29; N, 2.30; P, 5.08%.

*Reaction of **2** with **5**.* A mixture of **2** (0.77 g, 2.61 mmol) and **5** (2.18 g, 6.53 mmol) in xylene (100 ml) was heated under reflux for 8.5 h and the solvent was then evaporated. Chromatography of the residue with benzene-chloroform (2:1) gave **2** (0.195 g). An oil eluted with chloroform was re-chromatographed with benzene-chloroform (1 : 2) to give **7** (0.24 g, 21%) as a red oil, which on trituration in petroleum ether-dichloromethane partly solidified, mp 115—116 °C, NMR $\delta=3.63$ (3H, s), 3.82 (3H, s), 6.48 (2H, d, $J=8$ Hz), 6.83 (2H, d, $J=8$ Hz), 6.9—8.4 (19H, m); UV_{max} 266 nm (log ε 4.16), 312 (4.18), 360^{sh} (3.75), 383^{sh} (3.70), 464 (3.98); IR 2200 (C=N), 1650 cm^{-1} (C=O). Found: C, 76.42; H, 5.16; N, 4.07; P, 5.74%. Calcd for $C_{38}H_{29}N_2O_3P$: C, 77.02; H, 4.93; N, 4.73; P, 5.23%.[10] Elution with chloroform-ethyl acetate gave an inseparable mixture of **5** and **7**.

*Reaction of **3** with **5**.* A mixture of **3** (2.00 g, 10.6 mmol) and **5** (7.60 g, 22.8 mmol) in xylene (150 ml) was heated under reflux for 8.5 h, hydrolyzed with 10% aqueous sodium carbonate solution (*vide supra*), and worked up as above. Chromatography with benzene gave **11** (0.084 g, 7%), brownish violet prisms (from benzene), mp 219 °C, NMR $\delta=3.74$ (3H, s), 5.45 (1H, dd, $J=11$ and 8 Hz), 5.73 (1H, dd, $J=12$ and 8 Hz), 6.20 (1H, d, $J=11$ Hz), 6.58 (1H, d, $J=8$ Hz), 6.74 (1H, d, $J=8$ Hz), 7.27 (1H, d, $J=12$ Hz); UV_{max} 265 nm (log ε 4.43), 273 (4.45), 369 (4.03), 393 (4.08), 417 (4.09), 463 (2.96), 499 (3.03), 540 (3.04), 591 (2.94), 650 (2.65); IR 2200 (C≡N), 1690 cm^{-1} (C=O). Found: C, 63.43; H, 3.27; Cl, 12.54; N, 9.71%. Calcd for $C_{15}H_9ClN_2O_2$: C, 63.28; H, 3.19; Cl, 12.45; N, 9.84%. Elution with benzene-chloroform (3:1) gave **10** (0.083 g, 9%), mp 201 °C (lit,[9] mp 202 °C), Found: C, 65.16; H, 3.32; N, 13.92%. Further elution with benzene-chloroform (3:1) afforded **3** (1.19 g) and elution with benzene-chloroform (1:4) gave triphenylphosphine oxide (5.54 g). Elution with chloroform gave **8** (0.79 g, 38%), orange prisms (from cyclohexane-dichloromethane), mp 210 °C, NMR $\delta=3.65$ (3H, s), 7.3—7.9 (19H, m), 8.24 (1H, d, $J=9$ Hz); UV_{max} 269 nm (log ε 4.34), 307 (4.31), 318^{sh} (4.23), 354 (3.76), 450 (4.22); IR 2200 (C≡N), 1650 cm^{-1} (C=O). Found: C, 76.20; H, 4.52; N, 5.72; P, 6.64%. Calcd for $C_{31}H_{23}N_2O_2P$: C, 76.53; H, 4.77; N, 5.76; P, 6.37%.

*Reaction of **4** with **5**.* A mixture of **4** (2.00 g, 8.49 mmol) and **5** (6.60 g, 20.4 mmol) in xylene (150 ml) was heated under reflux for 18.5 h, hydrolyzed (*vide supra*), and worked up as above. Elution with chloroform-ethyl acetate (1:1) gave **4** (0.296 g) and triphenylphosphine oxide (3.07 g) and elution with ethyl acetate afforded **9** (0.53 g, 14%), orange needles (from cyclohexane), mp 198 °C, NMR $\delta=1.46$ (3H, t, $J=7$ Hz), 3.43 (3H, s), 4.43 (2H, q, $J=7$ Hz), 7.25—7.95 (19H, m), 8.75 (1H, dm, $J=10$ Hz); UV_{max} 272 nm (log ε 4.47), 309 (4.25), 354 (3.81), 448 (4.19); IR 1675 (C=O), 1615 cm^{-1} (C=O). Found: C, 74.16; H, 5.15; N, 2.51; P, 5.77%. Calcd for $C_{33}H_{28}NO_4P$: C, 74.28; H, 5.29; N, 2.63; P, 5.81%.

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References

1) Part III, N. Abe and T. Nishiwaki, *Bull. Chem. Soc. Jpn.*, **51**, 667 (1978).

2) For a review see H. J. Bestmann, *Angew. Chem.*, **77**, 651 (1965).

3) J. J. Pappas and E. Gancher, *J. Heterocycl. Chem.*, **5**, 123 (1968).

4) E. C. Taylor and S. F. Martin, *J. Am. Chem. Soc.*, **96**, 8095 (1974).

5) N. Abe, *Heterocycles*, **4**, 221 (1976).

6) M. A. Shaw, J. C. Tebby, R. S. Ward, and D. H. Williams, *J. Chem. Soc., C*, **1967**, 2442; J. J. Pappas and E. Gancher, *J. Org. Chem.*, **31**, 1287 (1966).

7) R. G. Cooks, R. S. Ward, D. H. Williams, M. A. Shaw, and J. C. Tebby, *Tetrahedron*, **24**, 3289 (1968).

8) G. A. Gray, *J. Am. Chem. Soc.*, **95**, 7736 (1973).

9) S. Seto and T. Nozoe, *Proc. Jpn. Acad.*, **32**, 765 (1956).

10) Compound **7** was not obtained in an analytically pure state as shown by microanalytical data and the presence of an additional small peak at δ 3.93 in its ^{1}H NMR spectrum. It was difficult to crystallize and to separate completely from **5**, which resulted in unsatisfactory analytical data.