intermediacy of a hemiaminal resulting from addition of O_1 in **17** to the imino carbon (C_3). The IRC data suggest that such an equilibrium must take place after the transition state. Collapse of product complex **17** to epoxide **18** is also excluded since the latter compound does not exist at the 4-31+G level of theory but optimizes directly to α-keto lithium alkoxide **15**.

In summary, the transition state for oxygen transfer to the lithium enolate is quite similar to that for epoxidation of ethylene where the oxygen approached the alkene over one carbon atom.[8e] In consonance with existing descriptions of this type of reaction,[1,3] this oxygen atom transfer most likely involves a "closed" transition state with the metal cation providing a stabilizing binding interaction to both partially negatively charged oxygen atoms in the transition state. If coordination of the metal cation to one of the sulfonyl oxygen atoms is important, then TS-3 should be favored. The stereochemistry of the resulting α-hydroxy carbonyl compound is determined by a balance between this oxyanion stabilization and steric effects with no special stereoelectronic effects being apparent.

Acknowledgment. This work was supported in part by a grant from the National Institutes of Health (CA 47348-02) and Ford Motor Company. We are very thankful to the Pittsburgh Supercomputing Center, the Ford Motor Company, and the Computing Center at Wayne State University for generous amounts of computing time. One of us (J.L.A.) gratefully acknowledges a fellowship from the CIRIT of the Generalitat de Catalunya (Catalonia, Spain) which has made his stay at Wayne State University possible.

Registry No. **1** (X = Cl), 127184-05-8; **12**, 6827-26-5; **13**, 2053-29-4; **14**, 67285-39-6; **15**, 136586-89-5.

On the Reaction of (Vinylimino)phosphoranes and Related Compounds. 20.[1] Syntheses and Properties of Methanocyclodeca[*b*]pyridine Ring Systems

Nobuhiro Kanomata, Hiroyuki Kawaji, and Makoto Nitta*

Department of Chemistry, School of Science and Engineering, Waseda University, Shinjuku-ku, Tokyo 169, Japan

Received July 2, 1991

Novel 2-[(triphenyl- and 2-[(tributylphosphoranylidene)amino]-1,6-methano[10]annulenes (**8x,y**) and 3-[(triphenyl- and 3-[(tributylphosphoranylidene)amino]-1,6-methano[10]annulenes (**9x,y**) were generated by the Staudinger reaction of 2- and 3-azido-1,6-methano[10]annulenes (**5** and **6**). The compound **8x** was inert to α,β-unsaturated ketones, while compounds **8y** and **9y** were found to react with α,β-unsaturated ketones in enamine–alkylation process followed by aza–Wittig reaction and dehydrogenation to give 7,12- and 5,10-methanocyclodeca[*b*]pyridines **20a–f** and **26a,f**, respectively. The reactivity of **8** and **9** as well as the site selectivity of **9** was suggested by their ^{13}C NMR spectra, in which the carbon signals of the nucleophilic center appear at higher field as compared to those of 1,6-methano[10]annulene. Structural properties of **20a–f** and **26a,f** were examined by ^1H NMR and UV spectra. The ^1H NMR spectra analyzing aromatic characters clarified both remarkable reduction of a ring current and appearance of bond alternation as compared to the parent 1,6-methano[10]annulene (**1**). The UV spectra exhibiting a prolonged cyclic conjugation are in contrast to their 10π electron analogues, 1,6-methano[10]annulene (**1**) and quinoline derivatives.

The chemistry of bridged annulenes has been developed widely and deeply, ever since Vogel et al. reported the synthesis of 1,6-methano[10]annulene (**1**) as the first stable aromatic cyclodecapentaene.[2] The aromatic nature concerning diatropicity and bond alternation is largely influenced by the fusion of another aromatic ring. A typical example is 2,3-benzo-1,6-methano[10]annulene (**2**),[3] which shows both remarkable reduction of a ring current and bond alternation in the 10π electron unit as compared to **1**. The fusion of a heteroaromatic ring, on the other hand, is expected also to cause variations of the physical properties of **1**. Although various kinds of heterocyclic annulations are possible in principle, only a few examples have been reported.[4] Our interest focused on the synthesis and spectroscopic properties of methanocyclodeca[*b*]pyridines in relation to our previous studies of azaazulene vinylogues **3** and **4**.[5] Recently, our research group has been studying synthetic utilities of (vinylimino)phosphoranes, equivalents of primary enamine, for construction of various kinds of heterocycles.[6–9] A typical example is the reaction with α,β-unsaturated ketones resulting in the formation of pyridine derivatives[7] in enamine alkylation process followed by aza–Wittig reaction and dehydrogenation. In this paper, we describe the preparation and reactions of novel 2- and 3-(phosphoranylideneamino)-1,6-methano[10]-annulenes (**8x,y** and **9x,y**), and spectroscopic properties

(1) Part 19: Nitta, M.; Mori, S.; Iino, Y. *Tetrahedron Lett.*, in press.
(2) (a) Vogel, E.; Roth, H. D. *Angew. Chem.* **1964**, *76*, 145. (b) Vogel, E.; Klug, W.; Breuer, A. *Organic Syntheses*; Wiley: New York, 1988; Collect. Vol. VI, p 731. (c) Vogel, E. *Chem. Soc. Spec. Publ.* **1967**, No. 21, 113. (d) Vogel, E. *Proc. Robart A. Welch Found. Conf. Chem. Res.* **1968**, *12*, 215.
(3) Tanimoto, S.; Schäfer, R.; Ippen, J.; Vogel, E. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 613.
(4) (a) Neidlein, R.; Lautenschläger, G. *Chem. Ber.* **1989**, *122*, 493. (b) Neidlein, R.; Tadesse, L. *Chem. Ber.* **1986**, *119*, 3862. (c) Neidlein, R.; Hartz, G. *Chem. Zeit.* **1984**, *108*, 366. (d) Brinker, U. H.; Jones, W. M. *Tetrahedron Lett.* **1976**, 577. Jones, M. W.; LaBar, R. A.; Brinker, U. H.; Gebert, P. H. *J. Am. Chem. Soc.* **1977**, *99*, 6379.
(5) Nitta, M.; Kanomata, N.; Masaru, T. *Tetrahedron Lett.* **1990**, *31*, 1291.
(6) Iino, Y.; Nitta, M. *J. Syn. Org. Chem. Jpn.* **1990**, *48*, 681.
(7) (a) Kobayashi, T.; Nitta, M. *Chem. Lett.* **1986**, 1549. (b) Kobayashi, T.; Iino, Y.; Nitta, M. *J. Chem. Soc. Jpn. (Nippon Kagaku Kaishi)* **1987**, 1237. (c) Iino, Y.; Nitta, M. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 2235. (d) Kanomata, N.; Nitta, M. *Tetrahedron Lett.* **1988**, *29*, 5957; *J. Chem. Soc., Perkin Trans. 1* **1990**, 1119. (e) Nitta, M.; Soeda, H.; Iino, Y. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 932. (f) Nitta, M.; Iino, Y. *J. Chem. Soc., Perkin Trans. 1* **1990**, 435. (g) Nitta, M.; Ohnuma, M.; Iino, Y. *Ibid.* **1991**, 1115.
(8) (a) Iino, Y.; Kobayashi, T.; Nitta, M. *Heterocycles* **1986**, *24*, 2437. (b) Iino, Y.; Hara, E.; Nitta, M. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 1913.
(9) (a) Nitta, M.; Kobayashi, T. *Chem. Lett.* **1986**, 463. (b) Nitta, M.; Iino, Y.; Hara, E.; Kobayashi, T. *J. Chem. Soc., Perkin Trans. 1* **1989**, 51. (c) Nitta, M.; Iino, Y.; Kamata, K. *Heterocycles* **1989**, *29*, 1655.

0022-3263/92/1957-0618$03.00/0

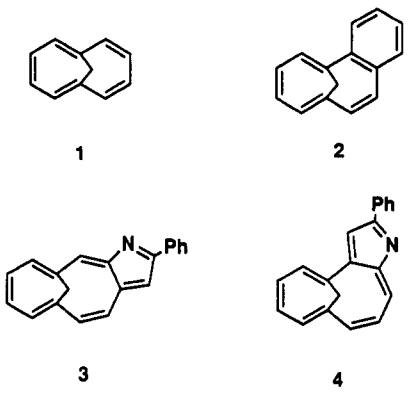
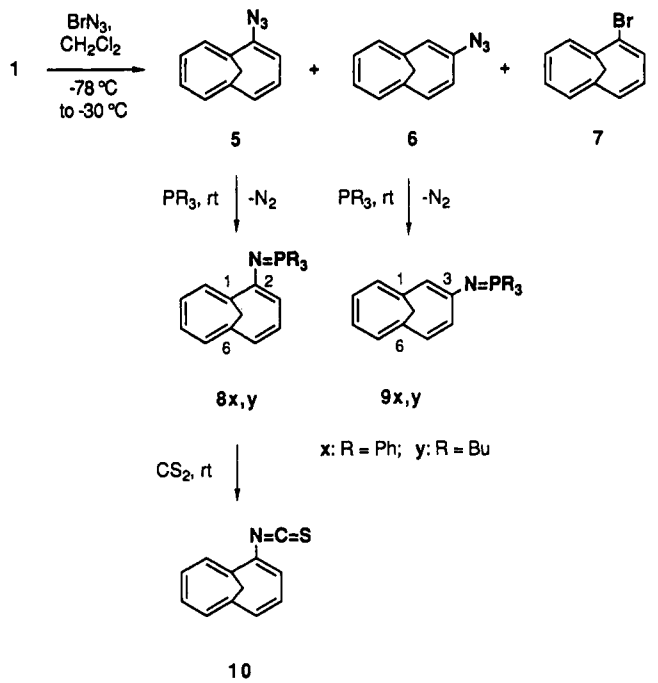


Figure 1.

Scheme I



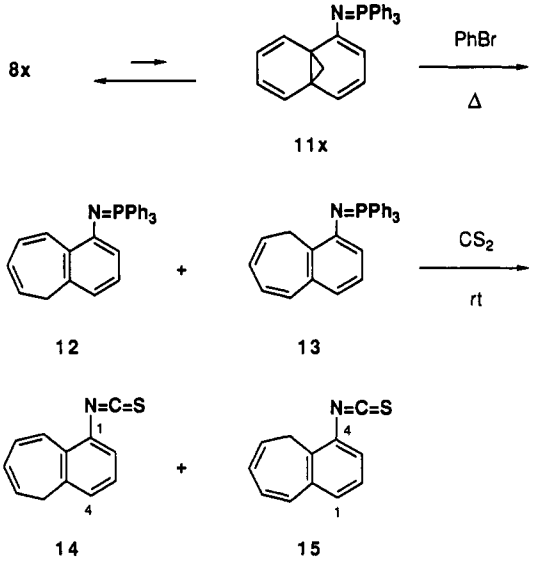
of the resulting 7,12- and 5,10-methanocyclodeca[*b*]-pyridine derivatives, **20a–f** and **26a,f**.

Results

Our synthetic strategy for methanocyclodeca[*b*]pyridines is the preparation of 2- and 3-(phosphoranylideneamino)-1,6-methano[10]annulenes (**8x,y** and **9x,y**) and their reaction with α,β-unsaturated ketones.

The iminophosphoranes, **8x,y** and **9x,y**, were prepared by the Staudinger reaction[10] of novel 2- and 3-azido-1,6-methano[10]annulenes (**5** and **6**). The azidoannulenes **5** and **6** were obtained by the reaction of **1** with bromine azide[11] in dichloromethane at low temperatures in 38% and 12% yields, respectively, in addition to 2-bromo-1,6-methano[10]annulene (**7**)[12] in a 10% yield (Scheme I). The compounds **5** and **6** seem to derive from 2,5- (1,4-addition) and 2,3-bromoazidation (1,2-addition) to **1** and following dehydrobromination. The preferential formation of **5** suggests that the 1,4-addition is predominant.[12] The structures of **5** and **6** are deduced from their ^{1}H NMR spectra and IR spectra (ν_{azide}: 2130 cm^{-1} for **5** and 2100 cm^{-1} for **6**). Since the azides **5** and **6** were unstable oily materials,[13] both of them were separated on TLC and used in the next step without further purification. The two azides reacted smoothly with triphenylphosphine at room temperature to give the iminophosphoranes **8x** and **9x** in 78% and 81% yields, respectively. The reaction of **8x** with carbon disulfide giving a known isothiocyanate derivative **10**[14] supports the structure of **8x**. Furthermore, all the spectral data of **8x** and **9x** are consistent with the proposed structures. The ^{1}H NMR spectral data provide no indication of an equilibrium between **8x** (or **9x**) and its norcaradiene form. Since most of iminotributylphosphoranes are quite labile toward water and workup conditions,[7g,8b,9c] tributyl analogues **8y** and **9y** were generated in situ by the reaction of the azides **5** and **6** with tributylphosphine at room temperature, respectively (Scheme I).

Scheme II



Our initial attempt at a pyridine annulation was made by the reaction of iminotriphenylphosphorane **8x** with an α,β-unsaturated ketone **16a** in refluxing toluene. The annulation reaction, however, did not proceed and benzocycloheptatriene derivatives **12** and **13** were obtained exclusively. Independent thermal isomerization of **8x** was completed with 20 h in refluxing bromobenzene to give a mixture of **12** and **13** in a ratio of 2/1 in a quantitative yield (Scheme II). On treatment with carbon disulfide, the mixture was converted into the mixture of isothiocyanate derivatives **14** and **15**. The structures of **14** and **15** were deduced from ^{1}H NMR spectra and the high-resolution mass spectra. The ^{1}H NMR spectrum of the mixture exhibited the methylene protons of **14** and **15** at δ 3.01 and δ 3.12, respectively, the latter of which is plausibly deshielded by an anisotropy effect of the isothiocyanate group of **15**. Although separation of the mixture was unsuccessful, the ^{1}H NMR spectrum clarified that the mixture contained **14** and **15** in a ratio of 2/1 and the position of the isothiocyanate groups. Thus, the structures of **12** and **13** were also deduced. The formation of **12** and **13** is explained by Berson–Willcott rearrangement[15] of a postulated norcaradiene intermediate **11x** which exists in an equilibrium with **8x** at a high temper-

(10) Gololobov, Y. G.; Zhmurova, I. N.; Kasukhin, L. F. *Tetrahedron* **1981**, *37*, 437.
(11) Hassner, A.; Boerwinkle, F. P.; Levy, A. B. *J. Am. Chem. Soc.* **1970**, *92*, 4879.
(12) (a) Vogel, E.; Böll, W. A. *Angew. Chem.* **1964**, *76*, 784. (b) Vogel, E.; Böll, W. A.; Biskup, M. *Tetrahedron Lett.* **1966**, 1569.
(13) ^{1}H NMR spectra (400 MHz) exhibited that the azides **5** and **6** separated by TLC are almost pure, and their satisfactory high-resolutional mass spectral data were obtained.
(14) Neidlein, R.; Constantinescu, T.; Boese, R.; Bläser, D. *Chem. Ber.* **1988**, *121*, 1699.
(15) Berson, J. A.; Willcott, M. R., III. *J. Am. Chem. Soc.* **1966**, *88*, 2494.

Scheme III

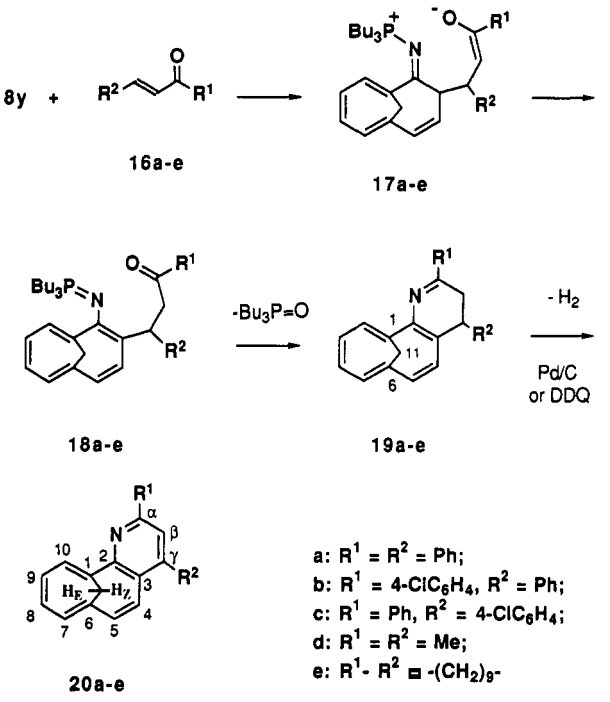


Table I. Reaction of 8y or 9y with 16a-f[a]

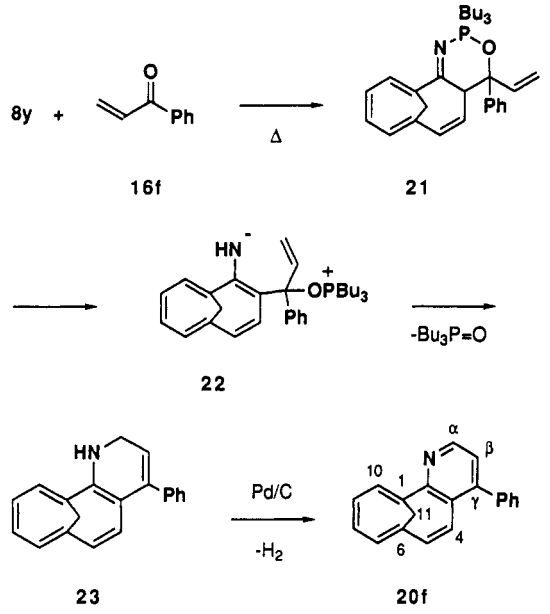
run	compd 8y/9y	16	R1	R2	condns time/h	condns oxidant	yields[b]/% 20	yields[b]/% 26
1	8y	16a	Ph	Ph	18	DDQ	47	
2	8y	16b	4-ClC6H4	Ph	15	DDQ	47	
3	8y	16c	Ph	4-ClC6H4	19	DDQ	52	
4	8y	16d	Me	Me	53	Pd/C	41	
5	8y	16e	-(CH2)9-		23	Pd/C	6	
6	8y	16f	Ph	H	22	Pd/C	8	
7	9y	16a	Ph	Ph	18	DDQ		48
8	9y	16f	Ph	H	4.5	Pd/C		42

[a] All the reactions were carried out in refluxing toluene. [b] Yields of the products are based on the azide 5 or 6 used.

ature. It is worthy to note that the isomerization of **8x** occurred at much lower temperature than that of **1**[1d] (above 250 °C) probably due to a substituent effect of an electron-donating phosphoranylideneamino group.

Since the replacement of —N=PPh$_3$ with —N=PBu$_3$ usually accelerates an enamine-type alkylation of (vinylimino)phosphoranes,[8b] the pyridine annulation using iminotributylphosphoranes **8y** and **9y** was investigated. The reaction of **8y**, which is prepared in situ, with α,β-unsaturated ketones **16a–f** in refluxing toluene and subsequent dehydrogenation gave 7,12-methanocyclodeca[*b*]pyridine derivatives **20a–f** (Schemes III and IV). The reaction conditions and the yields of the products (based on **5**) are summarized in Table I (runs 1–6). In the reaction with **16a–c**, postulated dihydropyridine derivatives **19a–c** were obtained as a mixture with **16a–c** and dehydrogenated to **20a–c**, respectively. Thus, the mixture was dehydrogenated subsequently by 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in refluxing benzene to give expected **20a–c** (runs 1–3). In the case of the reaction with **16a**, dihydropyridine derivative **19a** was isolated as a pure form after repeated chromatography (see Experimental Section). Thus, the intermediacy of dihydropyridine derivatives **19a–c** seemed to be supported. The dimethyl-substituted derivative **20d** and the nonamethylene-substituted derivative **20e** having an [9]metapyridinophane structure were obtained directly by the reaction of **8y** with **16d,e** in the presence of Pd/C as a dehydrogenating catalyst (runs 4 and 5). On the other hand, the reaction of **8y** with 1-phenyl-2-propenone (**16f**) in the presence of Pd/C resulted in the formation of **20f**, and not of the expected 2-phenyl isomer (run 6, Scheme IV).

Scheme IV



Structures of **20a–f** are deduced from their spectral data and elemental analyses (or high-resolution mass spectral data). The ^{1}H NMR spectral data for **20a–f** are listed in Table II. Unequivocal proton assignment was made by 2D ^{1}H–^{1}H and 2D ^{13}C–^{1}H correlation NMR spectra. All the chemical shifts for **20a–f** are in good accordance with the proposed structures. The structural assignment of the compounds **20b** and **20c** are quite important to discuss the reaction mechanism in Scheme III (vide infra). The ^{1}H NMR spectra of **20b** and **20c** showed that ortho protons of *p*-chlorophenyl groups appear at δ 8.21 for **20b** and δ 7.51 for **20c**. The former protons are deshielded by an electronic effect of a nitrogen atom; thus, the *p*-chlorophenyl groups are located at α- and γ-positions, respectively. In the case of **20f**, a pair of doublets appears at δ 8.81 and 7.41 (J = 4.8 Hz) which correspond to the α- and the β-protons of the annelated pyridine. Furthermore, ortho protons of the phenyl group, appearing in the range of δ 7.52–7.59, are not deshielded by an electronic effect of a nitrogen atom. Thus, the phenyl group of **20f** is located not at the α-position but at the γ-position.

The postulated reaction pathway[7a] for the formation of **20a–e** is shown in Scheme III. The enamine-type alkylation of the iminophosphorane **8y** to the β-carbon atom of **16a–e** gives **17a–e**, respectively. The following hydrogen transfer in **17a–e** gives the intermediates **18a–e**, which then undergo an intramolecular aza-Wittig reaction to produce dihydropyridines **19a–e**, respectively. The dehydrogenation of **19a–e** with DDQ or Pd/C results in the formation of **20a–e**. The plausible pathway for the formation of **20f** is depicted in Scheme IV. The C-3 carbon of **8y** attacks the carbonyl carbon of **16f** preferentially to give the intermediate **21**.[7g] We propose that the intermediate **21** then undergoes hydrogen migration and N–P bond cleavage to give the internal salt **22**, cyclization of which occurs to generate dihydropyridine derivative **23**, which is dehydrogenated with Pd/C to give the compound **20f**. The detailed reasons for the exceptional reactivity of **16f** are unclear at this stage.

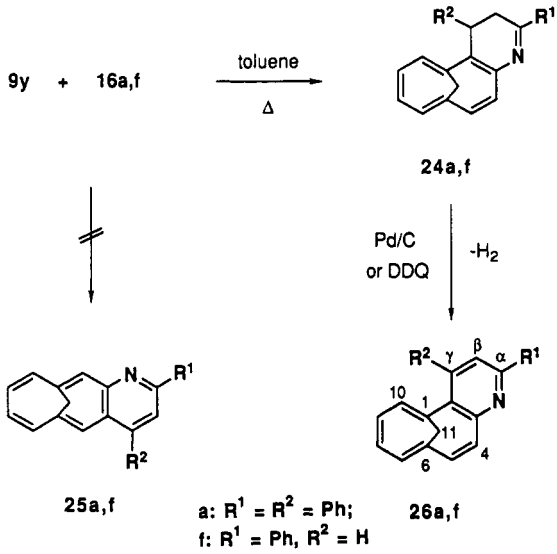
The reactivity of the iminophosphorane **9y** is interesting because both 2- and 4-positions are formally expected to

Table II. ^{1}H NMR (400 MHz, $CDCl_3$) Spectral Data (δ/ppm) for 20a–f and 26a,f[a]

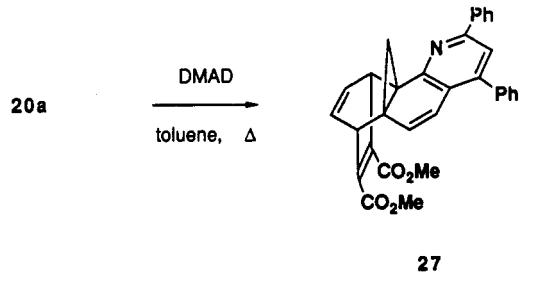
	aromatic protons						bridge protons			
compd	H-4	H-5	H-7	H-8	H-9	H-10	H_E-11	H_Z-11	δ_{av}[b]	other protons
20a	6.94	7.12	6.97	7.20	7.30	8.09	−0.04	1.35	0.66	7.44 (1 H, tt, J = 7.3, 1.5 Hz, Ph), 7.47–7.59 (7 H, m, Ph), 7.83 (H-β), 8.26 (2 H, dd, J = 7.3, 1.5 Hz, Ph)
20b	6.93	7.13	6.97	7.20	7.29	8.05	−0.04	1.33	0.65	7.48 (2 H, d, J = 8.4 Hz, 4-ClC_6H_4), 7.50–7.58 (5 H, m, Ph), 7.78 (H-β), 8.21 (2 H, d, J = 8.4 Hz, 4-ClC_6H_4)
20c	6.88	7.14	6.98	7.20	7.30	8.08	−0.05	1.30	0.63	7.44 (1 H, tt, J = 7.3, 1.8 Hz, Ph), 7.51 (4 H, s, 4-ClC_6H_4), 7.52 (2 H, t, J = 7.3 Hz, Ph), 7.78 (H-β), 8.25 (2 H, dd, J = 7.3, 1.8 Hz, Ph)
20d	7.07	7.23	6.95	7.16	7.22	7.80	−0.05	1.30	0.63	2.63, 2.67, 7.11 (H-β)
20e	7.11	7.23	6.95	7.16	7.22	7.80	−0.13	1.20	0.54	0.52–0.55 (1 H, m), 0.77–2.17 (13 H, m), 2.88–2.95 (1 H, m), 2.99–3.09 (2 H, m), 3.27–3.34 (1 H, m), 7.28 (H-β)
20f	6.99	7.19	7.02	7.27	7.35	7.97	−0.03	1.23	0.66	7.41 (H-β, J = 4.8 Hz), 8.81 (H-α, J = 4.8 Hz), 7.52–7.59 (5 H, m, Ph)
26a	*c*	*d*	6.72	6.91	6.64	6.11	0.04	1.37	0.71	7.39–7.43 (3 H, m, H-4, Ph), 7.46–7.56 (5 H, m, H-5, Ph), 7.65 (2 H, dd, J = 6.4 Hz, Ph), 7.70 (H-β), 8.14 (2 H, dd, J = 8.3, 1.5 Hz, Ph)
26f	7.47[e]	7.56[e]	7.06	7.29	7.33	7.39	−0.05	1.37	0.66	7.49 (1 H, tt, J = 7.0, 1.5 Hz, Ph), 7.57 (2 H, t, J = 7.0 Hz, Ph), 7.88 (H-β, J = 8.4 Hz), 8.20 (2 H, d, J = 7.0, 1.5 Hz, Ph), 8.64 (H-γ, J = 8.4 Hz)

[a] Numbering of each proton for **20a–f** and **26a,f** in a convenient manner is depicted in Schemes III–V. [b] The averaged chemical shifts of bridge protons (H_E-11 and H_Z-11). [c] The signal of H-4 is overlapping with the multiplet at δ 7.39–7.43. [d] The signal of H-5 is overlapping with multiplet at δ 7.46–7.56. [e] The H-4 and H-5 protons of **26f** were assigned by the pseudocontact ^{1}H NMR spectrum using Eu(fod)$_3$.

Scheme V



Scheme VI



react with electrophiles. The reaction of **9y**, which was prepared in situ, with **16a,f** was also carried out under the conditions similar to the case of **8y** (see Experimental Section). The products isolated after dehydrogenation by DDQ or Pd/C were identified as 5,10-methanocyclodeca[*b*]pyridines **26a,f** (Table I, runs 7 and 8, and Scheme V). The alternative products **25a,f** were not obtained. The results indicate that the nucleophilic attack of **9y** initially occurred at the C-2 position, and the reaction sequences similar to those depicted in Scheme III result in the formation of **26a,f**.

The chemical reactivity of methanocyclodeca[*b*]pyridine was also investigated. The Diels–Alder reaction of **20a** with dimethyl acetylenedicarboxylate (DMAD) in refluxing toluene gave an adduct **27** in a quantitative yield (Scheme VI). The structure of the product was assigned on the basis of the ^{1}H NMR and mass spectral data. The ^{1}H NMR spectra of **27** exhibited a loss of aromatic character of the [10]annulene system and suggested also an existence of a cyclopropane ring, which causes a small geminal coupling constant of methylene protons (J = 5.3 Hz). The result disclosed that both pyridine- and benzene-annelated 1,6-methano[10]annulenes have a similar reactivity in the Diels–Alder reaction.[3]

Finally, we investigated the reaction of tributylphosphoranylideneaminobenzene (**28**),[16] a reference molecule of **8y** and **9y**, to compare the difference of reactivity. The reaction of **28** with **16a**, however, underwent an aza-Wittig reaction to give chalcone anil (**29**)[17] in 91% yield and no quinoline derivative was obtained. Thus, the pyridine-annulation reaction seems to be largely dependent on the nature of the aromatic ring introduced on the nitrogen atom of the iminophosphoranes.

Discussion

Reactivity of (Phosphoranylideneamino)-1,6-methano[10]annulene. The compounds **8y** and **9y** are the first example of (vinylimino)phosphoranes, the double bond of which is contained in an aromatic system and can intervene in the pyridine-annulation reaction with α,β-unsaturated ketones. The enhanced reactivity of **8y** and **9y** as compared to **28** is ascribed to a lower resonance energy of 1 (17.2 kcal/mol) than that of benzene (26.1 kcal/mol).[18] The resonance energy per π-electron (REPE) of 1 (1.72 kcal/mol) is estimated as about 40% of that of benzene (4.35 kcal.mol) and is nearly equal to that of azulene[18] (1.61 kcal/mol). It is interesting to note that 2-[(tributylphosphoranylidene)amino]azulene reacts with 2-chlorotropone to undergo an annulation reaction giving azuleno[2,1-*b*]cyclohepta[*d*]pyrrole.[19]

The reactivity and site selectivity of **8** and **9** were evaluated also by ^{13}C NMR spectra (Figure 2).[8b] The signal of the C-3 carbon of **8x** (δ 116.6) shifted upfield by 10.0 ppm as compared to the corresponding carbon of **1** (δ 126.6).[20] The upfield shift suggests a high electron

(16) Wiegräbe, W.; Bock, H. *Chem. Ber.* **1968**, *101*, 1414.
(17) Eisch, J. J.; Sanchez, R. *J. Org. Chem.* **1986**, *51*, 1848.
(18) Roth, W. R.; Böhm, M.; Lennartz, H.-W.; Vogel, E. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 1007.
(19) Iino, Y.; Nitta, M. The 1989 International Chemical Congress of Pacific Basin Societies, Org. Chem. 157.

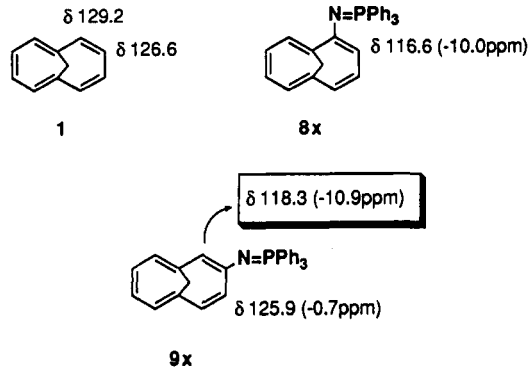


Figure 2. Chemical shifts of ^{13}C NMR. Relative chemical shifts are listed in parentheses.

Figure 3.

density on the C-3 carbon and enhanced nucleophilicity of [10]annulene ring of 8. The compound **9** has two possible reaction sites on C-2 and C-4 carbons. However, the reaction of **9y** with **16a,f** afforded **26a,f** exclusively and none of **25a,f**. The site selectivity of **9** is also rationalized by the ^{13}C NMR spectra. The signals of the C-2 and C-4 carbons of **9x** appear at δ 118.3 and 125.9, respectively. The significant upfield shift of the C-2 carbon (10.9 ppm) as compared to the corresponding carbon of **1** is compatible with the higher reactivity of the 2-position and enhancement of its intrinsic large coefficient of HOMO of **1**.[21]

As for the reaction pathway to give **20a–f**, one might consider that the norcaradiene form **11y** which could exist in an equilibrium with **8y** is an alternative reaction intermediate (Figure 3). Indeed, the thermal behavior of iminotriphenylphosphorane **8x** giving **12** and **13** (Scheme III) suggests the existence of norcaradiene form **11x** in an equilibrium with **8x** at a high temperature. Although the thermal reactions of **8y** and **9y** were not investigated, if the norcaradiene intermediate **11y** intervene in the pyridine-annulation reaction, concomitant methylene rearrangement should be expected. However, in the reactions of iminotributylphosphorane **8y** with enones **16a–f**, in contrast to those of **8x**, no methylene rearrangement was observed. Thus, the norcaradiene form **11y** seems inappropriate as the key intermediate in the present pyridine-annulation reaction. In the reaction of **9y** with enones **16a,f** giving **26a,f**, annulene form **9y**, not a norcaradiene form, could also be proposed for a key intermediate.

Spectroscopic Properties of Methanocyclodeca[*b*]pyridine. The ^1H NMR spectral data are informative to evaluate aromatic characters of methanocyclodeca[*b*]pyridines. All the spectral data clarified that **20a–f** and **26a,f** are aromatic molecules: (i) all the peripheral protons appear in an aromatic region ranging from δ 6.64 to 8.09 except the H-10 proton of **26a** (vide infra); (ii) the chemical shifts of bridge protons appearing at δ –0.13–0.04 (H_E-11) and 1.20–1.37 (H_Z-11) are shielded remarkably by a diatropic ring current; (iii) the geminal coupling constants of H-11 protons are 8.8–9.5 Hz, the values of which are large enough to exclude alternative norcaradiene structures. The most sensitive value to examine aromaticity is the average chemical shift (δ_{av} value) of H_E-11 and H_Z-11 protons, which reflects the degree of a diatropic ring current in methano[10]annulene systems (Table II).[2c] The δ_{av} values for **20a–f** and **26a,f** were found in a shielding region (δ_{av} = 0.54–0.71) but appeared at lower field than those of **1** (δ = –0.5) and dihydropyridine derivative **19a** (δ_{av} = 0.06). These findings indicate that a pyridine annulation on **1** decreases a diatropic ring current as in the case of benz[10]annulene **2** (δ_{av} = 0.66), and that the degree of diatropicity of **20a–f** and **26a,f** are almost the same to each other. The vicinal coupling constants of peripheral protons are diagnostic of bond alternation in methano[10]annulene systems. For compounds **20a–f** and **26a,f**, the coupling constants among H-7, H-8, H-9, and H-10 protons are $J_{8,9}$ (9.5–10.3 Hz) > $J_{7,8} \approx J_{9,10}$ (6.4–7.7 Hz) in a decreasing order, and these values suggest that there is remarkable localization of double bonds in their [10]annulene perimeters (Table III). Consequently, aromatic characters of the two types of methanocyclodeca[*b*]pyridines **20a–f** and **26a,f** were found to be similar to each other according to their tropicity and bond alternation.

Table III. Coupling Constants (Hz) of the ^1H NMR Spectra for 20a–f and 26a,f[a]

		annulene protons			
compd	bridge proton J_{11}	$J_{4,5}$	$J_{7,8}$	$J_{8,9}$	$J_{9,10}$
20a	9.2	10.6	7.7	9.7	7.7
20b	9.2	11.0	7.3	9.5	7.3
20c	9.2	11.0	7.3	9.5	7.3
20d	8.8	10.6	7.0	9.5	6.4
20e	8.8	11.0	7.3	9.9	7.3
20f	9.2	11.0	7.3	9.9	7.3
26a	9.5	*b*	6.8	10.3	7.3
26f	9.2	11.0	7.0	9.5	7.0

[a] Numbering of each proton for **20a–f** and **26a,f** in a convenient manner is depicted in Schemes III–V. [b] The signals of H-4 and H-5 are overlapping with phenyl protons.

Table IV. UV Spectra of 20a–f and 26a,f in EtOH

compd	λ_{max}/nm (log ϵ)		
20a	343 (4.40)	287 (4.82)	268 (4.80)
20b	345 (4.17)	288 (4.55)	267 (4.55)
20c	342 (4.18)	288 (4.61)	267 (4.61)
20d	325 (3.75, sh)	272 (4.57)	
20e	335 (3.26)	274 (3.92)	
20f	329 (4.01, sh)	277 (4.60)	
26a	294 (4.61)	268 (4.49, sh)	
26f	390 (2.72, sh)	284 (4.61)	

More information on the structures of **20a–f** and **26a,f** can be obtained from their UV spectra (Table IV). The UV spectra in ethanol support the structures of methanocyclodeca[*b*]pyridine systems having prolonged cyclic conjugations as compared to **1** (298 nm, ϵ = 6200) and related quinoline derivatives such as 2-phenylquinoline[22] (324 nm, log ϵ = 3.90) and 4-phenylquinoline[23] (286 nm, log ϵ = 3.85). However, the diphenyl-substituted derivative **26a** is an exception. The longest absorption maximum of **26a** appeared at 294 nm, which is shifted by 40 nm to shorter wavelength than that of **20a**. This hypsochromic shift of **26a** is probably due to lack of π-conjugation be-

(20) Kemp-Jones, A. V.; Jones, A. J.; Sakai, M.; Beeman, C. P.; Masamune, S. *Can. J. Chem.* **1973**, *51*, 767.
(21) (a) Klingensmith, K. A.; Puttmann, W.; Vogel, E.; Michl, J. *J. Am. Chem. Soc.* **1983**, *105*, 3375. (b) Boschi, R.; Schmidt, W.; Gfeller, J.-C. *Tetrahedron Lett.* **1972**, 4107. (c) Batich, C.; Heilbronner, E.; Vogel, E. *Helv. Chim. Acta* **1974**, *57*, 2288. (d) Andrea, R. R.; Cerfontain, H.; Lambrechts, H. J. A.; Louwen, J. N.; Oskam, A. *J. Am. Chem. Soc.* **1984**, *106*, 2531. (e) Suzuki, T.; Takase, K.; Takahashi, K. *J. Chem. Soc., Perkin Trans. 2* **1988**, 697.
(22) Moszew, J.; Sulko, ST.; Sledziewska, E. *Bull. Acad. Polon. Sci., Ser. Sci. Chim.* **1961**, *9*, 231.
(23) Sobczyk, L. *Bull. Acad. Polon. Sci., Ser. Sci. Chim.* **1961**, *9*, 237.

tween the annelated pyridine and the phenyl substituent at the γ-position, according to the strong steric repulsion between H-10 proton and the phenyl group. This expectation is also supported by the upfield shift of the H-10 proton for **26a** in the ^{1}H NMR spectra. Being located in the shielding region of the phenyl substituent, the H-10 proton appears at δ 6.11 shifted by ca. 1.3–2.0 ppm more upfield than that of other methanocyclodeca[*b*]pyridines (see Table II). Also interesting is the bathochromic shift in [9]metapyridinophane **20e**, the longest absorption maxima of **20e** appearing at 335 nm shifted by 10 nm to longer wavelength as compared to **20d** (325 nm, sh). This shift probably reflects a further increase of strain in the methanocyclodeca[*b*]pyridine structure of **20e** due to the incorporation of a strained metapyridinophane skeleton.[7d]

Experimental Section

IR spectra were recorded on a Shimadzu IR-400 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Hitachi R-90H and a JEOL GSX400 spectrometer. The chemical shifts are given in ppm (δ) relative to the internal $SiMe_4$ or CH_2Cl_2 standard. Mass spectra and high-resolution mass spectra were measured by a Shimadzu GCMS QP-1000 and a JEOL JMS-DX300 spectrometer. All the reactions were carried out in an anhydrous solvent under a dry nitrogen atmosphere. Microanalyses were performed at the Science and Engineering Research Laboratory of Waseda University. Melting points were recorded on a Büchi apparatus and are uncorrected.

2- and 3-Azido-1,6-methano[10]annulenes (5 and 6). To a solution of 1,6-methano[10]annulene **1** (166 mg, 1.17 mmol) in dichloromethane (3 mL) was added dropwise a solution of bromine azide (1.50 mmol) in dichloromethane at −78 °C. After the solution was warmed to −30 °C and stirred for 2 h, aqueous sodium thiosulfate was added to the reaction mixture and the aqueous layer was extracted with dichloromethane. The organic layer was washed with aqueous sodium hydrogencarbonate, dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was separated by TLC on alumina using hexane as a developer to afford 2-bromoannulene **7**[12] (25 mg, 10%), 2-azidoannulene **5** (81 mg, 38%), and 3-azidoannulene **6** (25 mg, 12%).

5: oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ −0.61 (1 H, d, J = 9.9 Hz, H_E-11), −0.22 (1 H, d, J = 9.9 Hz, H_Z-11), 6.82 (1 H, d, J = 9.9 Hz, H-3), 7.08 (1 H, dd, J = 9.9, 9.2 Hz, H-4), 7.17 (1 H, dd, J = 9.2, 8.4 Hz, H-9), 7.23 (1 H, dd, J = 9.2, 8.4 Hz, H-8), 7.33 (1 H, d, J = 9.2 Hz, H-5), 7.42 (1 H, d, J = 8.4 Hz, H-7), 7.61 (1 H, d, J = 8.4 Hz, H-10); ^{13}C NMR (100 MHz, $CDCl_3$) δ 33.1, 106.4, 115.5, 118.8, 126.9, 127.3, 127.6, 127.7, 128.0, 128.1, 137.2; IR (CCl_4) 2130, 1270 cm^{-1}; MS m/z (rel intensity) 183 (M^+, 4), 57 (100); HRMS m/z 183.0827, calcd for $C_{11}H_9N_3$ 183.0796.

6: oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ −0.33 (1 H, d, J = 9.0 Hz, H_E-11 or H_Z-11), −0.28 (1 H, d, J = 9.0 Hz, H_Z-11 or H_E-11), 6.74 (d, J = 9.3 Hz, H-4), 7.04 (t, J = 8.8 Hz, H-8 or H-9), 7.10 (t, J = 8.8 Hz, H-9 or H-8), 7.11 (1 H, s, H-2), 7.40–7.45 (3 H, m, H-5, H-7, and H-10); ^{13}C NMR (100 MHz, $CDCl_3$) δ 35.6, 114.2, 114.5, 117.7, 119.0, 126.2, 127.4, 129.1, 130.9, 138.1 (one peak is overlapping); IR ($CHCl_3$) 2100, 1275, cm^{-1}; MS m/z (rel intensity) 183 (M^+, 9), 154 (100); HRMS m/z 183.0789, calcd for $C_{11}H_9N_3$ 183.0796.

2-[(Triphenylphosphoranylidene)amino]-1,6-methano[10]annulene (8x). To a solution of azide **5** (65 mg, 0.355 mmol) in ether (2 mL) was added dropwise a solution of triphenylphosphine (93 mg, 0.355 mmol) in ether (2 mL) at room temperature, and the mixture was stirred for 2 h. The resulting precipitate was collected by filtration to give the product **8x** (115 mg, 78%).

8x: mp 164–166 °C dec; ^{1}H NMR (400 MHz, $CDCl_3$) δ −0.74 (1 H, d, J = 9.3 Hz, H_E-11), 0.23 (1 H, d, J = 9.3 Hz, H_Z-11), 6.16 (1 H, d, J = 9.3 Hz, H-3), 6.47 (1 H, t, J = 9.3 Hz, H-4), 6.77 (1 H, d, J = 9.3 Hz, H-5), 6.98 (1 H, dd, J = 9.3, 8.3 Hz, H-9), 7.12 (1 H, dd, J = 9.3, 8.3 Hz, H-8), 7.23 (1 H, d, J = 8.3 Hz, H-7), 7.41 (6 H, ddd, $J_{C,H}$ = 7.8, 7.3 Hz, $J_{C,P}$ = 2.9 Hz, *m*-Ph), 7.50 (3 H, td, $J_{C,H}$ = 7.3 Hz, $J_{C,P}$ = 1.5 Hz, *p*-Ph), 7.68 (6 H, m, $J_{C,P}$ = 12.2 Hz, *o*-Ph), 7.87 (1 H, d, J = 8.3 Hz, H-10); ^{13}C NMR (100 MHz, $CDCl_3$) δ 34.1 (C-11), 114.8 ($J_{C,P}$ = 18.7 Hz, C-1), 116.6 ($J_{C,P}$ = 10.4 Hz, C-3), 119.1 (C-6), 119.4, 119.5, 123.9, 125.3, 126.7, 127.28, 127.34, 128.3 (6 C, $J_{C,P}$ = 12.44 Hz, Ph), 130.4 (3 C, $J_{C,P}$ = 114.7 Hz, Ph), 131.5 (3 C, $J_{C,P}$ = 2.8 Hz, Ph), 132.4 (6 C, $J_{C,P}$ = 9.0 Hz, Ph), 152.6 ($J_{C,P}$ = 4.8 Hz, C-2); IR ($CHCl_3$) 1469, 1428, 1400, 1295, 1276, 1097 cm^{-1}; MS m/z (rel intensity) 417 (M^+, 76), 183 (100). Anal. Calcd for $C_{29}H_{24}NP$: C, 83.43; H, 5.79; N, 3.35. Found: C, 83.04; H, 6.07; N, 3.32.

3-[(Triphenylphosphoranylidene)amino]-1,6-methano[10]annulene (9x). To a solution of azide **6** (53 mg, 0.284 mmol) in ether (3 mL) was added dropwise a solution of triphenylphosphine (75 mg, 0.286 mmol) in ether (2 mL) at room temperature, and the mixture was stirred for 2 h. After the solvent was evaporated, the residue was purified by TLC on alumina using hexane–ethyl acetate (5/1) as a developer to afford the product **9x** (96 mg, 81%).

9x: oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ −0.50 (1 H, d, J = 8.6 Hz, H_E-11), −0.30 (1 H, d, J = 8.6 Hz, H_Z-11), 6.53 (1 H, s, H-2), 6.81 (1 H, t, J = 8.8 Hz, H-8 or H-9), 6.88 (1 H, t, J = 8.8 Hz, H-9, or H-8), 6.99 (1 H, dd, J = 9.3, 1.2 Hz, H-4), 7.10 (1 H, d, J = 8.8 Hz, H-7 or H-10), 7.18 (1 H, d, J = 9.3 Hz, H-5), 7.30 (1 H, d, J = 8.8 Hz, H-10 or H-7), 7.44 (6 H, m, Ph), 7.53 (3 H, m, Ph), 7.81 (6 H, m, Ph); ^{13}C NMR (100 MHz, $CDCl_3$) δ 36.7 (C-11), 111.7 (C-1 or 6), 116.7 (C-6 or 1), 118.3 ($J_{C,P}$ = 13.2 Hz, C-2), 123.2 (C-8 or 9), 125.9 ($J_{C,P}$ = 22.0 Hz, C-4), 126.0 (C-9 or 8), 127.9 (C-7 or 10), 128.5 (C-10 or 7), 128.6 (6 C, $J_{C,P}$ = 12.5 Hz, Ph), 129.2 ($J_{C,P}$ = 2.2 Hz, C-5), 130.7 (3 C, $J_{C,P}$ = 98.3 Hz, Ph), 131.7 (3 C, $J_{C,P}$ = 2.9 Hz, Ph), 132.8 (6 C, $J_{C,P}$ = 9.5 Hz, Ph), 151.9 ($J_{C,P}$ = 2.8 Hz, C-3); IR ($CHCl_3$) 1440, 1320, 1270, 1110 cm^{-1}; MS m/z (rel intensity) 417 (M^+, 76), 183 (100); HRMS m/z 417.1656, calcd for $C_{29}H_{24}NP$: 417.1647.

The Reaction of 8x with Carbon Disulfide. A solution of **8x** (100 mg, 0.240 mmol) in carbon disulfide (5 mL) was stirred for 2 days at room temperature. After removal of the solvent in vacuo, the resulting mixture was chromatographed on silica gel using hexane–ethyl acetate (10/1) as an eluent to give isothiocyanate **10** (36 mg, 75%). The structure of the product was identified by comparison of the spectroscopic data with those reported in the literature.[14]

Thermal Reaction of 8x. A solution of **8x** (208 mg, 0.500 mmol) in bromobenzene (5 mL) was heated under reflux for 20 h. After the reaction mixture was concentrated in vacuo, the residue was purified by TLC on silica gel using hexane–ethyl acetate (2/1) as a developer to give a mixture (208 mg, 100%) of 1- and 4-[(triphenylphosphoranylidene)amino]-5*H*-benzocycloheptatrienes (**12** and **13**) in 68% and 32% yields, respectively. Separation of **12** and **13** was unsuccessful.

12 and **13**: mp 83–88 °C; ^{1}H NMR (90 MHz, $CDCl_3$) δ 2.96 (0.68 H, d, J = 6.6 Hz, CH_2 for **12**), 3.45 (0.32 H, d, J = 6.8 Hz, CH_2 for **13**), 5.50–8.20 (22 H, m); IR (CCl_4) 1458, 1444, 1377, 1342, 1110 cm^{-1}; MS m/z (rel intensity) 417 (M^+, 27), 416 (100); HRMS m/z 417.1674, calcd for $C_{29}H_{24}NP$ 417.1646.

Reaction of 12 and 13 with Carbon Disulfide. A mixture of **12** and **13** (41 mg, 0.098 mmol) in a ratio of 2/1 in carbon disulfide (5 mL) was stirred at room temperature for 3 days. After the solution was concentrated in vacuo, the residue was separated by column chromatography on silica gel using hexane as an eluent to give a mixture (18 mg, 91%) of 5*H*-benzocycloheptatriene 1- and 4-isothiocyanates (**14** and **15**) in a ratio of 2/1. Separation of **14** and **15** was unsuccessful.

14 and **15**: oil; ^{1}H NMR (400 MHz, $CDCl_3$) for **14** δ 3.01 (2 H, d, J = 6.6 Hz, H-5), 5.82 (1 H, dt, J = 9.9, 7.0 Hz, H-6), 6.12 (1 H, dd, J = 9.9, 5.1 Hz, H-7), 6.67 (1 H, dd, J = 11.7, 5.1 Hz, H-8), 7.10 (1 H, d, J = 7.7 Hz, H-4), 7.15–7.33 (2 H, m, H-3 and H-4), 7.30 (1 H, d, J = 11.7 Hz); for **15** δ 3.12 (2 H, d, J = 7.0 Hz, H-5), 5.84 (1 H, dt, J = 9.9, 7.0 Hz, H-6), 6.16 (1 H, dd, J = 9.9, 5.5 Hz, H-7), 6.56 (1 H, dd, J = 11.7, 5.5 Hz, H-8), 7.08 (1 H, d, J = 11.7 Hz, H-9), 7.15–7.33 (3 H, m, H-1, H-2, and H-3); IR (CCl_4) 2100 cm^{-1}; MS m/z (rel intensity) 199 (M^+, 68) and 58 (100); HRMS m/z 199.0443, calcd for $C_{12}H_9NS$ 199.0455.

General Preparation of 2,4-Diaryl-7,12-methanocyclodeca[*b*]pyridine (20a–c). 2-[(Tributylphosphoranylidene)amino]-1,6-methano[10]annulene (**8y**) was prepared in situ by the reaction of the azide **5** (126 mg, 0.689 mmol) with tributylphosphine (210 mg, 1.04 mmol) in toluene under stirring for 1 h at room temperature. To the reaction mixture were added chalcone derivatives **16a–c** (1.38 mmol), and the mixture was

heated under reflux for 17 h. After removal of the solvent in vacuo, the residue was chromatographed on silica gel using benzene as an eluent to remove tributylphosphine oxide. The fractions gave a mixture of crude dihydropyridine derivatives **19a–c** and **16a–c**. In the case of the mixture of **19a** and **16a**, repeated chromatography (TLC) on silica gel using benzene–hexane (1/2) as a developer afforded a pure sample of **19a**, the spectral data of which are as follows: oil; ^{1}H NMR (90 MHz, $CDCl_3$) δ −0.34 (1 H, dd, J = 9.0, 0.9 Hz, H_E-11), 0.23 (1 H, d, J = 9.0 Hz, H_Z-11), 3.14 (1 H, dd, J = 15.6, 8.0 Hz, H-β), 3.55 (1 H, dd, J = 15.6, 2.2 Hz, H-β), 4.56 (1 H, broad d, J = 8.0 Hz, H-γ), 6.70–7.70 (13 H, m), 7.75–8.05 (2 H, m), 8.20–8.45 (1 H, m, H-10); IR (CCl_4) 3030, 1605, 1500, 1445, 1355 cm^{-1}; MS m/z (rel intensity) 347 (M^+, 22), 346 (100).

Then, the mixture of **19a–c** and **16a–c** was heated with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 156 mg, 0.687 mmol) in benzene (5 mL) under reflux for 2 h. After the reaction was completed, aqueous 5 N NaOH was added to the reaction mixture and stirred for several minutes. The benzene layer was separated, the aqueous layer was extracted with ether, and the combined organic layer was dried over $MgSO_4$. After the organic layer was concentrated in vacuo, the resulting mixture was separated by TLC on silica gel using hexane–benzene (2/1) as a developer to give **20a–c** and the recovery of **16a–c** (47%). The yields, ^{1}H NMR, and UV spectral data for **20a–c** are summarized in Tables I, II, and IV, respectively.

20a: mp 129–130 °C (from EtOH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 34.4 (C-11), 109.0 (C-6 or C-1), 111.2 (C-1 or C-6), 118.1 (C-β), 123.4 (C-7), 124.2 (C-4), 125.1 (C-3), 125.8 (C-10), 127.1 (3C, C-8 and Ph), 127.2 (C-9), 128.3 (Ph), 128.6 (2C, Ph), 128.7 (2C, Ph), 129.0 (Ph), 129.9 (2C, Ph), 130.5 (C-5), 139.2 (Ph), 140.8 (Ph), 152.2 (C-γ), 153.0 (C-α), 154.3 (C-2); IR (CCl_4) 3060, 3040, 1590, 1567, 1490, 1373 cm^{-1}; MS m/z (rel intensity) 345 (M^+, 100); HRMS m/z 345.1509, calcd for $C_{26}H_{19}N$ 345.1517.

Picrate of **20a**: mp 170–171 °C (dec, from EtOH). Anal. Calcd for $C_{32}H_{22}N_4O_7$: C, 66.90; H, 3.86; N, 9.75. Found: C, 66.65; H, 3.80; N, 9.60.

20b: mp 134–136 °C (from EtOH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 34.3 (C-11), 108.7 (C-6 or C-1), 111.0 (C-1 or C-6), 117.7 (C-β), 123.5 (C-7), 124.1 (C-4), 125.2 (C-3), 125.8 (C-10), 127.18 (C-8), 127.24 (C-9), 128.3 (2 C, Ar), 128.4 (Ar), 128.6 (2 C, Ar), 128.9 (2 C, Ar), 129.8 (2 C, Ar), 130.8 (C-5), 135.1 (Ar), 137.6 (Ar), 140.7 (Ar), 151.7 (C-γ), 152.3 (C-α), 154.3 (C-2); IR (CCl_4) 3020, 1487, 1370, 1095 cm^{-1}; MS m/z (rel intensity) 379 (M^+, 100). Anal. Calcd for $C_{26}H_{18}NCl$: C, 82.20; H, 4.78; N, 3.69. Found: C, 81.77; H, 4.86; N, 3.58.

Picrate of **20b**: mp 183–184 °C (dec, from EtOH). Anal. Calcd for $C_{32}H_{21}ClN_4O_7$: C, 63.11; H, 3.48; N, 9.20. Found: C, 63.15; H, 3.40; N, 9.15.

20c: mp 157–159 °C (from EtOH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 34.3 (C-11), 108.8 (C-6 or C-1), 111.1 (C-1 or C-6), 117.8 (C-β), 123.5 (C-7), 123.7 (C-4), 124.9 (C-3), 125.9 (C-10), 127.1 (2 C, Ar), 127.2 (C-8), 127.3 (C-9), 128.78 (Ar), 128.83 (2 C, Ar), 129.1 (2 C, Ar), 130.9 (C-5), 131.2 (2 C, Ar), 134.5 (Ar), 139.0 (Ar), 139.2 (Ar), 150.8 (C-γ), 153.1 (C-α), 154.4 (C-2); IR ($CHCl_3$) 3040, 1488, 1370, 1090 cm^{-1}; MS m/z (rel intensity) 379 (M^+, 100); HRMS m/z 379.1148, calcd for $C_{26}H_{18}NCl$ 379.1128.

Picrate of **20c**: mp 184–187 °C (dec, from EtOH). Anal. Calcd for $C_{32}H_{21}ClN_4O_7$: C, 63.11; H, 3.48; N, 9.20. Found: C, 62.80; H, 3.50; N, 9.08.

Preparation of 2,4-Dimethyl- and 4-Phenyl-7,12-methanocyclodeca[*b*]pyridine (20d,f). To a solution of **8y**, prepared in situ from the azide **5** (127 mg, 0.694 mmol) and tributylphosphine (210 mg, 1.04 mmol) in toluene (3 mL), was added α,β-unsaturated ketones **16d,f** (3.12 mmol) and heated under reflux for 53 h in the presence of 10% Pd/C (35 mg). After the reaction mixture was filtered through Celite, the filtrate was concentrated in vacuo and the resulting mixture was chromatographed on silica gel using hexane–ethyl acetate (5/1) as an eluent to remove phosphine oxide. The fractions were concentrated, and the residue was separated by TLC on silica gel using hexane–ethyl acetate (10/1) as a developer to give the product **20d,f**. The yields, ^{1}H NMR, and UV spectral data for **20d,f** are summarized in Tables I, II, and IV, respectively.

20d: oil; ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 24.5, 40.0, 109.8, 111.2, 121.2, 122.5, 123.1, 124.7, 125.3, 126.9, 127.0, 130.0, 146.6, 153.1, 155.2; IR ($CHCl_3$) 3050, 2960, 1600, 1580, 1450, 1375 cm^{-1}; MS m/z (rel intensity) 221 (M^+, 9), 58 (100); HRMS m/z 221.1196, calcd for $C_{16}H_{15}N$ 221.1205.

Picrate of **20d**: mp 164–167 °C (from EtOH). Anal. Calcd for $C_{22}H_{18}N_4O_7$: C, 58.67; H, 4.03; N, 12.44. Found: C, 58.64; H, 4.03; N, 12.50.

20f: mp 124–125 °C (from MeOH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 34.4 (C-11), 109.1 (C-6 or C-1), 111.8 (C-1 or C-6), 121.2 (C-β), 123.4 (C-7), 124.2 (C-4), 125.3 (C-10), 126.3 (C-3), 127.29 (C-8), 127.32 (C-9), 128.3 (Ph), 128.5 (2C, Ph), 129.8 (2C, Ph), 130.8 (C-5), 140.4 (Ph), 146.1 (C-α), 151.5 (C-γ), 154.4 (C-2); IR (CCl_4) 3045, 1630, 1427, 1228 cm^{-1}; MS m/z (rel intensity) 269 (M^+, 100); HRMS m/z 269.1207, calcd for $C_{20}H_{15}N$ 269.1204.

Preparation of 2,4-Nonamethylene-7,12-methanocyclodeca[*b*]pyridine (20e). A solution of **16e** (274 mg, 1.52 mmol) and **8y**, prepared in situ from azide **5** (186 mg, 1.02 mmol) and tributylphosphine (307 mg, 1.52 mmol), was heated under reflux in toluene (5 mL) for 23 h. After removal of the solvent in vacuo, the residue was separated by TLC on silica gel using hexane–ethyl acetate (10/1) as a developer to give a mixture of **20e** and 3-cyclododecenone[24] originated from **16e**. The mixture was then treated by $NaBH_4$ (12 mg, 0.31 mmol) in ethanol (2 mL) to reduce 3-cyclododecenone to the corresponding alcohol at room temperature overnight. After evaporation of the solvent, the residue was separated by TLC on silica gel using hexane–ethyl acetate (5/1) as a developer to give **20e**. The yield, ^{1}H NMR, and UV spectral data are listed in Tables I, II, and IV.

20e: oil; IR (CCl_4) 3030, 2940, 2855 cm^{-1}; MS m/z (rel intensity) 317 (M^+, 26), 56 (100); HRMS m/z 317.2138, calcd for $C_{23}H_{27}N$ 317.2144.

Preparation of 2,4-Diphenyl-5,10-methanocyclodeca[*b*]pyridine (26a). A solution of 3-(phosphoranylideneamino)-1,6-methano[10]annulene **9y** was prepared in situ by the reaction of the azide **6** (36 mg, 0.20 mmol) and tributylphosphine (48 mg, 0.24 mmol) in toluene (2 mL) with stirring for 1 h at room temperature. To the reaction mixture was added chalcone **16a** (41 mg, 0.20 mmol), and the mixture was heated under reflux for 18 h. After removal of the solvent in vacuo, the residue was chromatographed on silica gel using benzene as an eluent to remove tributylphosphine oxide. The fractions were concentrated and treated with DDQ (45 mg, 0.20 mmol) in benzene (2 mL) at room temperature for 1 h. After the reaction was completed, a few drops of 1,8-diazabicyclo[5.4.0]-7-undecene (DBU) in acetonitrile (1 mL) was added to the reaction mixture and stirred for several minutes. The reaction mixture was then extracted with dichloromethane, and the organic layer was dried over Na_2SO_4. The filtrate was concentrated in vacuo, and the resulting mixture was separated by TLC on silica gel using hexane–ethyl acetate (10/1) as a developer to give the product **26a**. The yield, ^{1}H NMR, and UV spectral data for are summarized in Tables I, II, and IV, respectively.

26a: mp 152–153 °C (from EtOH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 36.3 (C-11), 114.0 (C-1 or C-6), 116.3 (C-6 or C-1), 119.3 (C-β), 122.7 (C-7), 126.8 (C-10), 127.2 (3C, C-8, Ph), 127.7 (C-9), 128.1 (Ph), 128.71 (Ph), 128.74 (4C, Ph), 128.96 (Ph), 129.04 (Ph), 129.3 (C-4), 131.3 (C-2), 132.7 (C-5), 139.1 (Ph), 140.8 (Ph), 148.6 (C-γ), 151.7 (C-3), 153.7 (C-α); IR (CCl_4) 3030, 1570, 1375 cm^{-1}; MS m/z (rel intensity) 345 (M^+, 100). Anal. Calcd for $C_{26}H_{19}N$: C, 90.40; H, 5.54; N, 4.05. Found: C, 90.00; H, 5.54; N, 4.02.

Preparation of 2-Phenyl-5,10-methanocyclodeca[*b*]pyridine (26f). To a solution of **9y** prepared in situ from the azide **6** (59 mg, 0.322 mmol) and tributylphosphine (83 mg, 0.411 mmol) in toluene (1 mL) was added phenylpropenone **16f** (67 mg, 0.51 mmol), and the mixture was heated under reflux for 4.5 h in the presence of 10% Pd/C (18 mg). After removal of the solvent in vacuo, the resulting mixture was chromatographed on alumina using hexane–ethyl acetate (5/1) as an eluent to eliminate tributylphosphine oxide. After the fractions were concentrated, the residue was purified by TLC on silica gel using hexane–ethyl acetate (10/1) as a developer to give the product **26f**. The yield, ^{1}H NNR, and UV spectral data are summarized in Tables I, II, and IV, respectively.

26f: mp 109–110 °C (from EtOH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 36.2 (C-11), 113.1 (C-1 or C-6), 114.6 (C-6 or C-1), 117.1 (C-β),

(24) Marchesini, A.; Pagani, G.; Pagnoni, U. M. *Tetrahedron Lett.* **1973**, 1041.

123.4 (C-7), 123.7 (C-10), 127.2 (2 C, Ph), 127.5 (C-8), 127.7 (C-9), 128.8 (2 C, Ph), 128.9 (Ph), 129.0 (C-4), 132.70 (C-2 or C-5), 132.74 (C-5 or C-2), 133.6 (C-γ), 139.4 (Ph), 150.4 (C-3), 154.5 (C-α); IR (CCl_4) 3045, 1630, 1228 cm^{-1}; MS m/z (rel intensity) 269 (M^+, 100). Anal. Calcd for $C_{20}H_{15}N$: C, 89.19; H, 5.61, N, 5.20. Found: C, 88.96; H, 5.36; N, 5.14.

Reaction of 20a with Dimethyl Acetylenedicarboxylate (DMAD). A solution of **20a** (95 mg, 0.275 mmol) and DMAD (394 mg, 2.77 mmol) in toluene (2 mL) was heated under reflux for 4 h. After removal of the solvent in vacuo, the residue was separated by TLC on silica gel using hexane–ethyl acetate (3/1) as a developer to give the adduct **27** (113 mg, 99%).

27: mp 170–171 °C (from MeOH); ^1H NMR (90 MHz, $CDCl_3$) δ 0.44 (1 H, d, J = 5.3 Hz), 2.38 (1 H, d, J = 5.3 Hz), 4.14 (3 H, s), 4.22 (3 H, s), 4.37 (1 H, dd, J = 5.6, 2.3 Hz), 5.66 (1 H, dd, J = 5.5, 2.4 Hz), 6.39–6.55 (2 H, m), 7.30–7.60 (11 H, m), 8.10–8.25 (2 H, m); IR ($CHCl_3$) 1715, 1270 cm^{-1}; MS m/z (rel intensity) 487 (M^+, 63), 428 (100). Anal. Calcd for $C_{32}H_{25}NO_4$: C, 78.83; H, 5.17; N, 2.87. Found: C, 78.65; H, 5.39; N, 2.86.

Reaction of [(Tributylphosphoranylidene)amino]benzene (28) with 16a. To a solution of **28**, prepared in situ from azidobenzene (54 mg, 0.45 mmol) and tributylphosphine (145 mg, 0.72 mmol) in toluene (3 mL), was added **16a** (203 mg, 0.98 mmol), and the mixture was heated under reflux for 26 h. The reaction mixture was concentrated, and the residue was chromatographed on silica gel using benzene as an eluent to eliminate tributylphosphine oxide. The fractions were concentrated in vacuo and separated by TLC on silica gel using benzene–hexane (2/1) as a developer to give chalcone anil **29** (116 mg, 91%): mp 96–98 °C (from ether) (lit.[17] mp 99–101 °C); ^1H NMR (90 MHz, $CDCl_3$) δ 6.62–7.50 (15 H, m), 7.69–7.80 (2 H, m).

Acknowledgment. This work was financially supported by a Grant-in-Aid for Fundamental Science from Ministry of Education, Science and Culture and by Waseda University Grant for Special Research Projects.

Registry No. 1, 2443-46-1; 5, 134858-12-1; 6, 137594-06-0; 7, 15825-92-0; 8x, 134858-17-6; 8y, 137594-07-1; 9x, 137594-08-2; 9y, 137594-09-3; 10, 115163-02-5; 12, 137594-10-6; 13, 137594-11-7; 14, 137594-12-8; 15, 137594-13-9; 16a, 94-41-7; 16b, 956-02-5; 16c, 956-04-7; 16d, 625-33-2; 16e, 42858-38-8; 16f, 768-03-6; 19a, 137594-14-0; 19b, 137594-15-1; 19c, 137594-16-2; 20a, 137594-17-3; 20a·picrate, 137594-18-4; 20b, 137594-20-8; 20b·picrate, 137695-53-5; 20c, 137594-21-9; 20c·picrate, 137594-22-0; 20d, 137594-23-1; 20d·picrate, 137594-24-2; 20e, 137594-25-3; 20f, 137594-26-4; 26a, 137594-27-5; 26f, 137594-28-6; 27, 137594-29-7; 29, 64723-86-0; DMAD, 762-42-5; triphenylphosphine, 603-35-0; carbon disulfide, 75-15-0; tributylphosphine, 998-40-3; 3-cyclododecenone, 42858-38-8; azidobenzene, 622-37-7.

Supplementary Material Available: ^1H NMR and ^{13}C NMR spectra of azido[10]annulenes **5** and **6**, methanocyclodeca[*b*]-pyridines **20a–d,f**, and **26a,f** and ^1H NMR spectra of isothiocyanates **14** and **15** and methanocyclodeca[*b*]pyridine **20e** (20 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

On the Importance of Reactions of Carbocation Ion Pairs in Water: Common Ion Inhibition of Solvolysis of 1-(4-Methoxyphenyl)-2,2,2-trifluoroethyl Bromide and Trapping of an Ion-Pair Intermediate by Solvent

John P. Richard

University of Kentucky, Department of Chemistry, Lexington, Kentucky 40506-0055

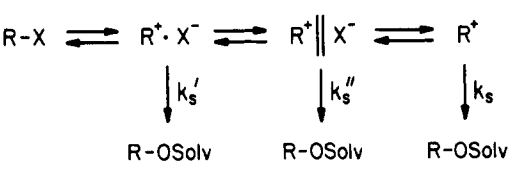
Received August 19, 1991

The effect of added bromide ion on the reactivity of 1-(4-methoxyphenyl)-2,2,2-trifluoroethyl bromide in water at 25 °C and I = 6.00 ($NaClO_4$) has been determined. The pseudo-first-order rate constant for this reaction decreases 300-fold as [NaBr] is increased from 0–5.00 M, which shows that ≥99.7% of the solvolysis reaction proceeds through the free carbocation intermediate, whose concentration is reduced by mass action of added bromide ion. At high [NaBr], the observed rate constants show a significant positive deviation from the rate law for a reaction in which solvolysis products are derived solely from capture of the free carbocation. This deviation is consistent with a second pathway for the formation of solvolysis products, by direct attack of solvent on an ion-pair intermediate. The limiting velocity through this pathway, approached at high concentrations of bromide ion, is estimated to be 0.06% of that through the liberated carbocation. It is concluded that the capture of ion-pair intermediates of solvolysis reactions by solvent water is normally an unimportant reaction.

Introduction

At least three intermediates may form in an S_N1 ($D_N + A_N$)[1] nucleophilic substitution reaction (Scheme I): the intimate ion pair, the solvent-separated ion pair, and the free ions.[2] In nonpolar solvents, the stabilizing electrostatic interactions between ions are relatively strong, so that solvent and other nucleophilic reagents may react directly with ion pair intermediates at a rate that is competitive with the dissociation of the ion pair to give free ions. In water, ion pairs are much more unstable and undergo rapid dissociation to give free ions. The capture of ion pair intermediates by this solvent will not be a significant reaction when the rate of dissociation of the intimate ion pair to form free ions is much faster than the capture of the ion pair by water.[3–5]

Scheme I



(1) Commission on Physical Organic Chemistry, IUPAC *J. Pure Appl. Chem.* **1989**, *61*, 23–36. Guthrie, R. D.; Jencks, W. P. *Acc. Chem. Res.* **1989**, *22*, 343–349.

(2) Harris, J. M. *Prog. Phys. Org. Chem.* **1974**, *11*, 89–173. Raber, D. J.; Harris, J. M.; Schleyer, P. v. R. In *Ions and Ion Pairs in Organic Reactions, Vol. 2: Role of Ions and Ion Pairs in Chemical Reactions*; Szwarc, M., Ed.; Wiley: New York, 1974.

(3) Jencks, W. P. *Chem. Soc. Rev.* **1981**, *10*, 345–375.

0022-3263/92/1957-0625$03.00/0