200 MHz) δ 6.51 (br, 1 H, NH), 5.63 (dd, 1 H, J = 8, 6 Hz, CHNH), 4.90 (dq, 1 H, J = 6, 8 Hz, CH_3CH), 2.09 (s, 3 H, CH_3CO), 1.44 (d, 3 H, J = 6 Hz, CH_3CH); FAB MS 144 (MH^+).

(3S,4R)-3-(Benzoylamino)-4-methyl-2-oxetanone (14). A suspension of **9a** (110 mg, 0.39 mmol) in 3 mL of CH_2Cl_2 at 0 °C under argon was treated with benzoyl chloride (0.07 mL, 0.60 mmol) followed by pyridine (0.06 mL, 0.74 mmol). The solution was stirred at 0 °C for 1 h and then warmed to 20 °C overnight. EtOAc was added and the solution was washed with water (3 × 10 mL). The organic extract was dried (Na_2SO_4) and evaporated. The resulting residue was triturated with diethyl ether to yield solid **14** (68 mg, 85%): mp 157–159 °C; IR (KBr) 3261, 1839, 1808, 1641, 1596, 1289, 720, 680 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 7.82 (m, 2 H, Ar H), 7.58 (m, 3 H, Ar H); 5.44 (dd, 1 H, J = 6, 8 Hz, CHNH), 5.00 (quint, 1 H, J = 6 Hz, CH_3CH), 1.45 (d, 3 H, J = 6 Hz, CH_3); MS (CI, NH_3) 223 (M + NH_4^+, 8.7), 206 (M + H^+, 100).

(3S,4R)-3-[[(N-(tert-Butoxycarbonyl)-D-phenylalaninyl]amino]-4-methyl-2-oxetanone (15). A solution of N-(tert-butoxycarbonyl)-D-phenylalanine (26.5 mg, 0.10 mmol) in CH_2Cl_2 (3.0 mL) at −5 °C was treated with triethylamine (10 mg, 0.10 mmol) and ethyl chloroformate (11 mg, 0.10 mmol). The solution was stirred for 20 min and **9a** (27.3 mg, 0.10 mmol) and pyridine (0.02 mL, 0.20 mmol) were added. After 30 min at −5 °C, the solution was allowed to warm to 20 °C overnight. The solvent was removed and the residue was triturated with EtOAc (3 × 5 mL). The combined organic extracts were washed with water, dried (Na_2SO_4), and concentrated to afford a solid. This was triturated with hexane and 10:1 hexane/ether (ca. 2 mL) to afford pure **15** (32.0 mg, 92%): mp 156–157 °C; IR ($CHCl_3$ cast), 3328, 2979, 1825, 1686, 1665 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.24 (m, 5 H, Ar H), 7.01 (d, 1 H, J = 8 Hz, NH), 5.57 (dd, 1 H, J = 8, 6 Hz, CHNH), 4.92 (d, 1 H, J = 8 Hz, NH), 4.80 (quint, 1 H, J = 6 Hz, CH_3CH), 4.38 (dd, 1 H, J = 8, 8 Hz, CHNHBoc), 3.06 (m, 2 H, $PhCH_2CH$), 1.40 (s, 9 H, $NHCOOC(CH_3)_3$), 1.22 (d, 3 H, J = 6 Hz, CH_3CH); FAB MS m/z 349 (MH^+). Anal. Calcd for $C_{18}H_{24}N_2O_5$: C, 62.05; H, 6.94; N, 8.04. Found: C, 62.13; H, 6.72; N, 8.06.

(3S,4R)-3-[[N-(tert-Butoxycarbonyl)-L-phenylalaninyl]amino]-4-methyl-2-oxetanone (16). The procedure used to prepare **15** was employed to condense N-(tert-butoxycarbonyl)-L-phenylalanine with **9a** to afford a 92% yield of **16**: mp 144–145 °C; IR ($CHCl_3$ cast), 3334, 1827, 1677 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.25 (m, 6 H, Ar H and NH), 5.52 (dd, 1 H, J = 8, 6 Hz, CHNH), 5.11 (d, 1 H, J = 8 Hz, NH), 4.85 (quint, 1 H, J = 6 Hz, CH_3CH), 4.39 (dd, 1 H, J = 8, 6 Hz, CHNHBoc), 3.07 (m, 2 H, $PhCH_2CH$), 1.40 (s, 9 H, $NHCOOC(CH_3)_3$), 1.33 (d, 3 H, J = 6 Hz, CH_3CH); FAB MS m/z 349 (MH^+). Anal. Calcd for $C_{18}H_{24}N_2O_5$: C, 62.05; H, 6.94; N, 8.04. Found: C, 61.73; H, 6.74; N, 7.92.

(2R,3S)-2-Amino-3-bromobutanoic Acid (17) from 8a. A 30% solution of HBr in acetic acid (0.11 mL, 1.70 mmol) was added to **8a** (86 mg, 0.34 mmol), and the mixture was stirred at 20 °C for 15 min. The acetic acid was evaporated and EtOAc (25 mL) was added. This solution was extracted with water (3 × 20 mL) and concentrated to yield solid **17** (42 mg, 68%): mp 179–183 °C dec (lit.[9] mp 198 °C); IR (KBr) 3067 (br), 1733, 1482, 1201 cm^{-1}; ^1H NMR (D_2O, 200 MHz) δ 4.60 (dq, 1 H, J = 8, 4 Hz, CH_3CH), 4.31 (d, 1 H, J = 4 Hz, $CHNH_3$), 1.72 (d, 3 H, J = 8 Hz, CH_3); FAB (glycerol) 181.96, 183.97 ($MH^+(^{79}Br)(^{81}Br)$).

Hydrobromide Salt of (2R,3S)-2-Amino-3-bromobutanoic Acid (17) from 9a. A 30% solution of HBr in acetic acid (0.13 mL, 1.90 mmol) was added to **9a** (100 mg, 0.37 mmol), and the mixture was stirred at 20 °C for 15 min. The solvent was evaporated to yield a solid, which after trituration with diethyl ether yielded **17** as its bromide salt (90 mg, 92%): mp 180–195 °C dec (lit.[9] mp 198 °C); IR (KBr), 3016–2800 (br), 1734, 1482, 1200; ^1H NMR (DMF-d_7, 360 MHz) δ 9.20 (br s, 1 H, CO_2H), 5.05 (dq, 1 H, J = 6, 5 Hz, CH_3CH), 4.75 (d, 1 H, J = 6 Hz, $CHNH_3$), 2.00 (d, 3 H, J = 6 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 90.5 MHz) δ 169.1, 60.2, 48.3, 24.4; FAB MS (HCOOH/glycerol) 181.98, 183.99 ($MH^+(^{79}Br)(^{81}Br)$).

(2R,3R)-2-Amino-3-bromobutanoic Acid (18). The procedure described above for preparation of **17** from **8a** was used to convert **8b** to **18** in 69% yield except that an 18-h reaction time was required: mp 165 °C dec; IR (CH_3CN cast) 3000–2800 (br), 1737, 1488, 1211 cm^{-1}; ^1H NMR (D_2O, 200 MHz) δ 4.75 (m, 1 H, CH_3CH), 4.20 (d, 1 H, J = 4 Hz, $CHNH_3$), 1.75 (d, 3 H, J = 7 Hz, CH_3); FAB MS 181.96, 183.96 ($MH^+(^{79}Br)(^{81}Br)$).

(2R,3S)-3-Bromo-2-(benzoylamino)butanoic Acid (19). A solution of **14** (65 mg, 0.32 mmol) in freshly distilled THF (5.0 mL) was added dropwise at 20 °C to a suspension of anhydrous $MgBr_2 \cdot OEt_2$ (1.30 mmol) (prepared by addition of freshly distilled 1,2-dibromoethane (0.12 mL, 1.3 mmol) to Mg metal (32 mg, 1.30 mmol) in diethyl ether (5.0 mL)). After 10 min, the mixture was cooled to 4 °C and acidified with 1 M H_3PO_4 (6 mL). The phases were separated and the aqueous phase was extracted with ether (3 × 10 mL). The organic extracts were combined, dried (Na_2SO_4), and concentrated to yield a colorless oil (**19**) (86 mg, 94%). This material could be purified by preparative TLC (formic acid/methanol/$CHCl_3$, 1:9:90) but was unstable and decomposed rapidly at room temperature: ^1H NMR ($CDCl_3$, 200 MHz) δ 8.80 (br s, 1 H, CO_2H), 7.85 (m, 2 H, Ar H), 7.52 (m, 3 H, Ar H), 7.00 (d, 1 H, J = 8 Hz, NH), 5.08 (dd, 1 H, J = 8, 4 Hz, CHNH), 4.55 (quint, 1 H, J = 4 Hz, CH_3CH), 1.95 (d, 3 H, J = 8 Hz, CH_3).

Acknowledgment. We are grateful to Merck Frosst Canada Inc. and the Natural Sciences and Engineering Research Council of Canada (Grants CRD0040921 and 0845) for generous financial support.

The Synthesis of 1*H*-, 3*H*-, and 5*H*-2-Benzazepine Derivatives in the Reaction of Bicyclic Aromatic Nitro Compounds with Dimethyl Phosphite and Amines in the Basic Conditions[1]

Witold Danikiewicz and Mieczysław Mąkosza*

Institute of Organic Chemistry, Polish Academy of Sciences, ul. Kasprzaka 44/52, PL-01-224 Warszawa, Poland

Received April 4, 1990

1- and 2-nitronaphthalenes and 5-, 6-, and 8-nitroquinolines react with dimethyl phosphite and various primary and secondary amines in the presence of NaOMe in MeOH to give 1*H*-, 3*H*, and 5*H*-2-benzazepine or pyridazepine derivatives. Some structural features of these compounds deduced from the NMR spectra and molecular mechanics calculations are discussed.

In our preliminary communication we have reported that 1-nitronaphthalene (**1a**) reacts with dimethyl phosphite in the presence of NaOMe in MeOH yielding three main products (**2**, **3**, and **4**) in a ratio depending on the reaction

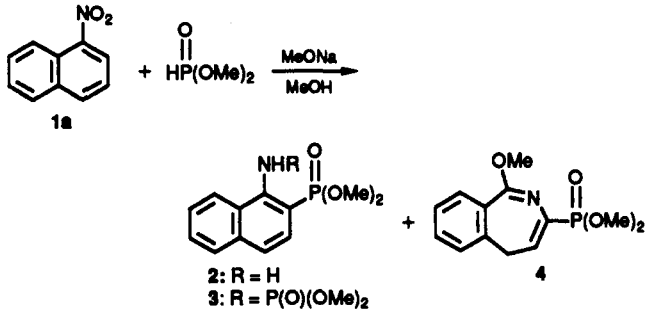
0022-3263/91/1956-1283$02.50/0

Table I.[a] Yields of the Products in the Reactions of 1-Nitronaphthalene Derivatives and Heteroanalogues with Dimethyl Phosphite and Amines

entry	nitroarene	X	Y	R	amine		products (yield,[b] %)
					R^1	R^2	
1	1a	CH	CH	H	CH_3	CH_3	**9a** (89)
2	1a	CH	CH	H	$-(CH_2)_4-$		**9b** (69),[c] **10b** (7)[c]
3	1a	CH	CH	H	C_2H_5	H	**9c** (66), **10c** (22)
4	1b	CH	CH	CH_3	CH_3	CH_3	**9d** (14), **10d** (34)
5	1b	CH	CH	CH_3	C_2H_5	H	**9e** (16), **10e** (72)
6	1c	CH	N	H	CH_3	CH_3	**9f** (90)
7	1d	N	CH	H	CH_3	CH_3	**9g** (81)

[a] X, Y, R, R^1, and R^2 as in Scheme III. [b] Yields of isolated products. [c] Isomer ratio calculated from the ^1H NMR spectrum; this mixture was not separated.

Scheme I

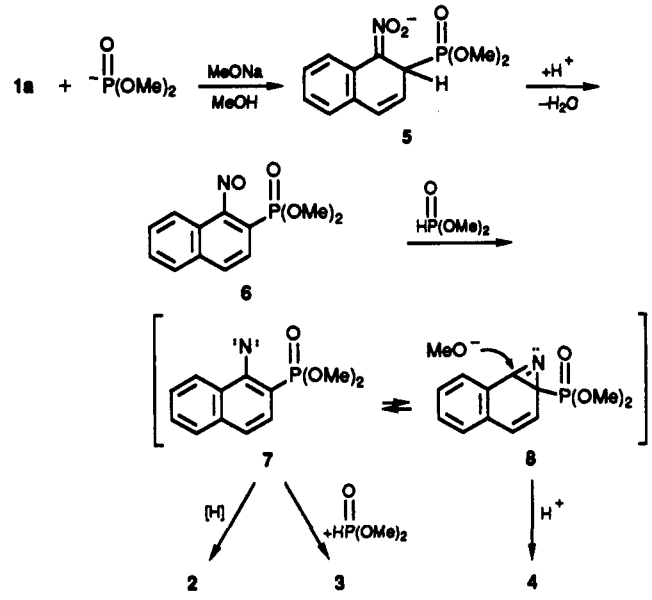


conditions (Scheme I).[2] Under these conditions similar products were obtained from 5- and 8-nitroquinolines, as well as from some 4-substituted 1-nitronaphthalene derivatives. Formation of these products was rationalized by the reaction path shown in Scheme II.

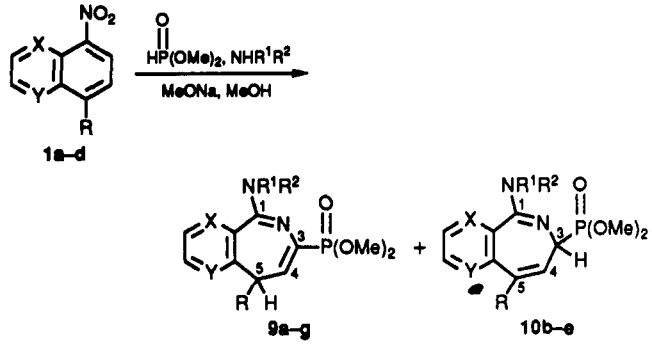
The key step in this complicated process —conversion of the anionic σ-adduct of the phosphite anion to **1a** (**5**) into the nitroso compound **6**—has no precedent in the literature; it resembles, however, transformations of σ-adducts of arylacetonitriles carbanions to nitroarenes.[3] On the other hand, rapid deoxygenation of nitrosoarenes to the corresponding nitrenes by trivalent phosphorus compounds is well documented.[4]

Scheme II implies that the crucial step in the benzazepine formation is a nucleophilic addition of the methoxide anion to the C=N bond of the intermediate azirine **8** (formed via reversible intramolecular addition of the nitrene **7**) leading to the aziridine which subsequently undergoes ring-opening reaction. It was shown that the ratio of the naphthylamine derivatives **2** and **3** and the benzazepine **4** can be manipulated by varying the concentration of sodium methoxide, thus indicating that the intramolecular addition of the nitrene **7** to form azirine derivative **8** is indeed a reversible process.[2] We have anticipated, therefore, that the presence in the reaction mixture of a nucleophile able to react rapidly with intermediate azirine **8** should direct the reaction course entirely toward the benzazapine at the expense of naphthylamine derivatives. From the literature it was known that aliphatic amines react readily with that type azirine intermediate.[5] Therefore, the reaction was attempted in the

Scheme II



Scheme III



presence of primary and secondary aliphatic amines.

Results and Discussion

1-Nitronaphthalene reacts smoothly with dimethyl phosphite and primary or secondary amines in the presence of NaOMe in MeOH solution at 5–10 °C, yielding dimethyl 5*H*-2-benzazepine-3-ylphosphonates (**9**), in which the alkylamino or dialkylamino substituent occupies position 1 (Scheme III). In some instances, isomeric dimethyl 3*H*-2-benzazpine-3-ylphosphonate derivatives (**10**) were formed together with **9**. Similar results were obtained in the analogous reactions of 5- and 8-nitroquinolines, and 1-methyl-4-nitronaphthalene. The results of this reaction series are collected in Table I.

2-Substituted 1-nitronaphthalene derivatives (e.g. 2-chloro-1-nitronaphthalene and 2-methyl-1-nitro-

(1) Part 175 in the series Reaction of Organic Anions. Part 174: Ostrowski, S.; Wojciechowski, K. *Can. J. Chem.*, in press.
(2) Danikiewicz, W.; Mąkosza, M. *J. Chem. Soc., Chem. Commun.* **1985**, 1792.
(3) Davis, R. B.; Pizzini, L. C. *J. Org. Chem.* **1960**, *25*, 1884. Mąkosza, M.; Jagusztyn-Grochowska, M.; Ludwikow, M.; Jawdosiuk, M. *Tetrahedron* **1974**, *30*, 3723.
(4) *Organophosphorus Reagents in Organic Synthesis*; Cadogan, J. I. G., Ed.; Academic Press: London, 1979; Chapter 6.
(5) Atherton, F. R.; Lambert, R. W. *J. Chem. Soc., Perkin Trans. 1* **1973**, 1079. De Boer, T.; Cadogan, J. I. G.; McWilliam, H. M.; Rowley, A. G. *J. Chem. Soc., Perkin Trans. 2* **1975**, 554.

naphthalene) do not undergo this reaction, which seems to proceed specifically in the ortho position to the nitro group. Under similar conditions we were unable to observe an analogous process for any monocyclic nitroarene. Nitrobenzene, p-chloronitrobenzene, and p-(trifluoromethyl)nitrobenzene were recovered unchanged in the standard reaction conditions. Refluxing the reaction mixture caused almost total consumption of nitroarene but only nonisolable, tarry products were obtained.

In all but one reaction of 1-nitronaphthalene and 1-nitro-4-methylnaphthalene, two isomeric products, **9** and **10**, were formed in a ratio depending on the amine and the substituent in position 4. Thus, the reactions with primary amines gave larger amounts of isomer **10** (Table I, entries 2 and 3, or 4 and 5). Also, a methyl group in position 4 exerts a favorable effect on formation of **10**. With 5- and 8-nitroquinolines, products of type **10** were not observed.

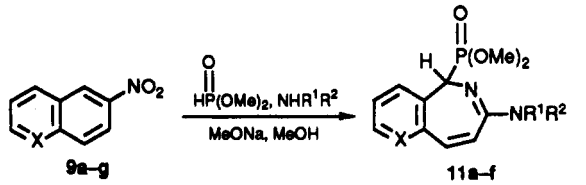
The structures of the products were established on the basis of their ^{1}H NMR spectra. These spectra show a number of interesting features which give important information about the geometry of the investigated molecules. In the series of 5H-2-benzazepine derivatives (**9**) produced for 1-nitronaphthalene and 5- or 8-nitroquinolines, the hydrogen atoms in position 5 are magnetically nonequivalent (with one exception) in spite of the formal symmetry of these molecules. The chemical shifts difference between these protons varies from 0 for compound **2c** to 0.47 ppm for compound **2f**. This phenomenon can be explained by taking into account that the 7-membered ring is not planar and that the energy barrier for the inversion is relatively high, so the inversion rate is slow in the NMR time scale.[6] This assumption was supported by molecular mechanics calculations. The PCMODEL-PI program using the MMX force field and VESCF π-electron calculations was applied.[7] The dihedral angles H4–C4–C5–H5 and H4–C4–C5–H5′ calculated from appropriate experimental coupling constants using a modified Karplus-type equation[8] indicate that in fact the azepine ring is bent about 10° more than indicated by the molecular mechanics calculations.

Another important feature of the ^{1}H NMR spectra of **9** is the nonequivalence of the methyl groups in the dimethyl phosphonate moiety (from $\Delta\delta$ = 0.20 ppm for **9e** to 0.38 ppm for **9f**). This phenomenon can be explained by taking into account that the molecule is chiral in its most stable conformation.

An interesting exception to the regularities described above is compound **9c**. In this case protons 5 and 5′ are magnetically equivalent, which indicates that the inversion of the azepine ring is much faster than for the other compounds investigated. This relatively fast inversion causes also very large broadening of the MeO groups signals. They appear in the spectrum (at 27 °C) as a singlet with a width at half height of 115 Hz.

In the derivatives of 3H-2-benzazepine the azepine ring is also strongly bent. Molecular mechanics calculations indicate that there is no significant difference in energies of two possible conformers, i.e. with the P(O)(OMe)$_2$ group in the quasiequatorial and quasiaxial positions. Calculated coupling constants between protons 3 and 4 in these conformers are, respectively, 5.7 and 6.6 Hz. Experimental values vary from 5.86 Hz for **10c** to 6.44 for **10e**, which is in good agreement with the calculated values. However, the differences in the coupling constants are too small to permit any insight into the relative populations of the conformers and the ring-inversion barrier.

Scheme IV



Scheme V

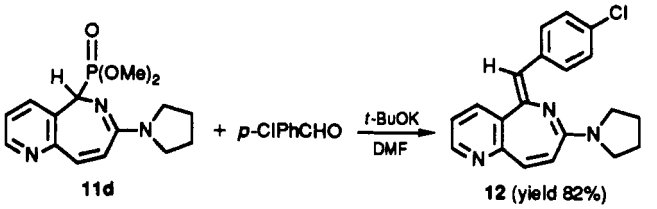


Table II. Yields of the Products in the Reactions of 2-Nitronaphthalene and 6-Nitroquinoline with Dimethyl Phosphite and Amines

entry	nitroarene		amine		product (yield, %)
		X	R^1	R^2	
1	**1e**	CH	CH_3	CH_3	**11a** (82)
2	**1e**	CH	n-C_4H_9	H	**11b** (81)
3	**1f**	N	CH_3	CH_3	**11c** (65)
4	**1f**	N	$-(CH_2)_4-$		**11d** (77)
5	**1f**	N	$-(CH_2)_5-$		**11e** (72)
6	**1f**	N	C_2H_5	H	**11f** (77)

In the reactions of 2-nitronaphthalene and 6-nitroquinoline with dimethyl phosphite and primary or secondary amines under similar conditions, dimethyl 1H-2-benzazepine-1-ylphosphonates with alkyl- or dialkylamino substituent in position 3 (**11**) are obtained in high yields (Scheme IV and Table II).

A characteristic feature of the ^{1}H NMR spectra of these products is the large broadening of the signals of H1 (e.g. for **11c**: 31 Hz, including coupling constant of about 15 Hz) and H9 (for **11c**: 18 Hz, including coupling constant of about 8 Hz) together with variable broadening of the OMe groups signals (for **11c**, 2.6 Hz for each line of the doublet of the downfield methyl group and 6.8 Hz for each line of the doublet of the upfield methyl group; for **11b**, about 8 and 20 Hz, respectively). These phenomena indicate that the ring inversion rate at room temperature is comparable with the NMR time scale, i.e. it is close to coalescence point. Molecular mechanics calculations show that P(O)(OMe)$_2$ group has to occupy preferentially the quasiaxial position. The calculated difference in energies of two conformers is about 1 kcal/mol. This value, however, may be questionable because for such complex molecules with large π-electron system, the accuracy of the molecular mechanics calculations (in terms of energies) is rather low.

The structure of products **11a–f**, with an acidic proton H1 in the α-position to the phosphonate group, suggests that these compounds should undergo the Wittig–Horner reaction. This was confirmed experimentally as shown in Scheme V. Only one isomer of **12** was formed in this reaction, but the spectral data are not sufficient to establish the geometry of the exocyclic double bond.

The results reported in this paper indicate interesting possibilities in the synthesis of some heterocyclic systems.

(6) *Comprehensive Chemistry of Heterocyclic Compounds*; Katritzky, A. R.; Rees, C. W., Eds.; Pergamon Press: Oxford, 1984; Part 5, Chapter 5.16.

(7) PCMODEL - Molecular Modeling Software for the IBM PC/XT/AT and Compatibles, Version 3.2. Serena Software, Box 3076, Bloomington, IN 47402-3076. PCMODEL-PI is a version of PCMODEL which performs VESCF π-electron calculations.

(8) Garbisch, E. W., Jr. *J. Am. Chem. Soc.* **1964**, *86*, 5561.

More important, they exemplify one of the general pathways of further transformations of the anionic σ^H adducts of nucleophiles to nitroarenes.[9]

Experimental Section

^1H NMR spectra were recorded with a Bruker AM-500 (500 MHz) spectrometer at 27 °C using $CDCl_3$ as a solvent and Me_4Si as an internal standard. All chemical shifts and coupling constants (hertz) were calculated using first-order approximations. The accuracy and reproducibility of the chemical shifts were better than ±0.002 ppm (except of the very broad lines). Coupling constants were reproduced with an accuracy ±0.03 Hz (for sharp lines). Full description and interpretation of the ^1H NMR spectra are given in the supplementary material.

Melting points are uncorrected.

Silica gel type 60 from Merck was used for column chromatography. 1- and 2-nitronaphthalenes and 5-, 6-, and 8-nitroquinolines are commercially available (Aldrich). 1-Methyl-4-nitronaphthalene was prepared according to ref. 10.

Reactions of Nitroarenes with Dimethyl Phosphite and Amines. General Procedure. To a solution (or suspension) of nitroarene (10 mmol), dimethyl phosphite (40 mmol), and amine (40 mmol) in anhydrous MeOH (12 mL) was added 15 mL of a 2 M solution of MeONa in MeOH (30 mmol) dropwise during 30 min at 5–10 °C. Low-boiling amines, e.g. dimethylamine, were used as ca. 25% solution in MeOH. The reaction mixture was stirred at 5–10 °C until TLC indicated total consumption of the nitroarene (usually 30 min to 1 h), concentrated in vacuo at 30 °C, diluted with 100 mL of saturated sodium bicarbonate solution, and extracted thoroughly with ethyl acetate or methylene chloride (most of the products are water soluble). The combined extracts were dried with sodium sulfate, and the solvent was evaporated in vacuo. Solid products were purified by boiling with hexane and filtration or by recrystallization from CCl_4 or CCl_4/hexane. Other products were purified by column chromatography on silica gel.

Dimethyl (1-(dimethylamino)-5*H*-2-benzazepin-3-yl)phosphonate (9a): pale yellow oil (column chromatography, hexane–EtOAc–EtOH, 10:20:1).

Dimethyl (1-Pyrrolidino-5*H*-2-benzazepin-3-yl)phosphonate (9b) and Dimethyl (1-pyrrolidino-3*H*-2-benzazepin-3-yl)phosphonate (10b). The mixture of these two compounds was obtained after column chromatography (hexane–EtOAc–EtOH, 10:20:1) as a pale yellow oil. It contains ca. 90% of **9b** and 10% of **10b** (on the NMR basis).

Dimethyl (1-(Ethylamino)-5*H*-2-benzazepin-3-yl)phosphonate (9c) and Dimethyl (1-(Ethylamino)-3*H*-2-benzazepin-3-yl)phosphonate (10c). These compounds were separated by column chromatography ($CHCl_3$–MeOH, 10:1).

9c (less polar): colorless crystals (CCl_4); mp 159–161 °C; ^1H NMR δ 1.28 (t, 3, J = 7.3), 3.13 (d, 2, J = 6.8), 3.51 (br s, 3), 3.70 (br s, 6), 4.77 (br s, 1), 6.20 (dt, 1, J = 12.9, 6.9), 7.14 (m, 1), 7.29 (m, 1), 7.41 (m, 1), 7.48 (m, 1). Anal. Calcd for $C_{14}H_{19}N_2O_3P$: C, 57.14; H, 6.51; N, 9.52. Found: C, 57.24; H, 6.63; N, 9.76.

10c (more polar): colorless crystals (CCl_4–hexane); mp 121–123 °C; ^1H NMR δ 1.20 (t, 3, J = 7.3), 3.27–3.45 (m, 2), 3.61 (m, 1), 3.89 (d, 3, J = 10.3), 3.92 (d, 3, J = 10.2), 4.23 (br s, 1), 6.45 (ddd, 1, J = 11.2, 9.9, 5.9), 6.76 (ddd, 1 J = 9.9, 4.3, 1.6), 7.30–7.35 (m, 2), 7.45 (m, 1), 7.72 (m, 1). Anal. Calcd for $C_{14}H_{19}N_2O_3P$: C, 57.14; H, 6.51; N, 9.52. Found: C, 56.89; H, 6.83; N, 9.61.

Dimethyl (1-(Dimethylamino)-5-methyl-5*H*-2-benzazepin-3-yl)phosphonate (9d) and Dimethyl (1-(Dimethylamino)-5-methyl-3*H*-2-benzazepin-3-yl)phosphonate (10d). These compounds were separated using column chromatography ($CHCl_3$–MeOH, 25:1).

9d (less polar): pale yellow oil.

10d (more polar): pale yellow oil.

Dimethyl (1-(Ethylamino)-5-methyl-5*H*-2-benzazepin-3-yl)phosphonate (9e) and Dimethyl (1-(Ethylamino)-5-methyl-3*H*-2-benzazepin-3-yl)phosphonate (10e). These compounds were separated using column chromatography ($CHCl_3$–MeOH, 25:1).

9e (less polar): pale yellow oil.

10e (more polar): pale yellow oil.

Dimethyl (6-aza-1-(dimethylamino)-5*H*-2-benzazepin-3-yl)phosphonate (9f): colorless crystals (CCl_4–hexane); mp 108–110 °C. Anal. Calcd for $C_{13}H_{18}N_3O_3P$: C, 52.88; H, 6.14; N, 14.23. Found: C, 52.63; H, 6.35; N, 14.27.

Dimethyl (9-aza-1-(dimethylamino)-5*H*-2-benzazepin-3-yl)phosphonate (9g): colorless crystals (CCl_4–hexane); mp 97–99 °C. Anal. Calcd for $C_{13}H_{18}N_3O_3P$: C, 52.88; H, 6.14; N, 14.23. Found: C, 52.83; H, 6.33; N, 14.49.

Dimethyl (3-(dimethylamino)-1*H*-2-benzazepin-1-yl)phosphonate (11a): colorless crystals (CCl_4–hexane); mp 130–131 °C. Anal. Calcd for $C_{14}H_{19}N_2O_3P$: C, 57.14; H, 6.51; N, 9.52. Found: C, 57.20; H, 6.66; N, 9.72.

Dimethyl (3-(*n*-butylamino)-1*H*-2-benzazepin-1-yl)phosphonate (11b): colorless crystals (CCl_4–hexane); mp 92–94 °C. Anal. Calcd for $C_{16}H_{23}N_2O_3P$: C, 59.62; H, 7.19; N, 8.69. Found: C, 59.34; H, 7.35; N, 8.56.

Dimethyl (6-aza-3-(dimethylamino)-1*H*-2-benzazepin-1-yl)phosphonate (11c): colorless crystals (CCl_4–hexane); mp 128–130 °C dec; ^1H NMR δ 2.78 (s, 6), 3.76 (br d, 3, J = 10.3), 3.84 (br d, 3, J = 10.3), 4.07 (br d, 1, J = 13.4), 6.64 (d, 1, J = 12.1), 7.16 (dd, 1, J = 8.0, 4.8), 7.27 (d, 1, J = 12.1), 8.10 (br d, 1, J = 8.0), 8.40 (dd, 1, J = 4.8, 1.5). Anal. Calcd for $C_{13}H_{18}N_3O_3P$: C, 52.88; H, 6.14; N, 14.23. Found: C, 52.67; H, 6.31; N, 14.33.

Dimethyl (6-aza-3-pyrrolidino-1*H*-2-benzazepin-1-yl)phosphonate (11d): colorless crystals (CCl_4–hexane); mp 109–111 °C dec. Anal. Calcd for $C_{15}H_{20}N_3O_3P$: C, 56.07; H, 6.27; N, 13.08. Found: C, 56.21; H, 6.41; N, 12.87.

Dimehyl (6-aza-3-piperidino-1*H*-2-benzazepin-1-yl)phosphonate (11e): colorless crystals (CCl_4–hexane); mp 134–135 °C dec. Anal. Calcd for $C_{16}H_{22}N_3O_3P$: C, 57.30; H, 7.09; N, 12.52. Found: C, 57.00; H, 6.96; N, 12.77.

Dimethyl (6-aza-3-(ethylamino)-1*H*-2-benzazepin-1-yl)phosphonate (11f): colorless crystals (CCl_4–hexane); mp 130–131 °C dec. Anal. Calcd for $C_{13}H_{18}N_3O_3P$: C, 52.88; H, 6.14; N, 14.23. Found: C, 52.68; H, 6.25; N, 14.29.

Wittig–Horner Reaction of 11d with *p*-Chlorobenzaldehyde. The solution of **11d** (0.321 g, 1.0 mmol) and *p*-chlorobenzaldehyde (0.155 g, 1.1 mmol) in anhydrous DMF (3 mL) was added dropwise during 3 min to the stirred solution of *t*-BuOK (0.224 g, 2.0 mmol) in DMF (5 mL) at 5–8 °C. The reaction mixture was stirred at 5 °C for 30 min and then at room temperature for 2 h. After a standard extractive workup the crude product was recrystallized form a hexane–ethyl acetate mixture to give 0.275 g of **12** (82%) as orange crystals: mp 188–190 °C dec; ^1H NMR ($CDCl_3$) δ 1.97 (m, 4 H), 3.56 (br s, 4 H), 5.520 (s, 1 H), 6.559 (d, J = 12.08, 1 H), 7.202 (d, J = 12.09, 1 H), 7.242 ($^1/_2$ of AA'XX' system, 2 H), 7.300 (dd, H = 7.74 and 4.80, 1 H), 7.740 (ddd, J = 7.74, 1.67, and 0.57, 1 H), 7.762 ($^1/_2$ of AA'XX' system, 2 H), 8.557 (dd, J = 4.80 and 1.67, 1 H). Anal. Calcd for $C_{20}H_{18}ClN_3$: C, 71.53; H, 5.40; Cl, 10.56; N, 12.51. Found: C, 71.24; H, 5.33; Cl, 10.54; N, 12.43.

Acknowledgment. This work was supported by Polish Academy of Sciences Grant CPBP 01.13. We express our thanks to Serena Software and personally to Professor Joseph J. Gajewski from the Department of Chemistry, Indiana University, Bloomington, for generous gift of the copy of PCMODEL-PI program.

Supplementary Material Available: Two tables containing full description and interpretation of the ^1H NMR spectra of compounds **9a–g**, **10b–e**, and **11a–f**; PCMODEL-PI geometry-optimized structures of **9a**, **10a** (quasiequatorial and quasiaxial conformers), and **11a** (quasiequatorial and quasiaxial conformers) (7 pages). Ordering information is given on any current masthead page.

(9) Mąkosza, M. Proceedings of 31 IUPAC Congress, Sofia 1987, Section 6, p 118.

(10) Dixon, E. A.; Fisher, A.; Robinson, F. P. *Can. J. Chem.* **1981**, *59*, 2629.