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A Convenient Route to Alkyl, Alkynyl and Aryl Substituted 7-Azabicyclo[2.2.1]heptadienes

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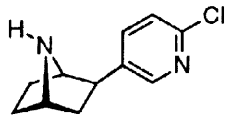
Abstract: 3-Bromopropiolates underwent a smooth [4+2] cycloaddition reaction with *N*-acylpyrroles to afford ***N*-acyl-2-alkoxycarbonyl-3-bromo-7-azabicyclo[2.2.1]heptadienes** in good yields. The 3-bromo-2,7-dimethoxycarbonyl-7-azabicyclo[2.2.1]heptadiene was further transformed to 3-alkyl-, 3-alkynyl- and 3-aryl-2,7-dimethoxycarbonyl-7-azabicyclo[2.2.1]heptadiene derivatives via palladium catalyzed and organocopper coupling reactions.

INTRODUCTION

Since Daly and coworkers reported the isolation and structural elucidation of the novel alkaloid epibatidine (**1**)[1], the synthesis of this highly potent non-opioid analgesic, nicotinic receptor agonist[2,3] has been the focus of numerous synthetic efforts. The synthesis of 7-azabicyclo[2.2.1]heptanes, 7-azabicyclo[2.2.1]-hepta-2,5-dienes and **1** has been the subject of several recent review articles[4-6] and continues to be of interest to synthetic chemists.[7-14]



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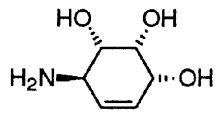

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Of the numerous methods developed for the construction of the 7-azabicyclo[2.2.1]heptane ring system the [4+2] cycloaddition reaction of *N*-protected pyrroles with a suitable acetylenic dienophile to afford 7-azabicyclo[2.2.1]heptadiene derivatives has been shown to be the most straightforward. Several highly reactive acetylenic dienophiles (acetylenic sulfones[11,15-18] and acetylenic dicarboxylate derivatives[19] have been successfully employed. Although substituted 7-azabicyclo[2.2.1]heptadiene derivatives have been employed as key intermediates in the synthesis of **1** and glycosidase inhibitory conduramine alkaloids (**2**)[20,21] further elaboration of the substituted 7-azabicyclo[2.2.1]heptadiene derivatives, especially removal of the sulfonyl moiety, has proven to be problematic.

Previous work in our laboratories has shown that *N*-Boc-pyrrole (**3a**) readily underwent a [4+2] cycloaddition reaction with methyl 3-bromopropiolate (**4a**) to give 3-bromo-7-*tert*-butoxycarbonyl-2-methoxycarbonyl-7-azabicyclo[2.2.1]hepta-2,5-diene (**5a**) in good yield.[7] The cycloaddition adduct **5a** was then converted into **1** via a short and facile synthetic sequence.[7] The ease and the good yield of the [4+2] cycloaddition reaction of **3a** and **4a** prompted us to explore the scope of this reaction as well as the synthetic

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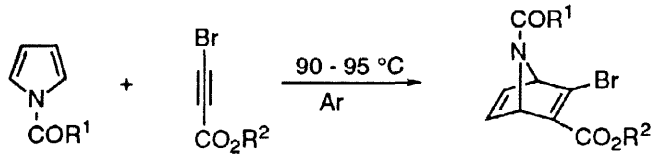
utility of the cycloaddition adducts for the preparation of analogues of epibatidine. Herein we wish to report that derivatives of 3-bromopropiolate **4** readily react with *N*-acylpyrroles **3** to give the corresponding *N*-acyl-3-bromo-2-alkoxycarbonyl-7-azabicyclo[2.2.1]hepta-2,5-dienes **5** in good yield. In addition, we have found that the cycloaddition adduct **5b** can be conveniently converted into a variety of functionalized 7-azabicyclo[2.2.1]heptadiene derivatives via palladium catalyzed and organocopper coupling reactions.

RESULTS AND DISCUSSION

Derivatives of 3-bromopropiolate **4** have been reported as good dienophiles in a variety of [4+2] cycloaddition reactions.[7,12,22-24] The 3-bromopropiolates **4a** and **4b** were conveniently prepared by the bromination of the corresponding propiolate esters with NBS in acetone in the presence of a catalytic amount of $AgNO_3$.[25] A typical [4+2] cycloaddition reaction was performed by heating **3** (5 equiv.) with the 3-bromopropiolate **4** (1 equiv.) at 90 – 95 °C under an argon atmosphere. The corresponding cycloaddition adduct **5** was then isolated in good yield by chromatography (Table 1). The carbamate (**3a**, **3b**) and amide (**3c**, **3d**) derivatives were equally effective at reducing the aromaticity of the pyrrole ring system and facilitating the cycloaddition reaction. The nature of the ester moiety of **4a** and **4b** also had little effect on the yield of cycloaddition adduct **5**. The reaction was found to give the highest yields of **5** when performed neat. The use of solvent (CH_2Cl_2, benzene, toluene, DMF) routinely lead to diminished yields of **5** (30 - 40%).

Table 1. [4 + 2] Cycloaddition Reactions.

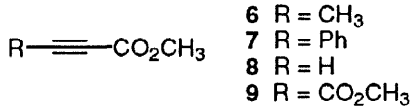


3 **4** **5**

entry	substrates		R^1	R^2	time (h)	adduct	yield (%)[a]
1	**3a**	**4a**	*t*-BuO	CH_3	33	**5a**	60
2	**3b**	**4a**	CH_3O	CH_3	30	**5b**	56
3	**3c**	**4a**	Ph	CH_3	40	**5c**	49
4	**3d**	**4a**	CH_3	CH_3	40	**5d**	45
5	**3a**	**4b**	CH_3O	CH_2Ph	44	**5e**	55

[a]Isolated yields after chromatography.

It was of interest to prepare alkyl and aryl substituted 7-azabicycloheptadiene derivatives as analogues of epibatidine. To this end, initial attempts to prepare these derivatives focused on the [4+2] cycloaddition reaction of 3-substituted methyl propiolates [methyl 2-butynoate (**6**) and methyl phenylpropiolate (**7**)] with *N*-acylpyroles **3a** and **3b**. Unfortunately, these acetylene derivatives were unreactive toward the *N*-acylpyrroles



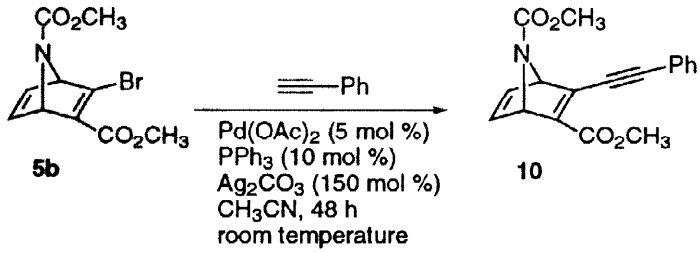
6 R = CH_3
7 R = Ph
8 R = H
9 R = CO_2CH_3

and only starting materials were recovered. Presumably the esters **6** and **7** were not sufficiantly activated to react with the deactivated pyrrole ring system. In addition, we found that methyl propiolate (**8**) reacted with **3b**

to give an intractable mixture of aromatic products which resulted from the Micheal addition reaction of the pyrrole with the acetylenic ester **8**. Moreover, we found and others have shown that the diester, dimethyl acetylenedicarboxylate (**9**) undergoes the [4+2] cycloadditon reaction with *N*-acylpyrrole derivatives **4** under a variety of conditions to give the corresponding cycloaddition adducts in good yields.[4]

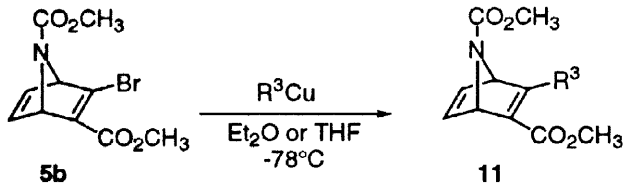
As an alternative approach to alkyl and aryl substituted 7-azabicycloheptadiene derivatives, it was of interest to explore the synthetic utility of the cycloaddition adducts **5**. Introduction of alkynyl, alkyl and aryl groups onto **5b** by displacement of the bromo substituent was envisaged to take place via transition metal mediated coupling reactions. An acetylenic moiety was successfully introduced under modified palladium catalyzed coupling conditions.[26] The palladium catalyzed coupling reaction of **5b** with phenylacetylene in the presence of $Pd(OAc)_2$ (5 mol %) and Ph_3P (10 mol %) using Ag_2CO_3 as the base furnished **10** in 73% yield (Scheme 1).

Scheme 1



Alternatively, alkyl and aryl groups were introduced into **5b** via an organocopper coupling reaction to afford the 3-alkyl- and 3-aryl-7-aza-bicyclo[2.2.1]hepta-2,5-dienes **11**. The alkyl- and arylcopper reagents which were prepared by the addition of alkyllithium or aryllithium to a suspension of $CuBr{\bullet}SMe_2$ in Et_2O at −78 °C reacted smoothly with **5b** to afford **11a – d** in good yields (Table 2). It is noteworthy that the 5-(2'-chloro)pyridinyl group, inherent to epibatidine **1**, was conveniently introduced by this method to give **11d** in 40% yield (Table 2, entry 4), while a previous attempt to introduce the 5-pyridyl group into a 7-aza-bicyclo[2.2.1]hept-2-ene system by the conjugate addition of 5-pyridyl cuprate was reported to be unsuccessful.[27] In addition, we found that reactions of **5b** with the lithium organocuprates $[(R^3)_2CuLi]$ gave consistently lower yields of **11a** (53%) and **11c** (22%) than with the corresponding organocopper reagents.

Table 2. Organocopper Coupling Reactions with **5b**.



entry	R^3	solvent	product	yield (%)[a]
1	CH_3	Et_2O	**11a**	74
2	n-C_4H_9	Et_2O	**11b**	78
3	Ph	Et_2O	**11c**	50
4	5-(2'-chloro)-pyridinyl	THF	**11d**	40

[a]Isolated yields after chromatography.

CONCLUSION

The [4+2] cycloaddition reaction of *N*-acylpyrroles with 3-bromopropiolates has provided versatile 2-alkoxycarbonyl-3-bromo-7-azabicyclo[2.2.1]hepta-2,5-dienes in good yields. These 7-azabicyclo[2.2.1]hepta-diene derivatives can then be readily converted into 3-alkynyl-, 3-aryl- and 3-alkyl-7-aza-bicyclo[2.2.1]heptadienes via organometallic coupling reactions. This synthetic sequence represents a new approach for the introduction of a variety of substituents on the 7-azabicyclo[2.2.1]heptadiene ring system and should prove to be useful for the construction of analogues of epibatidine and derivatives of conduramine alkaloids.

EXPERIMENTAL

All boiling and melting points were uncorrected. All chemicals were purchased from Aldrich Chemical Co. unless otherwise noted and used without further purification. Chromatography refers to flash chromatography on silica gel (Silica Gel 60, 230 – 400 mesh, E. M. Science). Diethyl ether and THF were dried by distillation over sodium and benzophenone ketyl under nitrogen. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian-300 in $CDCl_3$ with TMS as internal standard. Elemental analyses were obtained from Atlantic Microlab, Inc.

N-Boc-pyrrole (**3a**)[28], *N*-Methoxycarbonylpyrrole (**3b**)[29]*N*-acetylpyrrole (**3c**)[30], *N*-benzoylpyrrole (**3d**)[31] and methyl 3-bromopropiolate (**4a**)[25] were prepared according to literature methods. Benzyl 3-bromopropiolate (**4b**)[23] was prepared in 98% yield using a similar procedure as reported for **4a**[25].

Methyl 3-Bromo-7-*tert*-butoxycarbonyl-7-azabicyclo[2.2.1]hepta-2,5-diene-2-carboxylate (5a). 60% yield, slightly yellow oil.[7]

Methyl 3-Bromo-7-methoxycarbonyl-7-azabicyclo[2.2.1]hepta-2,5-diene-2-carboxylate (5b). Typical Procedure: A mixture of *N*-carbomethoxypyrrole (**3b**, 9.2 g, 73.5 mmol) and methyl 3-bromopropiolate (**4a**, 2.40 g, 14.7 mmol) was stirred at 90 – 95 °C under an argon atmosphere for 33 h. The resulting mixture was cooled to room temperature and subjected to column chromatography on silica gel (EtOAc/petroleum ether, 1:12). The first fractions contained the unreacted **3b** (7.5 g) followed by the adduct **5b** (2.40 g, 56% based on **4a**) as a slightly yellow oil. IR (NaCl) 1722, 1606, 1445, 1263, 1091 cm^{-1}; ^{1}H NMR δ 7.14 (br s, 2H), 5.56 (s, 1H), 5.22 (s, 1H), 3.79 (s, 3H), 3.67 (s, 3H); ^{13}C NMR δ 162.5, 154.8, 143.8, 143.5, 141.1, 140.8, 74.4, 68.3, 53.1, 51.8; MS(CI, CH_4) *m/z* (%) 290(M^+ + 1, 40), 258(87), 256(90), 208(100). Anal. Calcd. for $C_{10}H_{10}BrNO_4$ C, 41.69; H, 3.50; N, 4.86. Found C, 41.66; H, 3.45; N, 4.78.

Methyl 3-Bromo-7-benzoyl-7-azabicyclo[2.2.1]hepta-2,5-diene-2-carboxylate (5c). 49% yield, slightly yellow oil. IR (NaCl) 1722, 1606, 1450, 1217, 1090, 705 cm^{-1}; ^{1}H NMR δ 7.39 – 7.50 (m, 5H), 7.31 (s, 0.9H), 7.07 (s, 1.1H), 5.94 (s, 0.45H), 5.60 (s, 1.1H), 5.19 (s, 0.45H), 3.81 (s, 1.35H), 3.75 (s, 1.65H); ^{13}C NMR δ 167.7, 162.4, 145.3, 143.22, 143.18, 142.78, 142.74, 140.4, 133.2, 131.6, 128.6, 128.1, 75.9, 72.6, 70.2, 66.2, 51.9; MS(CI, CH_4) *m/z* (%) 336[M^+(^{81}Br) + 1, 46], 334[M^+(^{79}Br) + 1, 48], 255(42), 105(100). Anal. Calcd. for $C_{15}H_{12}BrNO_3$ C, 53.91; H, 3.62; N, 4.19. Found C, 53.89; H, 3.65; N, 4.12.

Methyl 3-Bromo-7-acetyl-7-azabicyclo[2.2.1]hepta-2,5-diene-2-carboxylate (5d). 45% yield, colorless oil. IR (NaCl) 1717, 1672, 1606, 1328, 1280 cm^{-1}; ^{1}H NMR δ 7.19 – 7.21 (m, 1H), 7.11 – 7.16 (m, 1H), 5.85 (s, 0.4H), 5.57 (s, 0.6H), 5.52 (s, 0.6H), 5.18 (s, 0.4H), 3.79 (s, 1.8H), 3.77 (s, 1.2H), 1.93 (s, 1.8H), 1.92 (s, 1.2H); ^{13}C NMR δ 166.9, 166.7, 162.2, 166.0, 149.1, 146.0, 145.0, 144.2, 143.2, 142.5, 142.3, 140.4, 74.2, 72.0, 68.2, 65.8, 52.6, 51.9, 21.32, 21.28; MS(CI, CH_4) *m/z* (%) 274[M^+(^{81}Br) + 1, 98], 272[M^+(^{79}Br) + 1, 100], 193(40). Anal. Calcd. for $C_{10}H_{10}BrNO_3$ C, 44.14; H, 3.70; N, 5.15. Found C, 44.07; H, 3.75; N, 5.07.

Benzyl 3-Bromo-7-methoxycarbonyl-7-azabicyclo[2.2.1]hepta-2,5-diene-2-carboxylate (5e). 55% yield, colorless oil. IR (NaCl) 1722, 1606, 1450, 1213, 1087, 708 cm^{-1}; ^1H NMR δ 7.30 – 7.40 (m, 5H), 7.14 (br s, 2H), 5.59 (s, 1H), 5.23 (m, 3H), 3.67 (s, 3H); ^{13}C NMR δ 161.9, 154.8, 143.3, 141.1, 140.7, 135.3, 128.5, 128.3, 128.1, 74.5, 68.3, 66.6, 53.1; MS(CI, CH_4) *m/z* (%) 364[M^+(^{81}Br) + 1, 43], 364[M^+(^{79}Br) + 1, 45], 284(100). Anal. Calcd. for $C_{16}H_{14}NBrO_4$ C, 52.77; H, 3.87; N, 3.84. Found C, 52.69; H, 3.92; N, 3.75.

Methyl 3-Phenylethynyl-7-methoxycarbonyl-7-azabicyclo[2.2.1]hepta-2,5-diene-2-carboxylate (10). To a solution of **5b** (290 mg, 1.0 mmol) and phenylacetylene (250 mg, 2.5 mmol) in MeCN (5 mL) under an argon atmosphere were added Ag_2CO_3 (415 mg, 1.5 mmol), $Pd(OAc)_2$ (11 mg, 0.05 mmol) and Ph_3P (26 mg, 0.1 mmol). The mixture was stirred at room temperature and monitored by TLC. After the reaction was completed (48 h), the mixture was filtered and concentrated. The residue was purified by column chromatography on silica gel (EtOAc/petroleum ether, 1:8) to afford **10** as a slightly yellow oil (230 mg, 73%). IR (NaCl) 2192, 1722, 1611, 1445, 1263, 693 cm^{-1}; ^1H NMR δ 7.35 – 7.53 (m, 5H), 7.10 (m, 2H), 5.62 (s, 1H), 5.37 (s, 1H), 3.82 (s, 3H), 3.67 (s, 3H); ^{13}C NMR δ 162.8, 154.77, 148.1, 147.9, 143.4, 141.8, 131.9, 129.5, 128.4, 128.3, 128.2, 122.2, 72.1, 67.2, 53.0, 51.9; MS(CI, CH_4) *m/z* (%) 309(M^+, 68), 278(46), 153(100). Anal. Calcd. for $C_{18}H_{15}NO_4$ C, 69.89; H, 4.89; N, 4.53. Found C, 69.33; H, 5.06; N, 4.40.

Methyl 3-Methyl-7-methoxycarbonyl-7-azabicyclo[2.2.1]hepta-2,5-diene-2-carboxylate (11a). Typical Procedure: MeLi (0.95 M solution in Et_2O, 2.1 mL, 2.0 mmol) was added to a suspension of CuBr•SMe_2 (450 mg, 2.2 mmol) in Et_2O (15 mL) at – 78 °C and the mixture was stirred for 15 min. Then a solution of **5b** (290 mg, 1.0 mmol) in Et_2O (3 mL, precooled to – 78 °C was added. After stirring at – 78 °C for 1 h, the reaction was quenched with aqueous NH_4Cl (5 mL). The water layer was extracted with Et_2O (3 × 10 mL). The combined organic layers were dried (Na_2SO_4) and concentrated. Chromatography on silica gel (EtOAc/petroleum ether, 1:5) afforded **11a** (165 mg, 74%) as a colorless oil. IR (NaCl) 1717, 1647, 1440, 1222, 1087 cm^{-1}; ^1H NMR δ 7.10 (s, 1H), 6.97 (s, 1H), 5.44 (s, 1H), 5.02 (s, 1H), 3.72 (s, 3H), 3.61 (s, 3H), 2.22 (s, 3H); ^{13}C NMR δ 164.4, 155.1, 144.8, 144.5, 141.1, 140.6, 71.9, 67.2, 52.7, 51.3, 16.1; MS(CI, CH_4) *m/z* (%) 224(M^+ + 1, 52), 223(M^+, 37), 192(100). Anal. Calcd. for $C_{11}H_{13}NO_4$ C, 59.19; H, 5.87; N, 6.27. Found C, 58.83; H, 5.97; N, 6.02.

Methyl 3-*N*-Butyl-7-methoxycarbonyl-7-azabicyclo[2.2.1]hepta-2,5-diene-2-carboxylate (11b). 78% yield, colorless oil. IR (NaCl) 1717, 1637, 1445, 1338, 1258, 1092 cm^{-1}; ^1H NMR δ 7.07 (s, 1H), 6.93 (s, 1H), 5.43 (s, 1H), 5.12 (s, 1H), 3.71 (s, 3H), 3.60 (s, 3H), 2.67 (m, 2H), 1.41 (m, 2H), 1.28 (m, 2H), 0.88 (t, J = 7.2 Hz, 3H); ^{13}C NMR δ 164.5, 155.2, 144.9, 144.2, 141.6, 140.8, 70.4, 67.1, 52.7, 51.3, 29.0, 28.4, 22.4, 13.7; MS(CI, CH_4) *m/z* (%) 266(M^+ + 1, 42), 265(M^+, 22), 234(100). Anal. Calcd. for $C_{14}H_{19}NO_4$ C, 63.38; H, 7.22; N, 5.28. Found C, 63.54; H, 7.27; N, 5.20.

Methyl 3-Phenyl-7-methoxycarbonyl-7-azabicyclo[2.2.1]hepta-2,5-diene-2-carboxylate (11c). 50% yield, colorless oil. IR (NaCl) 1717, 1621, 1450, 1222, 693 cm^{-1}; ^1H NMR δ 7.60 – 7.66 (m, 2H), 7.40 – 7.42 (m, 3H), 7.22 (s, 1H), 7.15 (s, 1H), 5.65 (s, 1H), 3.75 (s, 3H), 3.67 (s, 3H); ^{13}C NMR δ 164.1, 155.2, 144.3, 144.1, 141.5, 141.0, 132.8, 129.9, 128.2, 72.0, 68.7, 52.9, 51.7; MS(CI, CH_4) *m/z* (%) 285(M^+, 61), 214(47), 129(100). Anal. Calcd. for $C_{16}H_{15}NO_4$ C, 67.36; H, 5.30; N, 4.91. Found C, 67.25; H, 5.23; N, 4.63.

Methyl 3-[5-(2'-chloro)pyridinyl]-7-methoxycarbonyl-7-azabicyclo[2.2.1]hepta-2,5-diene-2-carboxylate (11d). 40% yield, oil. IR (NaCl) 1717, 1586, 1223, 1106 cm^{-1}; ^1H NMR δ 8.50 (s, 1H), 8.01 (d, J = 8.1 Hz, 1H), 7.32 (d, J = 8.1 Hz, 1H), 7.19 (s, 1H), 7.10 (s, 1H), 5.61 (s, 1H), 5.48 (s, 1H), 3.72 (s, 3H), 3.63 (s, 3H); MS(CI, CH_4) *m/z* (%) 321(M^+ + 1, 100), 289(30), 125(46). Anal. Calcd. for $C_{15}H_{13}N_2ClO_4$ C, 56.15; H, 4.08; N, 8.77. Found C, 55.94; H, 4.22; N, 8.49.

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