Generation and Trapping Reactions of 1-*tert*-Butoxycarbonyl-3,4-didehydro-1*H*-pyrrole†

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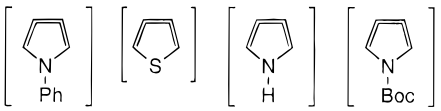
3,4-Bis(trimethylsilyl)-1*H*-pyrrole (**5**) was employed as a key precursor to generate a highly strained and reactive five-membered cyclic cumulene, namely 1-*tert*-butoxycarbonyl-3,4-didehydro-1*H*-pyrrole (**4**). The transient existence of **4** at room temperature was confirmed by trapping reactions with furan, acrylonitrile, and benzene, affording cycloadducts **13**−**15**. The choice of the electron-withdrawing *tert*-butoxycarbonyl group as the *N*-substituent was essential because it was able to adjust the electron density of **11a** and **11b**. As a result, monoiodonium triflates **12a** and **12b** were obtained, respectively. On the contrary, *N*-*tert*-butyl-3,4-bis(trimethylsilyl)-1*H*-pyrrole (**9**) led instead to the bisiodonium triflate **10** upon treatment with the Zefirov reagent.

Introduction

Over the last four decades, a great deal of research has been devoted to the generation and reactions of benzyne.[2,3] Didehydroheterocycles, which are also known as hetarynes, are related but less well-known intermediates.[4] Six-membered didehydrohetarynes,[5] such as 3,4-didehydropyridine, have been generated under several different conditions.[6] However, the attempts to identify five-membered hetarynes have met with immense difficulties. To our best knowledge, many methods have been tested without much success,[4,7] especially when highly strained heterocyclic cumulenes were involved. In the domain of carbocycles, only the isolable 1,2,3-cyclononatriene,[8] the moderately kinetically stable 1,2,3-cyclooctatriene,[9] and the fugitive 1,2,3-cycloheptatriene[10] and 1,2,3-cyclohexatriene[11] have been registered. In the field of heterocycles, the attempts to remove concurrently CO and CO_2 via thermolysis of the 1-phenyl-1*H*-pyrrole 3,4-anhydride and thiophene 3,4-anhydride had been performed, but none of these led eventually to the identification of 1-phenyl-3,4-didehydro-1*H*-pyrrole (**1**)[12] or 3,4-didehydrothiophene (**2**),[13] respectively.



1 **2** **3** **4**

Inspired recently by Kitamura's efficient generation of benzyne from (phenyl)[*o*-(trimethylsilyl)phenyl]iodonium triflate,[14] we successfully generated and trapped 3,4-didehydrothiophene (**2**) in our laboratory.[15] Interestingly, standard ab initio molecular orbital calculations,[15a,16] including geometry optimization and frequency computations, show that 3,4-didehydro-1*H*-pyrrole (**3**) should be more strained than 3,4-didehydrothiophene (**2**) and that the C_3-C_4 bond of **3** possesses slightly less π-character than that of **2**. These two factors indicate that the C_3 and C_4 of **3** should possess a fairly large radical nature, thereby leading to the conclusion that **3** should be much more difficult to trap as a normal cyclic cumulene. Herein, we would like to disclose the generation of 1-*tert*-

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† Dedicated to Professor Xiyan Lu on the occasion of his 70th birthday.

(1) To whom correspondence concerning X-ray crystallographic results should be addressed.

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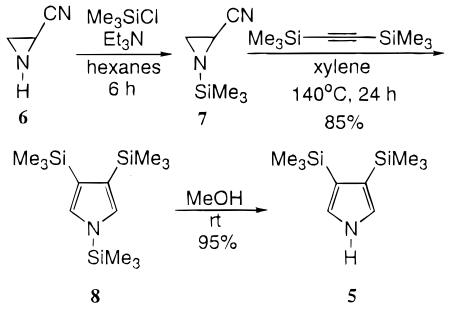
Scheme 1



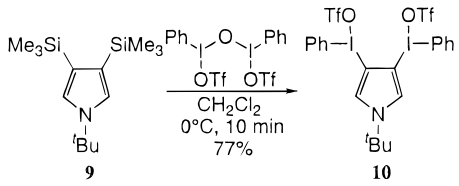
butoxycarbonyl-3,4-didehydro-1*H*-pyrrole (**4**) and its trapping reactions with three different alkenes.

Results and Discussion

Recently, 3,4-bis(trimethylsilyl)-1*H*-pyrrole (**5**)[17] was realized in our laboratory via a 1,3-dipolar cycloaddition pathway[18] as shown in Scheme 1. A trimethylsilyl group was chosen as the nitrogen substituent of aziridine **6**[19] for two reasons: first, the trimethylsilyl group is an electron-donating group which will stabilize the nitrogen ylide intermediate, and second, the trimethylsilyl group can easily be removed from the resulting pyrrole nucleus by treatment with a mild base. With 1-trimethylsilylaziridine-2-carbonitrile (**7**) in hand, we therefore set forth to examine its 1,3-dipolar reaction with bis(trimethylsilyl)acetylene.[18] Thus, treatment of the rather air- and moisture-sensitive **7** with bis(trimethylsilyl)acetylene in xylene at 140 °C furnished 1,3,4-tris(trimethylsilyl)-1*H*-pyrrole (**8**) in 85% yield. To avoid partial or total desilylation during the workup routine, flash chromatography was used. As expected, the desired **5** was easily obtained after removal of the *N*-trimethylsilyl group by stirring **8** in MeOH for 5 min (Scheme 1).[17]

After a reliable supply of **5** had been secured, we then focused our attention on the generation of 3,4-didehydro-1*H*-pyrrole from the corresponding iodonium triflate.[14,15] It is well known that pyrrole is a π-excessive aromatic compound,[20] because the resonance involving the lone-pair electrons on nitrogen results in an enhanced electron density on all of the carbon atoms of a pyrrole ring. Pyrrole itself has the tendency to polymerize[20] in acid, and there is the more serious possibility that the two trimethylsilyl groups of **5** can easily undergo a protodesilylation reaction. Consequently, the first major challenge in our quest of **3** is to generate the pyrrole monoiodonium triflate under acid conditions via an electrophilic aromatic substitution reaction. When 1-*tert*-butyl-3,4-bis(trimethylsilyl)-1*H*-pyrrole (**9**)[17] was allowed to react with the Zefirov reagent[21] at 0 °C, a bisiodonium salt, 1-*tert*-butyl-1*H*-pyrrole-3,4-diyl-bis(phenyliodonium) triflate (**10**) was unfortunately obtained (Scheme 2). The

Scheme 2



structure of **10** was substantiated by spectral analysis, as well as by an X-ray crystallographic study.[22]

In our attempts to achieve electrophilic substitution reactions of other *N*-substituted 3,4-bis(trimethylsilyl)-1*H*-pyrroles[17] with organoiodine(III) compounds, where the *N*-substituents are all of an electron-donating nature, we obtained in a very short reaction time only intractable dark sticky materials even at very low temperatures. These findings suggested that a suitable electron-withdrawing *N*-protecting group might be needed in order to reduce the electron density of the pyrrole ring. With this notion, the *tert*-butoxycarbonyl (Boc) group was chosen as the *N*-substituent. It was anticipated that the electron-withdrawing ability of the Boc group would lower the electron density of the pyrrole ring, therefore retarding the undesired protodesilylation and the bisiodonium salt formation. Despite our previous success[15] in utilizing iodobenzene diacetate,[14,15] the acid conditions involved in this pathway are unfavorable with the present pyrroles. Indeed, our first attempt at transforming **11a** to **12a** by using *p*TsOH as an acid was unfruitful. Compound **11a** was in turn obtained from **5** through a standard procedure.[23] The Zefirov reagent[21] was tried for **11a** without success. After much experimentation, we eventually uncovered that **12a** was provided when **11a** was treated with PhIO activated with $BF_3 \cdot Et_2O$, followed by an anion exchange reaction with NaOTf.[24] The yield of monoiodonium triflate **12a** was optimized to 78%, and the reaction was also improved to a multigram scale (Scheme 3). The structure of **12a** was confirmed by X-ray crystallography,[22] as well as by the usual spectroscopic techniques. In a similar manner, *N*-Ts protecting pyrrole **11b**[25] was also prepared from **5** and was likewise converted to the monoiodonium salt **12b** (Scheme 3).

With an effective preparation of **12a** at our disposal, we then started to examine the generation of 1-*tert*-butoxycarbonyl-3,4-didehydro-1*H*-pyrrole (**4**). The generation and trapping process was carried out as shown in Scheme 4. The reaction of **12a** with a large excess of KF in the presence of a catalytic amount of 18-crown-6 in anhydrous CH_2Cl_2 using furan as a trapping reagent was first studied. Unfortunately, the Diels–Alder adduct endoxide **13** was provided in only 1.4% yield, with the major side products being 1-*tert*-butoxycarbonyl-3-iodo-1*H*-pyrrole (**16**, 17%) and 1-*tert*-butoxycarbonyl-3-iodo-4-trimethylsilyl-1*H*-pyrrole (**17**, 28%). It was clear from

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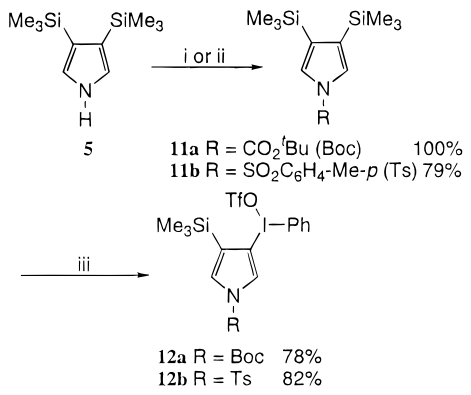
Scheme 3[a]



[a] Reagents and conditions: (i) $(t\text{-BuOCO})_2O$, DMAP, CH_2Cl_2, 30 min; (ii) NaH, DMF then TsCl, 0°C, 6 h; (iii) PhIO, 1.6 eqiv. $BF_3{\bullet}Et_2O$, CH_2Cl_2, rt, 30 min then NaOTf, MeOH, 30 min.

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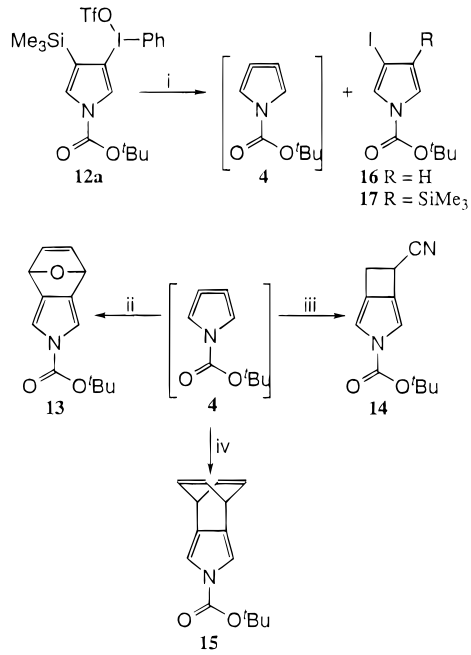
Scheme 4[a]



[a] Reagents and conditions: (i) KF, 18-Crown-6, CH_2Cl_2, r.t.; (ii) furan; (iii) CH_2=CHCN; (iv) C_6H_6.

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this endeavor that the cyclic cumulene **4** must be involved in this reaction as an elusive intermediate with a certain half-life at room temperature, and it was then trapped by furan. The structure of **13** was clearly indicated by its ^{1}H NMR spectroscopic data, which exhibit a two-proton singlet at δ 5.61 for the methine hydrogens. Though the extremely low yield of **13** prevented us from recording its elemental analysis, the ^{13}C NMR and high-resolution mass spectra of **13** confirmed its proposed structure. The optimal reaction temperature for the generation of **4** was maintained from room temperature to 40°C. Lower reaction temperatures were found to render no reaction, and higher temperatures proved to be detrimental. In addition to furan, the highly strained cyclic cumulene intermediate **4** was also trapped by acrylonitrile through a similar approach to afford the [2 + 2] adduct **14** in, again, a meager 1.4% yield, together with **16** (8%) and **17** (26%). It is interesting to note that **4** is so reactive that it could even be trapped by benzene to furnish a Diels−Alder adduct **15**, albeit in only 2.2% yield, again with **16** (10%) and **17** (25%). The structure of **15** was also confirmed by an X-ray crystallographic study.[22]

It is worthy to note that **16** and **17** were generated as the major side products in all the aforementioned trapping reactions, in which all starting material was consumed. Most of the missing products (approximately 60%) were found to be dark red intractable materials. In all the reactions, the isolable products were first purified by preparative TLC plates to separate the desired adducts from the mixtures of **16** and **17**. The final purification was then performed through careful column chromatography on silica gel. The generation of **16** and **17** from the aforementioned reactions is of no surprise, because it has been well established that organic polyvalent iodine compounds[26] are able to decompose to their corresponding iodides under a variety of conditions, the main driving force being the large nucleofugality[27] of the aryliodonio group.

In an attempt to improve the yields of **13**−**15**, we also employed a high dilution approach to keep **12a** at an extremely low concentration. Thus, slow addition (0.9 mL/h) through a syringe pump of a CH_2Cl_2 solution of **12a** to a mixture of KF, 18-crown-6, and furan in CH_2Cl_2 over 10 h gave **13** in 1% yield, along with **16** in 10% yield and **17** in 31% yield. When acrylonitrile was used as the trapping agent and **12a** was added at a rate of 0.2 mL/h, we obtained a similar result as that realized with a regular addition rate, i.e., **14** was generated in 0.9% yield, together with **16** (8%) and **17** (21%). Moreover, the use of benzene as a trapping agent gave **15** (2.3%) and also **16** (17%) and **17** (27%). It is therefore apparent that there was no significant difference between the high dilution method and the normal method.

From a mechanistic point of view, we would like to investigate whether the Diels−Alder adducts were formed through the first cleavage of C−I bond. However, it seems unlikely that the reaction involves an initial C−I bond cleavage rather than a C−Si bond cleavage due to the isolation of **16**. The isolation of **16** indeed provides a clue to the possible existence of phenyl [1-*tert*-butoxycarbonyl-1*H*-pyrrole-3-yl]iodonium triflate, a silicon-free analogue of **12a**.

The other topic we needed to investigate was whether **17** was a byproduct or an intermediate in the formation of Diels−Alder adducts. The results obtained under both normal and high dilution conditions prompted us to believe that compound **17** might be the precursor of **4**. However, when **17** was subjected to the same elimination condition for 30 h in the presence of furan, no reaction was observed and **17** remained intact. This result indicates that **17** is only a byproduct due to the decomposition of **12a**.

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Tetra-*n*-butylammonium fluoride (TBAF), a more soluble fluoride source, was also examined as a reagent for the generation of **4** in the presence of furan as a trapping agent. Thus, treatment of **12a** with 1.2 equiv of TBAF at room temperature in CH_2Cl_2 and furan furnished **16** and **17** in 8% and 11% yield, respectively. Adduct **13** was never isolated in this reaction. This result nonetheless means that the generation of **13** by TBAF was much less efficient than the combined use of KF and 18-crown-6.

Conclusion

As can be seen from the aforementioned results, it is obvious that **4** was formed and trapped not without difficulties. The major factor must be attributed to the geometric strain, as mentioned previously. The additional strain of **4** as compared to **2** might affect its stability[16] and may even result in the anticipated poorer overlap and therefore presumably poorer stabilizing interaction between the orbitals in the ring of **4**. Early research endeavors[28] have studied the relative degree of aryne orbital overlap according to the geometry of the parent aromatic compounds. One such empirical comparison[29] suggests that the overlap of aryne orbitals decreases in the order benzyne ≫ 3,4-didehydrothiophene (**2**) > 2,3-didehydrothiophene > 3,4-didehydro-1*H*-pyrrole (**3**) > 2,3-didehydro-1*H*-pyrrole. Moreover, the energy factor is also relevant in determining the ease with which **4** was generated. Because of the higher energy content of **3** as compared with **2**,[7] the rate of formation of **3** would be slower and other reactions such as ring opening, substitution by an addition−elimination pathway, and stepwise decomposition via nonaryne intermediates would have the opportunity to intervene prior to the formation of **3**.

In conclusion, the physical existence at room temperature of **4** as a reactive and highly strained cyclic cumulene has been verified by trapping reactions with furan, acrylonitrile, and benzene. The attempted generation of the last and most difficult member in this family, 3,4-didehydrofuran,[16] is in progress.

Experimental Section

1,3,4-Tris(trimethylsilyl)-1*H*-pyrrole (8). Me_3SiCl (14 mL, 110.7 mmol) was added dropwise to a solution containing 2-aziridinecarbonitrile (**6**)[19] (6 mL, 88.2 mmol) and Et_3N (12 mL, 86.6 mmol) in anhydrous hexanes (80 mL) at 0 °C under N_2. Precipitates formed immediately. After the addition, the reaction mixture was stirred at room temperature for 6 h. The precipitate was filtered under N_2, and the filtrate was evaporated in vacuo to give 1-trimethylsilyl-2-aziridinecarbonitrile (**7**) (13 mL) as an air- and moisture-sensitive residue. Compound **7** was then added to a stirred solution of bis(trimethylsilyl)acetylene (12 mL, 53 mmol) in xylene (60 mL), and the mixture was stirred at 140−150 °C for 24 h with N_2 bubbled continuously through the reaction solution. After evaporation of xylene, the brownish solution was purified through flash column chromatography on silica gel (15 g, hexanes) to give **8** (10.8 g, 85%) as white solids: mp 45−47 °C; ^{1}H NMR ($CDCl_3$) δ 0.26 (s, 18H), 0.42 (s, 9H), 6.93 (s, 2H); ^{13}C NMR ($CDCl_3$) δ −0.1, 1.0, 124.4, 132.7; MS *m*/*z* 283 (M^+, 100). Anal. Calcd for $C_{13}H_{29}NSi_3$: C, 55.05; H, 10.31; N, 4.94. Found: C, 55.35; H, 10.69; N, 4.93.

3,4-Bis(trimethylsilyl)-1*H*-pyrrole (5). 1,3,4-Tris(trimethylsilyl)-1*H*-pyrrole (**8**) (283 mg, 1 mmol) in MeOH (10 mL) was stirred at room temperature for 5 min. Evaporation of the solvent gave a white powder, which was recrystallized from MeOH−H_2O (7:1) to afford **5** (201 mg, 95%): mp 115−118 °C; ^{1}H NMR ($CDCl_3$) δ 0.28 (s, 18H), 7.01 (d, J = 2.2 Hz, 2H), 8.56 (br s, 1H); ^{13}C NMR ($CDCl_3$) δ 1.0, 121.7, 127.4; MS *m*/*z* 211(M^+, 41). Anal. Calcd for $C_{10}H_{21}NSi_2 \cdot 0.25H_2O$: C, 55.62; H, 10.03; N, 6.48. Found: C, 55.56; H, 10.29; N, 6.50.

1-*tert*-Butyl-1*H*-pyrrole-3,4-diyl-bis(phenyliodonium) Triflate (10). To a fine suspension of PhIO (330 mg, 1.50 mmol) in CH_2Cl_2 (6.0 mL) was added triflic anhydride (0.25 mL, 1.5 mmol) dropwise at 0 °C. After 10 min, 1-*tert*-butyl-3,4-bis(trimethylsilyl)-1*H*-pyrrole (**9**)[17] (510 mg, 3.0 mmol) in CH_2Cl_2 (6.0 mL) was added in a single portion, and an enormous white precipitate immediately appeared. The precipitate was collected on a sintered glass funnel and was recrystallized from MeOH−$CHCl_3$ to give **10** as colorless crystals: mp 231−233 °C; ^{1}H NMR ($CDCl_3$−CD_3OD) δ 1.61 (s, 9H), 7.34 (t, J = 7.8 Hz, 4H), 7.54 (t, J = 7.5 Hz, 2H), 7.77 (d, J = 7.7 Hz, 4H), 8.05 (s, 2H); ^{13}C NMR ($CDCl_3$−CD_3OD) δ 29.2, 59.8, 88.2, 115.1, 117.3, 122.3, 127.4, 131.6, 131.8, 133.2; MS *m*/*z* 678 [$(M - OSO_2CF_3)^+$, 100]. Anal. Calcd for $C_{22}H_{21}F_6I_2NO_6S_2$: C, 31.54; H, 2.56; N, 1.69. Found: C, 31.21; H, 2.28; N, 1.40.

1-*tert*-Butoxycarbonyl-3,4-bis(trimethylsilyl)-1*H*-pyrrole (11a). Pyrrole **5** (10.6 g, 0.05 mol) and Boc_2O (13.2 g, 0.05 mol) were dissolved in CH_2Cl_2. After DMAP (0.61 g, 5 mmol) was added, the solution was stirred at room temperature for 1 h. TMEDA (1.6 g) was added, and the resulting mixture was stirred for an additional 10 min. Et_2O (500 mL) and 1 M $KHSO_4$ (250 mL) was added to the reaction mixture. The organic phase was separated, washed consecutively with 1 M $KHSO_4$ (2 × 125 mL), H_2O (125 mL), 1 M $NaHCO_3$ (125 mL), brine (3 × 125 mL), and H_2O (125 mL), and dried over Na_2SO_4. The solvent was removed in vacuo, and the crude residue was purified by column chromatography on silica gel (250 g, hexanes−Et_2O 50:1) to yield **11a** (15.6 g, 100%) as white solids: mp 51 °C; ^{1}H NMR ($CDCl_3$) δ 0.30 (s, 18H), 1.62 (s, 9H), 7.39 (s, 2H); ^{13}C NMR ($CDC1_3$) δ 0.5, 28.0, 83.5, 126.1, 128.7, 148.5; MS *m*/*z* 311 (M^+, 10). Anal. Calcd for $C_{15}H_{29}NO_2Si_2$: C, 57.82; H, 9.38; N, 4.49. Found: C, 57.47; H, 9.58; N, 4.42.

1-Toluenesulfonyl-3,4-bis(trimethylsilyl)-1*H*-pyrrole (11b). NaH (1.44 g, 36 mmol) was placed in a 250 mL three-necked flask fitted with a thermometer and a dropping funnel and was washed with hexanes (2 × 8 mL). Then DMF (70 mL) was added. This NaH−DMF mixture was cooled to −10 °C, and a solution of **5** (6.33 g, 30 mmol) in DMF (50 mL) was added dropwise. After the addition, the reaction was stirred at 0 °C for 3 h. TsCl (5.72 g, 30 mmol) in DMF (50 mL) was added, and the mixture was stirred for an additional 2 h. It was then poured into ice water (250 mL), and Et_2O (300 mL) was added. The water layer was separated and washed with Et_2O (200 mL × 2). The combined Et_2O solution was washed with H_2O (2 × 200 mL) and brine (2 × 200 mL) and dried over $MgSO_4$. Recrystallization from hexanes afforded colorless crystals of **11b** (8.6 g, 79%): mp 108 °C; ^{1}H NMR ($CDCl_3$) δ 0.22 (s, 18H), 2.42 (s, 3H), 7.19 (s, 2H), 7.31 (d, J = 8.4 Hz, 2H), 7.77 (d, J = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 0.4, 21.3, 126.8, 127.5, 128.3, 129.8, 136.1, 144.7; MS *m*/*z* 365 (M^+, 64). Anal. Calcd for $C_{17}H_{27}NO_2SSi_2$: C, 55.83; H, 7.45; N, 3.83. Found: C, 56.01; H, 7.53; N, 3.72.

Phenyl [1-*tert*-butoxycarbonyl-4-(trimethylsilyl)-1*H*-pyrrole-3-yl]iodonium Triflate (12a). $BF_3 \cdot Et_2O$ (2.0 mL, 16 mmol) in CH_2Cl_2 (33 mL) was added dropwise to a stirred mixture of PhIO (2.2 g, 10 mmol) and **11a** (3.1 g, 10 mmol) in CH_2Cl_2 (70 mL) at −5 to 0 °C under N_2. The yellowish powder of PhIO gradually disappeared. After the addition, the brownish solution in the three-necked round-bottomed flask was allowed to stir for 30 min at room temperature. $NaOSO_2CF_3$ (5.0 g, 29.1 mmol) in MeOH (33 mL) was added in one portion, and the mixture was stirred for an additional 30 min. CH_2Cl_2 (100 mL) and H_2O (100 mL) were added. The aqueous phase was separated and extracted with CH_2Cl_2 (80 mL). The

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combined extracts were washed with H_2O (100 mL) and dried over $MgSO_4$. The solvent was evaporated, and the residue was crystallized from Et_2O to give **12a** (4.6 g, 78%) as colorless crystals: mp 128−130 °C; ^{1}H NMR ($CDCl_3$) δ 0.15 (s, 9H), 1.62 (s, 9H), 7.28 (d, J = 2.1 Hz, 1H), 7.38 (m, 2H), 7.49−7.55 (m, 1H), 7.80−7.84 (m, 2H), 8.13 (d, J = 2.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ −0.9, 27.7, 86.9, 89.5, 114.6, 118.1, 122.4, 125.0, 128.9, 131.8, 132.0, 132.4, 132.7, 146.5; MS m/z 442 (M^+ − OSO_2CF_3, 86). Anal. Calcd for $C_{19}H_{25}F_3INO_5SSi$: C, 38.58; H, 4.26; N, 2.37. Found: C, 38.59; H, 4.27; N, 2.21.

Phenyl [1-toluenesulfonyl-4-(trimethylsilyl)-1*H*-pyrrole-3-yl]iodonium Triflate (12b). Iodonium salt **12b** was prepared from pyrrole **11b** (1.1 g, 3 mmol) with PhIO (0.66 g, 3 mmol) in CH_2Cl_2 (21 mL) catalyzed by BF_3·Et_2O (0.57 mL, 4.5 mmol) in the same manner as for **12a**, yielding **12b** (1.6 g, 82%) as colorless crystals: mp 54−56 °C; ^{1}H NMR ($CDCl_3$) δ 0.10 (s, 9H), 2.41 (s, 3H), 7.08 (d, J = 2.1 Hz, 1H), 7.34−7.39 (m, 4H), 7.47−7.51 (m, 1H), 7.78 (d, J = 8.4 Hz, 2H), 7.87 (d, J = 8.4 Hz, 2H), 8.22 (d, J = 2.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ −1.0, 21.7, 91.0, 114.5, 117.9, 122.2, 126.2, 127.6, 128.1, 130.5, 131.7, 131.8, 132.4, 133.0, 133.9, 146.6; MS m/z 496 (M^+ − OSO_2CF_3, 100). Anal. Calcd for $C_{21}H_{23}F_3INO_5S_2Si$: C, 39.07; H, 3.59; N, 2.17. Found: C, 39.07; H, 3.50; N, 1.99.

***N-tert*-Butoxycarbonyl-7-oxabicyclo[2.2.1]hept-5-eno-2,3-[*c*]pyrrole (13).** To a well stirred solution of **12a** (295 mg, 0.5 mmol), 18-crown-6 (79 mg, 0.3 mmol), and furan (1 mL) in CH_2Cl_2 (5 mL) under N_2 was added KF (87 mg, 1.5 mmol). This mixture was stirred at room temperature for 17 h. The resulting precipitate was removed by filtration. After evaporation of the solvent, the residue was chromatographed on preparative TLC (20 × 20 cm^2) with hexanes−ethyl acetate (9:1) as eluent to afford two portions. The first portion was further purified on silica gel (7 g) with CH_2Cl_2−hexanes (4:1) to give **13** as a colorless oil (1.6 mg, 1.4%): ^{1}H NMR ($CDCl_3$) δ 1.59 (s, 9H), 5.61 (s, 2H), 6.85 (d, J = 0.6 Hz, 2H), 6.90 (s, 2H); ^{13}C NMR ($CDC1_3$) δ 28.0, 78.2, 83.1, 110.2, 136.3, 141.1, 149.8; MS m/z 233 (M^+, 30); high-resolution MS calcd for $C_{13}H_{16}NO_3$ (MH^+) m/z 234.1125, found 234.1127.

The second portion was further purified on silica gel (20 g) with hexanes−CH_2Cl_2 (33:4) as eluent to afford 1-*tert*-butoxycarbonyl-3-iodo-1*H*-pyrrole (**16**) as colorless oil (25 mg, 17%): ^{1}H NMR ($CDCl_3$) δ 1.59 (s, 9H), 6.29 (q, J = 1.5 Hz, 1H), 7.13 (t, J = 2.7 Hz, 1H), 7.32 (t, J = 1.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 27.9, 65.2, 84.4, 118.8, 121.4, 124.7, 147.5; MS m/z 293 (M^+, 100).

Another component of the second portion was 1-*tert*-butoxycarbonyl-3-iodo-4-trimethylsilyl-1*H*-pyrrole (**17**), which formed a colorless oil (51 mg, 28%): ^{1}H NMR ($CDCl_3$) δ 0.29 (s, 9H), 1.58 (s, 9H), 7.11 (d, J = 1.8 Hz, 1H), 7.40 (d, J = 1.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ −1.1, 27.8, 71.4, 84.2, 125.7, 126.4, 126.7, 147.3; MS m/z 365 (M^+, 27). Anal. Calcd for $C_{12}H_{20}INO_2Si$: C, 39.46; H, 5.52; N, 3.83. Found: C, 39.41; H, 5.55; N, 3.76.

***N-tert*-Butoxycarbonyl-3-cyanocyclobuteno[*c*]pyrrole (14).** This compound was prepared from the reaction of **12a** (1.2 g, 2 mmol), acrylonitrile (10 mL), and 18-crown-6 (317 mg, 1.2 mmol) with KF (348 mg, 6 mmol) in CH_2Cl_2 (20 mL), employing a procedure as described for the preparation of **13**, yielding **14** (6 mg, 1.4%) as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 1.59 (s, 9H), 3.56−3.61 (ddd, J = 13.8, 3.6, 1.2 Hz, 1H), 3.68−3.75 (ddd, J = 13.8, 6.0, 0.9 Hz, 1H), 4.24−4.28 (ddd, J = 6.0, 3.3, 0.9 Hz, 1H), 6.86 (d, J = 0.9 Hz, 1H), 6.99 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 26.7, 28.0, 34.9, 84.1, 111.8, 111.9, 119.3, 124.1, 126.5, 149.1; MS m/z 218 (M^+, 41); high-resolution MS calcd for $C_{12}H_{15}N_2O_2$ (MH^+) m/z 219.1128, found 219.1129. Compounds **16** (47 mg, 8%) and **17** (190 mg, 26%) were also obtained.

***N-tert*-Butoxycarbonylpyrro[*c*]bicyclo[2.2.2]octatriene (15).** This compound was prepared from the reaction of **12a** (1.2 g, 2 mmol), benzene (8 mL), and 18-crown-6 (634 mg, 2.4 mmol) with KF (696 mg, 12 mmol) in CH_2Cl_2 (20 mL), employing a procedure as described for the preparation of **13**, yielding **15** (10.7 mg, 2.2%) as colorless crystals: mp 118 °C; ^{1}H NMR ($CDCl_3$) δ 1.52 (s, 9H), 4.63 (tt, J = 3.6, 3.6, 3.6, 3.6 Hz, 2H), 6.79−6.82 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 28.0, 40.4, 82.4, 109.7, 135.6, 139.6, 145.0; MS m/z 243 (M^+, 100); high-resolution MS calcd for $C_{15}H_{18}NO_2$ (MH^+) m/z 244.1332, found 244.1328. Compounds **16** (59 mg, 10%) and **17** (182 mg, 25%) were also obtained.

***N-tert*-Butoxycarbonyl-7-oxabicyclo[2.2.1]hept-5-eno-2,3-[*c*]pyrrole (13) Prepared under High Dilution Condition.** To a well stirred solution of 18-crown-6 (295 mg, 0.5 mmol), KF (87 mg, 1.5 mmol), and furan (1 mL) in CH_2Cl_2 (5 mL) was added **12a** (295 mg, 0.3 mmol) in CH_2Cl_2 (9 mL) through a syringe pump at a rate of 0.9 mL/h in 10 h. The mixture was stirred for another 14 h after the addition. The resulting mixture was worked up as described above, yielding **13** (1.2 mg, 1%) as a colorless oil. The ^{1}H NMR ($CDCl_3$) and ^{13}C NMR ($CDCl_3$) spectra were identical to those of **13** obtained under the regular condition. Compounds **16** (15 mg, 10%) and **17** (57 mg, 31%) were also obtained, the ^{1}H NMR ($CDCl_3$) and ^{13}C NMR ($CDCl_3$) spectra of which were identical to those obtained from the regular condition.

***N-tert*-Butoxycarbonyl-3-cyanocyclobuteno[*c*]pyrrole (14) Prepared under High Dilution Condition.** Compound **14** was prepared by use of **12a** (1.2 g, 2 mmol) in CH_2Cl_2 (5 mL), 18-crown-6 (317 mg, 1.2 mmol), KF (348 mg, 6 mmol), and acrylonitrile (10 mL) in CH_2Cl_2 (20 mL). The syringe pump rate was 0.2 mL/h, and the addition time was 25 h, yielding **14** (3.9 mg, 0.9%) as a colorless oil. Compounds **16** (47 mg, 8%) and **17** (153 mg, 21%) were also obtained. The ^{1}H NMR ($CDCl_3$) and ^{13}C NMR ($CDCl_3$) spectra of **14**, **16**, and **17** were identical to those obtained under the regular condition.

***N-tert*-Butoxycarbonylpyrro[*c*]bicyclo[2.2.2]octatriene (15) Prepared under High Dilution Condition.** Compound **15** was prepared by use of **12a** (1.2 g, 2 mmol) in CH_2Cl_2 (5 mL), 18-crown-6 (634 mg, 2.4 mmol), KF (696 mg, 12 mmol), and benzene (8 mL) in CH_2Cl_2 (20 mL). The syringe pump rate was 0.2 mL/h, and the addition time was 25 h, yielding **15** (11 mg, 2.3%) as a colorless oil. Compounds **16** (100 mg, 17%) and **17** (197 mg, 27%) were also obtained. The ^{1}H NMR ($CDCl_3$) and ^{13}C NMR ($CDCl_3$) spectra of **15**, **16**, and **17** were identical to those obtained under the regular condition.

Attempted Generation of 4 from 17 by TBAF. To a solution of **17** (183 mg, 0.5 mmol) and furan (1 mL) in CH_2Cl_2 (2.5 mL) was added TBAF (0.6 mL, 0.6 mmol) slowly. After 30 h of stirring at room temperature and evaporation of the solvent, the resulting residue was chromatographed on a silica gel column (230−400 mesh, 50 g) eluted with hexanes−CH_2Cl_2 (33:4) to recover the starting material (179 mg, 98%) as a colorless oil, the ^{1}H NMR spectrum of which was identical to that of an authentic **17**.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra for the compounds prepared, as well as the X-ray structural results of **10**, **12a**, and **15** (33 pages). This material is contained in 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.

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