Ring-Opening Reactions of 3-Substituted 1-Azabicyclo[1.1.0]butane with Dichlorocarbene†

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Reaction of 3-ethyl-1-azabicyclo[1.1.0]butane (**1a**) with chloroform-potassium *tert*-butoxide afforded a ring-opened product, 1,1-dichloro-2-aza-4-ethylpenta-1,4-diene (**4a**), which was characterized *via* conversion to the corresponding *N*-substituted 5-chloro-1,2,3,4-tetrazole, **5a**. Reaction of 3-phenyl-1-azabicyclo-[1.1.0]butane (**1b**) with "Seyferth's reagent" ($PhHgCCl_2Br$) afforded 1,1-dichloro-2-aza-4-phenylpenta-1,4-diene (**4b**), which also was characterized *via* conversion to a tetrazole derivative, i.e., **5b**. Finally, the reaction of **1b** with dichlorocarbene generated under phase transfer conditions (chloroform-sodium hydroxide-TEBA) was studied. At short reaction times (0.5 hour), the major reaction product was **4b**. However, at longer reaction times (20-30 hours), two secondary products, **8** and **9**, were formed which resulted *via* subsequent dichlorocyclopropanation of **4b**.

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Recently, our respective laboratories at the University of Łódź and at the University of North Texas have actively pursued a variety of studies of additions of reagents of the type X-Y across the highly strained N-C(3) σ-bond in 3-substituted 1-azabicyclo[1.1.0]-butanes [1-6]. Thus, a variety of such reagents have been reacted with 3-ethyl-, 3-phenyl-, and 2,2-dimethyl-3-phenyl-1-azabicyclo[1.1.0]butane (**1a-1c**, respectively) to afford *N*-3-disubstituted azetidines, and the reaction products have been isolated and fully characterized.

Reactions of this type provide a simple and convenient strategy for preparing 3-substituted azetidines. Such compounds recently have found extensive application as intermediates in the synthesis of azetidine-containing energetic materials [7-12]. Nevertheless, surprisingly few studies of this kind have been reported. As part of our program to investigate reactions of 3-substituted-1-azabicyclo[1.1.0]butanes with electrophiles [1-6], we now report the results of a study of reactions of **1a** and **1b** with dichlorocarbene generated from various suitable precursors.

Bicyclo[1.1.0]butane, a carbocyclic analog of 1-azabicyclo[1.1.0]butane, has been reported to react with dichlorocarbene to afford 2,2-dichlorobicyclo[1.1.1]pentane along with the corresponding ring-opened product, *i.e.*, 1,1-dichloro-1,4-pentadiene [13-17]. Given the close structural analogy between substituted 1-azabicyclo-[1.1.0]butanes and bicyclo[1.1.0]butane, our interest in the corresponding reactions of **1a** and **1b** with dichlorocarbene was piqued by the fact that these reactions have the potential to provide a synthetic entry into the hitherto unreported 1-azabicyclo[1.1.1]pentane system.

I. Reaction of **1a** with Dichlorocarbene.

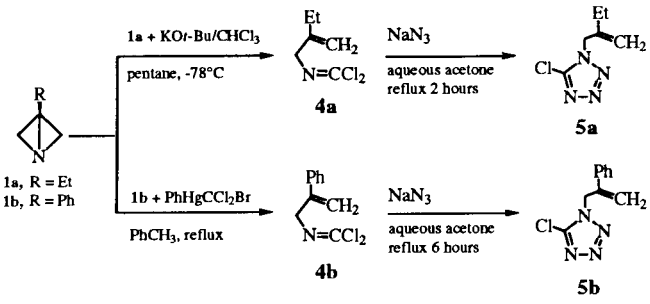
In order to study the reaction of **1a** with dichlorocarbene, the carbene was generated by reacting potassium *tert*-butoxide with chloroform in the presence of the substrate in pentane solution (Scheme 1). Workup of the reaction mixture afforded a yellow oil as the sole reaction product. Based upon our analysis of its ^1H and ^{13}C nmr spectra, the product thereby obtained was assigned structure **4a** [18]. However, this material proved to be unstable, and efforts to purify and to characterize this compound were not successful. Accordingly, the yellow oil was reacted with sodium azide to afford the corresponding substituted 5-chloro-1*H*-tetrazole [19], which was purified and subsequently was fully characterized.

II. Thermal Reactions of **1b-1d** with Seyferth's Reagent.

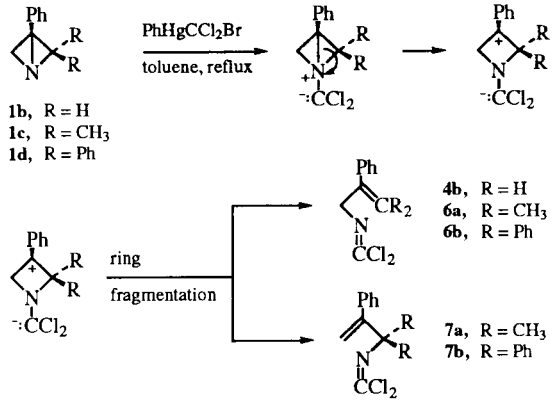
(Bromodichloromethyl)phenylmercury [20] (*i.e.*, $PhHgCCl_2Br$, one of "Seyferth's reagents" [21]) has been used frequently to generate dichlorocarbene in a manner that avoids the intermediacy of an anionic species (*i.e.* $Cl_3C^:$) [21-23]. In our hands, thermal reaction of equimolar quantities of **1b** and (bromodichloromethyl)-phenylmercury proceeded with concomitant ring-opening to afford **4b** (60%, Scheme 1) as the sole reaction product.

The corresponding reaction of **1c** and **1d** afforded mixtures of isomeric products that likewise resulted *via* ring-opening reactions [18]. The structures of the various reaction products were established *via* analysis of their ^1H and ^{13}C nmr spectra (see Experimental). A mechanism which accounts for the formation of **4b** from **1b**, **6a** + **7a** from **1c**, and **6b** + **7b** from **1d** is shown in Scheme 2.

Scheme 1



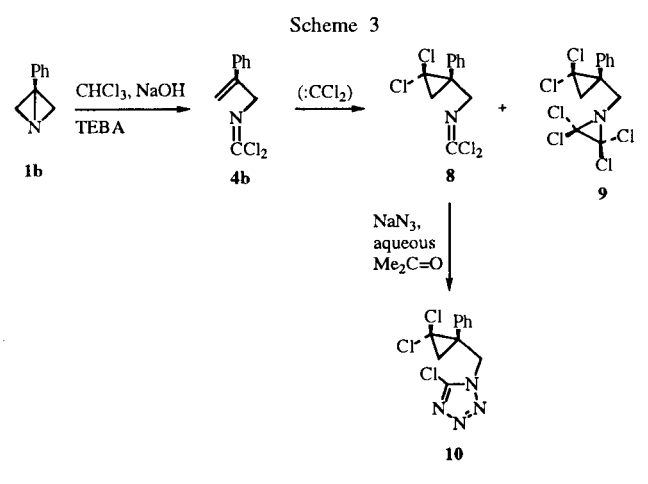
Scheme 2



III. Reaction of **1b** with Chloroform-Sodium Hydroxide-TEBAC.

Finally, **1b** was reacted with dichlorocarbene which was generated in a two-phase system in the presence of triethylbenzylammonium chloride (TEBAC, a phase-transfer catalyst; Makosza reaction [24, 25]). Under these conditions, the stoichiometry of the reaction can only be controlled by varying reaction conditions such as time and temperature. Thus, at short reaction times (0.5 hour), the major reaction product was found to be **4b**. However, at longer reaction times (20-30 hours), two secondary reaction products, **8** and **9** (Scheme 3), which resulted *via* subsequent dichlorocyclopropanation of **4b**, were formed. These products were characterized *via* analysis of their respective ^1H and ^{13}C nmr spectra (see Experimental). In addition, **8** was further characterized *via* subsequent conversion into the corresponding 5-chloro-1*H*-tetrazole (**10**, Scheme 3) [19].

Scheme 3



EXPERIMENTAL

Melting points are uncorrected. Proton and ^{13}C nmr spectra of **1a**, **4a**, and **5a** were obtained at 100 MHz and 25 MHz, respectively. The corresponding nmr spectra of the other compounds reported herein were obtained at 60 MHz and 20 MHz, respectively. Elemental microanalyses were performed by personnel at M-H-W Laboratories, Phoenix, AZ and at the Microanalytical Laboratory of the Polish Academy of Sciences (CBMM), Lodz.

Reaction of **1a** with Chloroform and Potassium *tert*-Butoxide.

A mixture of **1a** (830 mg, 10 mmoles) and potassium *tert*-butoxide (1.12 g, 10 mmoles) in pentane under argon was cooled to -78° *via* application of an external dry ice-acetone bath. To this cold mixture was added with stirring chloroform (810 mg, 6.85 mmoles) dropwise *via* syringe under argon. The resulting mixture was stirred for 1 hour at -78°, at which time the external cold bath was removed and the reaction mixture was allowed to warm gradually to room temperature. The reaction mixture was filtered through a Fluorisil pad, and the filtrate was concentrated *in vacuo*, thereby affording **4a** as a pale yellow, viscous oil. This material was unstable and gradually decomposed during attempts at further purification. Thus, it was used in the next step as obtained, without further purification. Compound **4a** was further characterized by converting it into the corresponding 5-substituted 1*H*-tetrazole, **5a** [19] (*vide infra*); ^1H nmr (deuteriochloroform): δ 1.05 (t, J = 7.6 Hz, 3 H), 2.08 (q, J = 7.6 Hz, 2 H), 4.02 (s, 2 H), 4.86 (br s, 1 H), 4.91 (br s, 1 H); ^{13}C nmr (deuteriochloroform): δ 11.9 (q), 27.0 (t), 59.4 (t), 110.3 (s), 124.6 (s), 145.7 (t).

Reaction of **4a** with Sodium Azide.

The sample of **4a** obtained *via* reaction of **1a** (830 mg, 10 mmoles) with chloroform-potassium *tert*-butoxide (1.12 g, 10 mmoles, *vide supra*) was dissolved in acetone (3 ml), and the resulting solution was added to a mixture of sodium azide (650 mg, 10 mmoles) in water (3 ml). The resulting mixture was refluxed for 2 hours and then was concentrated *in vacuo*. Water (25 ml) was added to the residue, and the resulting suspension was extracted with dichloromethane (3 x 10 ml). The combined organic layers were washed sequentially with water (25 ml) and brine (25 ml), dried (sodium sulfate), and filtered, and the filtrate was concentrated *in vacuo*. The dark red syrupy residue thereby obtained was purified *via* column chromatography on silica gel by eluting with 10% ethyl acetate-hexane). Pure tetrazole **5a** was thereby obtained as a pale yellow oil, bp 150° (2 mm Hg); yield 550 mg (46% overall yield from **1a**); ir (film): 2970, 1655, 1460, 1442, 1199, 910 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.08 (t, J = 7.3 Hz, 3 H), 2.02 (q, J = 7.3 Hz, 2 H), 4.81 (s, 1 H), 4.92 (s, 2 H), 5.08 (s, 1 H); ^{13}C nmr (deuteriochloroform): δ 11.5 (q), 26.1 (t), 52.2 (t), 113.8 (t), 142.2 (s), 146.0 (s).

Anal. Calcd. for $C_6H_9N_4Cl$: C, 41.75; H, 5.26. Found: C, 41.88; H, 5.40.

Reactions of Substituted 1-Azabicyclo[1.1.0]butanes with Seyferth's Reagent. General Procedure.

A solution of the substrate **1b-1d** (5 mmoles) and Seyferth's reagent [20] ($PhHgCCl_2Br$, 2.3 g, 5 mmoles) in toluene (20 ml) was refluxed under nitrogen for 18 hours. The reaction mixture was allowed to cool to ambient temperature and then filtered to remove precipitated bromophenylmercury. The precipitate was washed with a small amount of toluene, and the combined filtrates were concentrated *in vacuo*. The ^1H nmr spectrum of the residue was obtained, and the residue then was purified by distillation or by column chromatography.

Examination of the ^1H nmr spectrum of the product obtained *via* reaction of **1b** with Seyferth's reagent indicated the presence of a mixture of unreacted **1b** and the ring-opened product, **4b** (ratio 15:85). The major component of this mixture was collected *via* vacuum distillation in a Kugelrohr apparatus, thereby affording pure **4b** as a colorless oil, bp 90-95° (0.1 torr); yield 640 mg (60%); ir (film): 1660, 1650 cm^{-1}; ^1H nmr (deuteriochloroform): δ 4.50 (d, J = 1.0 Hz, 2 H), 5.32 (s, $W_{1/2}$ = 4.0 Hz, 1 H), 5.52 (s, $W_{1/2}$ = 3.0 Hz, 1 H), 7.25-7.55 (m, 5 H); ^{13}C nmr (deuteriochloroform): δ 58.2 (t), 61.7 (s), 114.3 (t), 114.9 (s), 126.2 (d), 128.0 (d), 128.6 (d), 139.8 (s); ms: m/z 215 [$(M+1)^+$, 2.2], 213 [$(M-1)^+$, 5.8], 154, 152 (100), 117, 115, 103, 78, 77.

Anal. Calcd. for $C_{10}H_9Cl_2N$: C, 56.10; H, 4.24; Cl, 33.12; N, 6.54. Found: C, 55.98; H, 4.14; Cl, 33.02; N, 6.58.

Examination of the ^1H nmr spectrum of the product obtained *via* reaction of **1c** with Seyferth's reagent indicated the absence of starting material and the presence of two products, **6a** and **7a** (ratio 75:25). The crude reaction product was purified *via* column chromatography on silica gel by using a dichloromethane-pentane gradient elution scheme. Pure **6a** was thereby obtained as a colorless oil, yield 480 mg (53%); ir (film): 1650 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.55 (s, 3 H), 1.85 (s, 3 H), 4.35 (s, 2 H), 7.10-7.40 (m, 5 H).

Anal. Calcd. for $C_{12}H_{13}Cl_2N$: C, 59.52; H, 5.41; Cl, 29.28; N, 5.78. Found: C, 59.68; H, 5.32; Cl, 29.38; N, 5.79.

The minor product of this reaction, *i.e.*, **7a**, was not isolated. It was identified *via* analysis of its ^1H nmr spectrum in admixture with **6a**; ^1H nmr (deuteriochloroform): δ 1.45 (s, 6 H), 5.15 (s, 1 H), 5.30 (s, 1 H), 7.00-7.50 (m, 5 H).

Examination of the ^1H nmr spectrum of the product obtained *via* reaction of **1d** with Seyferth's reagent indicated the absence of starting material and the presence of two products, **6b** and **7b** (ratio 85:15). The crude reaction product was purified *via* column chromatography on silica gel by using a dichloromethane-pentane gradient elution scheme. Pure **6b** was thereby obtained as a colorless microcrystalline solid, mp 81-82°; yield 730 mg (43%); ir (film): 1640 cm^{-1}; ^1H nmr (deuteriochloroform): δ 4.40 (s, 2 H), 6.95 (s, 5 H), 7.10 (s, 5 H), 7.25 (s, 5 H); ms: (m/z) 365 [$(M-1)^+$, 1.2), 356, 78, 77 (100), 51.

Anal. Calcd. for $C_{22}H_{17}Cl_2N$: C, 72.14; H, 4.68; Cl, 19.36; N, 3.82. Found: C, 72.40; H, 4.88; Cl, 19.30; N, 3.72.

The minor product of this reaction, *i.e.*, **7b**, was not isolated in pure form. It was identified *via* analysis of its ^1H nmr spectrum in admixture with **6b**; ^1H nmr (deuteriochloroform): δ 5.30 (s, 1 H), 5.70 (s, 1 H), 7.00-7.50 (m, 15 H).

Reaction of **4b** with Sodium Azide.

To a solution of sodium azide (130 mg, 2.0 mmoles) in water (1 ml) was added **4b** (428 mg, 2.0 mmoles), and the resulting mixture was refluxed for 6 hours. The reaction mixture was concentrated *in vacuo*, and the residue was extracted with dichloromethane, dried (magnesium sulfate), and filtered, and the filtrate was concentrated *in vacuo*. The residue was purified *via* vacuum distillation in a Kugelrohr apparatus, thereby affording pure 5-chloro-1-[(2-phenyl)propen-3-yl]-1*H*-tetrazole (**5b**) as a colorless oil, bp 150° (0.1 torr), yield 221 mg (50%). This material gradually solidified on standing to afford a colorless microcrystalline solid, mp 37°; yield 221 mg (50%); ir (potassium bromide): 1640, 1460, 1440, 1420, 1200, 1110, 920, 775, 705 cm^{-1}; ^1H nmr (deuteriochloroform): δ 5.10 (s, $W_{1/2}$ = 4.0 Hz, 1 H), 5.45 (s, $W_{1/2}$ = 4.0 Hz, 2 H), 5.65 (s, $W_{1/2}$ = 3.0 Hz, 1 H), 7.45 (s, 5 H); ms: m/z 222 [$(M + 2)^+$, 20.3], 220 (M^+, 60.7), 163, 157, 153, 130, 129, 128, 127, 103 (100), 91, 77, 51.

Anal. Calcd. for $C_{10}H_9ClN_4$: C, 54.43; H, 4.11; Cl, 16.07; N, 25.39. Found: C, 54.25; H, 4.10; Cl, 15.90; N, 25.32.

Reaction of **1b** with Chloroform-Sodium Hydroxide-TEBAC. Method A.

To a solution of **1b** (655 mg, 5.0 mmoles) in benzene (3 ml) was added a solution of triethylbenzylammonium chloride (TEBAC, 25 mg, catalytic amount) in 50% aqueous sodium hydroxide (5.0 ml, 190 mmoles). To this mixture was added chloroform (5.0 ml, 62 mmoles) dropwise with vigorous stirring at ambient temperature. After the addition of chloroform had been completed, the resulting mixture was stirred vigorously for 0.5 hour. Water (20 ml) was added, and the organic layer was separated. The aqueous layer was extracted with dichloromethane (3 x 25 ml), and these washings were combined and added to the chloroform layer. The combined organic extracts were dried (sodium sulfate) and filtered, and the filtrate was concentrated *in vacuo*. Analysis of the ^1H nmr spectrum of the residue thereby obtained revealed the presence of unreacted **1b** along with two reaction products, *i.e.*, **4b** and **8** (molar ratio 30:60:10, *vide infra*).

Method B.

The same general conditions were employed for the reaction of **1b** with chloroform-sodium hydroxide-TEBAC as described in Method A, above, with the exception that the reaction mixture was stirred at ambient temperature for 20 hours prior to workup. Analysis of the ^1H nmr spectrum of the product obtained after workup of the reaction mixture revealed no trace of **1b**; only **8** and **9** were present (molar ratio 80:20). The crude product was purified *via* column chromatography on silica gel by using a dichloromethane-pentane gradient elution scheme. Pure **8** was thereby obtained as a colorless oil, which was further purified *via* vacuum distillation on a Kugelrohr apparatus, yield 930 mg (63%), bp 105° (0.1 torr); ir (film): 1650 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.80 (AB, J_{AB} = 7.0 Hz, 1 H), 1.95 (AB, J_{AB} = 7.0 Hz, 1 H), 3.75 (AB, J_{AB} = 14.0 Hz, 1 H), 4.00 (AB, J_{AB} = 14.0 Hz, 1 H), 7.30 (s, 5 H); ^{13}C nmr (deuteriochloroform): δ 30.8 (t), 39.7 (s), 61.6 (t), 64.2 (s), 75.6 (s), 127.9 (d), 128.3 (d), 129.8 (d), 137.5 (s); ms: m/z 297 [$(M + 2)^+$, 0.8], 295 (M^+, 0.6), 262, 260, 224, 163 (100), 152, 149, 128, 117, 115, 103, 77, 51.

Anal. Calcd. for $C_{11}H_9Cl_4N$: C, 44.48; H, 3.05; Cl, 47.75; N, 4.71. Found: C, 44.30; H, 3.15; Cl, 47.98; N, 4.93.

Method C.

The same general conditions were employed for the reaction of **1b** with chloroform-sodium hydroxide-TEBAC as described in Method A, above, with the exception that the reaction mixture was stirred at ambient temperature for 30 hours prior to workup. Analysis of the ^1H nmr spectrum of the product obtained after workup of the reaction mixture revealed no trace of **1b**; only **8** and **9** were present (molar ratio 25:75). The crude product was purified *via* column chromatography on silica gel by using a dichloromethane-pentane gradient elution scheme. Compound **9** was thereby obtained as a colorless microcrystalline solid, yield 1.08 g (57%). Recrystallization of this material from hexane afforded analytically pure **9**, mp 80-81°; ir (potassium bromide): 1290, 845 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.85 (AB, J_{AB} = 8.0 Hz, 1 H), 2.05 (AB, J_{AB} = 8.0 Hz, 1 H), 3.35 (s, $W_{1/2}$ = 4.0 Hz, 2 H), 7.35 (s, 5 H); ^{13}C nmr (deuteriochloroform): δ 31.1 (t), 38.9 (s), 55.6 (t), 63.9 (s), 78.8 (s), 128.2 (d), 128.6 (d), 129.9 (d), 137.0 (s); ms: m/z (no molecular ion), 346, 344, 342 [(M - Cl)$^+$], 308, 306, 178, 165, 164, 163 (100), 128, 127, 113, 77, 51.

Anal. Calcd. for $C_{12}H_9Cl_6N$: C, 37.93; H, 2.38; Cl, 55.99; N, 3.68. Found: C, 38.21; H, 2.12; Cl, 55.82; N, 3.95.

Reaction of **8** with Sodium Azide.

To a solution of sodium azide (130 mg, 2.0 mmoles) in water (1 ml) was added **8** (594 mg, 2.0 mmoles), and the resulting mixture was refluxed for 6 hours. The reaction mixture was concentrated *in vacuo*, and the residue was extracted with dichloromethane, dried (magnesium sulfate), and filtered, and the filtrate was concentrated *in vacuo*. The residue was recrystallized from hexane, thereby affording pure 5-chloro-1-[(2,2-dichloro-1-phenyl)cycloprop-1-yl]methyl-1*H*-tetrazole (**10**) as a colorless microcrystalline solid, mp 115-117°, yield 423 mg (70%); ir (potassium bromide): 1460, 1445, 1415, 1200, 1125, 1030, 770, 695 cm^{-1}; ^1H nmr (deuteriochloroform): δ 2.05 (AB, J_{AB} = 8.0 Hz, 1 H), 2.30 (AB, J_{AB} = 8.0 Hz, 1 H), 4.65 (AB, J_{AB} = 14.0 Hz, 1 H), 5.00 (AB, J_{AB} = 14.0 Hz, 1 H), 7.00-7.40 (m, 5 H); ms: m/z 306 [(M + 4)$^+$, 0.2], 304 [(M + 2)$^+$, 0.7], 302 (M$^+$, 0.5), 200, 198, 178, 165, 163 (100), 128, 115, 103, 77, 51.

Anal. Calcd. for $C_{11}H_9Cl_3N_4$: C, 43.52; H, 2.99; Cl, 35.04; N, 18.46. Found: C, 43.28; H, 3.06; Cl, 34.89; N, 18.15.

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REFERENCES AND NOTES

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