0.528 ml (5.0 mmol) of redistilled **1**. After 30 min, 5.0 ml of D_2O was added and the mixture was saturated with NaCl at 25°. The ether layer was dried ($MgSO_4$) and concentrated under vacuum to yield 0.416 g of purified by preparative glc on a 5 ft × 0.25 in. column containing 15% SF-96 on 30/60 mesh support. One peak was observed corresponding to the retention time (R_T) of undeuterated **1**. Metalation of **1** with excess MeLi involved adding 0.503 g (4.7 mmol) of **1** in 3 ml of ether to a mixture of ether (10 ml) and 5 ml of 1.6 *M* MeLi in ether at 0°. Quenching with D_2O followed by ether extraction gave 0.463 g of crude **1**. Glc analysis indicated complete absence of by-products and provided pure samples for mass spectral analysis.

Metalation/Deuteration of 2. A solution of **2** (0.9994 g, 8.19 mmol) in 5 ml of ether was added dropwise at 0° to 5.0 ml of 1.6 *M* MeLi in ether, stirred for 1 hr, and at 0° 2 ml of D_2O was added followed by 30 ml of saturated brine. Rapid ether extraction (3×), drying ($MgSO_4$), and concentration under vacuum gave crude deuterated **2** which was purified by glc on a 20 ft × 0.25 in. column packed with 18% diethylene glycol succinate on 60/80 mesh support to provide a sample for pmr analysis. No peaks other than **2** were observed. Similarly addition of **2** (0.127 g) to ether (10 ml) and 10 ml of 1.6 *M* MeLi at 25° gave, after 24-hr reaction and work-up, 0.1184 g of deuterated **2**. Pmr of undeuterated **2**: δ 1.23 [t, J = 8 Hz, 3 H, CH_2CH_3], 2.43 [s, 3 H, ring CH_3], 2.72 [q, J = 8 Hz, 2 H, CH_2CH_3], 8.10 [d, J = 2.0 Hz (not completely resolved), ring H] and 8.15 [d, J = 3.0 Hz, ring H] ppm. The aromatic region of deuterated **2** exhibited two broad lines of approximately equal area centered at δ 8.12 and 8.14 ppm. The question of which ring hydrogen has the greater chemical shift remains to be resolved.

Methylation of Methylpyrazine with $NaNH_2/CH_3I$. To 100 ml of liquid NH_3 containing 2.34 g (0.060 mol) of sodamide was added 2.82 g (0.030 mol) of methylpyrazine. After 15 minutes, 3.9 ml (0.030 mol) of methyl iodide was added and stirring was continued until the initial intense red color faded. Excess NH_3 was evaporated and the residue was continuously extracted with ether for 24 hr. The ether was removed, and the residue was distilled to afford 2.84 g of oil, bp 58–69° (15 mm). Glc analysis on a 10 ft × 0.25 in. column containing 15% SF-96 on 30/60 mesh support at 135° resolved the following alkylpyrazines (% yield): methyl- (3.6), ethyl- (31.8), isopropyl- (42), and *tert*-butyl- (4.3). Similar experiments in which only the amounts of sodamide and methyl iodide were varied led to the data in Table III. Pyrazines were isolated by preparative glc technique for characterization. Methyl- and ethylpyrazine were identified by comparison of R_T and ir spectral data with those of authentic samples. Isopropylpyrazine was an oil at 25°: pmr δ 1.30 [d, J = 7 Hz, 6 H, $(CH_3)_2CH$], 3.03 [m, J = 7 Hz, 1 H, $(CH_3)_2CH$], 8.30 and 8.38 ppm (br s, total of 3 H, ring hydrogens).

Anal. Calcd for $C_8H_{12}N_2$: C, 70.6 H, 8.8, N, 20.6. Found: C, 70.11; H, 9.01; N, 21.02.

tert-Butylpyrazine was an oil at 25°: pmr δ 1.34 [s, 9 H, $(CH_3)_3C$] and 8.20–8.56 ppm (unresolved group of peaks, 3 H, ring hydrogens).

Anal. Calcd for $C_8H_{12}N_2$: C, 70.6 H, 8.8, N, 20.6. Found: C, 70.11; H, 9.01; N, 21.02.

Acknowledgments. The author gratefully acknowledges the helpful assistance of Mr. Fred Schroeder in obtaining the high resolution mass spectral data and of Mr. Norvin Gullion for performing the synthetic aspects of the work.

Registry No.—**1**, 5910-89-4; **2**, 15707-23-0; methylpyrazine, 109-08-0; isopropylpyrazine, 29460-90-0; *tert*-butylpyrazine, 32741-11-0; methyllithium, 917-54-4.

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A Convenient Synthesis of 2,3-Dihydroimidazo[1,2-*c*]quinazolines

Goetz E. Hardtmann* and Hans Ott

Sandoz, Inc., Pharmaceutical Division, East Hanover, New Jersey 07936

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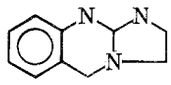
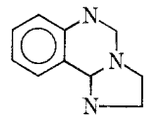
Recently several publications[1,2] have dealt with the preparation of the [2,1-*b*]imidazoquinazoline system (A). The isomeric [1,2-*c*] system (B) is known,[3,4] but no convenient synthetic approaches are available. We now wish to report a simple synthesis of this system utilizing the iodide-catalyzed rearrangement of aziridines originally used by Heine and coworkers[5] for the preparation of oxazolines.[6]

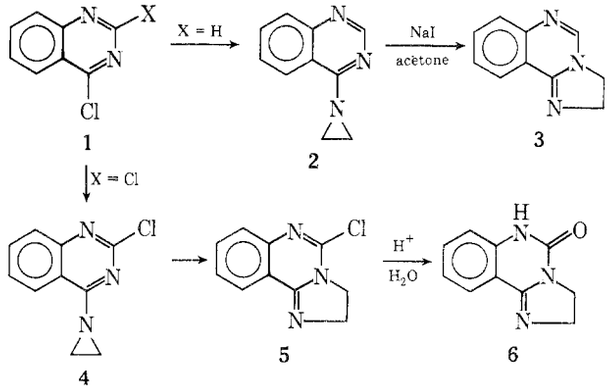


A [2,1-*b*]



B [1,2-*c*]

When 4-chloroquinazoline (1) was allowed to react at room temperature with an excess of ethylenimine, the expected aziridine **2** was formed. This product, when dissolved in acetone and stirred at room temperature in the presence of NaI, underwent rearrangement to the imidazo[1,2-*c*]quinazoline **3**.[3a] Similarly, 2,4-dichloroquinazoline reacted with ethylenimine, but only the 4-chloro substituent was replaced yielding **4**. Attempts to also replace the 2-chloro substituent by using elevated temperatures failed, resulting in the formation of ethylenimine polymers. The monosubstitution product **4** could be rearranged to **5** in the usual manner; treatment of **5** with acid gave the quinazolinone **6**.[4] Analogously 4-chloro- and 2,4-dichloro-6,7-dimethoxyquinazoline could be reacted with aziridines and the products rearranged to the corresponding imidazoquinazolines.



1 2 3 4 5 6

Experimental Section

The spectral data obtained from all products are in accordance with the assigned structure; nmr spectra were measured on a Varian A-60 instrument and the ir spectra with a Perkin-Elmer 137 spectrophotometer.

4-Aziridinoquinazoline (2). To a cooled solution of 4-chloroquinazoline (5 g, 0.03 mol) in methylene chloride (60 ml) ethylenimine (22 ml, 0.5 mol) dissolved in methylene chloride (50 ml) was added dropwise over a period of 30 min. The mixture was stirred at

ice-bath temperature for 90 min and then extracted consecutively with 10% sodium bicarbonate solution (three times), with NaCl solution (twice), and with water. After drying (sodium sulfate) the solvent was evaporated *in vacuo* and 4.5 g (85%) of a clear oil was obtained.

The 6,7-dimethoxy derivative prepared in analogous manner (60%) melted at 146–148°.

Anal. Calcd for $C_{12}H_{13}N_3O_2$: C, 62.3; H, 5.7; N, 18.2. Found: C, 62.5; H, 5.9; N, 18.5.

4-Aziridino-2-chloroquinazoline (4). To a suspension of 2,4-dichloroquinazoline (160 g, 0.8 mol) and anhydrous potassium carbonate (65 g) in 1.6 l. of benzene at 5° ethylenimine (88 ml, 2 mol) was added and the mixture was stirred at 5–10° for 30 min and then allowed to remain at room temperature overnight. The solvent was evaporated *in vacuo* and the crude residue treated with 500 ml of methylene chloride. The solids were removed by filtration and the filtrate was extracted twice with saturated NaCl solution, dried (sodium sulfate), and evaporated. The residue was crystallized from ethanol to obtain 134 g (81%) of **4**, mp 117–118°. (On heating above the melting point the product readily rearranged to **5**.)

Anal. Calcd for $C_{10}H_8N_3Cl$: C, 58.4; H, 3.9; Cl, 17.2. Found: C, 58.2; H, 4.2; Cl, 17.4.

The dimethoxy derivative prepared by the same procedure was used as the crude material for the next step.

2,3-Dihydroimidazo[1,2-*c*]quinazoline (3). A mixture of **2** (15 g, 0.087 mol) and NaI (16 g, 0.11 mol) in anhydrous acetone (150 ml) was stirred at 25° for 15 min followed by heating it under reflux for 60 min. The solvent was evaporated *in vacuo* and the residue treated with water. The slurry was repeatedly extracted with methylene chloride. The combined organic phases were washed with water, dried (sodium sulfate), and evaporated *in vacuo*. The crude product was recrystallized from ethyl acetate to yield 10.7 g (70%) of **3**, mp 128–129° (lit.[3a] mp 119–123°).

Anal. Calcd for $C_{10}H_9N_3$: C, 70.2; H, 5.3; N, 24.6. Found: C, 69.9; H, 5.6; N, 24.7.

The 8,9-dimethoxy analog prepared in the same manner in 61% yield melted at 250–251°.

Anal. Calcd for $C_{12}H_{13}N_3O_2$: C, 62.3; H, 5.7; N, 18.2. Found: C, 62.0; H, 5.9; N, 18.1.

2,3-Dihydro-5-chloroimidazo[1,2-*c*]quinazoline (5). Sodium iodide (15 g, 0.1 mol) was introduced into a solution of **4** (135 g, 0.65 mol) in 2 l. of anhydrous acetone. Methylene chloride (100 ml) was added to bring some newly formed precipitate back into solution and the mixture was stirred for 1 hr at room temperature. The residue obtained after evaporation was dissolved in methylene chloride (600 ml) and the solution extracted with saturated NaCl solution (three times, 200 ml). The organic phase was dried (sodium sulfate) and the solvent evaporated. After one recrystallization from methylene chloride–acetone, 131 g (97%) of **5**, mp 206–209°, was obtained.

Anal. Calcd for $C_{10}H_8N_3Cl$: C, 58.4; H, 3.9; Cl, 17.2. Found: C, 58.3; H, 4.2; Cl, 17.2.

The 8,9-dimethoxy analog was prepared in the same manner in 48% yield, mp 185–186°.

Anal. Calcd for $C_{12}H_{12}N_3O_2Cl$: C, 54.2; H, 4.6; Cl, 13.3. Found: C, 53.9; H, 4.8; Cl, 13.3.

2,3-Dihydroimidazo[1,2-*c*]quinazolin-6*H*-5-one (6). A solution of 10 g of **5** in dioxane (200 ml) was treated with 200 ml of 6 *N* hydrochloric acid. The mixture was heated under reflux for 1 hr, cooled, and neutralized with 50% NaOH solution. The crude reaction mixture was evaporated (to about 200 ml volume) and the crystalline precipitate was filtered off and thoroughly washed with water. This precipitate was dried *in vacuo* (70%) and recrystallized from ethanol to yield 8.0 g (90%) of **6**, mp 291–293° (lit.[4] mp 299–300°).

Anal. Calcd for $C_{10}H_9N_3O$: C, 64.2; H, 4.9; N, 22.5. Found: C, 64.1; H, 5.1; N, 22.3.

Registry No.—**1** (X = H), 5190-68-1; **1** (X = Cl), 607-68-1; **2**, 27114-97-2; **2**, 6,7-dimethoxy analog, 52842-99-6; **3**, 1010-62-4; **3**, 8,9-dimethoxy analog, 52843-00-2; **4**, 28320-12-9; **4** 6,7-dimethoxy analog, 27631-30-7; **5**, 27114-98-3; **5**, 8,9-dimethoxy analog, 27631-31-8; **6**, 38767-521.

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tert-Butylallene. Reversibility of Carbenoid Formation?

Kenneth C. Lilje and Roger S. Macomber*

Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221

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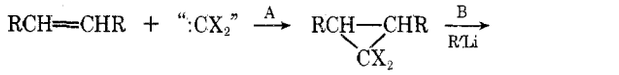
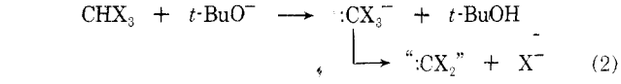
Without doubt the most generally applicable synthesis of allenes currently known involves the addition of a "dihalocarbene" to an olefin, then reaction of the *gem*-dihalocyclopropane with magnesium or an alkyllithium reagent (eq 1). Early work on these reactions was carried out by Doering,[1] Moore,[2] and Skattebol,[3] whose primary attention was directed to the second step. The source of "dihalocarbene" was the reaction of the appropriate haloform with potassium *tert*-butoxide (KO-*t*-Bu), as elucidated by Hine[4] and Skell[5] (eq 2). Although this method of dihalocarbenoid formation has been supplanted to some degree by the organometallic carbene transfer reagents of Seyferth,[6] the original method is still often employed.[7] We report here a complication attending reaction 2 which might have been anticipated from the earlier work[4,5] but which, to the best of our knowledge, has gone unrecognized or unreported.[8]



$$RCH{=}CHR + ":CX_2" \xrightarrow{A} RCH{-}CHR \xrightarrow[R'Li]{B} RCH{=}C{=}CHR + R'Br + LiBr \quad (1)$$



$$CHX_3 + t\text{-}BuO^- \longrightarrow :CX_3^- + t\text{-}BuOH \longrightarrow ":CX_2" + X^- \quad (2)$$

In connection with a study of homoconjugation in carbanions, we attempted to prepare *tert*-butylallene[9] (**1**) by reacting *tert*-butylethylene (**2**) with bromoform in the presence of KO-*t*-Bu. The yield of this reaction was expected to be low, as monosubstituted olefins are considerably less reactive than more electron rich alkenes.

The addition of bromoform to a mixture of **2** and KO-*t*-Bu (50% excess) in pentane at 0° was accompanied by the evolution of significant amounts of a gas.[10] Moreover, the crude product mixture comprised unreacted bromoform (54% by glc) and two products (A and B, 39 and 7%, respectively). The major product was found *not* to be the desired 1,1-dibromo-2-*tert*-butylcyclopropane (**3**), but rather a compound with molecular formula $C_5H_8Br_2$, an unspectacular infrared spectrum, and a lone singlet in its pmr spectrum (δ 1.45, CCl_4 solution). Identification of A was simplified when its pmr spectrum was reexamined using benzene as solvent. The original singlet resolved into two singlets at δ 1.11 (2 H) and 1.17 (6 H), identifying A as 1,1-dibromo-2,2-dimethylcyclopropane (**4**), and this proved to be identical with authentic **4**,[5b] which had been previously prepared by subjecting isobutylene to reaction 1-A.

In order to determine which factors influenced this reaction, it was repeated as above, except **2** was omitted. The evolved gas was trapped at −78°, and identified as isobutylene (*m/e* 56). No peak for carbon monoxide (*m/e* 28) could be detected at 15 eV.[8] The crude product mixture afforded a 49% recovery of bromoform, and a 25% yield (49% based on consumed bromoform) of **4**. No B was detected.