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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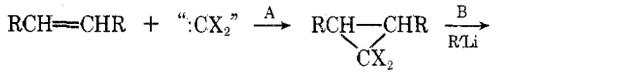
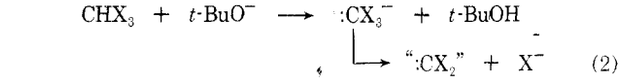
Without doubt the most generally applicable synthesis of allenes currently known involves the addition of a "dihalocarbene" to an olefin, then reaction of the *gem*-dihalocyclopropane with magnesium or an alkyllithium reagent (eq 1). Early work on these reactions was carried out by Doering,[1] Moore,[2] 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.

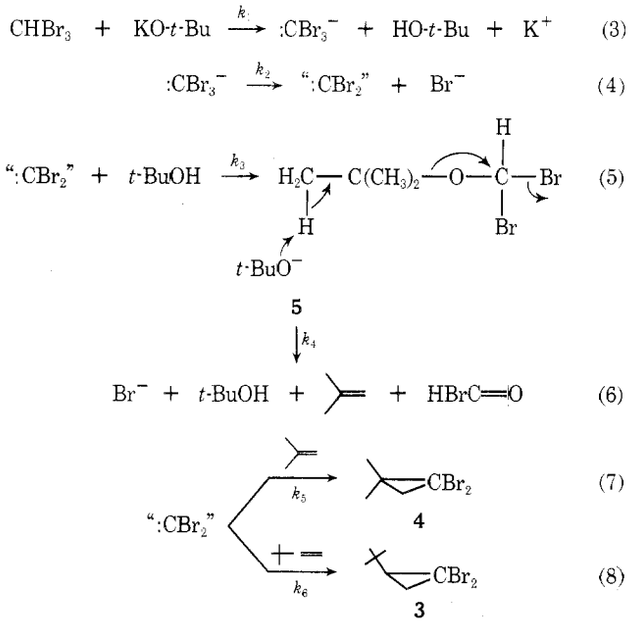
The addition of bromoform to a mixture of **2** and KO-*t*-Bu (50% excess) in pentane at 0° was accompanied by the evolution of significant amounts of a gas.[10] Moreover, the crude product mixture comprised unreacted bromoform (54% by glc) and two products (A and B, 39 and 7%, respectively). The major 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.

When a 4.7-fold excess of KO-*t*-Bu was employed, the yield of **4** was 30% based on consumed bromoform.

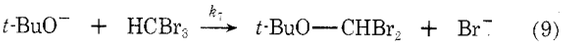
The formation of olefins from alcohols under conditions such as these has been documented,[4a,b,5c] and mechanisms have been advanced to rationalize their formation.[4b] We have found that **4** is the major product whether commercial KO-*t*-Bu or its 1:1 alcohol solvate is used. Furthermore, no gas is evolved *until the bromoform is added.* To account for these observations, it is necessary to invoke a mechanism where the carbenoid is partitioned between the intended carbenophile and the isobutylene produced in a side reaction. Since, with active carbenophiles, no isobutylene (or its adduct) is observed, the side reaction must be slower than addition under usual conditions. With compounds of low carbenophilicity, however, the side reaction becomes competitive, if not dominant.

One possible scheme accounting for these results has as its side reaction the insertion of dibromocarbenoid into the O–H bond of *tert*-butyl alcohol. In this scheme (assuming



k_4 and k_5 are relatively fast), the ratio k_3/k_6 determines the favorability of the outcome. The observation that added *tert*-butyl alcohol has no enhancing effect on the yield of isobutylene or its adduct suggests that *tert*-butyl alcohol may not be involved in the side reaction. An alternative mechanism substitutes reaction 9 for 5. Since it is usually assumed that k_1 is fast (certainly faster than k_7), this alternative mechanism would require reactions 3 and perhaps 4 to be *reversible.* Otherwise the side reaction would be inconsequential. It should be possible to test for the reversibility of carbenoid formation (reaction 4) by carrying out the reaction in the presence of labeled bromide, and looking for incorporation into **3** or **4**.

Although the evolution of isobutylene under these conditions has apparently escaped notice,[8] it is to be expected that reactions 5 and 8 (or reactions 3 and 9) will always compete, and the outcome will be determined by the carbenophilicity of the added olefin.



Product B (*vide supra*) was subsequently identified as the originally desired dibromocyclopropane **3**. This compound could be readily prepared in 45% yield by the reaction of **2** with one of Seyferth's reagents, phenyltribromomethylmercury(II), which is clearly the method of choice when dealing with olefins of low carbenophilicity. Treatment of **3** with methyllithium afforded **1** in 56% yield and >99% purity. Its physical and spectral properties are given in the Experimental Section.

Experimental Section

General. The following instruments were employed: ^{1}H nmr, Varian A-60 and T-60 (with samples in carbon tetrachloride solution containing TMS); ir, Perkin Elmer Models 237 and 700 (with samples in carbon tetrachloride solution); mass spectra, Hitachi Perkin Elmer RMU-7; glc, Hewlett-Packard Model 700 (TC detection) fitted with dual 8 ft × ⅛ in. columns packed with 12% squalane on 80–100 Chromosorb W AW/DMSC (column temperature 100°, injection port 140°, helium flow rate 30 ml/min), quoted product percentages are disc-integrated peak areas uncorrected for differences in response factor. Boiling points are uncorrected. Microanalyses were performed by Chemalytics, Tempe, Ariz.

Reaction of Bromoform–KO-*t*-Bu in the presence of *tert*-Butylethylene. A 250-ml flask fitted with gas inlet tube and vent, magnetic stirrer, and addition funnel was charged with 4.40 g (39 mmol) of commercial KO-*t*-Bu, 40 ml of dry pentane, and 1.18 g (14 mmol) of *tert*-butylethylene (Chemical Samples Co.). The stirred suspension was flushed with nitrogen, cooled to 0°, and 7.08 g (28 mmol) of freshly opened bromoform was added over 30 min. Gaseous evolution took place during addition as the mixture first thickened, then became more mobile. The mixture was allowed to warm to room temperature and stir overnight. Hydrolysis with 25 ml of water was followed by separation and washing of the organic phase with 3 × 20 ml of water, 2 × 20 ml of saturated sodium chloride (brine), then dried over anhydrous magnesium sulfate. Filtration and rotary evaporation left 4.36 g of a yellow oil comprising 54% bromoform (retention time 1.6 min), 39% A (2 min) and 7% B (4.4 min).

Reaction of Bromoform–KO-*t*-Bu without *tert*-Butylethylene. The above reaction was repeated with 29.2 mmol of KO-*t*-Bu-*t*-BuOH (substituted for the commercial material) and 20 mmol of bromoform in the absence of olefin. The liberated gas was collected at −78° and found to be isobutylene (*m/e* 56) by mass spectrometry at 15 eV. Work-up as above left 2.55 g of a mixture of bromoform (52%) and A (48%).

Preparation of 1,1-Dibromo-2-*tert*-butylcyclopropane. A 500-ml three-necked round-bottom flask equipped with magnetic stirrer, reflux condenser, septum cap, and gas inlet tube was charged with 52 g (98 mmol) of phenyltribromomethylmercury(II),[11] 24 g (283 mmol) of *tert*-butylethylene and 300 ml of benzene. The reaction vessel was flushed with nitrogen and heated to reflux. After 20 hr, tlc showed no starting material. The mixture was cooled and filtered to give 33.2 g (99% of theory) of a pale tan solid with mp 281–285° (C_6H_5HgBr). The filtrate was rotary evaporated and the remaining oil distilled to give 10.90 g (45% yield) of a colorless liquid (bp 60–61° (6 mm)). Use of the undistilled product increases the overall yield of allene. Spectral data: nmr δ 1.10 (s 9 H) and 1.59 (m, 3 H); ir 2850–2950, 1450, 1370 cm^{-1}.

Preparation of *tert*-Butylallene (1). A 100-ml three-necked round-bottom flask fitted with gas inlet tube, magnetic stirrer, and septum cap was charged with 12.87 g of the crude dibromocyclopropane (50 mmol) and 35 ml of anhydrous ether. The system was flushed with nitrogen, cooled to −78°, and 30 ml of 1.9 M methyllithium (Alfa Inorganics) was added dropwise *via* syringe; 3 hr after the addition was complete, during which the reaction mixture was allowed to warm to room temperature, tlc showed no remaining starting material. Water (30 ml) was cautiously added, the phases were separated, and the aqueous phase was extracted with 4 × 10 ml of ether. The combined ether phases were washed with 15 ml of water and 2 × 15 ml of brine, and dried over magnesium sulfate. After filtration the solution showed only one component other than ether by glc. Distillation through a 75-cm spinning band column afforded 2.66 g of >99% pure (glc) product (56% yield) with bp 77–78° (740 mm). Since the forecut and pot residue contained an estimated 0.68 g of impure **1** (raising the yield to 70%), it is likely that larger-scale preparations would substantially improve the recovery during distillation. Spectral data: nmr δ 1.03 (s, 9 H), 4.65 (d, J = 6.6 Hz, 2 H), 5.03 (dd, J = 6.6 Hz, 1 H);[12] ir 2850–2950, 1950, 1450–1470, 1365 cm^{-1}; mass spectrum *m/e* (rel abundance) 96 (36), 81 (89), 57 (28), 41 (100), 39 (65). *Anal.* Calcd for C_7H_{12}: C, 87.42; H, 12.58. Found: C, 87.15; H, 12.71.

Registry No.—**1**, 26981-77-1; **2**, 558-37-2; **3**, 52730-96-8; **4**, 32264-50-9; bromoform, 75-25-2; KO-*t*-Bu, 865-47-4; isobutylene,

115-11-7; phenyltribromomethylmercury(II), 3294-60-8; C_6H_5HgBr, 1192-89-8.

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(8) We thank Professor James A. Moore for calling to our attention the portion of the Ph.D. thesis of Thomas Newton (University of Delaware, 1973) wherein it is reported that *carbon monoxide* could be identified mass spectrometrically as a side product from the reaction of KO-*t*-Bu with bromoform. This finding was rationalized by a scheme similar to reaction sequence 3–6 (*vide infra*) followed by decomposition of the formyl bromide to CO and HBr.
(9) With the exception of one terse mention of its preparation by hydroboration [G. Zwerfel, A. Horng, and J. T. Snow, *J. Amer. Chem. Soc.*, **92**, 1427 (1970)], we have found no reports of the synthesis or properties of **1**.
(10) Even at −50°, evolution occurred at a rate of 7 ml/min.
(11) D. Seyferth and R. L. Lambert, *J. Organometal. Chem.*, **16**, 24 (1969).
(12) LAOCOON III (S. Castellano and A. A. Bothner-By, Quantum Chemistry Program Exchange, Department of Chemistry, Indiana University, Bloomington, Ind., Program No. 111) simulation was required to extract the exact chemical shifts and coupling constants of the A_2B allenic proton resonances.

A Facile One-Step Synthesis of 5-Silaspiro[4.4]nona-2,7-diene

Robert G. Salomon

Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106

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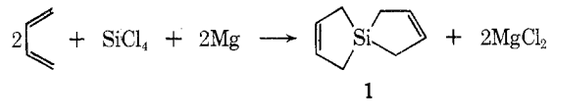
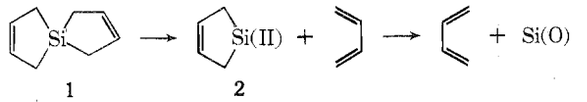
We wish to report a facile one step multiple annelation synthesis of the novel unsaturated heterocycle, 5-silaspiro-[4.4]nona-2,7-diene (**1**) from silicon tetrachloride and 1,3-butadiene. We find that a mildly exothermic reaction ensues upon stirring a suspension of "active magnesium"[1] in tetrahydrofuran under an atmosphere of butadiene. The resulting mixture reacts vigorously with silicon tetrachloride to give the title compound in preparatively useful yield.[2] The assignment of the structure is based on elemental analysis: nmr (CCl_4) δ 1.46 (8 H) and 5.86 (4 H), ir (neat) 839, 942, 1100, 1170, 1205, 1395, 1600, 2900, and 3040 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 53 (52), 54 (49), 55 (61), 67 (49), 81 (56), 82 (99), 83 (47), 108 (44), 136 (100), 137 (46).



1

The major fragmentation involves extrusion of a silylene **2** (*m/e* 82). Related thermal reductive cycloeliminations of dimethylsilylene from 1,1-dimethyl-1-silacyclo-3-pentene derivatives are well known.[3] Interestingly, in the case of **2**, atomic silicon would result from a second extrusion.



1 **2**

One feature of the present synthesis is especially noteworthy. This is the great reactivity of "active magnesium" toward 1,3-butadiene which allows the reductive silylation to be performed under unprecedentedly mild conditions. The reaction of butadiene, dichlorodimethylsilane, and ordinary magnesium powder in hexamethylphosphoric triamide requires several days at elevated temperatures.[4] The reaction must be conducted in an autoclave, and the yield for this single annelation giving 1,1-dimethyl-1-silacyclo-3-pentene is about the same as we obtain in our *double annelation.*

Experimental Section

5-Silaspiro[4.4]nona-2,7-diene. The reaction is conducted in a 2-l. three-neck flask equipped with a Dry Ice–acetone condenser which is topped by a head of nitrogen. One neck is stoppered and another is fitted with a rubber serum cap. Butadiene is introduced through the serum cap with a hypodermic needle and the reaction is stirred magnetically.

A suspension of "active magnesium" (0.25 mol) in tetrahydrofuran (500 ml) is stirred under an atmosphere of butadiene (32 g) until the exothermicity subsides. Then $SiCl_4$ (0.09 mol) is added dropwise with a hypodermic syringe. After stirring overnight at room temperature, cold 10% HCl (250 ml) is cautiously added (vigorous evolution of excess butadiene) followed by water (250 ml) and pentane (150 ml). The aqueous phase is extracted with pentane (200 ml) and the combined pentane extracts are washed with water (200 ml), saturated aqueous Na_2CO_3 (200 ml), and saturated aqueous NaCl (200 ml), and dried (Na_2SO_4). If greater quantities of aqueous washes are employed, voluminous sticky precipitates and emulsions result. Distillation gives **1**, bp 65–68° (13 mm), 21% based on $SiCl_4$. *Anal.* Calcd for $C_8H_{12}Si$: C, 70.51; H, 8.88. Found: C, 69.97; H, 8.86.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Registry No.—**1**, 52856-32-3; 1,3-butadiene, 106-99-0; magnesium, 7439-95-4; silicon tetrachloride, 10026-04-7.

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Reaction of *tert*-Butyl Hydroperoxide and α-Cumyl Hydroperoxide with Acetic Acid[1]

W. E. Cass* and Arun K. Bahl

Department of Chemistry, Northeastern University, Boston, Massachusetts 02115

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Following the chance observation that the hydroperoxide titer of a dilute solution of *tert*-butyl hydroperoxide in acetic acid decreased significantly on standing for several hours at room temperature, we investigated the system and found that direct esterification of the hydroperoxide occurred.[2,3] The reaction was strongly catalyzed by sulfuric acid. Equilibrium and kinetic data were obtained.

An investigation of the system, α-cumyl hydroperoxide–acetic acid, indicated that esterification probably occurred, but that the peroxy ester decomposed, as formed, *via* a