found 284.0048. Anal. Calcd for $C_{13}H_{15}BrS$: C, 55.13; H, 5.34; S, 11.32. Found: C, 55.15; H, 5.51; S, 11.32.

6-Bromo-1-[(4-methylphenyl)sulfonyl]-1-hexyne (8a'). A general literature procedure[28] was followed. *m*-Chloroperbenzoic acid (85%, 615 mg, 3.029 mmol) was added to a stirred and cooled (0 °C) solution of **14** (405 mg, 1.430 mmol) in chloroform (4 mL). The mixture was allowed to warm to room temperature, stirred for 16 h, taken up in ether (10 mL), and washed with saturated aqueous sodium bisulfite (2 × 5 mL), saturated aqueous sodium bicarbonate (5 mL), water (5 mL), and brine (5 mL). The organic solution was dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (2 × 15 cm) with 2:5 ethyl acetate–hexane gave **8a'** (415 mg, 92%) as a homogeneous oil (^1H NMR): FT-IR ($CHCl_3$ cast) 2200 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 1.65–1.76 (m, 2 H), 1.86–1.94 (m, 2 H), 2.41 (t, J = 6.8 Hz, 2 H), 2.46 (s, 3 H), 3.47 (t, J = 6.8 Hz, 2 H), 7.37 (d, J = 8.0 Hz, 2 H), 7.87 (d, J = 8.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 16.12, 21.65, 25.40, 31.30, 32.36, 78.97, 95.68, 127.24, 129.69, 138.95, 145.20; exact mass, m/z calcd for $C_{13}H_{15}{}^{81}BrO_2S$ 315.9946, found 315.9939. Anal. Calcd for $C_{13}H_{15}BrO_2S$: C, 49.53; H, 4.80; O, 10.15; S, 10.17. Found: C, 49.80; H, 4.87; O, 9.99; S, 10.35.

2-(4-Bromobutyl)-4,5-dimethyl-1-[(4-methylphenyl)-sulfonyl]cyclohexa-1,4-diene (8b). Sulfone **8a'** (178 mg, 0.565 mmol) and 2,3-dimethyl-1,4-butadiene (60 mg, 0.730 mmol) were dissolved in dry benzene (3 mL). The solution was sealed in a glass tube that had been flushed with argon and was heated in an oil bath at 140 °C for 20 h. The mixture was cooled, and the solvent was evaporated. Flash chromatography of the residue over silica gel (2 × 15 cm) with 1:9 ethyl acetate–hexane gave **8b** (187 mg, 83%) as a homogeneous (^1H NMR) oil. Crystallization from dichloromethane–hexane gave a homogeneous (^1H NMR) white solid: mp 98–102 °C; ^1H NMR ($CDCl_3$, 200 MHz) δ 1.54–1.72 (m, 2 H), 1.64 (broad s, 6 H), 1.92 (quintet, J = 7.1 Hz, 2 H), 2.46 (s, 3 H), 2.66 (t, J = 8.0 Hz, 2 H), 2.82 (t, J = 7.0 Hz, 2 H), 2.94 (t, J = 7.5 Hz, 2 H), 3.42 (t, J = 6.6 Hz, 2 H), 7.35 (d, J = 8.0 Hz, 2 H), 7.79 (d, J = 8.0 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 17.50, 17.84, 21.52, 27.08, 32.14, 32.54, 33.49, 34.16, 40.13, 121.33, 122.51, 127.09, 129.64, 131.56, 138.68, 143.85, 147.93; exact mass, m/z calcd for $C_{19}H_{25}{}^{81}BrO_2S$ 398.0735, found 398.0738. Anal. Calcd for $C_{19}H_{25}BrO_2S$: C, 57.43; H, 6.34; Br, 20.11; S, 8.07. Found: C, 57.39; H, 6.02; Br, 20.23; S, 8.09.

8,9-Dimethyl-6-[(4-methylphenyl)sulfonyl]spiro[4.5]dec-8-ene (8c). The general procedure for radical cyclization was followed using **8b** (103 mg, 0.259 mmol) in benzene (20 mL), triphenyltin hydride (100 μL, 137 mg, 0.390 mmol) in benzene (10 mL), and AIBN (6 mg, 0.036 mmol) in benzene (10 mL). The residue was taken up in ether (ca. 20 mL) and stirred with an aqueous solution (10 mL) containing an excess of potassium fluoride. The precipitated tributyltin fluoride was removed by filtration, and the ether layer was separated, dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (1 × 15 cm) with 1:9 ethyl acetate–hexane gave **8c** (50 mg, 61%): ^1H NMR ($CDCl_3$, 400 MHz) δ 1.48 (s, 3 H), 1.51 (s, 3 H), 1.60–1.86 (m, 8 H), 1.98–2.06 (m, 2 H), 2.12 (d, J = 10.0 Hz, 1 H), 2.36 (d, J = 10.0 Hz, 1 H), 2.43 (s, 3 H), 3.14 (t, J = 5.7 Hz, 1 H), 7.31 (d, J = 8.1 Hz, 2 H), 7.73 (d, J = 8.1 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 18.42, 18.91, 21.51, 23.30, 24.44, 32.05, 35.24, 38.98, 42.63, 44.75, 69.19, 121.26, 125.48, 128.45, 129.34, 137.76, 143.96; exact mass, m/z calcd for $C_{19}H_{26}O_2S$ 318.1653, found 318.1643. Anal. Calcd for $C_{19}H_{26}O_2S$: C, 71.66; H, 8.23; S, 10.07. Found: C, 71.69; H, 8.11; S, 10.05.

Acknowledgment of financial support is made to the Natural Sciences and Engineering Research Council of Canada.

Registry No. **1a**, 124781-90-4; (*E,E*)-**1a**, 124781-67-5; **1b**, 124781-80-2; **2b**, 124916-17-2; **2c**, 124781-86-8; **3a'**, 624-49-7; **3b**, 124916-18-3; **3b'**, 124781-69-7; **3c**, 124781-87-9; **3c'**, 124781-78-8; **4a'**, 4233-33-4; **4b**, 124781-81-3; **4c**, 124781-88-0; (*E*)-**5a**, 124781-70-0; (*Z*)-**5a**, 124781-75-5; **5b** (isomer 1), 124781-76-6; **5b** (isomer 2), 124781-82-4; **5c** (isomer 1), 124781-77-7; **5c** (isomer 2), 124916-19-4; (*E*)-**6a**, 54125-02-9; (*Z*)-**6a**, 124306-13-4; **6a**, 103971-83-1; **6b**, 124781-83-5; **6c**, 77745-32-5; **7a'**, 124854-74-6; **7b**, 124781-84-6; **7c**, 10469-63-3; **8a'**, 124781-79-9; **8b**, 124781-85-7; **8c**, 124781-89-1; **9**, 74785-89-0; (*E*)-**10**, 124781-71-1; (*Z*)-**10**, 124781-68-6; **11**, 124781-72-2; **12**, 124781-73-3; **13**, 66823-38-9; **14**, 124781-74-4; methyl α-(dimethylphosphono)propionate, 26530-60-9; 2,3-dimethyl-1,4-butadiene, 513-81-5; methyl 3-bromopropionate, 3395-91-3; maleic anhydride, 108-31-6; (methoxymethyl)triphenylphosphonium, 4009-98-7; 1,4-dibromobutane, 110-52-1; diphenyl diselenide, 1666-13-3; methyl 3-(phenylseleno)propionate, 67813-05-2; (*E,E*)-octa-4,6-dienol, 80106-30-5; phenyl selenocyanate, 2179-79-5.

(28) Snider, B. B.; Kirk, T. C.; Roush, D. M.; Gonzalez, D. *J. Org. Chem.* **1980**, *45*, 5015.

(29) After submission of this manuscript, the full paper corresponding to ref 5a appeared: Gosh, T.; Hart, H. *J. Org. Chem.* **1989**, *54*, 5073.

Olefins from Crowded Carbonyl Compounds with *tert*-Butyllithium (*tert*-Butylmagnesium Chloride)/Thionyl Chloride. Study of Carbocationic Reaction Intermediates and Rearrangement–Cleavage under Stable Ion Conditions Using ^{13}C NMR Spectroscopy[1]

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Received June 16, 1989

Crowded carbonyl compounds when reacted with *tert*-butyllithium or *tert*-butylmagnesium chloride followed by thionyl chloride treatment give in a one-pot reaction olefins in good to excellent yields. In the case of highly crowded tertiary systems the reaction occurs either by rearrangement followed by the loss of a *tert*-butyl group (as isobutylene) or rearrangement accompanied by deprotonation, indicating the carbocationic nature of the process. The nature of intermediate carbocations and their cleavage–rearrangement process was probed in SbF_5/SO_2ClF solution of the corresponding alcohols under stable ion conditions using ^{13}C NMR spectroscopy.

Introduction

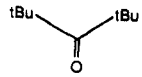
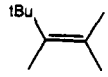
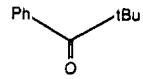
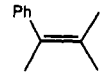
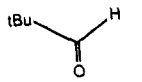
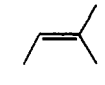
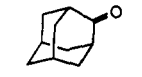
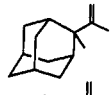
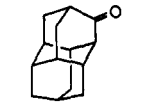
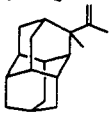
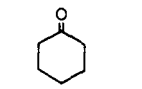
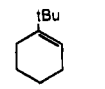
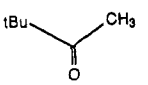
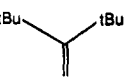
In the study of the dehydration of di-*tert*-butylmethyl alcohol to give trimethylethylene through elimination of a *tert*-butyl group (as isobutylene), Whitmore and Stahly[2a] established the common basis for intramolecular carbocationic rearrangements. Subsequently, in the solvolysis of (tri-*tert*-butylmethyl)-*p*-nitrobenzoate in a hydroxylic solvent under neutral conditions, Bartlett and Stiles[3]

(1) Synthetic Methods and Reactions. 146. For Part 145, see: Sassaman, M. B.; Prakash, G. K. S.; Olah, G. A. *Synthesis*, in press.

(2) (a) Whitmore, F. C.; Stahly, E. E. *J. Am. Chem. Soc.* **1933**, *55*, 4153. (b) Olah, G. A.; Wu, A.; Farooq, O. *J. Org. Chem.* **1989**, *54*, 1375.

0022-3263/90/1955-1792$02.50/0

Table I. Preparation of Olefins from Ketones with *tert*-Butyllithium/Thionyl Chloride

substrate ketone	product olefin	% yield[a]	reagent
		76 (70)	*t*-BuLi ; $SOCl_2$
		69 (76)	*t*-BuMgCl ; $SOCl_2$
		64 (61[b])	*t*-BuLi ; $SOCl_2$
		96 (90)	*t*-BuLi ; $SOCl_2$
		92 (90)	*t*-BuLi ; $SOCl_2$
		87 (64)	*t*-BuLi; $SOCl_2$
		82 (70)	*t*-BuLi; $SOCl_2$

[a] Values in parentheses are the isolated yields from the dehydration experiments using *p*-toluenesulfonic acid in benzene. [b] Only GC yield.

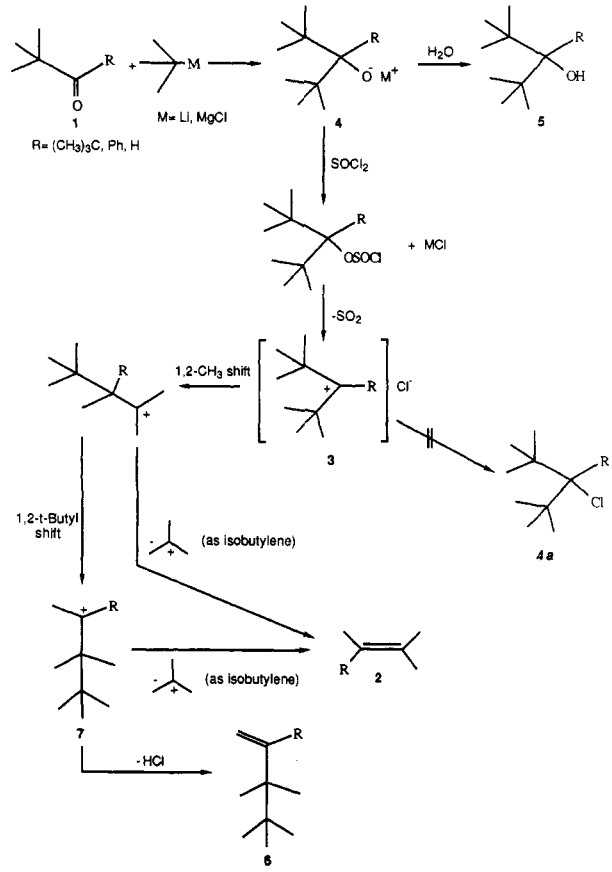
showed the product to be 3,3,4,4-tetramethyl-2-*tert*-butyl-1-pentene (a C_{13} olefin) formed via succcessive migration of methyl and *tert*-butyl group in the incipient tri-*tert*-butylmethyl cation. In the case of rigid cage systems, *tert*-butyl-substituted alcohols such as 2-*tert*-butyl-2-adamantanol and its analogues[4] undergo carbocation forming reactions extremely rapidly. The solvolysis of 2-*tert*-butyl-2-adamantyl-*p*-nitrobenzoate in aqueous medium gives a methyl-shifted alkene[5,6] (i.e. 2-isopropenyl-2-methyladamantane) as the major product similar to that obtained from the reaction of 2-*tert*-butyl-2-adamantanol with hydrogen halides and superacidic "Magic Acid" at ambient and subambient temperatures.[7]

Our continued interest in carbocationic rearrangements and our ongoing study of thionyl chloride induced dehydration of crowded carbinols[2b] led us to investigate the reaction of crowded carbonyl compounds with *tert*-butyllithium or *tert*-butylmagnesium chloride followed by thionyl chloride treatment, which gave olefins in a one-pot reaction. To understand the anamolous behavior of some *tert*-butylated crowded systems which lack α-hydrogens, we also undertook a ^{13}C NMR spectroscopic study of the mechanism of reaction by generating the respective carbocationic intermediates by the ionization of the corresponding tertiary alcohols under superacidic conditions.

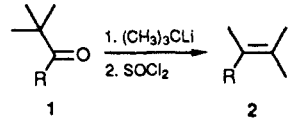
Results and Discussion

Nonenolizable carbonyl compounds such as **1** (R = *tert*-butyl, Ph, H) when reacted with *tert*-butyllithium or

Scheme I



tert-butylmagnesium chloride and subsequently with thionyl chloride, give 2-substituted 3-methyl-2-butene, **2**, as the only product in good to excellent yields. The results

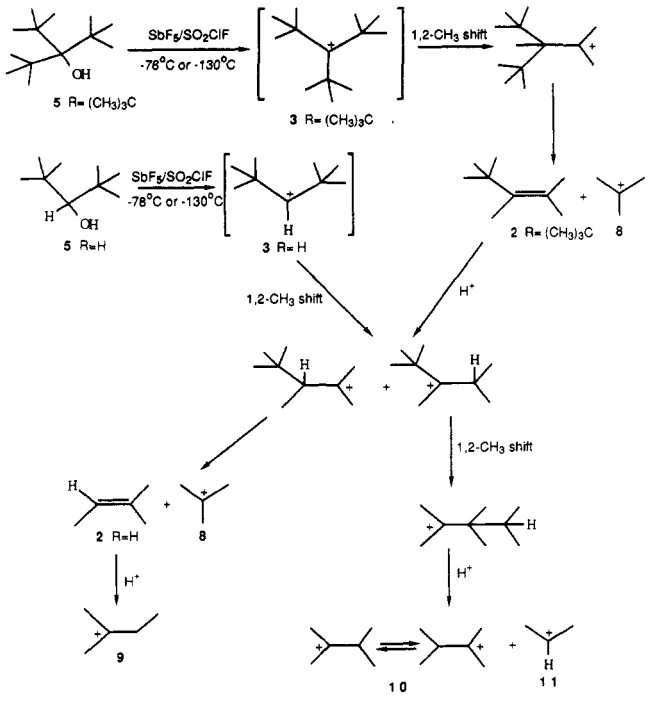


are summarized in Table I. Whereas the reaction mixtures did not show any other products (as analyzed by GLC), the gas phase above each reaction mixture showed the presence of isobutylene in all reactions. Thus, the formation of **2** can be rationalized through the involvement of substituted di-*tert*-butylmethyl cation **3**, which is generated by the treatment of the intermediate lithium aloxide adduct **4** with thionyl chloride (Scheme I). The crowded carbocation **3** upon successive methyl shift followed by *tert*-butyl group elimination, provides the olefin **2**. The olefin **2** (R = H) has been earlier observed by Whitmore in the dehydration of the di-*tert*-butylmethyl alcohol [**5** (R = H)]. We have observed the same olefin products (see Table I) in the dehydration of alcohols **5** catalyzed by *p*-toluenesulfonic acid, giving credence to the intermediacy of the cation **3** (see Scheme I) in the present reaction with thionyl chloride. Bartlett and Stiles[3] previously reported the isolation of olefin **6** [R = $(CH_3)_3C$] formed by the intermediacy of the cation **7**. The cation **7** is obtained by successive 1,2-methyl and *tert*-butyl shifts from cation **3**. However, under our conditions **7** can also eliminate a *tert*-butyl cation to give olefin **2**.

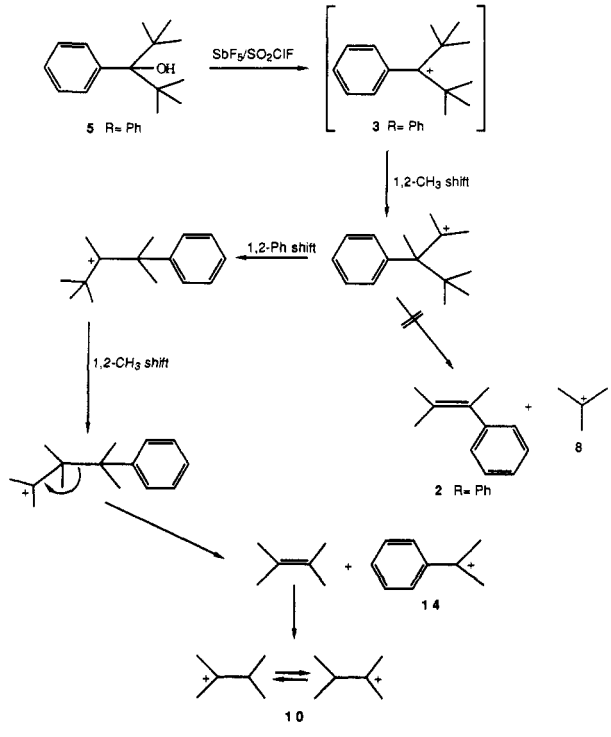
To further probe the intermediacy of carbocation **3** we ionized the *tert*-butyl-substituted alcohols **5** under superacidic stable ion conditions at low temperatures. Careful ionization of **5** [R = $(CH_3)_3C$] in SbF_5/SO_2ClF either at −78 °C or −130 °C gave a pale yellow solution. The 50-

(3) Bartlett, P. D.; Stiles, M. *J. Am. Chem. Soc.* **1955**, *77*, 2806.
(4) Fry, J. L.; Engler, E. M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1972**, *94*, 4628.
(5) Badger, R. C.; Fry, J. L. *J. Am. Chem. Soc.* **1979**, *101*, 1680.
(6) Lomas, J. S.; Luong, P. K.; Dubois, J. E. *J. Am. Chem. Soc.* **1977**, *99*, 5478; *J. Org. Chem.* **1979**, *44*, 1647.
(7) Saba, J. A.; Fry, J. L. *J. Am. Chem. Soc.* **1983**, *105*, 533.

Scheme II

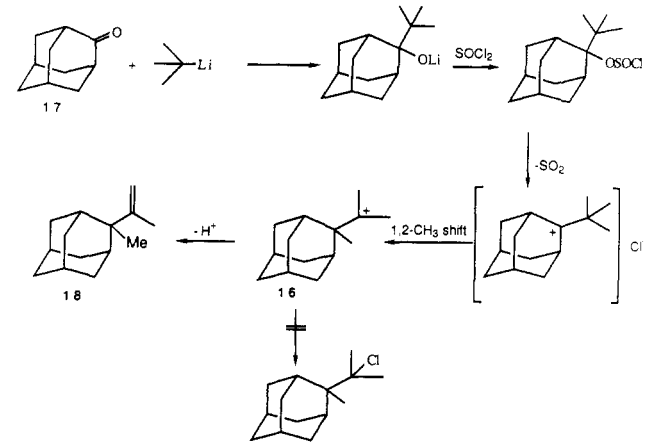


Scheme III



MHz ^{13}C NMR spectrum of the solution showed the presence of a mixture of *tert*-butyl cation **8**,[8] the *tert*-amyl cation **9**,[8] the *tert*-hexyl cation **10**, and the isopropyl cation **11**. Even at very low temperatures (−130 °C) we were unable to observe the parent cation **3** [R = $(CH_3)_3C$]. The formation of ions **8**, **9**, **10**, and **11** can be rationalized through the intermediacy of the tertiary cation **3** as shown in Scheme II. The intermediately formed olefin **2** [R = $(CH_3)_3C$] undergoes further protonation under the superacid conditions to give ions **8** and and **9** through the cation **12**. The ions **10** and **11**, on the other hand, are formed through the isomeric cation **13**, as depicted in the Scheme II.

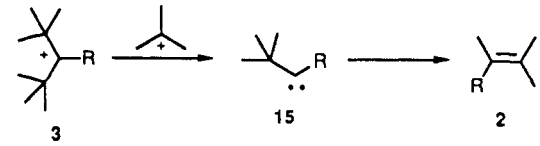
Scheme IV



Ionization of α,α-di-*tert*-butylbenzyl alcohol **5** (R = Ph) in SbF_5/SO_2ClF gave cleanly a mixture of *tert*-cumyl cation **14** and *tert*-hexyl cation **10**.[8] Again their formation is rationalized through the carbocation **3** (R = Ph), as shown in Scheme III. However, under the superacid conditions no evidence is obtained for cleavage of *tert*-butyl cation **8** from ion **3** to provide olefin **2** (R = Ph). Apparently under stable ion conditions the reaction takes a different course as outlined in Scheme III.

On the other hand, di-*tert*-butylmethyl alcohol **5** (R = H) under stable ion conditions undergoes clean ionization to a mixture of *tert*-butyl cation **8** and *tert*-amyl cation **9**[8] through the intermediacy of the olefin **2** (R = H), formed by the cleavage of *tert*-butyl cation from **12** (see Scheme II). These results agree well with our reported studies of the reaction of carbonyl compounds with *tert*-butyllithium (*tert*-butylmethylmagnesium chloride) as well as with the previous dehydration studies by Whitmore and Stahly.[2a]

An alternative mechanism that can be considered for the formation of olefin **2** from the cation **3** is the involvement of a carbene intermediate **15**. Cleavage of *tert*-butyl cation directly from **3** can give the carbene **15**, which then could undergo rearrangement to give olefin **2**. Fry and co-



workers[7] have considered such a pathway to account for the formation of methyleneadamantane in the reaction of 2-*tert*-butyl-2-adamantanol with hydrogen halides in solvents such as CH_2Cl_2, $CHCl_3$, and CCl_4. Such an α-fragmentation of a carbocation has precedence in gas-phase (mass spectral) fragmentations.[9] However, under our reaction conditions, such carbene intermediates appears to be unlikely, especially based on the results from stable ion studies.

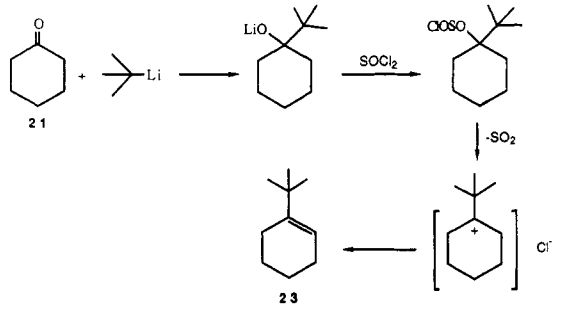
Thionyl chloride induced substitution reactions of alcohols (so-called S_Ni reactions) possess considerable ionic character[11] involving carbocations or ion pairs as inter-

(8) The corresponding cations were identified by their ^{13}C NMR spectroscopic characteristics. All these carbocations have been characterized earlier by ^{13}C NMR spectroscopy. See: Olah, G. A.; Donovan, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 5026.

(9) Olah, G. A.; Prakash, G. K. S.; Sommer, J. *Superacids*; Wiley Inter-Science: New York, 1985.

(10) Stahl, D.; Gäumann, T. *Adv. Mass Spectrom.* **1978**, *7*, 1190.

Scheme V



mediates[11-15] in the case of secondary and tertiary systems. Rearrangement–substitution products involving carbocations[11,12] were observed in the reaction of stereoisomeric 3-phenyl-2-butenol, 2-phenyl-3-pentanol, 3-methyl-2-butanol, and 3-phenyl-2-pentanol with thionyl chloride. It is significant to note that in our presently studied reactions (Scheme I) no substitution products such as **4a** or other isomers have been observed.

In the reaction of 2-adamantanone (**17**) with *tert*-butyllithium/thionyl chloride, the only isolated product was olefin **18** (see Scheme IV), which is formed through deprotonation of the intermediate cation **16**. In this case, no other products were identified. Reaction of 3-diamantanone **19** with *tert*-butyllithium $SOCl_2$ gave an olefinic product **20** similar to **18** (see Table I).

In the case of enolizable ketones such as cyclohexanone **21** or *tert*-butylmethyl ketone **22** the *tert*-butyllithium/thionyl chloride reaction gave the corresponding *tert*-butyl-substituted olefins, **23** and **24**. The reaction for cyclohexanone **21** is depicted in the Scheme V. The yields of the *tert*-butyl-substituted olefins are higher than those obtained from *p*-toluenesulfonic acid dehydrations of the corresponding alcohols (see Table I).

The present study shows that carbocations are generated from the hindered lithium alkoxide (Grignard) adducts of carbonyl compounds with thionyl chloride. Depending upon the steric crowding around the cationic center, rearrangement–cleavage occurs leading to the olefinic products. The intermediacy of carbocationic intermediates was further studied under stable ion conditions by ^{13}C NMR spectroscopy. Although thionyl chloride in general is used as a chlorinating agent for alcohols, elimination products are observed in crowded tertiary or secondary systems and the reaction can be advantageously employed to prepare some crowded olefins.

Experimental Section

Most of the starting ketones were purchased from Aldrich. Thionyl chloride was distilled prior to use. Diethyl ether was dried through refluxing over sodium metal. 3-Diamantanone was prepared according to a literature procedure.[16]

Boiling points are uncorrected. GC analysis was carried out on a Varian Associate Model 3700 gas chromatograph using a 30-m capillary column (quartz silica DB-1). ^{13}C NMR spectra were recorded on a Varian Associates Model VXR-200 superconducting spectrometer equipped with a variable-temperature broad-band probe. Infrared spectra were obtained on a Perkin-Elmer Model 1550 FT infrared spectrometer. Mass spectra were obtained on a Finnigan Matt mass spectrometer (Model INCOS-50). Elemental analysis was performed in Galbraith Laboratories, Inc., Knoxville, TN.

General Procedure. To a dry ice/acetone (−78 °C) cooled solution of the carbonyl compound (10 mmol) in dry diethyl ether (20 mL) was added *tert*-butyllithium (1.7 M in cyclohexane; 6.0 mL, 10.2 mmol) through a syringe with stirring under dry nitrogen atmosphere over a period of 5 min. After the addition, the mixture was stirred at −78 °C for another 30 min. Thereupon freshly distilled thionyl chloride (1.80 g, 15.1 mmol) was added dropwise with stirring over a period of 5 min. After the resulting mixture was stirred for 30 min at −78 °C, the ice bath was removed and the mixture was slowly warmed up and stirred at ambient temperature for 2 h. The resulting mixture was filtered, the filtrate was concentrated, and the residue was fractionated to provide the olefinic products. Reactions were carried out using the ketones listed in Table I.

2,3,4,4-Tetramethyl-2-pentene [2 [R = $(CH_3)_3C$]]. The residue was distilled at 42–44 °C (40 mm) to afford 2,3,4,4-tetramethyl-2-pentene[17] (0.95 g, 75% yield from 2,2,4,4-tetramethyl-3-pentanone) as a colorless liquid.

2-Methyl-3-phenyl-2-butene [2 (R = Ph)]. The reaction was carried out with *tert*-butylmagnesium chloride in diethyl ether. The residue was distilled at 65–67 °C (40 mm) to afford 2-methyl-3-phenyl-2-butene[18] (1.02 g, 70% yield from dimethylpropiophenone as a colorless oil.

2-Methyl-2-butene [2 (R = H)]. The reaction was carried out in *n*-heptane media, and *n*-heptane was also used in the extraction. The combined organic solution was dried over anhydrous magnesium sulfate and filtered. The filtrate was distilled at 35–38 °C to afford 2-methyl-2-butene (0.45 g, 64% yield from trimethylacetaldehyde) as a colorless liquid.

2-Isopropenyl-2-methyladamantane (18). The residue was distilled at 93–94 °C (0.1 mm) to afford 2-isopropenyl-2-methyladamantane[6] (1.7 g, 9.4 mmol; 94% yield from 2-adamantanone) as a colorless liquid. All spectral data were consistent with those given for 2-isopropenyl-2-methyladamantane in the literature.[7]

3-Isopropenyl-3-methyldiamantane (20). The residue was distilled at 130–132 °C (0.5) mm to afford 3-isopropenyl-3-methyldiamantane (2.23 g, 9.2 mmol; 92% yield from diamantanone[14]) as a colorless liquid. IR (neat): 3070 (w), 1630 (m). ^{13}C NMR ($CDCl_3$): δ 152.2 (s), 109.9 (t), 45.4, 43.2, 38.4, 38.1, 37.5, 36.9, 34.7, 33.8, 33.4, 32.4, 31.6, 30.9, 29.8, 26.3 (13 carbons on diamantane), 25.2 (q), 19.4 (q). GC/MS *m/e* (70 eV): 242 (M^+, 39.0), 227 (98.6), 187 (27.1), 131 (28.8), 117 (23.1), 105 (48.5), 91 (100.0), 77 (56.0), 41 (96.3). Anal. Calcd: C, 89.26; H, 10.74. Found: C, 89.39; H, 10.56.

1-*tert*-Butyl-1-cyclohexene (23). The residue was distilled at 76–78 °C (40 mm) to give 1-*tert*-butyl-1-cyclohexene as a colorless liquid (1.2 g; 87% yield from cyclohexanone). The material showed spectral data consistent with the literature values.[19]

1,1-Di-*tert*-butylethylene (24). The residue was distilled at 64–66 °C (40 mm) to give 1,1-di-*tert*-butylethylene[20] (1.15 g; 82% yield from pinacolone) as a colorless liquid. The material was identical with an authentic sample obtained commercially.

Preparation of *tert*-Butyl-Substituted Methanols. To an ethereal solution of the appropriate carbonyl compound (10 mmol in 20 mL) was added a solution of *tert*-butyllithium or *tert*-butylmagnesium chloride (10.2 mmol) as described in the general procedure. After the addition, the mixture was stirred for 0.5–1 h followed by workup with water. The organic phase was extracted in ether, dried over $MgSO_4$, and evaporated to a residue. The residue was purified via column chromatography on silica gel (20% EtOAc/hexane). The alcohols were satisfactorily characterized by NMR spectroscopy and GC/MS.

Dehydration of Alcohols. A solution of the appropriate alcohol (10 mmol) in 100 mL of benzene with a catalytic amount

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of *p*-toluenesulfonic acid (50 mg) was heated to reflux in a Dean-Stark apparatus for 4 h to remove water. After the reaction, the dry benzene layer was evaporated to obtain the olefin. The olefin was further purified by column chromatography on silica gel (hexane). The respective yields are shown in Table I. In the case of low boiling alkenes, the yields were obtained by GC analysis with internal standards.

Preparation of Carbocations. SbF_5 was freshly distilled before use. To SbF_5 dissolved in a 3-fold excess amount of SO_2ClF at either dry ice/acetone temperature (-78 °C) or pentane/liquid nitrogen slush (ca. -130 °C) was slowly added with vigorous stirring a cooled slurry or solution of the appropriate precursor in SO_2ClF, resulting in an approximately 10-15° solution of the ion. The solutions were then studied by ^{13}C NMR spectroscopy.

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Registry No. 1 (R = *t*-Bu), 815-24-7; 1 (R = Ph), 938-16-9; 1 (R = H), 630-19-3; 2 (R = *t*-Bu), 30436-14-7; 2 (R = Ph), 769-57-3; 2 (R = H), 513-35-9; 5 (R = *t*-Bu), 41902-42-5; 5 (R = Ph), 15656-90-3; 5 (R = H), 14609-79-1; 8, 14804-25-2; 9, 17603-15-5; 11, 19252-53-0; 14, 16804-70-9; 17, 700-58-3; 18, 38172-64-4; 19, 30545-23-4; 20, 125280-72-0; 21, 108-94-1; 22, 75-97-8; 23, 3419-66-7; 24, 5857-68-1; *t*-$Bu_2C(Me)OH$, 5857-69-2; $(CH_3)_2CHC^+(CH_3)_2$, 17603-18-8; 2-*tert*-butyl-2-adamantanol, 38424-20-3; 3-*tert*-butyl-3-diadamantanol, 125280-73-1; 1-*tert*-butyl-1-cyclohexanone, 20344-52-9.

Anomalous Reaction of Pentafluorophenacyl Bromide with Hexamethylenetetramine. Structure of the Product[1]

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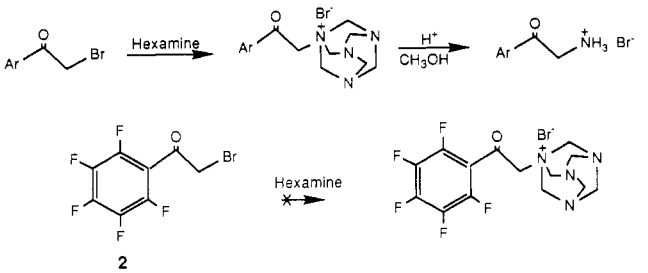
The title compounds condense in chloroform to yield tetrafluorobenzo[*b*]-1,3,5,7-tetraazatetracyclo-[7.3.1^{3,7}.1^{5,9}.0^{1,9}]tetradecan-10-one (1), a reaction proposed to involve both an ortho fluorine elimination and two Stevens type rearrangements. Structural assignment of the fluorescent product was based upon ^1H, ^{13}C, ^{19}F, and ^{15}N NMR spectra and a complete X-ray crystallographic determination. Additional studies supported the proposed mechanism and allowed improvements and modifications of the Delepine reaction as applied to phenacyl halides.

While preparing a series of substituted phenacylamine hydrochlorides by the Delepine synthesis[2] (Scheme I), it was noted that pentafluorophenacyl bromide (2) behaved anomolously. First, the condensation of the latter compound with hexamethylenetetramine (hexamine) in chloroform yielded a fluorescent, yellow salt (3) rather than the expected nonfluorescent, white or colorless salt. Second, the room temperature hydrolysis step in methanolic hydrochloric acid failed to cleave the initial bromide adduct, only transforming it to the corresponding chloride salt. Third, the adduct was not a quaternary ammonium salt as it readily furnished a stable, crystalline, free-base (1), which could be reconverted to the chloride or to other salts. Elemental analyses of the free base and of its various salts indicated that the compound had the formula $C_{14}H_{12}F_4N_4O\cdot(HX)$.

Besides the expected hexamine addition, attack on the pentafluorophenyl ring with loss of a fluoride had also occurred. Although displacement of the para or one of the ortho fluorine atoms seemed most logical, this could not be concluded unambiguously as 2-fluorophenacyl bromide (4) and hexamine behaved normally in the Delepine synthesis, yielding 2-fluorophenacylamine hydrochloride (5, no involvement of the ortho fluorine) (Scheme II). No reaction was observed between pentafluoroacetophenone (6) and hexamine in chloroform after 6 days at room temperature (Scheme II).

The structure of the unknown compound has now been elucidated by NMR studies (proton, carbon, fluorine, and nitrogen) and confirmed by a complete X-ray crystallographic structure determination. This paper summarizes the structure-determination studies and presents experimental investigations in support of a mechanism (Scheme III) by which the product, tetrafluorobenzo[*b*]-1,3,5,7-tetraazatetracyclo[7.3.1^{3,7}.1^{5,9}.0^{1,9}]tetradecan-10-one (1), is proposed to form. Literature precedents exist for both the intramolecular cyclization reaction[3] and the Stevens-type

Scheme I



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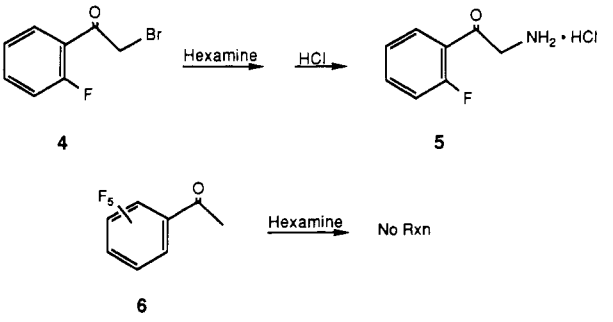
Scheme II



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