tion mixture was then treated as described under General Procedure. Analysis by gas chromatography showed only one component in the product. This component had a retention time identical with that of the major product from the chlorination of isobutyl bromide. Injections of mixtures of this component with 1-chloro-2-bromo-2-methylpropane gave two peaks. The nmr spectrum of this component is similar to that of 1-chloro-2-bromo-2-methylpropane but the chemical shifts for the two signals at τ 8.3 (six protons) and τ 6.37 (two protons) in the former differ significantly from those in the latter compound. This product is assumed to be 1-bromo-2-chloro-2-methylpropane. The chlorination of *t*-butyl bromide was relatively faster than the halogenations of other alkyl halides reported here.

Chlorination of Isobutyl Bromide. Gas chromatographic analysis of the products of this reaction showed three peaks: (1) 1-bromo-3-chloro-2-methylpropane, 33%, was identical in retention time as well as in nmr spectrum with the major product obtained by the addition of hydrogen bromide to methallyl chloride in the presence of peroxides; (2) 1-bromo-2-chloro-2-methylpropane, a major product, 59%, was identical with the product obtained by chlorinating *t*-butyl bromide; and (3) 1-chloro-2-bromo-2-methylpropane, present in a small quantity, 8%, was identical with the product obtained by the addition of hydrogen bromide to methallyl chloride in the dark as well as the product of bromination of isobutyl chloride. A complete resolution of 1-chloro-2-bromo-2-methylpropane and 1-bromo-2-chloro-2-methylpropane was not achieved although enough separation was achieved to show the two peaks.

Bromination of *t*-Butyl Chloride. Bromination of *t*-butyl chloride was extremely slow. In a typical run, 0.4 g of liquid bromine was added to a solution of 2 ml of *t*-butyl chloride in 2 ml of carbon tetrachloride. After being degassed, the solution was irradiated with ultraviolet light for 36 hr. Since the solution still retained the color of bromine it was washed with aqueous potassium iodide and sodium thiosulfate and extracted with ether. The ether solution was dried with Drierite and evaporated. One product comprising 98% of the reaction mixture was characterized as 1,2-dibromo-2-methylpropane by its identity with the product obtained by the polar addition of bromine to isobutylene.

Bromination of Isobutyl Chloride. The principal product (98–99%) from this reaction (0.84 g of isobutyl chloride and 0.3 g of bromine in 1 ml of carbon tetrachloride) was found to be 1-chloro-2-bromo-2-methylpropane. This compound was identical in retention time and nmr spectrum with the 1-chloro-2-bromo-2-methylpropane which was formed by the addition of hydrogen bromide to methallyl chloride in the dark.

Acknowledgment. The authors are pleased to acknowledge the financial assistance of the Research Foundation and the Graduate College of Oklahoma State University. We thank Dr. Stuart Scheppele for his interest in this work.

Stable Carbonium Ions. XLV.[1] Benzyl Cations

J. Martin Bollinger, Melvin B. Comisarow, Chris A. Cupas, and George A. Olah

Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. *Received June 28, 1967*

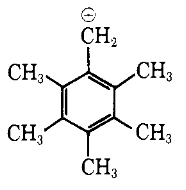
Abstract: A series of ring-substituted benzyl cations (phenylcarbonium ions) were obtained by ionization of the corresponding benzyl chlorides in SbF_5–SO_2 solution at −60°. Nmr and ultraviolet spectra of the ions were investigated. The geminal proton–proton magnetic resonance coupling constants of 2,6-disubstituted benzyl cations as well as the carbon–hydrogen couplings further prove the planar sp² hybridization nature of carbonium ions.

Various attempts to generate and observe the spectral properties in solution of the benzyl cation have thus far been unsuccessful.[2-4] Further reaction pathways open to the benzyl cation following ionization, such as intermolecular alkylation, undoubtedly contribute to its apparent instability.

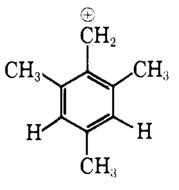
Results and Discussion

Using methods developed in our previous studies to observe stable, long-lived carbonium ions in solution[5] we were able to achieve the observation of the benzyl cations I–VI, VIII, XI, XII, and XIV. These benzyl cations were prepared by careful addition of the corresponding benzyl chlorides to well-stirred SbF_5–SO_2 solutions at −75°.

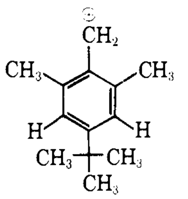
Introduction of alkyl substituents not only impede side reactions such as alkylation, but also further increase the stability of the benzyl cation inductively.



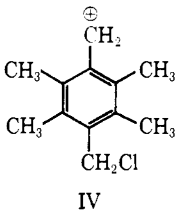
I



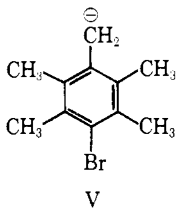
II



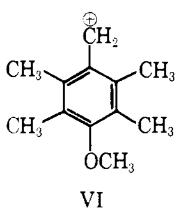
III



IV



V



VI

In all cases the nmr spectra of the solutions of the ions at −65° exhibited well-resolved, substantially deshielded peaks which could be assigned from their position and their integrated areas in most cases. With the exception of ion II which slowly decomposes over a 0.5-hr period at −65°, all ions were stable indefinitely at this temperature. The thermal stability of the pentamethylbenzyl cation (I) is characteristic of the remarkable stability of the benzyl cations studied. Sub-

---

[1] Part XLIV: G. A. Olah, M. Calin, and D. H. O'Brien, *J. Am. Chem. Soc.*, **89**, 3591 (1967); for a preliminary communication see *ibid.*, **88**, 361 (1966).

[2] N. C. Deno, P. T. Groves, J. J. Jaruzelski, and M. N. Lugasch, *ibid.*, **82**, 4217 (1960).

[3] J. F. A. Williams, *Tetrahedron*, **18**, 1487 (1962).

[4] I. Hanazaki and S. Magakura, *ibid.*, **21**, 2441 (1965).

[5] For a summary see G. A. Olah, *Chem. Eng. News*, **45**, 76 (March 27, 1967).

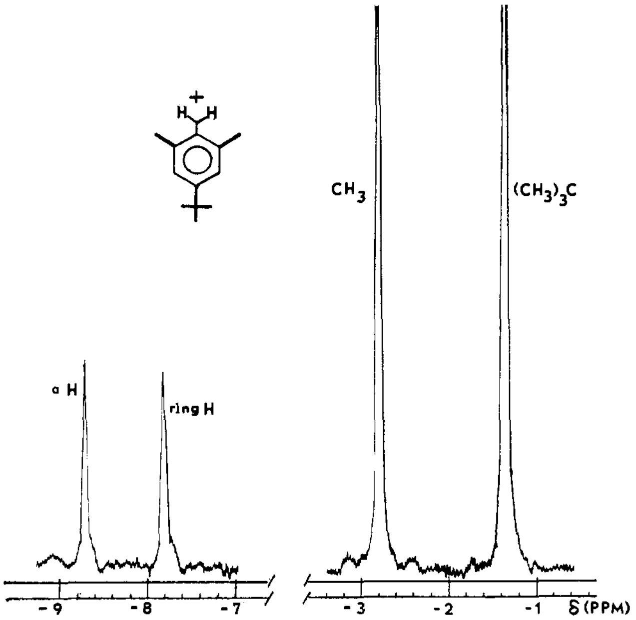
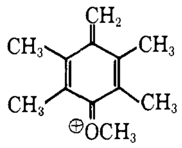


Figure 1. Pmr spectrum of 2,6-dimethyl-4-*t*-butylbenzyl cation (III).

stantial concentrations of this ion could still be detected after heating the ion in a sealed nmr tube at 75° for 15 min.

A summary of the nmr band positions and assignments for ions I–VI, VIII, XI, XII, and XIV are shown in Table I; an example of the simple spectra exhibited by all these ions is shown in Figure 1.

The positively charged benzylic hydrogens in ions I–VI, VIII, XI, XII, and XIV exhibit large downfield shifts compared with the position of the benzylic hydrogens in the covalent benzyl chlorides (Table I). As charge delocalization in the carbonium ion increases, the benzylic hydrogens will be expected to be less deshielded. Thus, these hydrogens are least deshielded in ion VI (8.2 ppm), which suggests that resonance structure VII makes an important contribution to the stabilization of the ion.



VII

The benzyl cations I and II have also been recently reported to exist in aluminum chloride–methylene chloride solutions.[6] However, the fact that under these conditions the most deshielded peak in the nmr spectrum of the 2,4,6-trimethylbenzyl cation (II) is due to the ring protons rather than the benzylic hydrogens strongly suggests that un-ionized species (possibly donor–acceptor complexes) were observed by these workers.

The chemical shift variations in these ions suggest the possibility of obtaining a correlation between charge densities and chemical shifts.[7] The examples which we have thus far studied are certainly in qualitative agreement with this idea. Further studies of *para*- and *meta*-substituted benzyl cations are necessary, however, before any attempt can be made at quantitative correlations.

In the benzyl cations I–VI, there was no evidence for ring expansion to tropylium derivatives, a facile process for benzyl cations under mass spectral conditions.[8] In

Table I. Nuclear Magnetic Proton Resonance Shifts of Benzyl Cations[a]

Compound	δ benzyl chloride	δ carbonium ion	Δδ
I			
CH_2^+	4.70	8.66	3.96
2,6-CH_3	2.05	2.72	0.67
3,5-CH_3	2.17	2.30	0.13
4-CH_3	2.05	2.72	0.67
II			
CH_2^+	4.58	8.50	3.92
2,6-CH_3	2.20	2.66	0.46
3,5-H	6.91	7.47	0.56
4-CH_3	2.07	2.66	0.59
III			
CH_2^+	4.67	8.67	4.00
2,6-CH_3	2.33	2.80	0.47
3,5-H	7.22	7.80	0.58
4-$C(CH_3)_3$	1.20	1.33	0.13
IV			
CH_2^+	4.64	9.05	4.41
2,6-CH_3	2.17	2.78	0.61
3,5-CH_3	2.17	2.38	0.21
4-CH_2Cl	4.64	4.78	0.14
V			
CH_2^+	4.55	8.89	4.34
2,6-CH_3	2.22	2.73	0.51
3,5-CH_3	2.22	2.54	0.32
VI			
CH_2^+	4.93	8.20	3.27
2,6-CH_3	2.29	2.95	0.66
3,5-CH_3	2.37	2.65	0.28
4-OCH_3	3.75	5.07	1.32
VIII			
CH_2^+	4.48	8.00	3.52
2-CH_3	2.01	3.06	...
3-CH_3		2.90	...
4-CH_3	2.10	2.20	...
5-CH_3		2.16	...
6-H	6.95	7.40	0.45
XI			
CH_2^+	4.84[b]	8.74	3.90
	5.07	9.00	3.93
2-CH_3	2.32	2.84	0.47
3,5-H	7.37	7.84 (broad)	0.63
	7.11		
4-$C(CH_3)_3$	1.26	1.42	0.16
6-$C(CH_3)_3$	1.42	1.58	0.16
XII			
CH_2^+	4.93	8.76	3.83
		8.84	3.91
2,4-CH_3	2.19	2.76	...
3-CH_3	2.28	2.34	...
5-CH_3	2.42	2.52	...
XIV			
CH_2^+	5.37	9.04	3.67
2,6-$C(CH_3)_3$	1.54	1.62	0.08
3,5-H	7.49	8.04	0.55
4-$C(CH_3)_3$	1.31	1.44	0.13

[a] In parts per million from external TMS at 60 Mc. [b] This compound exhibits magnetic nonequivalence because of the methylene protons of hindered rotation. We shall report in detail these results at a later time.

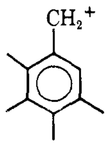
---

[6] I. Hazazaki and S. Magakura, *Tetrahedron*, **21**, 2441 (1965).

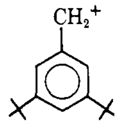
[7] T. Schaefer and W. G. Schneider, *Can. J. Chem.*, **41**, 966 (1963), and references therein cited.

[8] R. N. Rylander, S. Meyerson, and H. M. Grubb, *J. Am. Chem. Soc.*, **79**, 842 (1957); H. M. Grubb and S. Meyerson in "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press Inc., New York, N. Y., 1963; F. Meyer and G. Harrison, *J. Am. Chem. Soc.*, **86**, 4757 (1964).

view of the fact that these ions were all *ortho* disubstituted, the question remained whether the benzyltropylium rearrangement was impeded by these substituents. That this latter factor might not be important was shown by lack of rearrangement of 2,3,4,5-tetramethylbenzyl cation (VIII) having one *o*-methyl group.



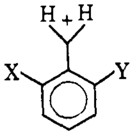
VIII



IX

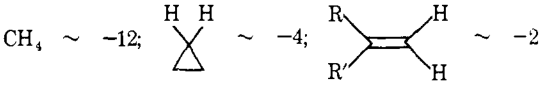
Attempts to generate 3,5-di-*t*-butylbenzyl cation IX in SbF_5–SO_2 even at −80° resulted in concurrent dealkylation and polymerization.

A further area of investigation of our work is concerned with the direct nmr observation of carbonium ions of type X



X

where magnetic nonequivalence of the benzylic hydrogen atoms is induced by substituents in the 2 and 6 positions of the benzene ring and which permits J_{gem} to be determined. The magnitude of geminal proton–proton coupling constants has been shown to be remarkably sensitive to a variety of geometrical and substituent effects.[9] For example, an increase in the H–C–H angle (or increasing s character of the carbon) results in an algebraic increase in J_{gem}[10]



An electronegative substituent can cause an increase or decrease in J_{gem} depending on whether the substituent is directly bonded to the carbon bearing the geminal protons[9,11] or one atom further removed.[12] The effect of adjacent π bonds has also been noted to cause an algebraic decrease in J_{gem}[13] and a theory has been developed which indicated a dependence of J_{gem} on the inclination of the H–H internuclear axis to the nodal plane of the π orbitals.[14] Recently Pople and Bothner-By have developed a molecular orbital treatment of coupling between geminal hydrogen atoms which provides a qualitative interpretation of the trends noted above.[9,15]

No data have been available, however, concerning the magnitude of J_{gem} in a primary carbonium ion. Here values typical of other sp^2-hybridized systems might be anticipated if overwhelming substituent effects are not operating.[16]

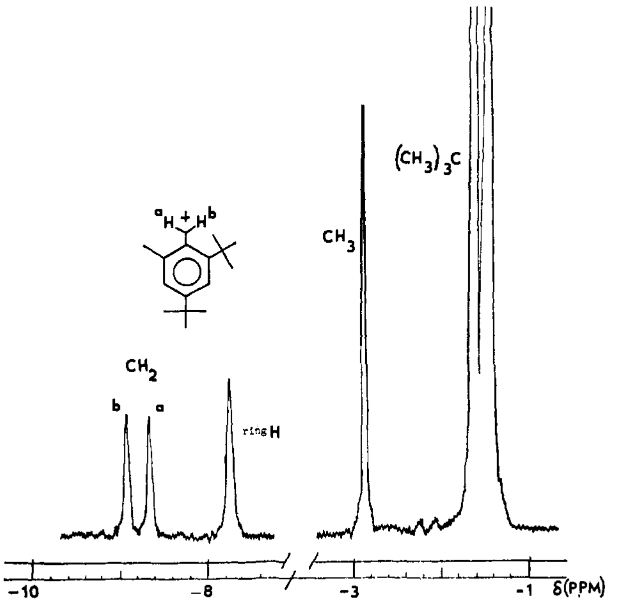
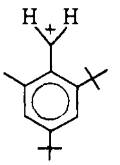
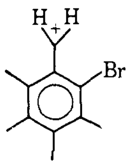


Figure 2. Pmr spectrum of 2,4-di-*t*-butyl-6-methylbenzyl cation (XI).

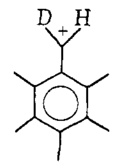
Treatment of 2,4-di-*t*-butyl-6-methylbenzyl chloride with SbF_5–SO_2 at −60° resulted in the formation of the corresponding benzyl cation (phenylcarbonium ion) XI. The nmr spectrum of this ion is shown in Figure 2. As anticipated from our previous studies of symmetrically substituted benzyl cations, the hydrogens directly bonded to the carbonium ion center experience the greatest deshielding, falling in the range of 8–9 ppm.[17]



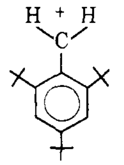
XI



XII



XIII



XIV

Presumably the benzylic hydrogen adjacent to the *t*-butyl group experiences the greater deshielding and appears at 9.00 ppm while the proton adjacent to the methyl appears at 8.74 ppm (support for this assignment is provided by ion XIV). From the line width of these absorptions $^2J_{H-H} \leqq \pm 1.5$ Hz can be estimated.[18,19] Because of the relatively small differences in chemical shifts of the α-hydrogens in ion XI (δ 16 Hz) a large value of $^2J_{H-H}$ could sufficiently mask (under our experimental conditions) the outer peaks of an AB quartet. That this was not the case was shown by observing XI at 100 MHz.[20]

---

(9) For recent reviews see A. A. Bothner-By, *Advan. Magnetic Resonance*, **1**, 195 (1965); R. C. Cookson, T. A. Crabb, J. J. Frankel, and J. Hudec, *Tetrahedron Suppl.*, No. 7, 355 (1967).

(10) H. J. Bernstein and N. Sheppard, *J. Chem. Phys.*, **37**, 3012 (1962).

(11) C. N. Banwell and N. Sheppard, *Discussions Faraday Soc.*, **34**, 115 (1962).

(12) K. L. Williamson, C. A. Lanford, and C. R. Nicholson, *J. Am. Chem. Soc.*, **86**, 762 (1964).

(13) M. Barfield and D. M. Grant, *ibid.*, **45**, 1899 (1963).

(14) M. Barfield and D. M. Grant, *Advan. Magnetic Resonance*, **1**, 149 (1965).

(15) J. A. Pople and A. A. Bothner-By, *J. Chem. Phys.*, **42**, 1339 (1965).

(16) For example, J_{H-H} = +41 Hz in formaldehyde: B. L. Shapiro R. M. Kopchik, and S. J. Ebersole, *J. Chem. Phys.*, **39**, 3154 (1963).

(17) External TMS at 60 MHz.

(18) The broadening observed in ion II could also be caused by long-range coupling.

(19) This value is to be compared with that of the precursor to ion X where $^2J_{H-H}$ = 11.4 Hz.

(20) We are indebted to Mr. Ross Pitcher of Varian Associates Applied Spectroscopy Laboratory, Pittsburgh, Pa., for the 100-MHz spectrum. In this spectrum $^1J_{^{13}C-H}$ = 169 Hz, 33.8% s character, was measured.

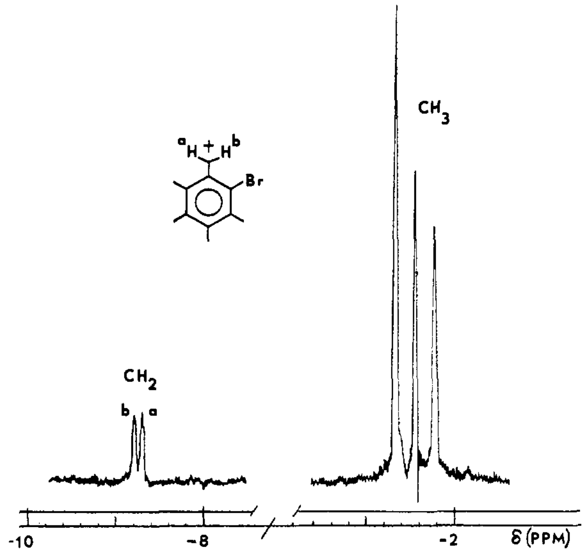


Figure 3. Pmr spectrum of 2-bromotetramethylbenzyl cation (XII).

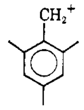
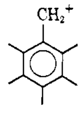
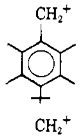
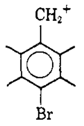
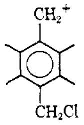
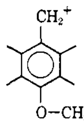
Treatment of 2-bromotetramethylbenzyl chloride with SbF_5-SO_2 at −60° produced ion XII which also showed magnetic nonequivalence of the benzylic hydrogens (Figure 3) appearing at 8.71 and 8.86 ppm. Here, too, $^2J_{H-H}$ is small and similar in range to ion VI. Finally, the deuterated benzyl cation, cation XIII, was prepared but no J_{H-D} coupling was observable.[21] The magnitude of J_{gem} in the carbonium ions XI and XII thus falls within the range of other sp^2-hybridized systems having no important substituent effects. We feel that the magnitude of these values provides another nmr criterion for carbonium ion formation along with large downfield shifts,[22] long-range coupling through the sp^2-hybridized center,[23] and magnitudes of $J_{^{13}C-H}$ coupling constants.[24]

Temperature-dependence studies of these ions were also carried out. However, no line coalescence was observed from −60 to 0° dec.

Ultraviolet Investigations

The electronic spectral properties of carbonium ions I–VI were also investigated and are summarized in Table II. The carbonium ions having halogen or methoxy groups in the ring absorb at longer wavelength than the hydrocarbon ions, indicating that these donor heteroatoms stabilize the excited state more than the ground state. It is of interest that λ_{max} for these substituted benzyl cations occurs near that reported for benzyllithium, which has strong absorption in the 330–340-mμ region in tetrahydrofuran.[25] This is undoubtedly fortuitous considering the extreme differences in media and degree of substitution, although it is in agreement with simple MO considerations.

Table II. Electronic Absorption of Stable Benzyl Cations[a]

	λ_{max}, mμ	ε
	480 370 318	1.2 × 10^3 4.4 × 10^3 1.1 × 10^4
	520 392 338 329[b]	2.1 × 10^3 2.1 × 10^3 1.6 × 10^4 1.7 × 10^4
	455 362	1.5 × 10^3 7.2 × 10^3
	540 364	2.4 × 10^3 1.2 × 10^4
	338	OD increased with time (initial) = 8 × 10^3 (22 min) = 1.2 × 10^4
	412–420 334	0.7 × 10^3 2.4 × 10^4

[a] All were prepared from the respective chloride in $FHSO_3$-SbF_5 at −60°. Spectra were determined at ∼−50°. [b] Double max.

Experimental Section

The following compounds were prepared by literature methods: pentamethylbenzyl chloride,[26] 2,3,4,5-tetramethylbenzyl chloride,[26] 2,4,6-trimethylbenzyl chloride,[27] 2,6-dimethyl-4-*t*-butylbenzyl chloride,[28] bischloromethyldurene,[29] and 2,4-di-*t*-butyl-6-methylbenzyl chloride.[30]

Chloromethylbromodurene. To 8.6 g (0.04 mole) of bromodurene[31] in 50 ml of glacial acetic acid were added 3.6 g of chloromethyl methyl ether (Aldrich) and 0.5 g of zinc chloride. The reaction mixture was stirred and heated at 100° for 24 hr. The reaction mixture was cooled and poured into cold water, and the precipitated solid was filtered and dried. After five recrystallizations from 90–100° petroleum ether there was obtained 3.4 g, 32% pure material of mp 106.5–108°.

Anal. Calcd for $C_{11}H_{14}ClBr$: C, 50.50; H, 5.39; Cl, 13.56; Br, 30.55. Found: C, 50.29; H, 5.43; Cl, 13.50; Br, 30.44.

4-Methoxytetramethylbenzyl Chloride. To 20 g (0.12 mole) of durophenol methyl ether[32] in 100 ml of concentrated hydrochloric acid was added 20 g of formalin (37% formaldehyde in water). This mixture was heated to 65–70° for 3 hr with vigorous stirring. At the end of this time, solid material was visible. The solution

---

(21) Cation XIII was studied as a further check against a small J_{H-H} value obscuring an AB pattern.

(22) G. A. Olah, E. B. Baker, J. C. Evans, W. S. Tolgyesi, J. S. McIntyre, and I. J. Bastien, *J. Am. Chem. Soc.*, **86**, 1360 (1964).

(23) J. M. Bollinger, C. A. Cupas, K. J. Friday, M. L. Woolfe, and G. A. Olah *ibid.*, **89**, 156 (1967).

(24) G. A. Olah and M. B. Comisarow, *ibid.*, **88**, 1818 (1966).

(25) R. Waack and M. A. Doran, *ibid.*, **85**, 1651 (1963).

(26) F. Benington, R. D. Morin, and L. C. Clark, Jr., *J. Org. Chem.*, 23, 2034 (1958).

(27) W. T. Nauta and J. W. Dienske, *Rec. Trav. Chim.*, **55**, 1000 (1936).

(28) R. C. Fuson, J. J. Denton, and J. W. Kneisley, *J. Am. Chem. Soc.*, 63, 2652 (1941).

(29) R. R. Aitken, G. M. Badger, and J. W. Cook, *J. Chem. Soc.*, 331 (1950).

(30) M. G. J. Beets, W. Meerburg, and H. van Essen, *Rec. Trav. Chim.*, **78**, 570 (1959).

(31) Prepared by the procedure described by L. I. Smith, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p 95.

(32) 2,3,5,6-Tetramethylphenol (Aldrich) was converted to its methyl ether by treatment with dimethyl sulfate and sodium hydroxide solution according to the method of C. Graebe, *Ann.*, **340**, 208 (1905).

was allowed to cool and the solid material filtered and washed with water. The solid was then taken up in benzene, washed with sodium carbonate solution, and dried over anhydrous potassium carbonate. Removal of benzene left 15 g of a solid of mp 75–97°. Three recrystallizations from methylene chloride (at low temperature) gave 6.5 g of pure compound, 24%, mp 102–104°.

Anal. Calcd for $C_{12}H_{17}ClO$: C, 67.76; H, 8.05; Cl, 16.67; O, 7.52. Found: C, 67.48; H, 7.94; Cl, 16.58.

2-Bromotetramethylbenzyl Chloride. To 10.6 g (0.05 mole) of bromoprehnitene[33] (2,3,4,5-tetramethylbromobenzene) in 50 g of chloroform were added 5.4 g (0.05 mole) of chloromethyl methyl ether and 5.2 g (0.05 mole) of stannic chloride. This solution was stirred at room temperature for 14 hr, then poured into cold water. The organic material was taken up in 100 ml of ether, washed with sodium bicarbonate solution, and dried over sodium sulfate. Removal of solvent left a crystalline solid which, after two recrystallizations from hexane, amounted to 7.4 g, 57%, and had mp 113–114°.

Anal. Calcd for $C_{11}H_{14}ClBr$: C, 50.50; H, 5.39; Cl, 13.56; Br, 30.55. Found: C, 50.45; H, 5.40; Cl, 13.36; Br, 30.47.

3,5-Di-*t*-butylfluoromethylbenzene. In 100 ml of carbon tetrachloride were dissolved 22.0 g (0.11 mole) of 3,5-di-*t*-butyltoluene[34] and to this solution was added 19.6 g (0.11 mole) of N-bromosuccinimide (Arapahoe). The reaction mixture was refluxed for 5 hr and filtered; the solvent was removed on a rotary evaporator. Distillation of the residual oil yielded 21.8 g, 70%, of 3,5-di-*t*-butylbenzyl bromide of bp 75–80° (0.1 mm). Its nmr spectrum (δ 1.32 (s), 4.38 (s), 7.14, and 7.26 (A_2B) ppm) confirmed the assigned structure.

Twenty grams (0.07 mole) of 3,5-di-*t*-butylbenzyl bromide was dissolved in 100 ml of anhydrous acetonitrile and to this solution was added 30.5 g (0.23 mole) of argentous fluoride (Harshaw). A precipitate began to form immediately. The reaction mixture was stirred for 4 hr, then filtered. The filtrate was poured into water and the organic material taken up in pentane. Removal of pentane left a dark oil which was distilled (0.8 mm), the portion boiling from 74 to 80° being collected as the desired product. This fraction solidified in the refrigerator and after recrystallization from methanol had mp 40–42°. It amounted to 10.5 g, 68%. The analytical sample was sublimed under vacuum.

Anal. Calcd for $C_{15}H_{23}F$: C, 81.03; H, 10.43; F, 8.54. Found: C, 80.89; H, 10.48; F, 8.33.

2,4,6-Tri-*t*-butylbenzyl Chloride. 2,4,6-Tri-*t*-butylphenyllithium was prepared by the procedure of Barclay and Betts[35] from 6.5 g (0.02 mole) of 2,4,6-tri-*t*-butylbromobenzene[36] and 50 ml of *n*-butyllithium (1.6 *M* in hexane, Foote) in 100 ml of dry ether. To this was added gaseous formaldehyde generated by heating 4.8 g (0.6 mole) of paraformaldehyde which had been dried over phosphorus pentoxide under vacuum for 30 hr. When all the formaldehyde had been added, the solution was refluxed for 2 hr, then hydrolyzed with 100 ml of cold water. Separation of the layers followed by drying and distillation of solvent yielded 7.0 g of oil. This oil was chromatographed on Woelm silica gel of activity I. Hexane rapidly eluted 1,3,5-tri-*t*-butylbenzene and then methanol removed the desired alcohol. In this way there was obtained 2.3 g of 2,4,6-tri-*t*-butylbenzyl alcohol of mp 180–181.5°; nmr in CCl_4: δ 1.27 (s) 6-*t*-butyl, 1.48 (s) 2- and 4-*t*-butyl, 4.98 (s) benzylic, 7.27 (s) aromatic, 1.70 (s) hydroxyl. In the infrared spectrum in CCl_4, the hydroxyl stretching appeared as a sharp band at 3640 cm.

Conversion to the chloride was accomplished with neat thionyl chloride at room temperature. Removal of excess thionyl chloride under vacuum left a solid which after recrystallization from hexane had mp 141.5–143.5°. The analytical sample was sublimed without change of melting point.

Anal. Calcd for $C_{19}H_{31}Cl$: C, 77.38; H, 10.60; Cl, 12.02. Found: C, 77.20; H, 10.63; Cl, 11.95.

Pentamethyl-2-*d*-benzyl Chloride. Pentamethylbenzaldehyde[37] was prepared in 60% yield from pentamethylbenzyl chloride[26] by oxidation with 2-nitropropane by the procedure described by Betts[30] for a similar preparation. Reduction with lithium aluminum deuteride gave pentamethyl-2-*d*-benzyl alcohol in 85% yield, mp 158.5–159° (lit. for protium compounds[38] 159–160°). Conversion to the chloride was accomplished with thionyl chloride in nearly quantitative yield, mp 82–83° (lit. for the protium compound[26] 81–82°).

Spectral Measurements. Solutions of the carbonium ions were prepared by adding the organic halide to antimony pentafluoride–sulfur dioxide solution while maintaining vigorous stirring with a homogenizer. It was possible to prepare all of these ions without high-speed stirring, but those precursors containing *t*-butyl groups showed substantial de-*t*-butylation under these conditions. Nmr spectra were measured either on Varian A-60 or A56-60A spectrometers equipped with variable-temperature probes. Ultraviolet spectra were recorded on a Cary 14 spectrophotometer by the procedure described previously.[39]

Acknowledgment. Support of this work by grants of the National Science Foundation and the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

---

(33) A. Töhl, *Chem. Ber.*, **25**, 1526 (1892).

(34) J. Geuze, C. Ruinard, J. Soeterbroek, P. E. Verkade, and B. M. Wepster, *Rec. Trav. Chim.*, **75**, 301 (1956).

(35) L. R. C. Barclay and E. E. Betts, *Can. J. Chem.*, **33**, 672 (1955).

(36) L. R. C. Barclay and E. E. Betts, *ibid.*, **33**, 672 (1955).

(37) L. I. Smith and J. Nichols, *J. Org. Chem.*, **6**, 489 (1941).

(38) M. S. Newman and N. C. Deno, *J. Am. Chem. Soc.*, **73**, 3644 (1951).

(39) G. A. Olah and C. U. Pittman, Jr., R. Waack, and M. Doran, *ibid.*, **88**, 1488 (1966).