$$\log (K_{CO_2^-}/K_i) = \frac{e\mu \cos \theta}{2.3kTR^2D_E} + \frac{e^2}{2.3kTRD_E} \qquad (6)$$

group, the calculation is based on eq 6 as outlined by Wilcox and McIntyre[14] with $\mu = 3.50$.

Tanner and Gilman report the dipole moment of dibenzobicyclo-[2.2.2]octa-2,5-diene is 0.81 D. and propose that the angle between the planes of the aromatic nuclei is about 110–120° to account for the dipole moment on the basis of two *o*-xylene units.[61] The C_1C_4 distance for this structure is 2.4 A, with the carbon atoms of the ethano bridge separated by 1.5 A. Further, the $H_1C_1C_4H_4$ nuclei are nearly colinear. The only deviation from normal bond angles is the $C_1C_2C_3$ angle of 110°. This structure requiring small angle deformation was adopted for the calculations. The values of *R* and the bond moments are presented in Table VIII. The results of the calculation are summarized in Table V.

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[61] D. D. Tanner and T. S. Gilman, *J. Am. Chem. Soc.*, **85**, 2982 (1963).

Chlorination and Bromination of Isobutyl and *t*-Butyl Chlorides and Bromides[1]

Prem S. Juneja and Ernest M. Hodnett[2]

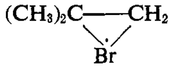
Contribution from the Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma. *Received May 1, 1967*

Abstract: Photochlorination of *t*-butyl bromide at room temperature gives only 1-bromo-2-chloro-2-methylpropane probably through a bridged-bromine radical. Chlorination of isobutyl bromide gives 1-bromo-2-chloro-, 1-bromo-3-chloro-, and 1-chloro-2-bromo-2-methylpropane. Photobromination of *t*-butyl chloride at room temperature yields a single organic product, 1,2-dibromo-2-methylpropane; isobutyl chloride under the same conditions gives exclusively 1-chloro-2-bromo-2-methylpropane. Mechanisms of the reactions are discussed.

Neighboring group participation has been proposed in the halogenation of some alkyl halides. When *t*-butyl bromide is chlorinated with *t*-butyl hypochlorite at −78° a 92% yield of 1-bromo-2-chloro-2-methylpropane[3] is obtained; this product could come from an intermediate having a bridged bromine atom. Thaler[4] found that bromocyclohexane and bromocyclopentane gave on photobromination at 60° predominantly the *trans*-1,2-dibromo derivatives, probably *via* a bridged intermediate. Skell[5] found that the bromination (photochemical or with *t*-butyl hypobromite) of (+)-1-bromo-2-methylbutane at 25° gave (−)-1,2-dibromo-2-methylbutane of high optical purity. When (+)-1-chloro-2-methylbutane is photobrominated, (−)-1-chloro-2-bromo-2-methylbutane is the sole dihalide (about 97%). However, reaction of *t*-butyl hypochlorite or chlorine with (+)-1-bromo-2-methylbutane is said to give only inactive products. Conversely Haag and Heiba[6] have shown that photobromination of (+)-1-cyano-2-methylbutane gives (+)-1-cyano-2-bromo-2-methylbutane. Further, when *t*-butyl bromide reacts with *t*-butyl hypochlorite at −78° bromine atoms can be trapped with allene, indicating that elimination of bromine atoms occurs to some extent.[7]

We here report two examples of halogenation reactions that appear to proceed by way of a bridged-bromine radical: the photochlorination of isobutyl bromide and of *t*-butyl bromide with elemental chlorine.

t-Butyl bromide was photochlorinated at 24° in carbon tetrachloride at an initial concentration of 0.3 g/ml with sufficient chlorine to react with 30% of the *t*-butyl bromide. Only one product was shown by gas chromatographic analysis of the reaction mixture; this component was identified as 1-bromo-2-chloro-2-methylpropane. The production of this compound is explained most easily by assuming the formation of an intermediate bridged radical



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This would open preferentially at the tertiary position when attacked by a chlorine atom because of the electron-releasing ability of the methyl groups. Although the $(CH_3)_2CBrCH_2\cdot$ radical could eliminate a bromine atom and form isobutylene, the latter would probably add a molecule of chlorine very quickly. Since no dichloro isomer was obtained, it seems unlikely that the elimination and addition mechanism[7] was operative.

It is interesting to note that Skell[3] found only one product, 1-bromo-2-chloro-2-methylpropane, in the reaction of *t*-butyl hypochlorite with *t*-butyl bromide at −78°. When the reaction was carried out in carbon disulfide solution, Haag and Heiba[7] found both 1-bromo-2-chloro-2-methylpropane and 1-chloro-2-bromo-2-methylpropane; the concentration of the latter compound increased with the proportion of *t*-butyl hypochlorite used.

When isobutyl bromide was subjected to photochlorination at 24° in carbon tetrachloride three products were obtained: 1-bromo-2-chloro-2-methylpropane, 59%; 1-bromo-3-chloro-2-methylpropane, 33%; and 1-chloro-2-bromo-2-methylpropane, 8%. The 1-bromo-3-chloro-2-methylpropane comes from reaction

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[1] Abstracted from a portion of the Ph.D. dissertation of P. S. J., Oklahoma State University, May 1967.

[2] Author to whom communications should be addressed.

[3] P. S. Skell, R. G. Allen, and N. D. Gilmour, *J. Am. Chem. Soc.*, **83**, 504 (1961).

[4] W. Thaler, *ibid.*, **85**, 2607 (1963).

[5] P. S. Skell, D. L. Tuleen, and P. D. Readio, *ibid.*, **85**, 2849 (1963).

[6] W. O. Haag and E. I. Heiba, *Tetrahedron Letters*, 3679 (1965).

[7] W. O. Haag and E. I. Heiba, *ibid.*, 3683 (1965).

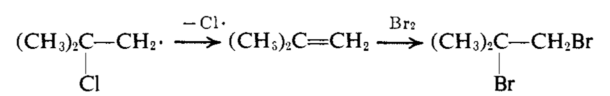
of the radical $\cdot CH_2CH(CH_3)CH_2Br$ with chlorine. The 1-bromo-2-chloro-2-methylpropane could have resulted from the attack of chlorine on the bridged radical I or the radical $(CH_3)_2\dot{C}CH_2Br$ or on both. It seems unlikely that this major product could have been derived by the elimination and addition reactions since again no dichloro product was detected by gas chromatography.

The origin of the 1-chloro-2-bromo-2-methylpropane produced in a small but significant amount in the reaction is uncertain. It could arise from an attack of chlorine on the primary carbon of the bridged radical I, but if this were the case some of this compound would have appeared in the chlorination of *t*-butyl bromide. It could come from the free-radical addition of Br:Cl to isobutylene (if the latter were formed during the reaction), but this seems unlikely.[3]

The chlorination of isobutyl bromide appears to be much slower than the chlorination of *t*-butyl bromide. This may be attributed to the more difficult formation of the bridged radical I from the relatively stable tertiary radical $(CH_3)_2\dot{C}-CH_2Br$ as compared to its formation from the primary radical $(CH_3)_2C(Br)-CH_2\cdot$. The proportion of 1-bromo-2-chloro-2-methylpropane to 1-bromo-3-chloro-2-methylpropane (59:33) is greater than might be expected. Although the tertiary hydrogen is more reactive than the primary hydrogens, the amount of 1,3 isomer would be greater than the 1,2 isomer since there are six primary hydrogens. Since the electronegative bromine normally deactivates the carbon-2 to substitution, this is further substantiation of the anchimeric assistance of the bromine.

Skell[3] also found 1-bromo-2-chloro-2-methylpropane, 57%, in the reaction of *t*-butyl hypochlorite with isobutyl bromide at −78°. However, he reported 20% of 1-bromo-1-chloro-2-methylpropane in the same reaction and no 1-bromo-3-chloro-2-methylpropane, although direct photochlorination at room temperature gives 33% 1-bromo-3-chloro-2-methylpropane and no 1-bromo-1-chloro-2-methylpropane.

Photobromination of *t*-butyl chloride with elemental bromine at room temperature is a very slow reaction which results in the exclusive production of 1,2-dibromo-2-methylpropane. The mechanism of this reaction must be that of elimination and addition



$$(CH_3)_2\underset{\displaystyle Cl}{C}-CH_2\cdot \xrightarrow{-Cl\cdot} (CH_3)_2C{=}CH_2 \xrightarrow{Br_2} (CH_3)_2\underset{\displaystyle Br}{C}-CH_2Br$$

The slowness of the reaction indicates the lower reactivity of the bromine atom with the primary hydrogen atoms. The absence of chloro bromo products indicates the lack of anchimeric assistance of the substituted chlorine atom.

The reaction of bromine with isobutyl chloride at room temperature gives one product, 1-chloro-2-bromo-2-methylpropane. This product results from the great specificity for tertiary hydrogen atoms which bromine has shown in other reactions.[8]

It should be noted that photochlorinations of isobutyl chloride and bromide produce small amounts of isobutane. The source of this product and the mechansm of its formation are being investigated further.

Experimental Section

General Procedure. All halogenations were performed in carbon tetrachloride solution with a 200-w incandescent light unless otherwise stated. The samples were either flushed with nitrogen or degassed on the vacuum line prior to the reaction. Chlorine was added as a solution in carbon tetrachloride; bromine was added either as a pure liquid or in carbon tetrachloride solution. After the color of the halogen had disappeared (except in bromination of *t*-butyl chloride), the reaction mixtures were treated with solid potassium bicarbonate and dried over Drierite.

Materials. Eastman isobutyl and *t*-butyl bromides (97.9 and 99.6%, respectively, by gas chromatography), Eastman spectroscopy grade carbon tetrachloride, and pure isobutyl and *t*-butyl chlorides (99.68 and 99.71%, respectively, by gas chromatography) were used in this investigation. *n*-Butyl bromide (1.8%) was the major impurity in isobutyl bromide.

Identification of Products. The samples were analyzed on an Aerograph Model A-90P gas chromatograph using a 15-ft × 0.25-in. column containing Resoflex-728 (30% on Firebrick) as the stationary phase. The retention times at 112° of 1-chloro-2-bromo-2-methylpropane, 1-bromo-2-chloro-2-methylpropane, 1,2-dibromo-2-methylpropane, and 1-bromo-3-chloromethylpropane were respectively 7 min 30 sec, 8 min, 13 min 12 sec, and 20 min 54 sec. The nmr spectra were obtained with a Varian A-60 nuclear magnetic resonance spectrometer; carbon tetrachloride was used as the solvent and tetramethylsilane as the internal reference.

Addition of Hydrogen Bromide to Methallyl Chloride in the Dark. Methallyl chloride (15 ml, Eastman practical grade, containing 7% isocrotyl chloride) and 66 g of 48.8% hydrogen bromide were placed in a flask covered with foil to exclude light, and the mixture was stirred at room temperature for 7.5 hr. The organic layer was washed with aqueous sodium bicarbonate solution and with water. The mixture was extracted with ether which was dried over Drierite, and the ether was evaporated. Analysis of this mixture showed that 90% of it was one component. The mixture was fractionated at reduced pressure, and the major product was identified as 1-chloro-2-bromo-2-methylpropane by its nmr spectrum. This spectrum shows a singlet at τ 8.17 (six protons) and a singlet at τ 6.13 (two protons).

Addition of Hydrogen Bromide to Methallyl Chloride in the Presence of Peroxide.[9] Dry hydrogen bromide[10] was prepared by dropping 48% aqueous hydrobromic acid on phosphorus pentoxide and passing the vapors through a trap containing more phosphorus pentoxide. This gas mixed with nitrogen was bubbled through 10 ml of methallyl chloride (Eastman practical grade) containing 200 mg of benzoyl peroxide cooled in an ice bath. The solution was washed with aqueous sodium bicarbonate solution and extracted with ether. The ether solution was dried with Drierite and evaporated; the residue was distilled under reduced pressure. Gas chromatography showed three components in this residue: (1) 1-chloro-2-bromo-2-methylpropane, 15.5%; (2) 1-bromo-3-chloro-2-methylpropane, 81.5%; and (3) an unidentified product, 3%. The first product was identified by comparison with an authentic sample. The nmr spectrum of the second sample shows a triplet at τ 6.46, J = 5.9 cps (four protons), a doublet at τ 8.86, J = 6.5 cps (three protons), and a multiplet centered at τ 7.8 (one proton). Integration of the triplet gives an intensity ratio of 1:2:1 which seems to arise from the overlap of one peak of the two doublets from the pair of hydrogen atoms on each of the first and third carbons.

Addition of Bromine to Isobutylene in the Dark. A solution of isobutylene (CP grade, Matheson) in carbon tetrachloride was placed in a 50-ml, round-bottomed flask which was covered with aluminum foil. Liquid bromine (0.4 ml) was added dropwise as the mixture was stirred. Analysis of the product by gas chromatography showed two products: (1) 1,2-dibromo-2-methylpropane, 85%, and (2) methallyl bromide, 15%. The nmr spectrum of the major product has a singlet at τ 8.13 (six protons) and a singlet at τ 6.15 (two protons). The minor product had a retention time in the gas chromatograph slightly longer than that of carbon tetrachloride but much shorter than that of the dibromide.

Chlorination of *t*-Butyl Bromide. *t*-Butyl bromide (0.6 g) and 0.12 g of chlorine in 2 ml of carbon tetrachloride were irradiated at room temperature until the chlorine color disappeared; the reac-

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[8] M. S. Kharash, W. Hered, and F. R. Mayo, *J. Org. Chem.*, **6**, 818 (1941); B. H. Eckstein, H. A. Scheraga, and E. R. Van Artsdalen, *J. Chem. Phys.*, **22**, 28 (1954).

[9] B. A. Kazanskii and M. Y. Lukina, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 47 (1951); *Chem. Abstr.*, **46**, 4491 (1952).

[10] R. T. Dillon and W. G. Young, *J. Am. Chem. Soc.*, **51**, 2389 (1929).

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.

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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*

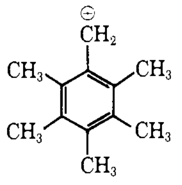
Abstract: A series of ring-substituted benzyl cations (phenylcarbonium ions) were obtained by ionization of the corresponding benzyl chlorides in SbF_5–SO_2 solution at $-60°$. Nmr and ultraviolet spectra of the ions were investigated. The geminal proton–proton magnetic resonance coupling constants of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



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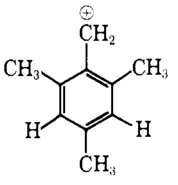

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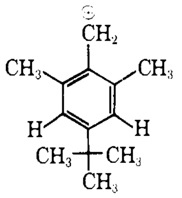

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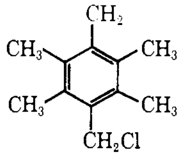

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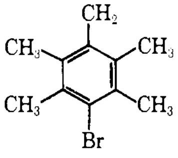

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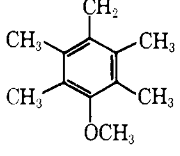

VI

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-

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[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).

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[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).