added slowly to a solution of 1.04 g (4.1 mmol) of **5** in a solution of 6 ml of water and 5 ml of dioxane until the bromine was no longer rapidly decolorized. Product isolation as in the reaction in ethanol gave 0.56 g (69%) of crude bromoacetophenone and a mixture of esterified acids shown by vpc (10 ft × $^3/_8$ in. SE-52 on Chromosorb W, 155°, 120 ml/min) to consist of 80% diethyl methyl phosphate and 20% methyl benzoate. Both products were isolated and identified by comparison with authentic specimens.

Reaction of 0.487 g (1.9 mmol) of **5** with bromine in 3 ml of dioxane and 4.1 g of water containing ^{18}O was carried out by the procedure above.

Diphenylphosphoric acid was prepared by stirring 10 g of diphenyl chlorophosphate (Aldrich) overnight with an equimolar amount of water in a flask equipped with a drying tube. The resultant oil crystallized on standing, and was treated with 100 ml of benzene which was distilled away to remove excess water and HCl. The residue was recrystallized from a mixture of 5 ml of chloroform and 45 ml of hexane. A second recrystallization gave long white needles, mp 66–68° (lit.[26] mp 70° (anhydrous), lit.[27] 68°, lit.[28] 51–52° (dihydrate)). Labeled material was prepared by the use of ^{18}O-enriched water. The acid was converted to its methyl ester for isotopic analysis by treatment with ethereal diazomethane.

Benzoic acid-^{18}*O* was prepared by stirring benzoyl chloride with a slight excess of ^{18}O-enriched water in dioxane for 4 days, followed by evaporation of the solvent and sublimation.

Diphenyl α-ethoxyvinyl phosphate (6) was prepared by the reaction of diphenylphosphoric acid with excess ethoxyacetylene (Chemical Samples Co.) in dichloromethane or CCl_4 by the published procedure:[20] nmr (CCl_4) δ 1.14 (t, 3, J = 7 Hz, Me), 3.70 (q, 2, J = 7 Hz, OCH_2), 3.5–3.9 (m, 2, vinyl H), and 7.10 (s, 10, Ar). The vinyl and methylene resonances overlap, but the overlap is somewhat reduced in solvent benzene.

Reaction of 6 and benzoic acid[20] could be carried out in an nmr tube in CCl_4 solvent. As soon as an equimolar amount of benzoic acid had been added the aliphatic absorptions moved about 0.05 ppm upfield, the vinyl absorption disappeared, the aromatic absorption (now 15H) became several multiplets, and a new absorption due to the acetyl methyl appeared at δ 1.96. This spectrum is assigned to benzoyl diphenyl phosphate (**7**)[20] and ethyl acetate. In preparative experiments (in CH_2Cl_2), addition of 2 equiv of cyclohexylamine gave an exothermic reaction. After the reaction mixture had stood overnight a white precipitate of *N*-cyclohexylammonium diphenyl phosphate was collected and recrystallized from 1-propanol, mp 191–193° (lit.[20] mp 192°). The filtrate was distilled leaving a residue which was sublimed (120° (0.05 Torr)) to yield *N*-cyclohexylbenzamide, mp 145–148° (lit.[29] mp 149°). This melting point was apparently incorrectly transcribed in ref 20.

Methylation of diphenylphosphoric acid was accomplished by dissolving the cyclohexylammonium salt in boiling water and adding an equivalent amount of HCl just as the salt began to reprecipitate from the cooling solution. The solution was stirred and ethereal diazomethane was added. The product was extracted into ether which was dried and evaporated, leaving diphenyl methyl phosphate for mass spectral examination. Alternatively, the salt was dissolved in hot ethanol which was acidified on cooling, followed by alternate acidification with HCl and neutralization with diazomethane. Isotopic analyses of products from the two procedures were the same within experimental error, but higher recoveries of product were realized by the former method.

The last portion of the distillate from the filtrate from the isolation of the phosphate salt consisted of a mixture of ethyl acetate and CH_2Cl_2. The ethyl acetate was isolated by vpc (10 ft × $^3/_8$ in. SE-30 on Chromosorb W, 80°, 65 ml/min) for mass spectral analysis.

Acknowledgment. We are indebted to Professor A. G. Harrison for assistance with the interpretation of the mass spectral analyses.

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(26) J. M. A. Hoeflake, *Recl. Trav. Chim. Pays-Bas*, **36**, 24 (1916).

(27) P. W. C. Barnard, C. A. Bunton, D. Kellerman, M. M. Mhala, B. Silver, C. A. Vernon, and V. A. Welch, *J. Chem. Soc. B*, 227 (1966).

(28) R. L. Baylis, T. H. Bevan, and T. Malkin, *Chem. Ind.* (*London*), 67 (1955).

(29) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th ed, Wiley, New York, N. Y., 1956.

Electrophilic Reactions at Single Bonds. IX.[1a] Intermolecular Hydrogen Exchange and Alkylation (Alkylolysis) of Alkanes with Alkylcarbenium Fluoroantimonates[1b,c]

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Abstract: Intermolecular hydrogen exchange and alkylation of alkanes with their parent carbenium ion salts, such as the dimethyl-, trimethyl-, dimethylethyl-, and dimethylisopropylcarbenium fluoroantimonates, were studied under stable ion conditions in SO_2ClF and SO_2 solution (by nmr and glc methods). From the study of the temperature-dependent ^1H nmr spectra, the energies of activation, E_a, for the exchange reaction between the trimethylcarbenium ion and 2-methylpropane as well as 2-deuterium-2-methylpropane were determined. The highly hindered dimethyl-*tert*-butylcarbenium ion shows no hydrogen exchange with its parent hydrocarbon, 2,2,3-trimethylbutane (triptane). The intermolecular hydrogen exchange reactions are always accompanied by alkylation of alkanes by the carbenium ions, even though the former reactions are much faster. All data are in accord with reactions involving electrophilic attack by the carbenium ions on the C–H or C–C bonds *via* triangular three-center bonded carbonium ion transition states.

Intermolecular hydride transfers from isoalkanes to trivalent carbenium ions in acid-catalyzed media are well known from the work of Bartlett, Nenitzescu, and Schmerling, and have been reviewed.[2] More recently, we were able to develop superacid solvent systems allowing us to study stable carbocations and

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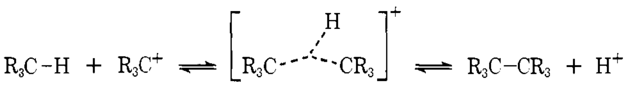
(1) (a) Part VIII: G. A. Olah and Y. K. Mo, *J. Amer. Chem. Soc.*, in press. (b) For a differentiation of trivalent carbenium ions from tetra- or pentacoordinated carbonium ions and a discussion of the general concept and naming of carbocations, see G. A. Olah, *ibid.*, **94**, 808 (1972). (c) Partially reported in preliminary form: G. A. Olah and J. A. Olah, *ibid.*, **93**, 1256 (1971).

(2) C. D. Nenitzescu in "Carbonium Ions," Vol. II, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N. Y., 1970, p 463.

Table I. Exchange Reaction of Alkylcarbenium Ions with Their Parent Alkanes

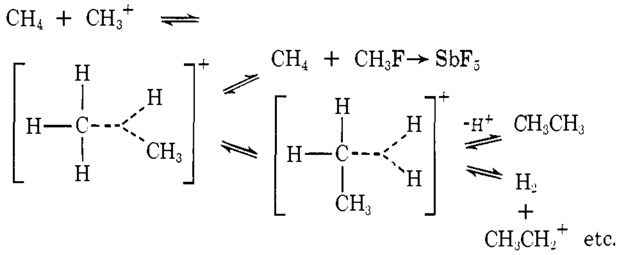
	Alkane	Alkyl carbenium ion	Experimental conditions	Observed reaction
1.	$CH_3CH_2CH_3$	$CH_3\overset{+}{C}HCH_3$	a. excess propane in $FSO_3H-SbF_5-SO_2ClF$ (1:1 mol/mol) b. $CH_3CHClCH_3$ in SbF_5-SO_2ClF, −78° with propane added	Exchange
2.	$(CH_3)_3CH(D)$	$(CH_3)_3\overset{+}{C}$	a. excess $(CH_3)_3CH(D)$ in $FSO_3H-SbF_5-SO_2ClF$ (1:1 mol/mol), −78° b. $(CH_3)_3$ in SbF_5-SO_2ClF, −78°, with $(CH_3)_3CH(D)$ added	Exchange
3.	$(CH_3)_2CHC_2H_5$	$(CH_3)_2\overset{+}{C}CH_2CH_3$	a. excess 2 methylbutane in $FSO_3H-SbF_5-SO_2ClF$ (1:1 mol/mol) b. neopentyl chloride in $FSO_3H-SbF_5-SO_2ClF$ (1:1 mol/mol) with 2-methylbutane added	Exchange
4.	$(CH_3)_2CHCH(CH_3)_2$	$(CH_3)_2\overset{+}{C}CH(CH_3)_2$	Excess 2,3-dimethylbutane in $FSO_3H-SbF_5-SO_2ClF$ (1:1 mol/mol) at −78°	Exchange
5.	$(CH_3)_3CCH(CH_3)_2$	$(CH_3)_3C\overset{+}{C}(CH_3)_2$	Excess 2,2,3-trimethylbutane in $FSO_3H-SbF_5-SO_2ClF$ (1:1 mol/mol), at −78°	No exchange

their reactions. Our investigation of the protolysis of alkanes in superacids[3] and their alkylations by carbenium ions[1b] extended the scope and understanding of hydrocarbon reactions. These studies have shown that intermolecular hydrogen transfer involves not linear but triangular, three-center bonded pentacoordinated carbonium ion transition states (or intermediates). Particularly in tertiary–tertiary systems, due



to steric reasons, only highly unsymmetrically bridged carbonium ions can be formed. A series of bicyclic three-center bonded carbonium ion intermediates in norbornyl, cyclopropylcarbinyl, and related systems have been, however, directly observed and characterized in our previous studies.[4]

To study the reaction of alkanes with alkylcarbenium ions both with regard of intermolecular hydrogen transfer and "direct" alkylation, it was necessary to find carbocation reaction conditions excluding olefin formation in order to eliminate the reaction pathway for olefin–isoalkane alkylation. To our knowledge, the only alkane alkylation reported so far in the literature fulfilling these conditions was our recently discovered methane and methyl fluoride condensation reactions.[5] The methyl cation (CH_3^+) formed in the course of the reactions methylates excess methane (or methyl fluoride) in the key step.



The only previous study of intermolecular hydrogen transfer between carbenium ions and alkanes under stable ion conditions was that of Brownstein and Bornais[6] who reported the study of the exchange reaction between trimethylcarbenium ion and isobutane in $AsF_5-SO_2-CH_2Cl_2$ solution. They have, however, not studied the mechanism of the exchange reaction. Further, in the case of isopropyl chloride–AsF_5–SO_2–CH_2Cl_2–propane system, Brownstein and Bornais suggested that the $(CH_3)_2CHCl-AsF_5$ complex was exchanging with the propane. However, our investigation of this system clearly proved that the exchanging complex was actually the diisopropylchloronium ion.[7]

We now report in full our studies on the alkylation of alkanes with alkylcarbenium ions[1c] and a detailed study of the accompanying intermolecular hydrogen exchange reaction.

Results and Discussion

In the present study we undertook an investigation at low temperature in superacids (*i.e.*, under stable ion conditions) of the reactions between stable alkylcarbenium ions and their parent alkanes. Our studies included investigation of the site of carbenium ion attack on the alkanes (C–H or C–C bond), hydrogen exchange, alkylation (isomerization, polymerization), and the determination of the energy of activation, E_a, for the exchange processes. The experimental technique used for exchange studies was primarily proton nuclear magnetic resonance (pmr) spectroscopy. Alkylates were analyzed by glc. The carbenium ions used were known from our previous studies to be stable, long-lived species under the experimental conditions. The pmr spectra of all these cations have been reported.

The exchange reactions of carbenium ions with alkanes were studied in the following two ways: (i) to excess alkane was added $FSO_3H-SbF_5-SO_2ClF$ or $HF-SbF_5-SO_2ClF$ to effect ionization and formation of the parent carbenium ions and (ii) the alkylcarbenium ion was prepared from the corresponding alkyl halides and $FSO_3H-SbF_5-SO_2ClF$ or $HF-SbF_5-SO_2ClF$ solution and then treated in the same solvent system with the corresponding alkane at −78° (Table I). For alkylation the same solutions, as well as those made up in SO_2 as solvent, were allowed to warm up to −20°, were kept generally for 5 min, cooled back to −78°, quenched (cold methanol-water), and analyzed (by gas chromatogaphy).

In the course of our investigations we found that all

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[3] G. A. Olah, Y. Halpern, J. Shen, and Y. K. Mo, *J. Amer. Chem. Soc.*, **93**, 1251 (1971).

[4] (a) G. A. Olah, A. M. White, J. R. DeMember, A. Commeyras, and C. Y. Lui, *ibid.*, **92**, 4627 (1970); (b) G. A. Olah, D. P. Kelly, C. L. Jeuell, and R. D. Porter, *ibid.*, **92**, 2544 (1970).

[5] G. A. Olah and R. H. Schlosberg, *ibid.*, **90**, 2726 (1968); **91**, 3261 (1969).

[6] S. Brownstein and J. Bornais, *Can. J. Chem.*, **49**, 7 (1971).

[7] G. A. Olah and Y. K. Mo, submitted for publication in *J. Amer. Chem. Soc.*

studied alkylcarbenium ion–alkane systems undergo fast intermolecular hydrogen exchange, as observed by the temperature-dependent pmr spectra of the systems. Alkylation of alkanes by alkylcarbenium ions is a concurrent, although much slower, reaction. By carrying out the study of exchange reactions at low temperature and for short periods of time, alkylation generally was less than 5% and consequently did not interfere with the study of the fast hydrogen exchange reactions. At the same time, by raising the temperature of the systems, alkylation was becoming more predominant.

A systematic study of the direct akylation of alkanes (both of straight and branched chain) by alkylcarbenium ion salts using aprotic solvent, SO_2ClF, was carried out. Whereas the system is aprotic initially, as the alkylation reaction proceeds proton elimination produces fluoroantimonic acid. Protolytic side reactions are thus possible, but in the relatively low concentrations of acid formed and at low temperatures used, they are of no major importance except in case of very acid sensitive hydrocarbons.

Intermolecular hydrogen transfer between tertiary and secondary alkycarbenium fluoroantimonates and alkanes is always the fast reaction in the systems, with the alkylation reactions being generally much slower. Consequently, alkylation products are also those derived from the new alkanes and carbenium ions formed in the hydrogen transfer reaction (*i.e.*, secondary alkylation products). Relative rates of hydrogen transfer and alkylation determine product compositions. Furthermore, isomerization of the carbenium ions and to some degree the alkanes, through usual intramolecular processes, causes further diversification of the alkylation mixture. Products result from all hydrocarbons and carbenium ions present in the system. Isomerization of alkanes can be depressed, although not completely eliminated, by carrying out the alkylation at low temperatures (generally −78 to −20°) and for only short reaction times (1 min).

Typical examples of alkylation of alkanes are those of propane, 2-methylpropane, or *n*-butane by dimethylcarbenium ion or the alkylation of propane and butanes by trimethylcarbenium ion or methylethylcarbenium ion, systems made somewhat interchangeable by competing hydrogen transfer and rearrangement of carbenium ions (although product compositions depend to a large extent on the relative rates of all competing processes). Whereas product compositions were determined with high accuracy using gas–liquid chromatography (see Experimental Section) in individual runs, it must be emphasized that due to the complexity of the systems data should be considered only representative, as even smallest changes in conditions can cause changes. From the point of view of our studies the emphasis clearly is on relative product compositions and not so much on absolute, quantitative yields of individual components of mixtures, which are always extremely difficult to define in this type of alkylative systems.

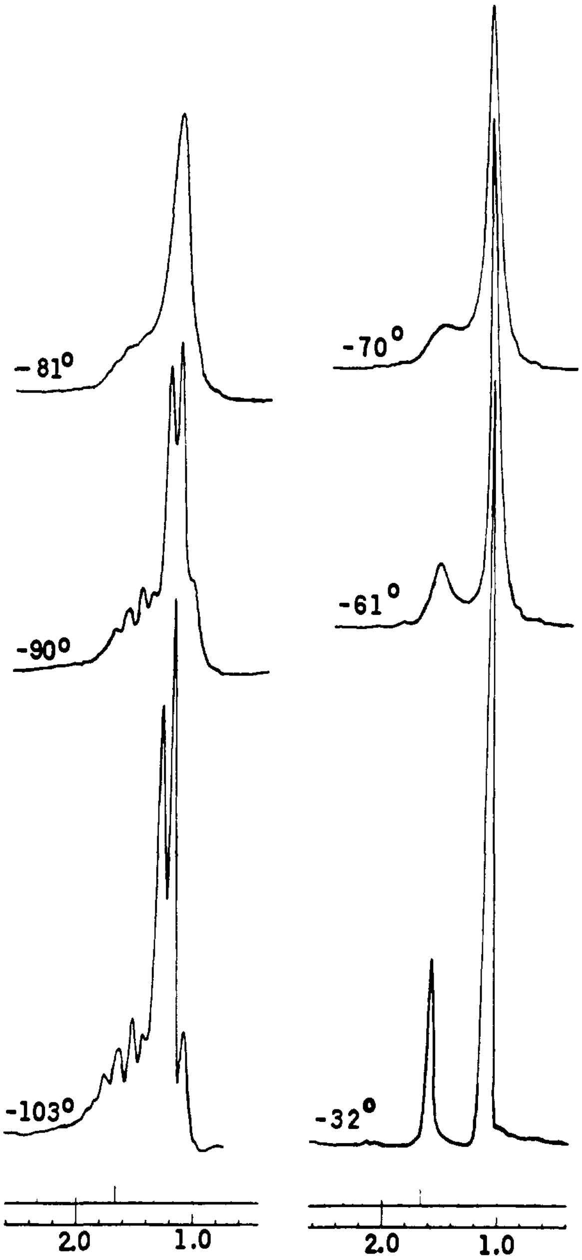
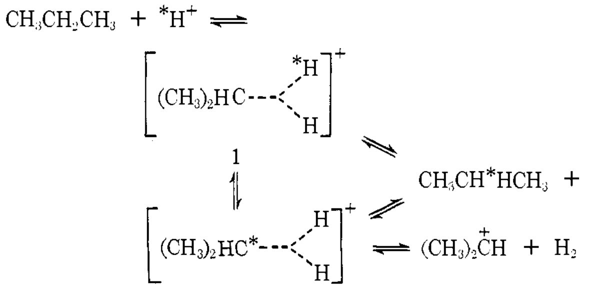


Figure 1. Temperature-dependent pmr spectra of propane exchanging with trace of dimethylcarbenium ion.

Dimethylcarbenium Ion–Propane (C_3^+–C_3). Cold propane in SO_2ClF was mixed with 2 mol % FSO_3H–SbF_5 (1:1 mol/mol) which was diluted with SO_2ClF (v/v 1:2) at −78°. The pmr spectrum of the resulting solution is temperature dependent (Figure 1) and can be interpreted as the methylene protons of propane exchanging with either the acid system (eq 1) or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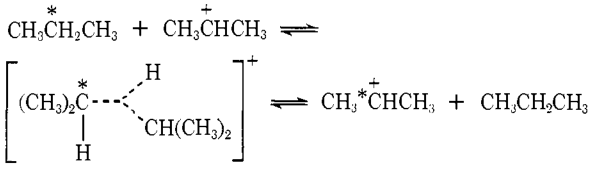
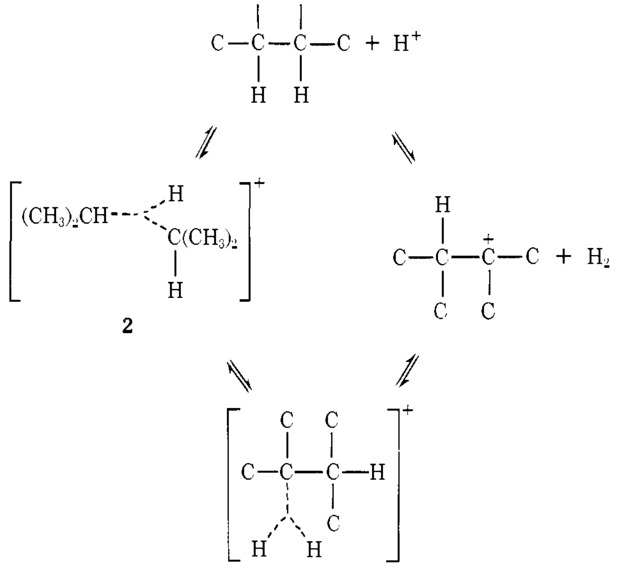

(2)

the small concentration of dimethylcarbenium ion present in the system (eq 2) through the two-electron three-center bonded transition states **1** and **2**, respectively. The former possibility is ruled out because a small amount of isopropyl alcohol is found after quenching the solution with ice–water (also see subsequent discussion). In Figure 1, the pmr spectrum at −103° is identical with that of propane in SO_2ClF solution indicating the exchange reaction between propane and dimethylcarbenium ion has not occurred. The pmr absorptions of dimethylcarbenium ion are too weak to be observed since its concentration is not more than 2 mol %. As the solution is warmed to −81°, the triplet of propane collapsed and became a broadened singlet absorption. When the solution was further heated to higher temperatures (*ca.* −32°), the pmr spectrum showed two sharp singlet absorptions at δ 1.12 (CH_3) and 1.63 (CH_2) for the rapidly hydrogen exchanging propane and dimethylcarbenium ion (eq 2).

When further $FSO_3H–SbF_5–SO_2ClF$ (total of 4 mol %) was added to the solution, the pmr spectrum was temperature independent and showed two slightly deshielded singlet absorptions at δ 1.26 (CH_3) and 2.10 (CH_2). The deshielding is more pronounced in the lower field singlet (CH_2). No acid peak was observed in the pmr spectrum under these conditions. The acid is thus completely used up in the ionization. These data indicate that the hydrogen exchange rate between propane and dimethylcarbenium ion is extremely rapid even at the lowest possible temperature (*ca.* −103°). The deshielding effect of the two temperature-dependent singlet absorptions is proportional to the amount of superacid added. By subsequent addition of up to 20 mol % $FSO_3H–SbF_5–SO_2ClF$ to the solution, the two singlet absorptions were deshielded to δ 1.93 and 3.07, respectively. This is the limiting concentration because adding more $FSO_3H–SbF_5–SO_2ClF$ to the solution changes the two singlet absorptions to temperature dependent nature (see subsequent discussion). On the other hand, the absorptions become shielded when adding propane to the solution. Thus, the process is reversible. In addition, hydrogen evolution was observed in the system. Consequently, hydrogen exchange between superacid and propane (eq 1) is less likely as dehydrogenation of **1** (ionization of propane to H_2 and dimethylcarbenium ion) seems more favorable than hydrogen exchange with the superacid system, although a small degree of hydrogen–deuterium scrambling has been observed in the propane–$DF–SbF_5–SO_2ClF$ system.[3]

As mentioned, no solvent acid pmr absorption was observed when 4 mol % or less $FSO_3H–SbF_5–SO_2ClF$ was used in relation to propane. The acid peak is, however, observed when the molar concentration of superacid is greater than 4%. Under these conditions, ionization of propane by superacid is slow (even at −30°) and incomplete, presumably because the hydrogen exchange reaction between dimethylcarbenium ion and propane (eq 2) is the fast and more favorable process. For example, when 20 mol % $FSO_3H–SbF_5–SO_2ClF$ is used to ionize propane, only 12% of dimethylcarbenium ion is formed.

When propane with 50 mol % $FSO_3H–SbF_5–SO_2ClF$ was treated at −10° for 1 min and then cooled to −90°, it resulted in a pmr spectrum of the solution showing the presence of both propane and dimethylcarbenium ion. The ratio of propane to dimethylcarbenium ion was dependent on the amount of $FSO_3H–SbF_5–SO_2ClF$ used in the ionization of propane. The pmr spectrum of the solution is now temperature dependent. The methyl resonance of propane (δ 1.20) and dimethylcarbenium ion (δ 4.20) became broadened and collapsed to a singlet at higher temperature (*e.g.*, −10°). The temperature-dependent pmr spectra of the solution indicate that the intermolecular hydrogen exchange process is reversible. However, besides the degenerate hydrogen exchange reaction, C–H and C–C bond alkylations involving two-electron three-center bonded carbonium ion transition states **2** and **4** also occur. Evidence for C–H alkylation through **2** came from the observation of dimethylisopropylcarbenium ion in the pmr spectrum. An appreciable amount (∼20%) of this ion was formed when the sample was warmed to −10° for 5 min. The carbonium ion transition state **2** can either deprotonate to 2,3-dimethylbutane which then ionizes in the superacid to the dimethylisoproplycarbenium ion or undergo "bond-to-bond" rearrangement to **3** which then dehydrogenates to give the dimethylisopropylcarbenium ion. Other carbenium (trimethyl- and dimethylethylcarbenium) ions were also formed indicating C–C alkylation (*via* transition state **4**) but are less predominant (∼5%). Carbonium ion **4** can again undergo



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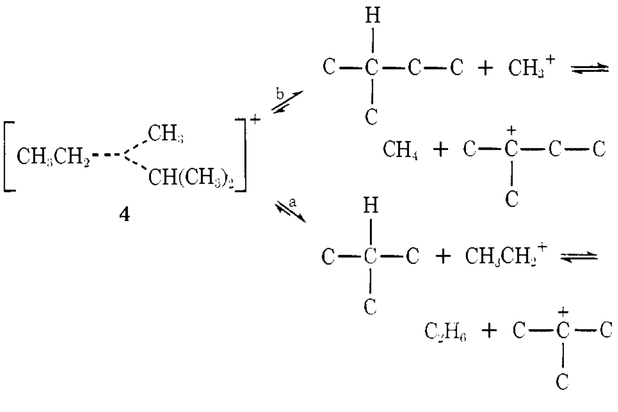
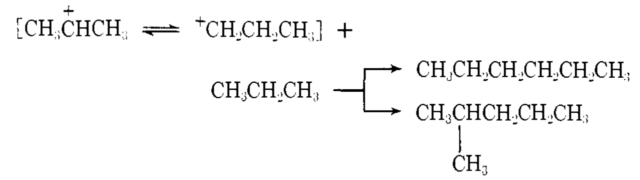


4

two cleavage pathways (depicted as a and b) to give trimethyl- and dimethylethylcarbenium ions, respectively. The amount of methane and ethane formed is relatively small compared to the ionic species and also depends on the reaction conditions. Some polymeric products were also obtained partially precipitating from the solution and showing broadened pmr absorptions in the alkane region, if propane was in a large excess over carbenium ions in the solutions, in accord of our previous observation of polycondensation of excess alkanes with carbenium ions.[1c]

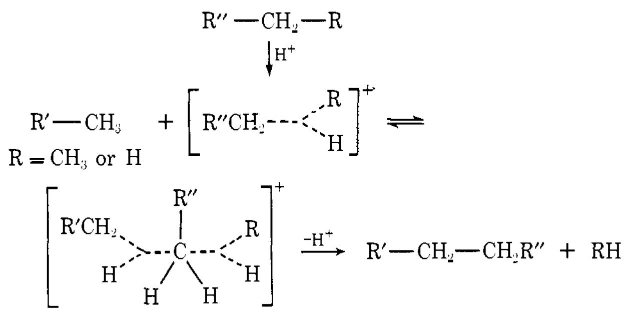
When dimethylcarbenium ion was treated with propane in sulfuryl chloride fluoride solution at −78°, warmed up to −20° (5 min), and then quenched with cold methanol–water, about 20% (based on dimethylcarbenium ion) C_6 alkylates were obtained (analyzed by capillary glc, compared with authentic pure alkanes) containing 26% 2,3-dimethylbutane, 28% 2-methylpentane, 14% 3-methylpentane, and 32% *n*-hexane. (It must be emphasized that product compositions in all alkylations are dependent on reaction conditions; therefore, only results of typical experiments can be given.) 2,3-Dimethylbutane is clearly a primary alkylation product formed by deprotonation of **2** and **3**.

The high amount of *n*-hexane formed indicates that not only the dimethylcarbenium ion but also the ethylcarbenium ion (as shown by C_2–C_1 scrambling in the long-lived dimethylcarbenium ion[8]) is also involved in the alkylation.



The absence of 2,2-dimethylbutane from the alkylate hexanes indicates predominantly nonisomerizing conditions, as this isomer is important in the acid-catalyzed isomerization of hexanes. The alkylation products also show the presence of *n*-butane, isobutane, *n*-pentane, and isopentane and small amounts of C_7 and C_8 alkylates (which are formed through hydrogen transfer and alkylation involving butanes and pentanes). Formation of *n*-butane and *n*-pentane as well as isobutane and isopentane is rationalized by *C–C bond alkylation* of propane (alkylolysis)[9] or protolysis (by the acid generated in the alkylation step) of formed alkylates.

One of the referees objected to our suggestion that incipient primary carbenium ions (*i.e.*, RCH_2^+) are involved in the alkylative formation of straight chain alkanes. It was pointed out that formation of primary carbenium ions energetically is difficult to visualize, as they would require about 30 kcal/mol which under the used reaction conditions and temperatures is hardly feasible. It should be, however, pointed out that developing primary carbenium ion centers could undergo either intra- or intermolecular delocalization with C–H or C–C bonds, thus showing substantial S_N2 type character with σ-donor single bonds acting as displacing nucleophiles.

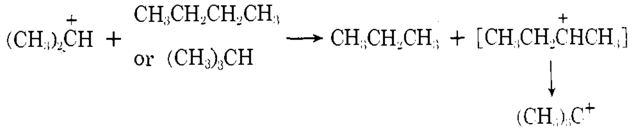


In view of the previously developed general concept of carbocations and their role in electrophilic reactions,[1b] we find no contradiction in the fact that S_N2 type reactions are taking place not only with n-donor (usual S_N2 type displacements) and π-donor (aromatic substitutions, for example, with primary alkyl halide–Lewis acid halide systems), but also with σ-donor systems (alkylation of alkanes with incipient primary carbenium ion systems).

Experimental evidence for the possibility of forming primary alkylcarbenium ions under stable ion conditions, indeed, was obtained in the case of the ethyl fluoride–antimony pentafluoride complex, which undergoes rapid intramolecular equilibration (both carbon and hydrogen scrambling) through the primary ethyl cation. When no external nucleophile is present in the system, the internal C–H bonds are the only available nucleophiles for delocalization, resulting in rapid degenerate 1,2-hydrogen shifts.[10a]

If, however, alkanes are present in the system as external σ nucleophiles, the incipient ethyl cation will readily be undergoing intermolecular displacement with them, resulting in alkylation.[10b]

Dimethylcarbenium Ion–2-Methylpropane (C_3^+–C_4) and Trimethylcarbenium Ion–Propane (C_4^+–C_3). Under stable ion conditions when dimethylcarbenium fluoroantimonate (in SO_2ClF solution at −78°) was treated with butane or 2-methylpropane, the pmr spectrum of the solutions showed the immediate formation of propane and trimethylcarbenium ion. When the solution was allowed to warm to −10° for 5 min, alkylation (of propane and butanes, respectively, by trimethyl(methylethyl)carbenium and dimethylcarbenium fluoroantimonates) took place yielding complex product mixtures. Hexanes (C_6 fraction), heptanes (C_7 fraction), and octanes (C_8 fraction) are the major alkylates formed in varying ratios (see Table II) reflecting relative rates of alkylation and hydrogen transfer.



The relative amount of C_7 alkylates in the C_3^+–C_4 and C_3–C_4^+ systems is relatively low (10–25% of combined C_6–C_8 alkylates), reflecting the faster intermolecular hydrogen transfer compared to alkylation.

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(8) G. A. Olah and A. M. White, *J. Amer. Chem. Soc.*, **91**, 5801 (1969).

(9) We define C–H bond substitution (*i.e.*, replacement of hydrogen) as *alkylation* and C–C bond substitution (involving C–C bond cleavage) as alkylolysis (similarly to protolysis, nitrolysis, chlorolysis, etc.).

(10) (a) G. A. Olah, J. R. DeMember, R. H. Schlosberg and Y. Halpern, *J. Amer. Chem. Soc.*, **94**, 156 (1972); (b) G. A. Olah, J. R. DeMember, and J. Shen, *ibid.*,**95**, 4952 (1973).

Table II. Relative Amounts of C_6, C_7, and C_8 Alkylates

Alkyl fluoro-antimonate	Alkane	Amount of alkylate fraction (%)		
		C_6	C_7	C_8
$(CH_3)_2CH^+$	$(CH_3)_3CH$	70	10	20
$(CH_3)_3C^+$	$(CH_3)_2CH_2$	22	25	53
$(CH_3)_3C^+$	$CH_3CH_2CH_2CH_3$	58	17	25
$(CH_3)_3C^+$	$(CH_3)_3CH$	29	12	59
$CH_3CH_2C^+HCH_3$	$CH_3CH_2CH_2CH_3$	23	4	73
$CH_3CH_2C^+HCH_3$	$(CH_3)_3CH$	16	9	75

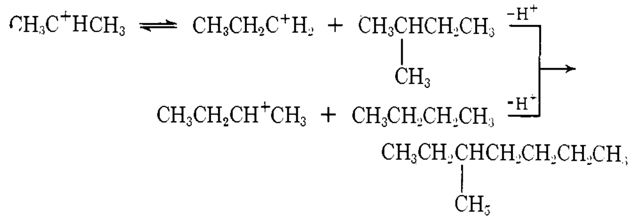
This point is particularly emphasized in the reaction of 2-methylpropane with dimethylcarbenium ion. Only 10% of heptanes are formed, due to the particularly fast hydrogen transfer reaction between 2-methylpropane and the dimethylcarbenium ions, which gives propane. The dimethylcarbenium ion then reacts with propane giving 70% hexanes. Under the reaction conditions, 2,3-dimethylbutane and 2-methylpentane are the main products in 41 and 54% yield, respectively, and only 2% *n*-hexane is formed. In the C_7 fraction there is 5–12% 2,2,3-trimethylbutane (triptane), depending on reaction conditions, indicating direct primary alkylation of the tertiary C–H bond by the dimethylcarbenium ion.

$$(CH_3)_3CH + CH_3C^+HCH_3 \xrightarrow{-H^+} (CH_3)_3CCH(CH_3)_2$$

Typical C_7 isomer distributions obtained are summarized in Table III. Among the 13 isomeric octanes formed 3-methylheptane (21%), 2,2,4-trimethylpentane (17%), and 2-methylheptane (14%) are the major products. Octanes are formed by secondary alkylation (C_3–C_5 and C_4–C_4 systems). For example, 3-methylheptane can be formed either by propylation of 2-methylbutane or butylation of butane.

Table III. Isomeric Heptane Compositions Obtained in Typical Alkylations of Propane by Butyl Cations and Butanes by Propyl Cations

Heptanes	C_3^+–C_4 or C_3–C_4^+			
	$(CH_3)_3CH$ $(CH_3)_2CH^+$	$CH_3CH_2CH_2CH_3$ $(CH_3)_2CH^+$	$CH_3CH_2CH_3$ $(CH_3)_3C^+$	$CH_3CH_2CH_3$ $(CH_3CH_2CH^+CH_3$
2,2-Dimethylpentane	17	69.9	23	41.1
2,4-Dimethylpentane	15.7	1.4	14.4	14.9
2,2,3-Trimethylbutane	5.2	2.1	9.1	23.9
3,3-Dimethylpentane	18.7	1.8	Trace	
2-Methylhexane	14.6	5.5	19.2	2.6
2,3-Dimethylpentane	17	2.7	19.1	12.3
3-Methylhexane	3.8	7.4	11.6	0.4
3-Ethylpentane	Trace		0.7	
Heptane	8	9.2	2.9	4.1



$$\left.\begin{array}{l} CH_3C^+HCH_3 \rightleftharpoons CH_3CH_2C^+H_2 + \underset{\displaystyle CH_3}{\underset{|}{CH_3CHCH_2CH_3}} \xrightarrow{-H^+} \\ CH_3CH_2CH^+CH_3 + CH_3CH_2CH_2CH_3 \xrightarrow{-H^+} \end{array}\right] \rightarrow \underset{\displaystyle CH_5}{\underset{|}{CH_3CH_2CHCH_2CH_2CH_2CH_3}}$$

Trimethylcarbenium Ion–2-Methylpropane (C_4^+–C_4). The exchange reaction of trimethylcarbenium ion and 2-methylpropane (isobutane) was found to be similar to that of dimethylcarbenium ion and propane. The exchanging system can be generated from 2-methylpropane and FSO_3H–SbF_5–SO_2ClF.

$$(CH_3)_3{}^*C^+ + (CH_3)_3CH \rightleftharpoons (CH_3)_3\overset{*}{C}H + (CH_3)_3C^+$$

The ratio of $(CH_3)_3C^+$ and $(CH_3)_3H$ can be regulated by the amount of FSO_3H–SbF_5 used in the reaction systems. In the case when the molar ratio of FSO_3H–SbF_5 to 2-methylpropane was 0.5:9.5, thus 2-methylpropane was exchanged with 5% of trimethylcarbenium ion, the temperature-dependent pmr spectra shown in Figure 2 were observed. The doublet of methyl protons in 2-methylpropane moved slightly downfield and collapsed to a singlet as the temperature was raised from −110 to −41°. The multiplet of the methine proton also collapsed to a singlet.

Temperature-dependent pmr spectra were also observed with other molar ratios of trimethylcarbenium ion and 2-methylpropane. The molar ratio can be changed from 0.5:9.5 to 9.5:0.5 dependent on the relative amounts of 2-methylpropane and superacid used. Figure 3 shows the temperature-dependent pmr spectra of 55% trimethylcarbenium ion exchanging with 45% of 2-methylpropane. These spectra are similar to those reported by Brownstein and Bornais[6] in AsF_5–SO_2–CH_2Cl_2 but have better resolution. Theoretical spectra were calculated[11] to fit the experimental ones. From these, the energy of activation, E_a, for the exchange process can be estimated to be 4.3 ± 0.6 kcal/mol with a preexponential factor of $A = 10^{7.7\pm0.8}$.

In the case when a large excess of 2-methylpropane (more than 95 mol %) over trimethylcarbenium ion was present in the system, it formed two separate layers and polycondensation occurred at −30°. If HF–SbF_5–SO_2ClF is used as the superacid, ionization as well as polycondensation of 2-methylpropane took place more rapidly than in FSO_3H–SbF_5–SO_2ClF. These observations further substantiate our previously reported observation of the superacid catalyzed polycondensation of alkanes.[3] The mechanism of the exchange reaction could involve hydrogen transfer from the methine or the methyl group through three-center bound carbonium transition states **5** and **6**, respectively. The latter possibility can be eliminated by the absence of hydrogen–deuterium scrambling in

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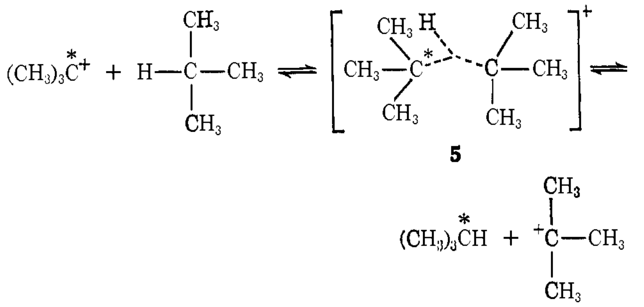
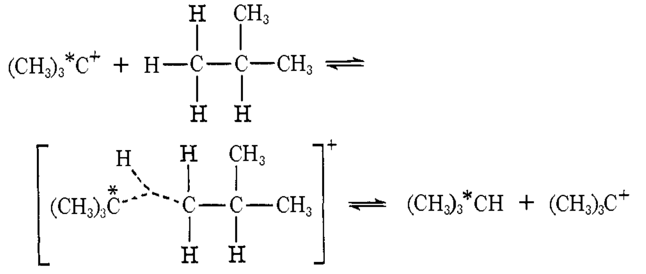
(11) The theoretical spectra for various rate constants were calculated by use of a multiple site exchange program originally obtained from Dr. T. Gerig and was adapted to the Univac 1108 computer by Dr. W. E. Heyd.





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the exchange reaction of $(CH_3)_3C^+$ and $(CH_3)_3CD$. The deuterium remained exclusively at the tertiary carbon even at −20°. Figure 4 shows the temperature-dependent pmr spectra of $(CH_3)_3CD$ exchanging with $(CH_3)_3C^+$ in a ratio of 7:3. These spectra show the absence of the methine singlet at δ 2.0 which was observed in the temperature-dependent pmr spectra of $(CH_3)_3C^+$ and $(CH_3)_3CH$ (Figure 3). In addition, if there were hydrogen–deuterium scrambling, a doublet for the methyl proton absorption should be observed in the spectrum taken under condition of no exchange (Figure 4 shows, however, at −118°, only a singlet.) In Figure 4 there are also given the calculated spectra for each temperature. By comparing the calculated with the experimental spectra and using best fits, the energy of activation, E_a, can be estimated to be 4.6 ± 0.5 kcal/mol with a preexponential factor, $A = 10^{7.3\pm0.6}$. The energies of activation, E_a, of both $(CH_3)_3CH$ and $(CH_3)_3CD$ exchanging with trimethylcarbenium ion are about the same, within experimental error. Our values (in FSO_3H–SbF_5–SO_2ClF media) are slightly higher than the value obtained by Brownstein and Bornais (3.6 kcal/mol) in AsF_5–SO_2–CH_2Cl_2.[6] This may be due to the lesser nucleophilicity of our reaction media. The exchange rate, k, for each temperature is about five times faster in the case of $(CH_3)_3CH$ than for $(CH_3)_3CD$. In other words, the exchange reactions show a primary kinetic hydrogen isotope effect of $k_H/k_D = \sim 5$, in accordance with the suggested involvement of the C–H (C–D) bond in forming the carbonium ion transition state **5** in the rate-determining step of the reactions.

When the SO_2ClF solution of trimethylcarbenium ion–2-methylpropane was allowed to warm up to −20° for 5–10 min, the trimethyl- or methylethylcarbenium ion, formed *via* hydrogen transfer, reacted with 2-methylpropane or butane to give varying proportions of hexanes, heptanes, and octanes. Table II summarizes the relative amount of hexanes, heptanes, and octanes obtained in typical butylation experiments of butanes. The amount of heptanes is always considerably less than that of hexanes and octanes. Octanes are formed by direct alkylation of butanes by butyl cations (trimethyl-, methylethyl-and isopropylcarbenium ion). C_6 and C_7 fractions are formed by secondary alkylation and/or alkylolysis.

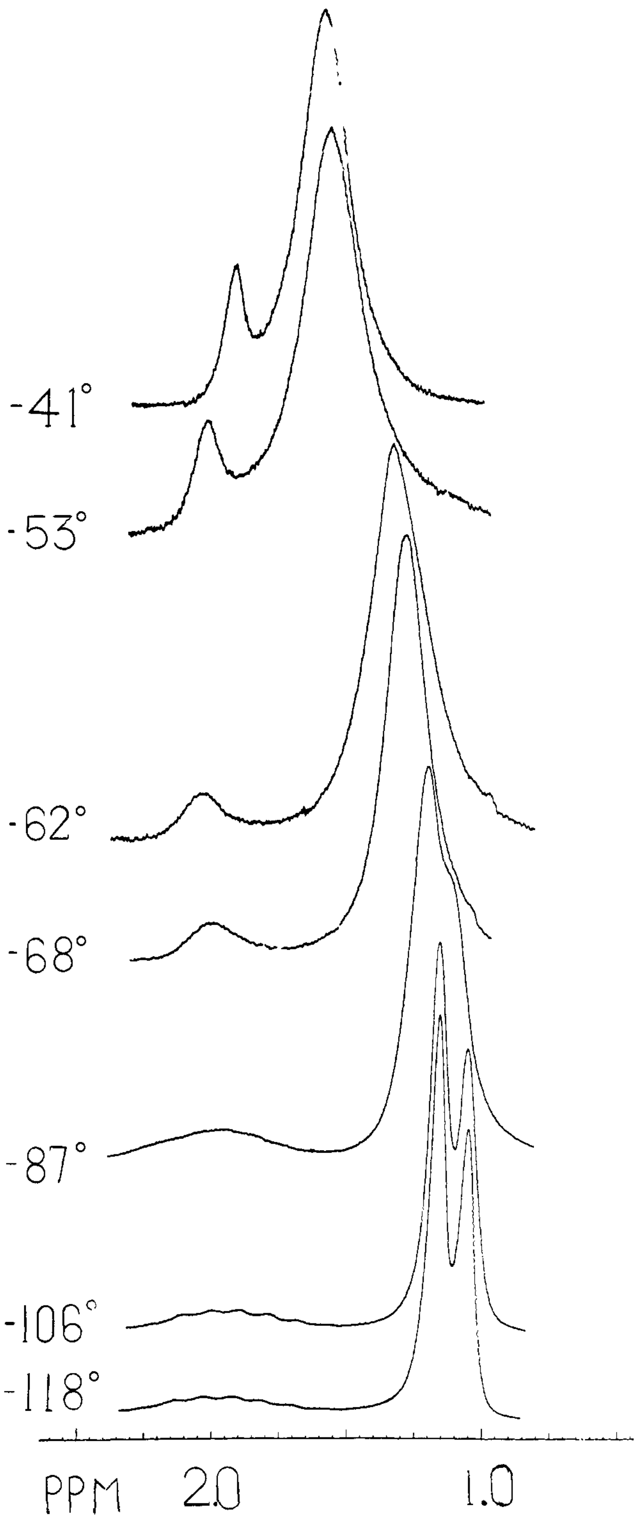


Figure 2. Temperature-dependent pmr spectra of 2-methylpropane (95%) exchanging with trimethylcarbenium ion (5%).

A key aspect in our studies is the assumption that under the used low nucleophilicity, stable ion conditions no alkene formation is involved in the systems. This is indicated from the previously discussed lack of deuterium incorporation into the methyl groups of the exchanging $(CH_3)CD + {}^+C(CH_3)_3$ system. Further decisive proof was obtained that alkene formation is, indeed, absent in the studied systems: when 2-

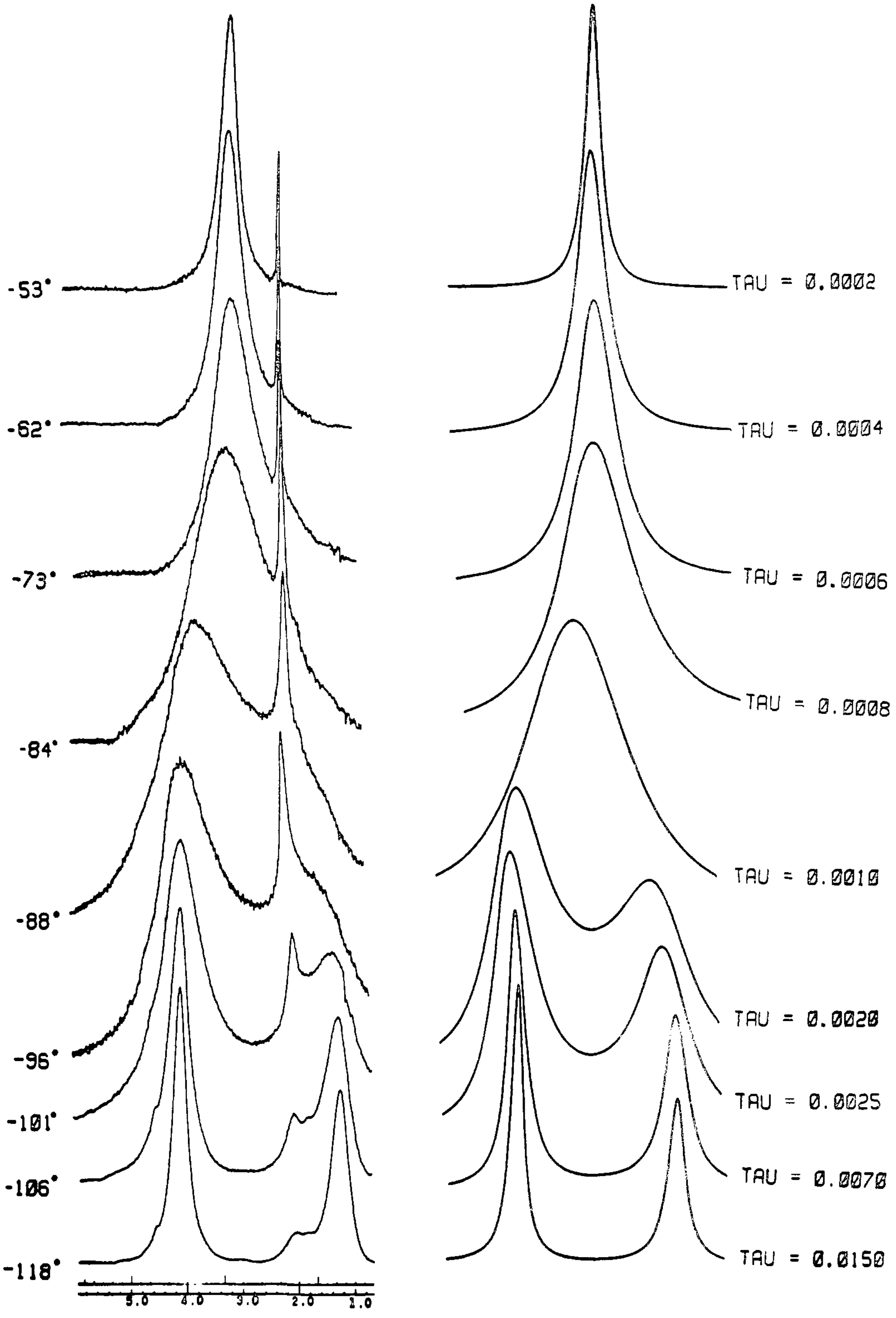


Figure 3. Temperature-dependent pmr spectra of 55 mol % trimethylcarbenium ion exchanging with 45 mol % 2-methylpropane (left) and calculated spectra (right). The methine proton absorption is omitted in the calculated spectra.

methylpropane was treated with either DF–SbF$_5$–SO$_2$ClF or FSO$_3$D–SbF$_5$–SO$_2$ClF at room temperature (in a pressure bomb) for 30 min, only exchange of the tertiary methine hydrogen was observed (by ^{1}H and ^{2}H nmr spectroscopy). Any intermediate formation of isobutylene in the system should have resulted in methyl hydrogen–deuterium exchange. Further, when perdeuterated *tert*-butyl cation $(CD_3)_3C^+$ (prepared from $(CD_3)_3COH$ in HF–SbF$_5$ or FSO$_3$H–SbF$_5$ solution) was kept even at room temperature for 48 hr, essentially no hydrogen–deuterium exchange could be detected (by nmr or mass spectrometry of quenching products). We thus are convinced that alkylation of alkanes with alkylcarbenium ions in the present work was carried out under conditions where alkene formation is absent, and the data, therefore, indeed, reflect single bond alkylations by carbenium ions.

Regardless of whether starting from 2-methylpropane or butane, both alkanes are always present in equilibrium due to hydrogen transfer and carbenium

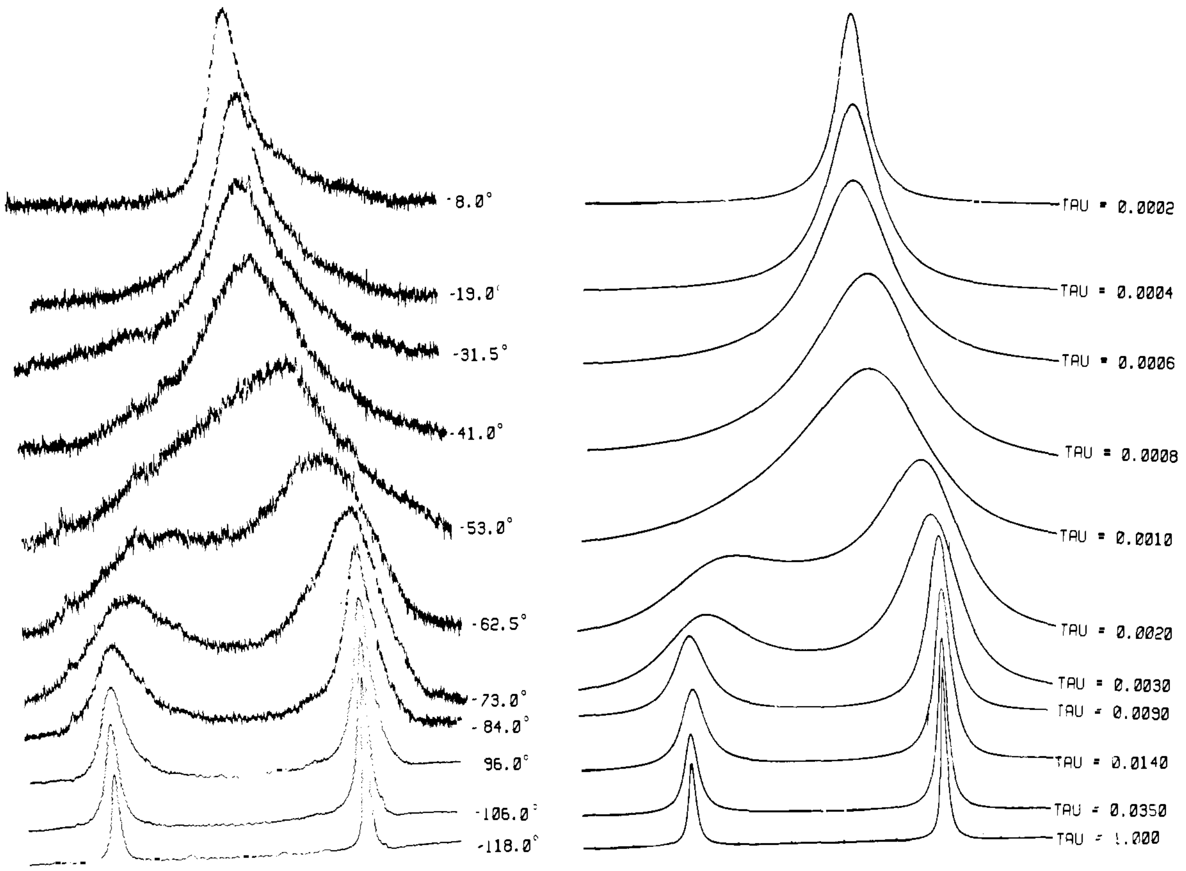


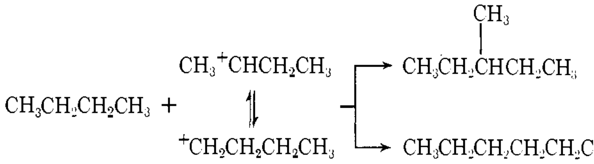
Figure 4. Temperature-dependent pmr spectra of trimethylcarbenium ion (70%) exchanging with 2-deuterated-2-methylpropane (30%) (left), and calculated spectra (right).

ion rearrangements taking place in the systems. Alkylation products, consequently, are also derived from methylethyl- and isopropylcarbenium ions (protonated methylcyclopropane can be involved in the ion rearrangement). Indeed, we feel that direct alkylation by bulkier *tert*-alkylcarbenium ions (like the trimethylcarbenium ion) is limited because of steric reasons and owing to the much faster intermolecular hydrogen transfer reactions gives more reactive and sterically less hindered secondary and even (through rearrangements involving protonated cyclopropanes) incipient primary carbenium ions. That tertiary carbenium ions themselves can act as alkylating agents is clearly proven, however, by the formation of small but important amounts (1–2% of the C_8 fractions) of 2,2,3,3-tetramethylbutane in the alkylation of 2-methylpropane with trimethylcarbenium ion. We can visualize no other way than direct alkylation of the C–H bond in 2-methylpropane for its formation.

$$(CH_3)_3CH + {}^+C(CH_3)_3 \xrightleftharpoons{-H^+} (CH_3)_3CC(CH_3)_3$$

Due to the extreme acid sensitivity of 2,2,3,3-tetramethylbutane, the observation of even a small amount in the alkylation products is very definite proof for the direct alkylation process. The actual yield may be much higher, but unavoidable protolytic cleavage in the system (where *via* proton elimination a strong acid is formed in the alkylation process) as well as isomerization decrease the observable amount.

Very different hexane isomer distributions were obtained in the C_6 fractions of alkylation of 2-methylpropane or *n*-butane with trimethyl- or methylethylcarbenium ion. For example, when *n*-butane is allowed to react with methylethylcarbenium fluoroantimonate, the hexane fraction, depending on reactions, contains 57–88% of 3-methylpentane and 38–7% *n*-hexane, with only 3 or 4% 2,3-dimethylbutane and about 1% 2-methylpentane. These data strongly indicate alkylolysis of C–C bonds of *n*-butane by methylethylcarbenium ion.



$$CH_3CH_2CH_2CH_3 + \begin{matrix} CH_3{}^+CHCH_2CH_3 \\ \Updownarrow \\ {}^+CH_2CH_2CH_2CH_3 \end{matrix} \longrightarrow \begin{matrix} CH_3CH_2\overset{CH_3}{\overset{|}{C}}HCH_2CH_3 \\ CH_3CH_2CH_2CH_2CH_2CH_3 \end{matrix}$$

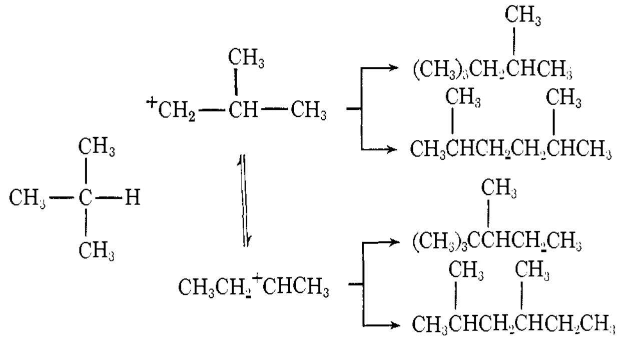
The formation of C_7 alkylates indicates initial alkylolysis followed by alkylation in the C_4–C_3 system. Table III summarizes typical isomeric heptanes formed in the C_4–$C_3{}^+$ and $C_4{}^+$–C_3 systems. Isomer distributions depend not only on the alkylating reaction conditions but also the initial C_4 alkanes and C_4 carbenium ions.

The major C_8 products of the reaction of 2-methylpropane and trimethylcarbenium ion are 2,2,4-trimethylpentane (18%), 2,5-dimethylhexane (43%) as well as 2,4-dimethylhexane (7.5%), and 2,2,3-trimethylpentane (3%), indicating alkylation by the methylethyl- and isopropylcarbenium ions (protonated methylcyclopropane) (Scheme I). Isomeric octanes obtained in the alkylation of 2-methylpropane and *n*-butane with trimethyl- and methylethylcarbenium ions are summarized in Table IV.

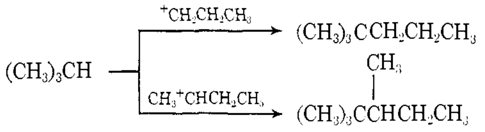
Table IV Isomeric Octane Compositions Obtained in Typical Alkylations of Butanes with Butyl Cations

	C_4–C_4			
Octane	$(CH_3)_3CH$ $(CH_3)_3{}^+C$	$CH_3CH_2CH_2CH_3$ $(CH_3)_3{}^+C$	$CH_3CH_2CH_2CH_3$ $CH_3{}^+CH_2CHCH_3$	$(CH_3)_3CH$ $CH_3{}^+CHCH_2CH_3$
2,2,4-Trimethylpentane	18.0	4.0	3.8	8.5
2,2-Dimethylhexane			0.4	
2,2,3,3-Tetramethylbutane	1–2		Trace	1–2
2,5-Dimethylhexane	43.0	0.6	1.6	29.0
2,4-Dimethylhexane	7.6	Trace		6.6
2,2,3-Trimethylpentane	3.0	73.6	40.6	3.2
3,3-Dimethylhexane			12.3	7.1
2,3,4-Trimethylpentane	1.5	7.2	15.5	6.2
2,3,3-Trimethylpentane	3.6		3.8	8.8
2,3-Dimethylhexane	4.2	6.9		12.8
2-Methylheptane		Trace	10.3	6.7
3-Methylheptane	19.3	7.6	6.8	9.5
n-Octane	0.2		4.8	Trace

Scheme I



The bulky trimethylcarbenium ion plays only a relatively minor role in alkylations of alkanes, but produces secondary cations with ease in intramolecular hydrogen transfer reactions. Consequently, we interpret formation of 2,2-dimethylpentane (a major product in C_4–C_3 alkylation and of 2,2,3-trimethylpentane in C_4–C_4 alkylation) not as tertiary butylation by the trimethylcarbenium ion, but as propylation or butylation of 2-methylpropane by the more reactive and less bulky secondary or incipient primary ions.

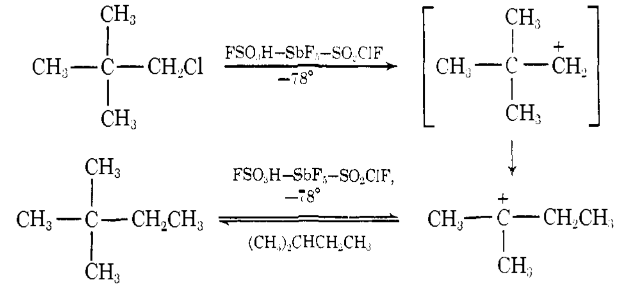


In all these reactions C–C bond alkylation (alkylolysis) by the secondary alkylcarbenium ions is always observed and thus plays an important role.

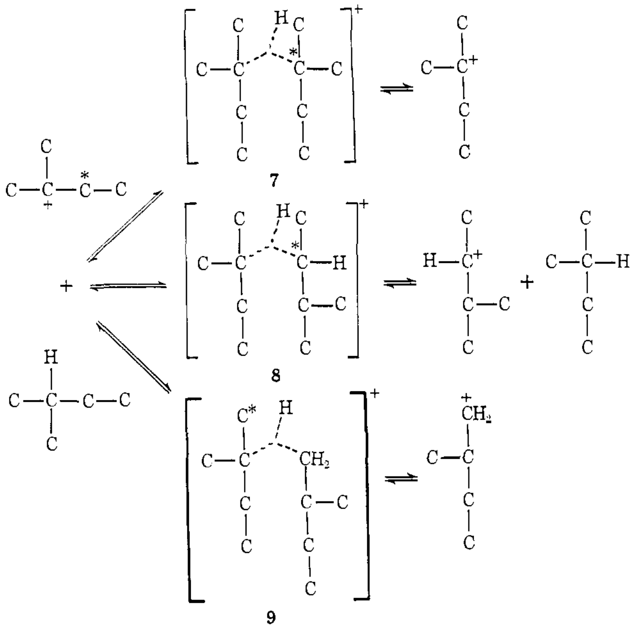
The trimethylcarbenium ion does not alkylate methane and ethane under the reaction conditions (in SO_2ClF solution at low temperature). In contrast, the dimethylcarbenium ion reacts with ethane showing hydrogen transfer and alkylation (products being propane with some 2-methylpropane and 2-methylbutane also formed). The methylethylcarbenium ion generally shows reactivity similar to that of the dimethylcarbenium ion.

Dimethylethylcarbenium Ion–2-Methylbutane. The exchanging system can be generated either from the ionization of excess of 2-methylbutane in FSO_3H–SbF_5–SO_2ClF or by generating the dimethylethylcarbenium ion (preferentially from neopentyl chloride with FSO_3H–SbF_5) and then adding 2-methylbutane (Scheme II). The former conditions are less favorable,

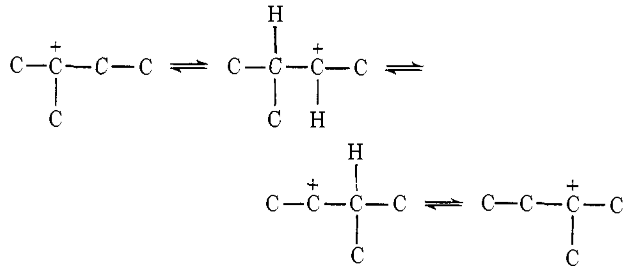
Scheme II



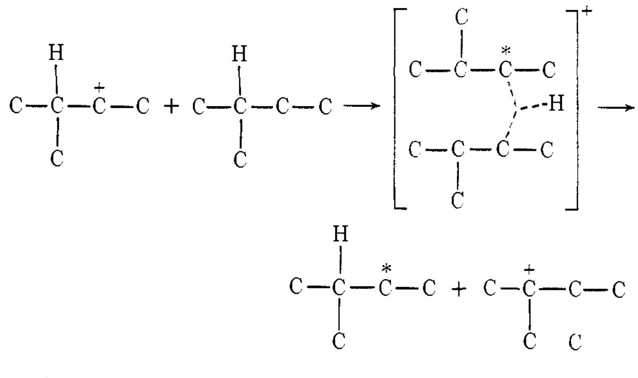
because of ready polycondensation which occurs even at −30°. The temperature-dependent pmr spectra of the-$(CH_3)_2CHCH_2CH_3$–$(CH_3)_2C^+CH_2CH_3$ exchange system are shown in Figure 5. At −90°, the exchange rate seems to be slow because both dimethylethylcarbenium ion and 2-methylbutane are separately observed in the pmr spectrum. The absence of observable spin–spin coupling may be, however, due to slow exchange or/and viscosity of the medium. Upon further cooling to −110°, the sample started to freeze, and only broadened resonances were observed. Upon heating, the α-methyl and methylene protons of dimethylethylcarbenium ion became broadened and finally collapsed with the corresponding resonance absorptions of 2-methylbutane at −20° to form a broad peak at δ 3.2. The β-methyl proton absorption is slightly shielded from δ 1.80 to 1.60 and shows a spin–spin splitting (J_{HH} = 6 Hz) pattern indicating that these proton absorptions are not involved in the exchange reaction. The observed spin–spin coupling between β-methyl and the methylene protons shows that the hydrogen exchange rate of the involved methylene protons (both intra- and intermolecular in dimethylethylcarbenium ion and 2-methylbutane) must be slow compared to that of the methine proton. On the other hand, if the hydrogen exchange rate was rapid enough to wash out the proton–proton coupling, the β-methyl proton would have shown a pmr singlet absorption. If only the tertiary methine proton is involved in the hydrogen transfer reaction, one would observe a singlet absorption for this proton as was observed in the case of trimethylcarbenium ion. Thus, the broadened resonance at δ 3.2 could be due to the rapid proton exchange reactions between all *gem*-methyl, methylene, and methine protons in both the dimethylethylcarbenium ion and 2-methylbutane. Hence the following hydrogen exchange reactions involving three-center bonded carbonium ion transition states 7, **8**, and 9 may be considered.



Alternatively, intramolecular hydrogen shift in the dimethylethylcarbenium ion can be involved as studied by Saunders in the temperature-dependent pmr spectra of the ion.[12] In the presence of excess 2-methylbutane, both intra- and intermolecular hydrogen shifts are



expected to occur. In this case, the more reactive methylisopropylcarbenium ion can attack the tertiary C–H bond of 2-methylbutane. Thus, the methylene protons of the dimethylethylcarbenium ion, the



methylene, and also the methine protons of 2-methylbutane can all be involved in rapid equilibration. Consequently, a broadened absorption would be expected as the *gem*-methyl protons of both the dimethylethylcarbenium ion and 2-methylbutane would be expected to show broadened resonance absorptions. Thus, the broadened absorption at δ 3.2 can be a combination of these two broadened peaks.

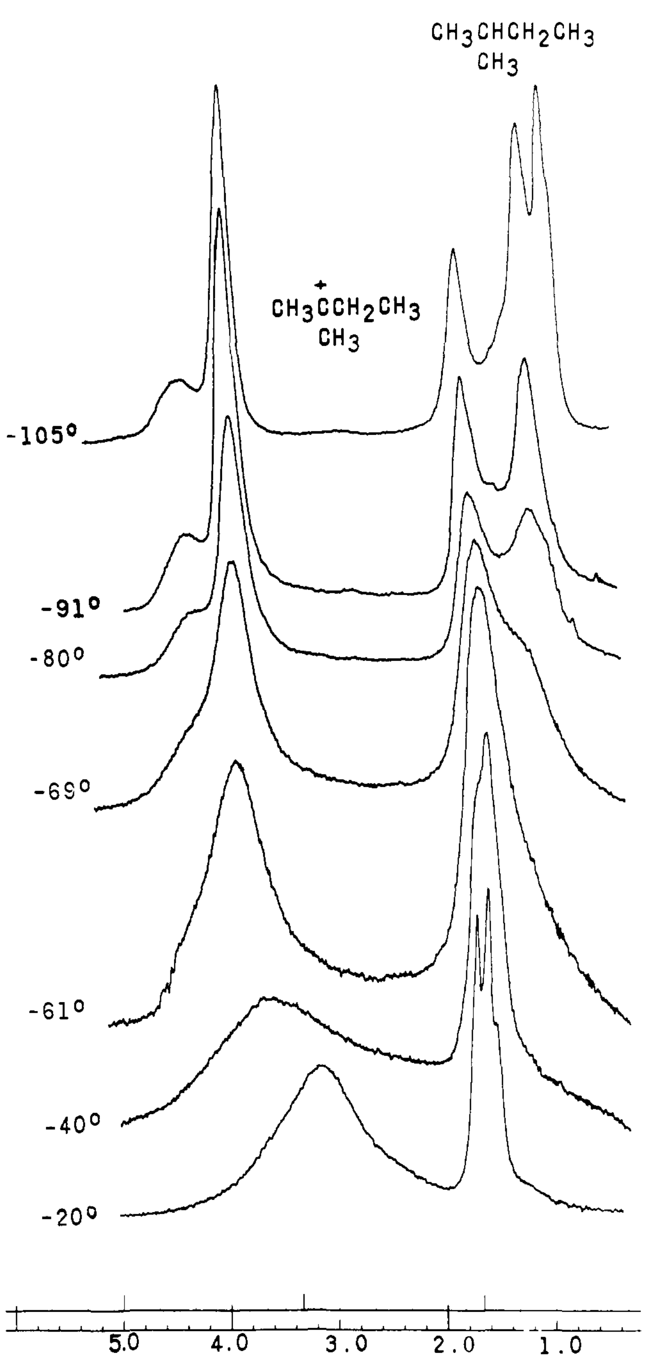


Figure 5. Temperature-dependent pmr spectra of 2-methylbutane exchanging with dimethylethylcarbenium ion.

The energy of activation for the intramolecular hydrogen transfer was estimated by Saunders to be 11.7 ± 0.2 kcal/mol.[13] It is relatively high when compared with that of the intermolecular hydrogen transfer of trimethylcarbenium ion and 2-methylpropane (see previous discussion). Due to the higher steric hindrance of dimethylethylcarbenium ion and 2-methylbutane, the barrier to intermolecular hydrogen transfer would be expected to be higher than that in the trimethylcarbenium ion, but still be lower than 11.7 ± 0.2 kcal/mol. We thus conclude from

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(12) M. Saunders and E. L. Hagen, *J. Amer. Chem. Soc.*, **90**, 2436 (1968).

(13) M. Saunders, *Tetrahedron Lett.*, 1699 (1963).

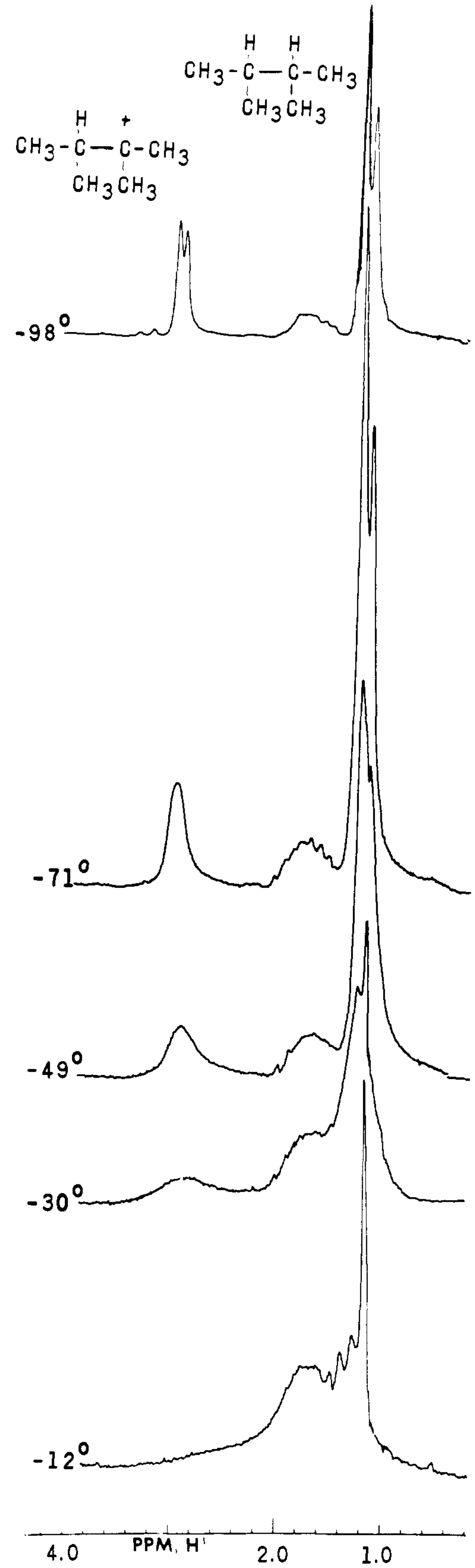
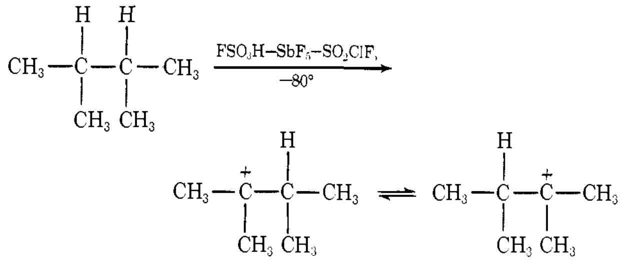


Figure 6. Temperature-dependent pmr spectra of 2,3-dimethylbutane exchanging with dimethylisopropylcarbenium ion.

study of the temperature-dependent pmr spectra that the exchange reaction between dimethylethylcarbenium ion and 2-methylbutane is dominated by the intermolecular process at lower temperature (< −60°) and becomes competative for both inter- and intramolecular processes at higher temperature (> −40°).

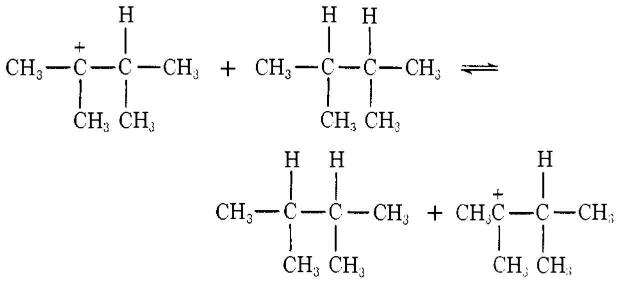
Dimethylisopropylcarbenium Ion–2,3-Dimethylbutane. The ionization of 2,3-dimethylbutane in excess $FSO_3H-SbF_5-SO_2ClF$ solution below −60° yields the dimethylisopropylcarbenium ion.[14] When an equal molar amount of 2,3-dimethylbutane was added to the $FSO_3H-SbF_5-SO_2ClF$ solution at −80°, the pmr spectrum showed both dimethylisopropylcarbenium ion and



$$CH_3-\underset{CH_3}{\overset{H}{C}}-\underset{CH_3}{\overset{H}{C}}-CH_3 \xrightarrow[-80^\circ]{FSO_3H-SbF_5-SO_2ClF}$$

$$CH_3-\underset{CH_3}{\overset{+}{C}}-\underset{CH_3}{\overset{H}{C}}-CH_3 \rightleftharpoons CH_3-\underset{CH_3}{\overset{H}{C}}-\underset{CH_3}{\overset{+}{C}}-CH_3$$

un-ionized 2,3-dimethylbutane separately in the solution. The pmr spectrum of the solution is temperature dependent as shown in Figure 6, indicating that by raising the temperature the dimethylisopropylcarbenium ion undergoes exchange with 2,3-dimethylbutane with no simultaneous intramolecular rearrangement of the dimethylisopropylcarbenium ion to the methyldiethyl- or dimethylpropylcarbenium ion.[7] Upon cooling back the solution to −90°, pmr shows again only the dimethylisopropylcarbenium ion and 2,3-dimethylbutane.



$$CH_3-\underset{CH_3}{\overset{+}{C}}-\underset{CH_3}{\overset{H}{C}}-CH_3 + CH_3-\underset{CH_3}{\overset{H}{C}}-\underset{CH_3}{\overset{H}{C}}-CH_3 \rightleftharpoons$$

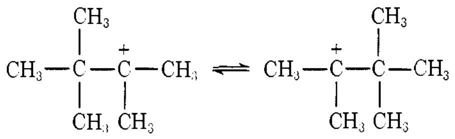
$$CH_3-\underset{CH_3}{\overset{H}{C}}-\underset{CH_3}{\overset{H}{C}}-CH_3 + CH_3\underset{CH_3}{\overset{+}{C}}-\underset{CH_3}{\overset{H}{C}}-CH_3$$

Due to the low energy barrier for 1,2-hydrogen shift in the dimethylisopropylcarbenium ion (it cannot be frozen out even at −100°), both intra- and intermolecular exchange would be expected at higher temperature. The singlet absorption in the spectrum at δ 1.10 at −10° is assigned to the three exchangeable methine protons. The methyl protons show a broadened absorption at δ 1.6.

Dimethyl-*tert*-butylcarbenium Ion–2,2,3-Trimethylbutane. The most stable *tert*-heptyl cation, the dimethyl-*tert*-butylcarbenium ion, is obtained upon ionization of 2,2,3-trimethylbutane in $FSO_3H-SbF_5-SO_2ClF$ at −60°. It shows in the pmr spectrum a sharp singlet absorption at δ 2.86.[13] When an excess of 2,2,3-trimethylbutane was added to this solution with good mixing at −78°, the pmr spectrum of the solution shows the separate, nonexchanging dimethyl-*tert*-butylcarbenium ion and 2,2,3-trimethylbutane throughout the temperature range from −80 to −10°. The absence of hydrogen exchange between dimethyl-*tert*-butylcarbenium ion and 2,2,3-trimethylbutane indicates that the very bulky tertiary cation

(14) G. A. Olah and J. Lukas, *J. Amer. Chem. Soc.*, **89**, 2227, 4739 (1967).

and alkane prevent the approach of the empty p_z orbital of the carbenium center to the tertiary C–H bond. In this case, thus, the rapid intramolecular equilibration of the methyl group in the cation has a lower energy barrier (estimated to be less than 4 kcal/mol) than the intermolecular hydrogen exchange.



$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\underset{CH_3}{\overset{+}{C}}-CH_3 \rightleftharpoons CH_3-\underset{CH_3}{\overset{+}{C}}-\underset{CH_3}{\overset{CH_3}{C}}-CH_3$$

We found that intermolecular hydrogen exchange between carbenium ions and their parent alkanes also takes places in the case of cycloalkyl systems.

Conclusion

Using stable ion conditions, we were able to study the exchange reaction and alkylations between alkylcarbenium ions and their parent alkanes.

The major reactions in the interaction of alkanes with alkylcarbenium ions are: (1) fast intermolecular hydrogen transfer, (2) direct alkylation and/or alkylolysis, and (3) secondary alkylation and/or alkylolysis. The nature of the transition state in all of these reactions is considered to involve electrophilic frontside attack on covalent C–H or C–C bonds by the carbenium ions. The three-center bonds in the triangular transition states are not considered symmetrical, particularly when steric hindrance, like in tertiary–tertiary systems, makes this difficult. In the transition states, however, attack by the electrophile still is on the main lobes of the bonding orbitals, where the electron density resides (the back lobes of the orbitals are considered poor electron donors, since probably less than 10% of the overall electron density is to be found in them). The role of steric hindrance is well demonstrated by the relatively small amount of 2,2,3,3-tetramethylbutane formed in the reaction of isobutane with trimethylcarbenium ion. The sterically less hindered dimethylcarbenium ion with 2-methylpropane gives higher yields of 2,2,3-trimethylbutane, as does the reaction of methylethylcarbenium ion with 2-methylpropane.

As shown in the present study, aliphatic electrophilic alkylation of alkanes by alkylcarbenium ion is a general reaction which can proceed without involvement of olefins and represents a significant example of electrophilic reactions at single bonds.

Reactions involving the formal transfer of a hydride ion from a neutral donor molecule to an electron deficient trivalent carbenium ion or strong protic acid are generally called hydride abstractions. We feel that the experimental data presented in our work indicate an electrophilic hydrogen transfer mechanism involving pentacoordinated carbonium ions and not simple, direct hydride ion transfer. Therefore, it is suggested that hydride ion abstraction (or transfer) should be more properly named "hydrogen transfer."

Experimental Section

Materials. All alkanes and alkyl halides used were commercially available. 2-Deuterio-2-methylpropane was obtained from Merck Sharp and Dohme of Canada Ltd.

Preparation of Alkylcarbenium Ions and Their Reaction with Alkanes. (a) In a typical experiment, 0.1 mol of alkane and 0.05 mol of superacid (1:1 FSO_3H–SbF_5 or HF–SbF_5) in SO_2ClF were mixed with vigorous stirring at −78°. A homogeneous colorless mixture was generally formed. When using gaseous alkanes they were introduced into the acid mixture in a slow stream. (b) Alkyl halide (0.01 mol) was ionized in 1:1 FSO_3H-SbF_5–SO_2ClF solution at −78°. This solution was then mixed with 0.01 mol of the parent alkanes with good stirring at the same temperature. The exchange reactions were followed in the nmr experiments by taking the temperature-dependent spectra in the range given. For alkylations, the reaction mixtures were allowed to warm up to −20 to −0° for 10 min and then were quenched with cold methanol–water; the organic phase was extracted with ether, dried, and analyzed by gas–liquid chromatography.

Gas–Liquid Chromatographic Analysis. The analyses of all products were carried out by gas–liquid chromatography using a Perkin-Elmer Model 226 gas chromatograph equipped with a hydrogen flame ionization detector system and open tubular capillary columns. Peak areas were obtained with an Infotronics Model CRS-1 electronic printing integrator. Characteristic retention times using a 150-ft, 0.01-in. diameter Squalene capillary column at 35° initial temperature for the first 20 min, increased to 60° at a rate of 0.75°/min, with 8 psi carrier gas pressure, are given in Table V.

Table V. Characteristic Gas–Liquid Chromatographic Retention Times of Alkanes

Alkane	Retention time, sec	Alkane	Retention time, sec
Propane	396	Heptane	1781
2-Methylpropane	427	2,2,4-Trimethylpentane	1668
Butane	432	2,2-Dimethylhexane	2006
2,2-Dimethylpropane	432	2,2,3,3-Tetramethylbutane	2046
2-Methylbutane	496	2,5-Dimethylhexane	2092
Pentane	558	2,4-Dimethylhexane	2126
2,2-Dimethylbutane	677	2,2,3-Trimethylpentane	2178
2,3-Dimethylbutane	765	3,3-Dimethylhexane	2326
2-Methylpentane	777	2,3,4-Trimethylpentane	2369
3-Methylpentane	836	2,3,3-Trimethylpentane	2468
Hexane	918	2,3-Dimethylhexane	2499
2,2-Dimethylpentane	1069	2-Methylheptane	2586
2,4-Dimethylpentane	1103	4-Methylheptane	2644
2,2,3-Trimethylbutane	1168	3,4-Dimethylhexane	2703
3,3-Dimethylpentane	1360	3-Methyl-3-ethylpentane	2731
2-Methylhexane	1450	3-Methylheptane	2746
2,3-Dimethylpentane	1483	3-Ethylhexane	2746
3-Methylhexane	1539	Octane	3690
3-Ethylpentane	1761		

Carbenium ions in SO_2ClF or SO_2 solutions were studied by nmr spectroscopy. All nmr spectra were obtained on a Varian Associates Model A56/60A nmr spectrometer equipped with a variable-temperature probe. External capillary TMS was used as reference. The probe temperature was calibrated before and after temperature-dependent experiments with a fitting thermometer. All the ions involved were reported in our previous studies.

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