Reaction of 2-Nitro Ketones in Methanol at Room Temperature. A. 2-Nitrocycloheptanone (4).—Compound **4** (0.8 g, 0.005 mol) and 5 drops of concentrated sulfuric acid were added to 50 ml of absolute methanol and the mixture was allowed to stir for 20 hr. After neutralization with sodium acetate, 200 ml of ether was added to precipitate inorganic salts. The reaction mixture was filtered and the solvent evaporated. Distillation of the residue gave 0.9 g of material, bp 60–80° (0.2 mm). Glpc analysis revealed four components: **4** (50%), dimethyl pimelate (28%), methyl 7-nitroheptanoate (12%), and 2,2-dimethoxynitrocycloheptane (4%). The retention times of these compounds were identical with those of authentic samples.

B. 2-Nitro-3,5,5-trimethylcyclopentanone (2).—Compound **2** (1.5 g, 0.0088 mol) was added to 25 ml of absolute methanol followed by 5 drops of concentrated sulfuric acid. After being stirred for 96 hr the reaction mixture was worked up in the manner as described in experiment A. Distillation gave 0.8 g of material, bp 45–62° (0.5 mm), and 0.5 g of a high boiling material which solidified in the distilling head.

Glpc analysis of the fraction, bp 45–62°, revealed two components, unreacted **2** (46%) and dimethyl 2,2,4-trimethylglutarate (5%). The ester was purified by glpc: $n^{20}\text{D}$ 1.4305 (lit.[12] $n^{21.5}\text{D}$ 1.4309).

Recrystallizing the high boiling material from *n*-heptane gave 0.4 g (33%) of 2,6-dioxo-3,3,5-trimethyl-1-hydroxy-1-azacyclohexane (**6**): mp 118–119.5°; ir (Nujol) 3350 (OH) and 1740 and 1665 cm^{-1} (C=O); nmr (CDCl$_3$) δ 1.32 [t, 9, C(CH$_3$)$_2$ and C(CH$_3$)], 1.69 (d, 1, J = 3 Hz, H, equatorial in CH$_2$), 1.83 (s, 1, H axial in CH$_2$), 2.80 (m, 1, CH), and 7.60 (s, 1, OH).

Anal. Calcd for $C_8H_{13}NO_3$: C, 56.14; H, 7.60; N, 8.18. Found: C, 56.35; H, 7.68; N, 8.19.

When the reaction was carried out in refluxing methanol for 20 hr, 1.0 g of **2** yielded 0.7 g (58%) of diester and 0.25 g (25%) of **6**.

When 0.5 g of **2** was allowed to stir at room temperature for 12 hr in 10 ml of concentrated hydrochloric acid, 0.35 g (70%) of **6**, mp 118–119°, was obtained after evaporation of the aqueous solution and sublimation of the residue at 40° (0.05 mm).

Acetate of 6.—To 10 ml of acetic anhydride was added 0.1 g of **6** and, after the mixture stirred for 24 hr, excess acetic anhydride was removed *in vacuo*. The residue, 0.11 g (100%) was purified by glpc: $n^{20}\text{D}$ 1.4680.

Anal. Calcd for $C_{10}H_{15}NO_4$: C, 56.34; H, 7.04; N, 6.57. Found: C, 56.44; H, 7.08; N, 6.33.

2,2-Dimethoxynitrocycloheptane.—To a mixture of 10 g of absolute methanol, 7.0 g of methyl orthoformate, and 3 drops of concentrated sulfuric acid was added 1.0 g (0.0062 mol) of **4**. After 12 hr at room temperature sodium bicarbonate was added to neutralize the acid, the reaction mixture filtered, and the solvent was evaporated. Distillation gave 1.2 g of material, bp 55–62° (0.4 mm). Glpc analysis revealed the presence of three components: **4** (10%), dimethyl pimelate (18%), and 2,2-dimethoxynitrocycloheptane (72%). Dimethyl pimelate and **4** were identified by comparison of their retention times with those of authentic samples. 2,2-Dimethoxynitrocycloheptane was purified by glpc: $n^{20}\text{D}$ 1.4760; ir (neat) 1550 and 1370 (NO$_2$) and 1110 cm^{-1} (OCH$_3$).

Anal. Calcd for $C_9H_{17}NO_4$: C, 53.20; H, 8.37; N, 6.90. Found: C, 53.34; H, 8.21; N, 6.83.

Similarly was prepared **2,2-dimethoxynitrocyclohexane** (83%), mp 53–54° after recrystallization from methanol.

Anal. Calcd for $C_8H_{15}NO_4$: C, 50.79; H, 7.94; N, 7.41. Found: C, 50.74; H, 8.08; N, 7.20.

2-Bromo-2-nitro-3,5,5-trimethylcyclopentanone (7).—Potassium 2-keto-3,3,5-trimethylcyclopentanenitronate[2] (2.1 g 0.01 mol) was placed in 25 ml of carbon tetrachloride and bromine was added until a faint yellow color persisted. The mixture was filtered and the filtrate was evaporated. The residual solid was recrystallized from hexane to give 2.0 g (67%) of compound **7**: mp 49–51°; ir (melt) 1515 and 1350 (NO$_2$) and 1755 cm^{-1} (C=O).

Anal. Calcd for $C_8H_{12}BrNO_3$: C, 38.40; H, 4.80; N, 5.60; Br. 32.00. Found: C, 38.44; H, 4.91; N, 5.63; Br, 32.40.

Registry No.—2,2-Dimethoxynitrocycloheptane, 20642-76-6; 2,2-dimethoxynitrocyclohexane, 20642-78-8; **6**, 20642-75-5; **7**, 20642-77-7.

Acknowledgment.—We are indebted to the Office of Naval Research for the financial support of this work.

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[11] E. Huntress and S. Mulliken, "Identification of Pure Organic Compounds," John Wiley & Sons, Inc., New York, N. Y., 1941, Order I.

[12] G. R. Enser and W. Wilson, *J. Chem. Soc.*, 4068 (1956).

Carbonium-Ion Behavior in Aluminum Bromide–1,2,4-Trichlorobenzene

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Nmr spectroscopy was used to monitor the catalytic activity of the aluminum bromide–1,2,4-trichlorobenzene system and to study long-chain hydride-transfer reactions between paraffins and cations. Compounds containing tertiary C–H bonds generally participate in extremely rapid reactions converting all the paraffins into ions in moments. Rearrangement of the intermediates to ions with a different number of branches is slower and usually rate determining. Ionic rearrangements leading to similarly branched species, however, are fast and these studies do not distinguish between these rates and those of hydride transfer. Normal paraffins appear to react much more slowly, probably because both the rates of forming and rearranging secondary ions are slow.

Aluminum bromide has a long history as an exceedingly active Friedel–Crafts catalyst. It is able to support the formation of alkyl cations which undergo extensive intramolecular isomerization and intermolecular reactions. The intermolecular reactions are generally of two types depending on the presence of unsaturated reactants in the system. When olefinic compounds are present, polymerization usually predominates, although cracking of high molecular weight ions and hydride abstraction reactions from the olefin also are often observed.

In the absence of olefins or other bases the alkyl ions enter into hydride abstraction reactions with paraffins.[1] This reaction is often considered the rate-determining step in the isomerization of paraffins, particularly when a normal paraffin is the hydride donor. Alkyl cations formed over AlBr$_3$ are known to be efficient at abstracting either tertiary or secondary hydride ions and thus participating in long-chain isomerization processes.

A major result of earlier work with this system was the finding that nmr spectroscopy could be used to study long-chain intermolecular hydride-transfer processes between isobutane and low concentrations of *t*-butyl cations,[2] eq 1. It can be shown that the doublet of

$$i\text{-}C_4H_{10} + t\text{-}C_4H_9^+ \rightleftharpoons t\text{-}C_4H_9^+ + i\text{-}C_4H_{10} \qquad (1)$$

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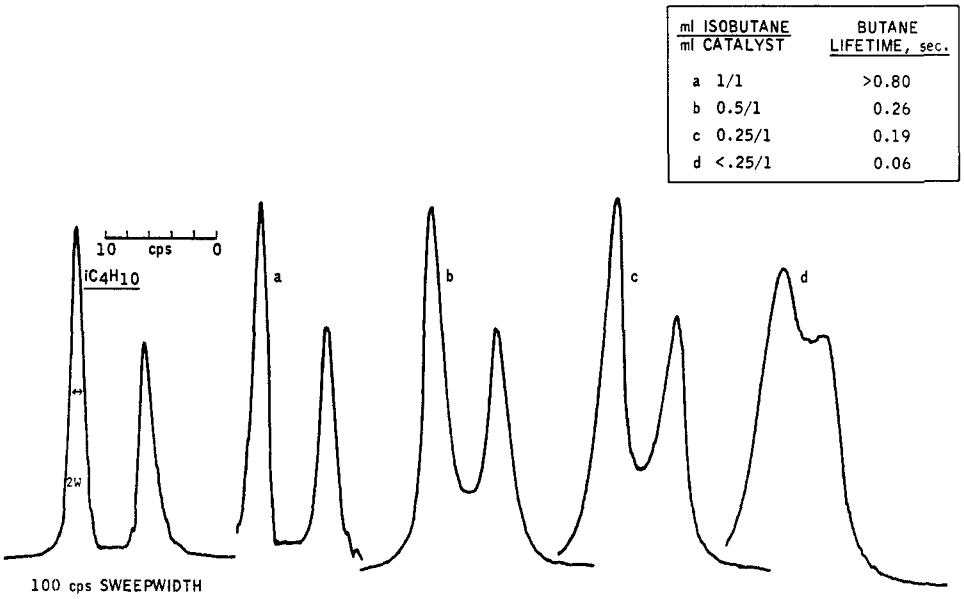
[1] P. D. Bartlett, F. E. Condon, and A. Schneider, *J. Amer. Chem. Soc.*, **66**, 1531 (1944).

[2] G. M. Kramer, B. E. Hudson, and M. T. Melchior, *J. Phys. Chem.*, **71**, 1525 (1967).



	ml ISOBUTANE / ml CATALYST	BUTANE LIFETIME, sec.
a	1/1	>0.80
b	0.5/1	0.26
c	0.25/1	0.19
d	<.25/1	0.06

Figure 1.—Nmr spectra of isobutane reacting in 0.5 *M* aluminum bromide–1,2,4-trichlorobenzene; 0.1 *M* water. The effect of lowering the isobutane/catalyst ratio upon the methyl resonance.

isobutane's methyl resonance will coalesce to a singlet when the average lifetime of isobutane molecules is about 0.06 sec. This condition can be approached with about 3.0 *M* solutions of isobutane in 1,2,4-trichlorobenzene containing 0.5 *M* aluminum bromide and about 0.1 *M* water. When the singlet is obtained all isobutane molecules on the average are converted into ions in this time. The lifetime of the ions is much below 0.06 sec and could be calculated if their steady-state concentration was known, *i.e.*, $\tau_{\text{ion}} = 0.06 \times [\text{ions}]/[i\text{-C}_4\text{H}_{10}]$. In any event an active $AlBr_3$ catalyst will convert isobutane into an ion at a high rate and for exceedingly long periods of time, one sample maintaining activity for more than 1 month.

The *t*-butyl cations show little evidence of isomerizing to *s*-butyl ions and isobutane is not isomerized to *n*-butane at any significant rate with this catalyst. This is probably related to a sizable energy difference between *t*-butyl and isobutyl cations which are the likely intermediates in the isomerization.

The present work is mainly concerned with the problems of preparing reproducibly active catalysts and of establishing the scope of the long-lived hydride-transfer reaction. In addition, some information concerning the fate of cations which can isomerize by energetically feasible paths will be discussed.

Preparing "Reproducibly Active Aluminum Bromide–Trichlorobenzene."—A major difficulty with utilizing aluminum bromide–1,2,4-trichlorobenzene for nmr studies has been that of preparing catalysts of essentially equivalent reactivity. This problem has in great part been solved by preparing large quantities of aluminum bromide and trichlorobenzene solutions, promoting with different amounts of water, and utilizing the behavior of isobutane as a barometer of catalyst activity. The test is simply to prepare a standard solution of isobutane in the catalyst system and then to examine the nmr spectrum for evidence of exchange. Any solution exhibiting detectable line broadening is an active catalyst, and an estimate of the activity can easily be made.

Suitable catalysts have been prepared by slowly adding water to a vigorously stirred solution of 30 g of aluminum bromide in 225 ml of 1,2,4-trichlorobenzene. The preparation is done in an otherwise inert atmosphere and any hydrogen bromide evolved is allowed to weather off. Redistilled aluminum bromide and various commercial reagents were all inactive until promoted in this way. Catalysts containing about 0.1 *M* water and 0.5 *M* aluminum bromide exhibit sufficient activity to substantially broaden isobutane's nmr spectrum and this composition was used in most of the subsequent work. An indication of the effect of water upon the reaction is given in Table I.

Table I
Effect of Water Promotion on the Spectrum of Isobutane

	1:1[a]		0.25:1[a]	
$[H_2O]$, *M*	Doublet separation, cps	Butane lifetime, sec	Doublet separation, cps	Butane lifetime, sec
Blank	5.96	∞	5.96	∞
0.0494	5.82	$\gg 0.8$	5.76	0.8
0.0988	5.76	≥ 0.8	5.50	0.19

[a] Volume ratio of isobutane/catalyst.

The main factor affecting isobutane's broadened spectra with a given catalyst appears to be the isobutane/catalyst ratio. Lowering the ratio results in broader spectra which is consistent with a decreased lifetime for the butane molecules, Figure 1.

It thus becomes possible to study the behavior of a series of hydrocarbons over an essentially uniformly active catalyst containing aluminum bromide. The catalyst yielding a minimum activity when employed with isobutane was arbitrarily chosen for this purpose.

The Behavior of Alkanes Containing Tertiary C–H Bonds.—The existence of a long-chain hydride-transfer process between isobutane and *t*-butyl ions appears to be a single example of a general reaction between paraffins containing tertiary C–H bonds and their corresponding cations. Eight C_5 through C_8 paraffins, methylcyclopentane, and methylcyclohexane all gave evidence of participating in the hydride-transfer process.

Some spectral changes were induced in all of the compounds upon contact with the catalyst. Isomerization is often found to accompany the hydride-transfer reaction and affect the nmr spectrum. The extent of isomerization over the water-promoted catalyst during the nmr scan often appears to be somewhat restricted to simple carbonium-ion rearrangements involving hydride and methide shifts along a chain. Processes leading to a change in branching appear to be slower and of minor importance with respect to influencing signal shape in the spectrometer. These interpretations are in accord with established cation behavior.

Spectral observations were made on mixtures of the catalyst and paraffin prepared in an inert atmosphere. The catalyst, 0.5 ml, was first added to an nmr tube and frozen at −80°. Then 0.5 ml of paraffin was added and the mixture was kept cold until the spectrometer was tuned. The contents of the tube were then thawed and shaken once or twice and the spectrum was recorded within several minutes.

Estimates of the lifetimes of the paraffins were made by comparing their spectra with calculated line shapes of exchanged broadened multiplets.[3]

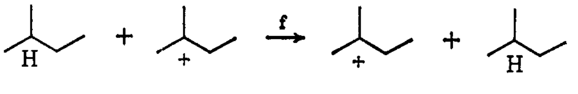
These estimates are tabulated in Table II and the behavior of the hydrocarbons is discussed below.

TABLE II

LIFETIME OF HYDROCARBONS IN 0.5 *M* ALUMINUM BROMIDE–1,2,4-TRICHLOROBENZENE, 0.1 *M* WATER

Compound	Registry no.	Lifetime, sec
Isobutane	75-28-5	>0.8
Isopentane	78-78-4	>0.8
2,3-Dimethylbutane	79-29-8	0.7
3-Methylpentane	96-14-0	0.7
2-Methylpentane	107-83-5	
2,4-Dimethylpentane	108-08-7	>0.7
2,2,3-Trimethylbutane	464-06-2	>0.7
2,2,4-Trimethylpentane	540-84-1	0.5
2,3,4-Trimethylpentane	565-75-3	?
Methylcyclopentane	96-37-7	0.13
Methylcyclohexane	108-8 2	?

Isopentane.—Isopentane gave a slightly broadened spectra. The half-widths of the methyl doublet increased about 10% while the doublet separation decreased very slightly. The lifetime of isopentane is roughly about 0.8 sec. Broadening of the spectrum is postulated as due to intermolecular hydride transfer, eq 2.



(2)

It is also assumed that the spectrum of isopentane is unaffected by the presence of a low concentration of reactive *t*-amyl ions. Any intramolecular rearrangements which the ion may undergo before being trapped as isopentane should have no sensible effect on the spectrum. Isopentane slowly isomerizes to *n*-pentane with this catalyst but the *n*-pentane concentration is negligible during the nmr scan.

2,3-Dimethylbutane.—The spectrum of this hexane is substantially broadened and some isomerization is noticeable. Isomerization appears to be considerably slower than hydride transfer because the lifetime of 2,3-dimethylbutane is short and it would be expected to reach at least a pseudoequilibrium with the methylpentanes in moments if ionic rearrangements were facile. The average lifetime of 2,3-dimethylbutane is estimated as ~0.7 sec.

2-Methylpentane and 3-Methylpentane.—2-Methylpentane's spectrum undergoes moderate change. There is some broadening and a decided shift in the intensity of the alkyl bands upon reaction of 3-methylpentane with the catalyst. It is apparent that 2- and 3-methylpentane are rapidly interconverting so that one observes the spectra of an equilibrating system containing predominantly 2-methylpentane.

It does not seem possible to decide upon the relative rates of the intermolecular hydride transfer and the intramolecular isomerization paths from this spectrum as both processes are fast on the nmr time scale. It is interesting to note that isomerization to 2,3-dimethylbutane does not occur so rapidly as the methylpentane equilibration. Thus there must be substantial barrier to rearrangement to the 2,3-dimethylbutyl cation.

2,3,3-Trimethylbutane.—Triptane's nmr spectrum broadens upon contact with the aluminum bromide–1,2,4-trichlorobenzene catalyst. Isomerization is difficult to detect and the spectrum gives little evidence of reactions other than hydride transfer. Rearrangement of the ion, if it were occurring, would not affect the spectra. The observed broadening is interesting because it suggests that steric barriers to the hydride-transfer reaction are not prohibitive in what might have been expected to be a rather strained transition state.

2,4-Dimethylpentane.—This paraffin appears to isomerize rapidly upon contact with the catalyst. As with the methylpentanes it is not possible to decide which reaction may be rate determining.

2,2,4-Trimethylpentane and 2,3,4-Trimethylpentane.—Both octanes undergo immediate reaction with the aluminum bromide–1,2,4-trichlorobenzene catalyst. The nmr spectrum changes rapidly upon contact of the reactants and products recovered from the solution indicated that extensive isomerization and cracking had occurred.

Methylcyclopentane.—The methyl doublet of methylcyclopentane broadens substantially and hydride transfer is clearly faster than rearrangement to a cyclohexyl ion. Cyclohexane is the favored isomer at equilibrium but rearrangement to the secondary ion is evidently slow. The lifetime of methylcyclopentane is estimated at 0.13 sec.

Methylcyclohexane.—The spectrum of this compound is very slightly altered. The main changes appear to be shifts in the relative intensities of the methylene proton bands, although some broadening of the methyl doublet can also be seen.

Discussion

Hydride transfer between tertiary cations and paraffins containing tertiary C–H bonds thus appears to be a generally rapid reaction leading to the nearly instantaneous conversion of paraffins into ions. Many of the

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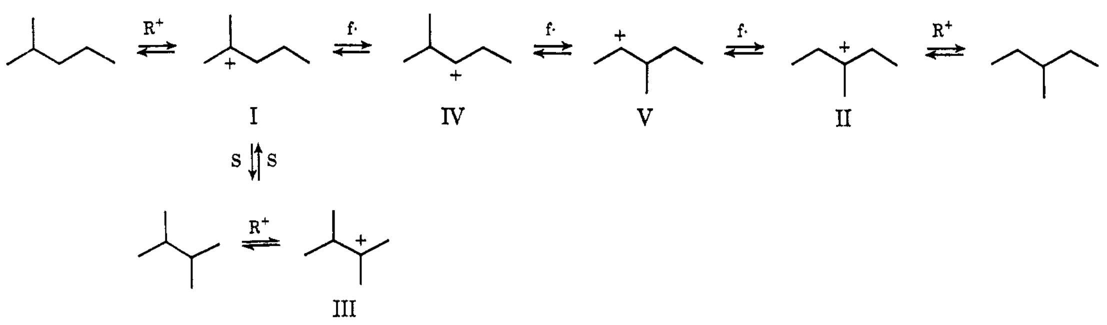
(3) Tables of Exchange Broadened NMR Multiplets, Technical Note 2, Contract No. AF 61 (052)-03, Weizmann Institute, Rehovoth, Israel, 1961.

SCHEME I



cations recapture hydride ions before rearranging but those which can isomerize by simple 1,2-hydride and alkyl shifts to other tertiary cations without undergoing a change in branching do so with surprising ease. In the latter case it is not possible to decide if hydride transfer or the rearrangement is rate determining as both reactions are rapid on the nmr time scale and one observes an equilibrium mixture of the participating isomers.

These observations lead to Scheme I for the interconversion of hexanes over the water-promoted aluminum bromide–1,2,4-trichlorobenzene system. Either 2- or 3-methylpentane may be converted into a tertiary cation *via* a rapid bimolecular hydride transfer to another ion in the system. The newly formed ion may isomerize by rapid intramolecular hydride and methide shifts to an equilibrium mixture of secondary and tertiary cations.

Conversion of the methylpentyl cations into the 2,3-dimethylbutyl cation or the reverse, however, is slower than either of the previous reactions. Thus the rate-determining process in isomerizing methylpentanes to 2,3-dimethylbutane is the rearrangement of the methylpentyl cations, not their formation. The slow step in the reverse reaction must necessarily lie in the isomerization of the 2,3-dimethylbutyl cation to the same transition state reached in the forward reaction and thus it is not surprising that this rearrangement is also more difficult than intermolecular hydride transfer.

It should be noted that the solutions studied contained equal volumes of the hydrocarbons and the catalyst. These solutions lead to the nearly instantaneous equilibration of 2-methylpentane and 3-methylpentane at ambient conditions. Isomerizations requiring more involved skeletal rearrangements are much slower. Thus, isobutane, isopentane, and the methylpentanes do not readily isomerize to *n*-paraffins, although there is no difficulty in forming the tertiary cations. The problem with isobutane may be that a primary isobutyl cation is too highly energetic relative to *t*-butyl but the *t*-amyl and methylpentyl ions should have little difficulty on energetic grounds of forming secondary *n*-alkyl cations. That these rearrangements are slow implies the existence of an energy barrier between the tertiary and secondary ions substantially exceeding the difference in stability of the product ions.

Secondary Ion Sources.—All of the paraffins containing tertiary C–H bonds thus appear readily to undergo reactions leading to the formation of cations and to participate in rapid long-term intermolecular hydride-transfer reactions with them. Hydrocarbons which are secondary ion precursors, however, generally appear to react more slowly with the same catalyst, Table III. Thus normal butane, pentane, and hexane show few spectral changes. The latter compounds undergo a slow isomerization, but *n*-butane does not form isobutane at a significant rate. It would be interesting to see if *n*-butane-1-^{13}C isomerizes to *n*-butane-2-^{13}C, but this has not been investigated in trichlorobenzene. In other systems this isomerization proceeds faster than the conversion of *n*-butane into isobutane.[4-6] The apparent reluctance of *n*-paraffins to react more readily is probably due to both the difficulty of generating a sufficiently high concentration of secondary ions and the existence of barriers to their rearrangement.

TABLE III

BEHAVIOR OF SECONDARY ION PRECURSORS

Compound	Observation
n-C_4H_{10}	Relative changes in CH_2 fine structure and the chemical shift
n-C_5H_{12}	Difficult to see a change initially. Sample is heavily isomerized to *i*-C_5H_{12} after 72 hr
n-C_6H_{14}	Spectra may be sharper initially, but after 72 hr *n*-hexane is heavily reacted
$C_yC_5H_{10}$	Little change is seen
$C_yC_6H_{12}$	Little change in initial sample. Some isomerization in 72 hr
$C_yC_7H_{14}$	Considerable isomerization to MC_yC_6 upon mixing
$C_yC_8H_{16}$	Isomerizes upon contact
Norbornane	No detectable change
Bicyclo[2.2.2]octane	Extremely reactive. An equilibrium product composition seems to be present upon contact

Cyclic compounds show more signs of reaction, particularly large-ring compounds which can undergo exothermic rearrangements to alkylcyclohexanes. Thus, while cyclopentane appears unreactive and cyclohexane slowly isomerizes to methylcyclopentane, cycloheptane and cyclooctane react and isomerize upon contact with the catalyst. Bicyclo[2.2.2]octane which also ought to generate a secondary ion capable of isomerizing to a more stable tertiary structure undergoes immediate isomerization at a rapid rate. The half-lives of the latter compounds appear to be on the order of minutes

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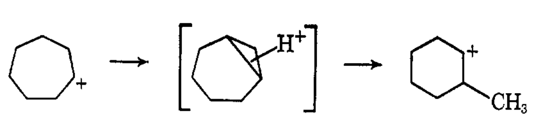
(4) D. M. Brouwer and J. M. Oelderik, *Rec. Trav. Chim. Pays-Bas*, **87**, 732 (1968).

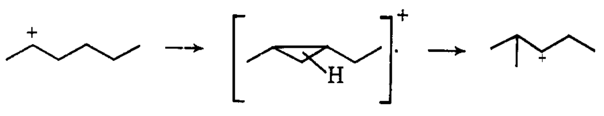
(5) J. W. Otvos, D. P. Stevenson, C. D. Wagner, and O. Beeck, *J. Chem. Phys.*, **16**, 745 (1948).

(6) M. Saunders, E. L. Hagen, and J. Rosenfeld, *J. Amer. Chem. Soc.*, **90**, 6882 (1968).

or less which suggests that hydride transfer from the naphthene to either secondary or tertiary ions is facile. It should be noted that, if the *n*-paraffins also had half-lives of this magnitude, essentially no broadening would have been detected with them.

Rearrangement of cycloheptane presumably occurs through a protonated cyclopropane intermediate or transition state without the formation of a primary ion (eq 3). A similar mechanism can be written for secondary hexyl ions but rearrangement in this case is relatively slow (eq 4). It is not clear if the apparent difference in reactivity of cycloheptane and the *n*-paraffins is due primarily to a difference in ease of ion formation or in behavior of the ion once formed.


(3)


(4)

There is no obvious reason why hydride transfer from cyclopentane to cyclopentyl ions should be any more difficult than transfer from cycloheptane to a cycloheptyl or methylcyclohexyl ion. Similarly there is no reason why *n*-butane or *n*-hexane should be reacting at much different rates than the cycloparaffins. Thus it is likely that the half-lives for all of these compounds are similar and of the order of minutes. If this is so, then the slow isomerization of *n*-butane, *n*-pentane, and *n*-hexane ought to be attributed to a relatively high activation energy for rearrangement of the secondary ion.

The behavior of secondary ion precursors may consequently be explained by assuming that (a) it is difficult to generate secondary cations whose steady-state concentration is appreciably lower than that of tertiary ions obtained from branched paraffins and that (b) branching of the secondary ion has a high energy barrier. The intermediacy of secondary ions is best seen by examining systems where rearrangement to a tertiary cation can take place easily. Such systems are found with large cycloparaffins. It is not obvious why larger barriers exist for the rearrangement of *s*-alkyl ions but the rearrangement of *n*-paraffins is generally slow. A tentative reason for this may be that the alkyl cations rearrange through the intermediacy of protonated cyclopropanes whose formation requires a relatively free cation. The cation–anion interaction in this solvent may be sufficiently strong to prevent the rearrangement unless the cation is predisposed to cyclize. Such a situation is favored where a secondary ion is generated on a naphthene since cyclization is favored by the relatively rigid framework and is subject to little steric interference by either an anion or solvent.

In summary it has been found that long-chain hydride-transfer reactions between paraffins containing tertiary C–H bonds and tertiary cations occur readily over a water-promoted aluminum bromide catalyst in 1,2,4-trichlorobenzene. The ions may undergo rapid intramolecular rearrangements which do not lead to a change in the degree of branching. Normal paraffins and naphthenes generally react more slowly, although naphthenes which can rearrange to more stable products do so easily.

Registry No.—Aluminum bromide, 7727-15-3; 1,2,4-trichlorobenzene, 120-82-1.

Anodic Oxidations. V. The Kolbe Oxidation of Phenylacetic Acid and 1-Methylcyclohexaneacetic Acid at Platinum and at Carbon

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The Kolbe oxidations of phenylacetic acid and 1-methylcyclohexaneacetic acid have been studied at both platinum and carbon anodes. At platinum, the products are derived from both free-radical and cationic intermediates, with products resulting from free radicals predominating. At a carbon anode, almost all of the products result from the generation of carbonium ions at the electrode. It is suggested that this unique ability of a carbon anode to promote the generation of carbonium ions is due to the presence within carbon of paramagnetic centers which bind the initially formed radicals, impede their desorption, and, therefore, promote a second electron transfer.

The remarkable effect on the product composition in the Kolbe reaction that results from substituting a carbon anode for the usual platinum electrode was first reported by Koehl.[1] In the case of acetate oxidation, for example, the anodic products are ethane and carbon dioxide on platinum, but almost entirely methyl acetate on carbon. The product composition in this Kolbe oxidation, as well as in others that have been studied,[1] has been rationalized by assuming that, except for special substrates where the greater stability of the carbonium ion compared with its related free radical affords driving force for a second electron transfer,[2] the predominant reaction mode on platinum is a one-electron transfer to give free-radical, product-forming intermediates. On carbon, on the other hand, the preferred reaction path appears to be a two-electron transfer at the anode to give cationic, product-forming intermediates.

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(1) W. J. Koehl, Jr., *J. Amer. Chem. Soc.*, **86**, 4686 (1964).

(2) E. J. Corey, N. L. Bauld, R. T. LaLonde, J. Casanora, Jr., and E. J. Kaiser, *ibid.*, **82**, 2645 (1960); E. J. Corey and J. Casanova, Jr., *ibid.*, **85**, 165 (1963).