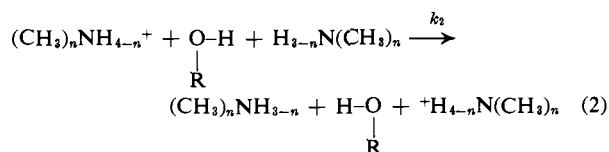analogous reaction (eq. 2) involving dissociated ions in solvents of higher dielectric constant are listed in Table II. The values of k_2 are quite nonspecific,

$$(CH_3)_nNH_{4-n}{}^+ + \underset{R}{O-H} + H_{3-n}N(CH_3)_n \xrightarrow{k_2}$$

$$(CH_3)_nNH_{3-n} + \underset{R}{H-O} + {}^+H_{4-n}N(CH_3)_n \quad (2)$$

depending only slightly on the number of methyl groups in the ammonium ion. Furthermore for trimethylammonium ion, the values in water and methanol are almost the same.

Table I. Values of k_2' for Methyl-Substituted Ammonium Salts in t-Butyl Alcohol at 35°

Cation	Anion	$k_2' \times 10^{-5}$, M^{-1} sec.$^{-1}$	$k_2(H_2O)/$ $k_2'(t\text{-BuOH})$
$(CH_3)_3NH^+$	Cl$^-$	1.1 ± 0.12	3500
	TFA^{-a}	1.8 ± 0.4	2200
	Br$^-$	5.3 ± 0.7	740
	OTs^{-b}	7.0 ± 0.7	560
$(CH_3)_2NH_2^+$	Cl$^-$	270 ± 40	38
	OTs^{-b}	310 ± 30	33
	TFA^{-a}	220 ± 20	46
$CH_3NH_3^+$	Cl$^-$	260 ± 30	23
	OTs^{-b}	240 ± 40	25

^{a} Trifluoroacetate. ^{b} p-Toluenesulfonate.

Table II. Values of k_2 for Methyl-Substituted Ammonium Ions in Water and Methanol at 35°^{a}

Cation	$k_2 \times 10^{-8}$, M^{-1} sec.$^{-1}$	Solvent	Ref.
$CH_3NH_3^+$	6.1	H_2O	2
$(CH_3)_2NH_2^+$	10.3	H_2O	3
$(CH_3)_3NH^+$	3.9	H_2O	4
$(CH_3)_3NH^+$	3.7	MeOH	5

^{a} Extrapolated from 25° using the activation energies given in ref. 3 and 4.

The values of k_2' in t-butyl alcohol are considerably smaller than those of k_2 and show a distinctive dependence on the nature of the reactant. For the mono- and dimethylammonium salts, the values are nearly identical and quite independent of the nature of the anion. For the trimethylammonium salts, the values depend strongly on the nature of the anion and are significantly smaller than those for the mono- and dimethylammonium salts.

These results can be explained adequately by the following theory. In the ion pair, one of the NH protons is hydrogen bonded to the anion; any others are hydrogen bonded to solvent molecules. An example is

$$(CH_3)_2\overset{+}{N}{-}H{-}{-}{-}{-}X^-$$
$$\underset{t\text{-BuOH}}{\overset{\displaystyle |}{\underset{\displaystyle |}{\overset{\displaystyle H}{\vphantom{|}}}}}$$
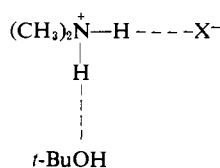
Also, an NH proton that is hydrogen bonded to an anion is considerably less reactive than one that is hydrogen bonded to a solvent molecule.

The data in Table I are consistent with this theory. For the mono- and dimethylammonium salts, the values

of k_2' are nearly identical, and the relative rates k_2'/k_2 (relative to water) are in the ratio $(1/24):(1/39)$ or 1.62. This ratio is very close to the ratio of statistical factors, $(2/3):(1/2)$, or 1.33, that would be expected if one of the NH bonds which is reactive in water becomes unreactive in t-butyl alcohol. After statistical correction, k_2'/k_2 for both the mono- and dimethylammonium salts is around $1/17$. This reduction could be due to a number of factors: the lower dielectric constant, the greater steric bulk of the t-butyl alcohol molecule, and the proximity of the anion (which could reduce the acidity of the NH protons).

For trimethylammonium salts, k_2'/k_2 is appreciably smaller than $1/17$ and depends strongly on the nature of the anion. These results indicate that the sole NH proton of the cation interacts strongly with the anion (probably through a hydrogen bond). In further support of this theory, the chemical shifts of NH vs. OH protons for the trimethylammonium salts were found to depend on the anion.

The rates of NH–OH proton exchange were measured by n.m.r. spin-echo techniques similar to those described previously.[6] These rates were measured at electrolyte concentrations between 10^{-3} and 10^{-1} M and at a number of acid–base ratios, and they followed good second-order kinetics. These results and further measurements with added common ion salts (to be reported more fully later) have convinced us that the proton exchange involves ion pairs (BH^+X^-) rather than dissociated ions (BH^+).

In conclusion, proton exchange provides a tool for probing the structure of ion pairs formed from ammonium salts. When the solvent is t-butyl alcohol and the anion is Cl$^-$, Br$^-$, OTs$^-$, or TFA$^-$, the anion appears to be hydrogen bonded to just one NH proton of the ammonium cation. Further work is in progress.

(6) E. Grunwald and E. Price, J. Am. Chem. Soc., 86, 2965 (1964).

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α-Silyl Radicals. The Peroxide-Induced Decarbonylation of Triphenylsilylacetaldehyde

Sir:

The free-radical rearrangement of phenyl in a 1,2-shift from carbon to carbon is well known in certain organic substances,[1] but no work appears extant on the analogous organosilicon systems.[2] We report here a preliminary result which demonstrates a decided difference between carbon and organosilicon compounds in this regard.
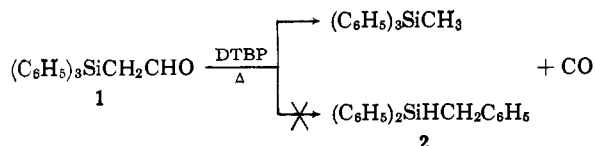
Free-radical decarbonylation of triphenylsilylacetaldehyde (1)[3,4] with di-t-butyl peroxide at 150° yielded *no* rearranged product. Methyltriphenylsilane[4] was

(1) C. Walling in "Molecular Rearrangements," Vol. 1, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, pp. 407–412.
(2) However, such rearrangements are known in ionic processes with organosilicon compounds. Cf. C. Eaborn, "Organosilicon Compounds," Academic Press Inc., New York, N. Y., 1960, pp. 434–441.
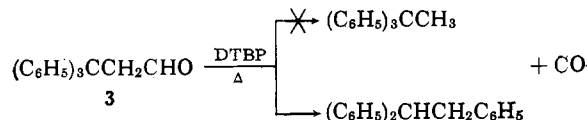(3) J. J. Eisch and J. T. Trainor, J. Org. Chem., 28, 2870 (1963).
(4) All compounds described were satisfactorily characterized by comparisons with known samples or, if new, by combustion analysis and concordant infrared and n.m.r. spectra.
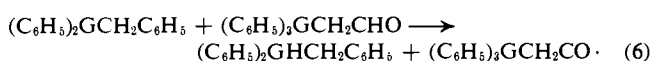
$$(C_6H_5)_3SiCH_2CHO \xrightarrow[\Delta]{DTBP} \begin{array}{c} \longrightarrow (C_6H_5)_3SiCH_3 \\ \\ \xcancel{\longrightarrow} (C_6H_5)_2SiHCH_2C_6H_5 \end{array} + CO$$
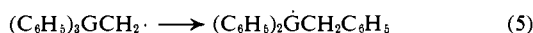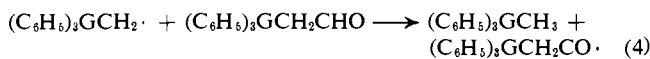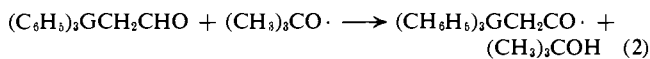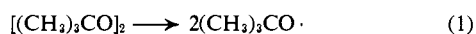
1 ... 2

formed (48%) with the evolution of carbon monoxide (52%). The heretofore unreported benzyldiphenylsilane (2),[4] a possible rearrangement product (synthesized by reaction of benzylmagnesium chloride with diphenylsilane), was not detected in the reaction product even though 2 was not destroyed under the reaction conditions used. Control studies indicated that *ca.* 5% rearrangement was detectable *via* infrared and n.m.r. spectroscopy.

Furthermore, no rearrangement of 1 was detected when decarbonylation was achieved in refluxing chlorobenzene under dilute conditions Methyltriphenylsilane again resulted (35%). No evidence was found in this reaction for silyl radical intervention *via* attack on either chlorobenzene[5] or the peroxide.

In striking contrast to the above results, decarbonylation of β,β,β-triphenylpropionaldehyde (3) with di-*t*-butyl peroxide at 140° has been shown[6] to afford essentially *completely rearranged* hydrocarbon products.

$$(C_6H_5)_3CCH_2CHO \xrightarrow[\Delta]{DTBP} \begin{array}{c} \xcancel{\longrightarrow} (C_6H_5)_3CCH_3 \\ \\ \longrightarrow (C_6H_5)_2CHCH_2C_6H_5 \end{array} + CO$$

3

On the plausible assumption that the decarbonylation reactions of 1 and 3 do not differ mechanistically, the following course for the reactions may be written.

$$[(CH_3)_3CO]_2 \longrightarrow 2(CH_3)_3CO \cdot \qquad (1)$$

$$(C_6H_5)_3GCH_2CHO + (CH_3)_3CO \cdot \longrightarrow (C_6H_5)_3GCH_2CO \cdot + (CH_3)_3COH \qquad (2)$$

$$(C_6H_5)_3GCH_2CO \cdot \longrightarrow (C_6H_5)_3GCH_2 \cdot + CO \qquad (3)$$

$$(C_6H_5)_3GCH_2 \cdot + (C_6H_5)_3GCH_2CHO \longrightarrow (C_6H_5)_3GCH_3 + (C_6H_5)_3GCH_2CO \cdot \qquad (4)$$

$$(C_6H_5)_3GCH_2 \cdot \longrightarrow (C_6H_5)_2\dot{G}CH_2C_6H_5 \qquad (5)$$

$$(C_6H_5)_2GCH_2C_6H_5 + (C_6H_5)_3GCH_2CHO \longrightarrow (C_6H_5)_2GHCH_2C_6H_5 + (C_6H_5)_3GCH_2CO \cdot \qquad (6)$$

The results indicate clearly that process 5 does not occur under the conditions studied when G is silicon. When G is carbon, process 5 not only occurs but it occurs to the virtual exclusion of process 4.[6]

Several factors may be involved in the lack of rearrangement of the triphenylsilylmethyl radical (4). A type of "back bonding"[7] of the unpaired electron on carbon through delocalization into an adjacent d-orbital of silicon could stabilize 4 and remove some of the driving force associated with the rearrangement of 3. Also, the decreased steric compression of the phenyls in 4 (because of the larger size of silicon) may be important.[8] In addition, the "push–pull" mechanism[9]

(5) J. Curtice, H. Gilman, and G. S. Hammond, *J. Am. Chem. Soc.*, 79, 4754 (1957).

(6) D. Y. Curtin and M. J. Hurwitz, *ibid.*, 74, 5381 (1952); D. Y. Curtin and J. C. Kauer, *J. Org. Chem.*, 25, 880 (1960). In the latter paper the authors report some spectral evidence for perhaps 10% unrearranged product in the hydrocarbon fraction.

(7) C. Eaborn, pp. 91–103 of ref. 2.

(8) E. S. Gould, "Mechanism and Structure in Organic Chemistry," H. Holt and Co., New York, N. Y., 1959, p. 756. Such compression

used to explain the *ionic* migration of phenyl from silicon to carbon may be needed in its radical migration also. If so, such a process is not readily achieved in decarbonylation.

Present work is aimed at determining which of these (or other) factors are really involved in the decarbonylation of 1. In addition, other organosilicon substrates (presumably) prone to radical rearrangement are being investigated.

increases rearrangement but is not necessary for it to occur. *Cf.* L. H. Slaugh, *J. Am. Chem. Soc.*, 81, 2262 (1959), and W. A. Bonner and F. D. Mango, *J. Org. Chem.*, 29, 29 (1964).

(9) A. G. Brook, K. H. Pannell, G. E. LeGrow, and J. J. Sheeto, *J. Organometal. Chem.*, 2, 493 (1964).

J. W. Wilt, O. Kolewe
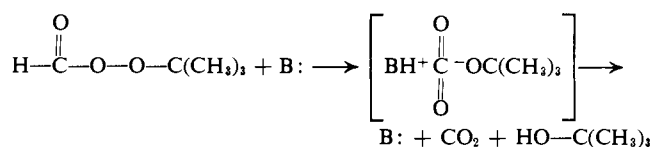Department of Chemistry, Loyola University
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Received March 24, 1965

Bimolecular Reactions in Frozen Organic Solutions[1]

Sir:

In organic solutions the base-catalyzed decomposition of *t*-butylperoxy formate (TBF) proceeds with pseudo-first-order formation of *t*-butyl alcohol and carbon dioxide.[2] This bimolecular reaction involves attack by base on the formate hydrogen with concerted development of carbon dioxide in the rate-determining step.[3]

$$H\overset{O}{\underset{\|}{C}}-O-O-C(CH_3)_3 + B: \longrightarrow \left[BH^+ \overset{O}{\underset{\underset{O}{\|}}{\overset{\|}{C}}}{}^- OC(CH_3)_3 \right] \longrightarrow$$

$$B: + CO_2 + HO-C(CH_3)_3$$

In liquid *p*-xylene at 70°, samples of a solution 0.031 M in TBF and 0.012 M in 2,6-lutidine gave an observed pseudo-first-order rate constant of 28.2×10^{-5} sec.$^{-1}$. If identical samples were first frozen at $-70°$ then held at 0° and defrosted at various times, the peroxide disappeared in the frozen samples with a first-order rate constant of 50.2×10^{-5} sec.$^{-1}$.

In frozen *p*-xylene (m.p. 13.25°) solutions, the reaction was quenched simply by defrosting the individual samples of a run. Except at high base concentrations there was little loss of peroxide at room temperature and samples were analyzed for TBF as previously described.[2] Comparisons of frozen samples with identical, but unfrozen (*i.e.*, supercooled), samples held at the temperature of the run also double-checked that loss of TBF occurred only in frozen samples. The 2,6-lutidine-catalyzed pseudo-first-order decomposition of TBF occurs at 0° and with accelerated rates in frozen dioxane, benzene, nitrobenzene, *p*-chlorotoluene, and diphenylmethane solutions.

Reactions catalyzed by pyridine and by 2,6-lutidine in *p*-xylene have been extensively investigated and show the following features as illustrated by the data in Table I. (A) All runs gave good straight plots of log

(2) R. E. Pincock, *J. Am. Chem. Soc.*, 86, 1820 (1964).

(3) R. E. Pincock, *ibid.*, 87, 1274 (1965).