Table I. Reaction Parameters of Gas-Phase 1,3-Silyl Rearrangements

Substrate	Silane	Temp range, C°	C_e %[a]	E_a, kcal/mol[b]	Log A	$\Delta S^{\ddagger}$, eu[c]	Product, % cis	Compd, % trans
Trimethyl-α-methylallyl	**1**	506–567	5.4	47.7 ± 0.3	12.3$_2$ ± 0.07	−6.2 ± 0.3	64	36
Dimethylphenyl-α-methylallyl	**2**	500–572	5.5	47.2 ± 0.2	12.1$_9$ ± 0.06	−6.8 ± 0.3	60	40
Dimethylphenyl-α,β-dimethylallyl	**3**	516–577	5.3	47.7 ± 0.3	12.2$_6$ ± 0.07	−6.6 ± 0.3	50	50
Trimethyl-α-phenylallyl	**4**	420–480	1.9	42.5 ± 0.2	11.9$_7$ ± 0.07	−7.4 ± 0.3	41	59

[a] Per cent unrearranged starting material at equilibrium, the specific rate constant for disappearance of starting material being calculated; $k = -\log [(C - C_e)/(C_0 - C_e)]/t$. [b] E_a was calculated by linear regression analysis of the plot of log k *vs.* $10^3/T$. A minimum of 20 experimental determinations of k was encompassed in this analysis. [c] The entropy of activation at 500° (calculated in the usual way from E_a and log A).

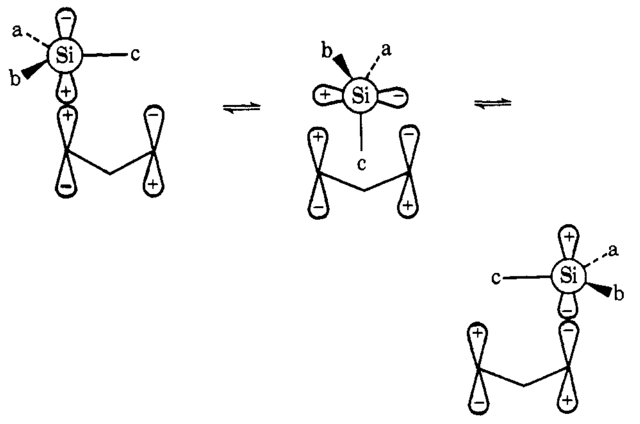
tion was unimolecular up to (at least) 90% rearrangement. Analysis of the rate data yielded E_a = 47.7 kcal/mol and $\Delta S^{\ddagger} = -6.2$ eu at 500° (see Table I). The negative activation entropy suggested a cyclic concerted transition state, as opposed to a radical dissociation mechanism previously[4] considered for other thermolysis reactions of the allylsilanes. Furthermore, the absence of cross-products,[1] when two differently substituted allylic silanes were cothermolyzed, provides additional support for the intramolecular process of rearrangement. It is also to be noted that the activation energy determined is considerably below the bond dissociation energy of Si–C even allowing for allylic stabilization of the carbon radical.

A series (**2–4**) of substituted allylic silanes was prepared and subjected to kinetic studies in an effort to distinguish between the various mechanistic courses by which the rearrangement could occur. The results summarized in Table I provide convincing evidence for a symmetrical transition state of sigmatropic migration of silicon. Thus, substitution of a phenyl for methyl on the silicon has no appreciable effect on the activation parameters. A homolytic or heterolytic mechanism of rearrangement would demand a very considerable response of rate to such a wide variation in the nature of substituents bonded to the migrating atom. Moreover, the formation of an intermediate of the type suggested by the results obtained in thermal rearrangement of allylic sulfides[1] is also ruled out. The complete lack of charge or radical development on silicon during the course of rearrangement, such as has been identified in the sulfur rearrangement process,[1] is also confirmed by the total absence (see Table I) of any rate or activation effects resulting from substitution of methyl at the β carbon (in **3**).

The only substituent influences on the rates and activation parameters (to be perceived in the reaction series studied) are those anticipated on the basis of prior results and considerations in well-established concerted rearrangement processes.[7] Thus, in the absence of significant steric factors, in cases where substitution results in a large degree of stabilization of the product relative to the reactant, the symmetrical transition state reflects this factor in a lowering of E_a without influencing the sign or magnitude of $\Delta S^{\ddagger}$, while shifting the equilibrium composition in favor of the product. This effect is clearly a rate-controlling factor in the case of **4**, the α-phenylallyltrimethylsilane rearrangement to the γ isomer. Here conjugation of the aromatic ring with the allylic double bond has decreased E_a by more than 5 kcal, with very little change in $\Delta S^{\ddagger}$, while the amount of unrearranged (α) isomer at equilibrium has declined to less than 2%.

A final point for comment is related to the observed cis/trans product ratios. Since the silyl group can migrate either above or below the plane of the allyl framework (in the HOMO) one might have expected a 50:50 cis–trans mixture of γ isomers. Reference to Table I indicates that although the product compositions in all instances studied are not far from 50:50, conformational factors arising from eclipsing and other nonbonded interactions in the transition states can result in some preference for forming one of the alternative configurations of the product.

On the basis of orbital symmetry considerations, a suprafacial 1,3 sigmatropic rearrangement involving an antisymmetric 3p silicon orbital is expected to occur with inversion of configuration (as illustrated below).



Experiments to test this hypothesis have been initiated. These results will be discussed together with the full details of the current work in a future article.

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(7) H. M. Frey and R. Walsh, *Chem. Rev.*, **69**, 103 (1969).

Acyl and Alkyl Tetracarbonylferrate(0) Complexes as Intermediates in the Synthesis of Aldehydes and Ketones

Sir:

Disodium tetracarbonylferrate(−II) is an inexpensive, selective reagent for the high yield conversion of aliphatic halides and tosylates into aldehydes and unsymmetrical ketones.[1,2] Earlier we proposed that alkyl and

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(1) M. P. Cooke, *J. Amer. Chem. Soc.*, **92**, 6080 (1970).

(2) J. P. Collman, S. R. Winter, and D. R. Clark, *ibid.*, submitted for publication.

Table I. Yield and Infrared Data for Acyltetracarbonylferrate Salts

Compound	Route a	Route b	Route c	Terminal ν_{CO}, cm^{-1}	Acyl ν_{CO}, cm^{-1}
[$CH_3C(=O)Fe(CO)_4$] $(Ph_3P)_2N$	81	35	20	1998 (m), 1890 (m, sh), 1870 (vs)	1592 (w-m)
[n-$C_4H_9C(=O)Fe(CO)_4$] $(Ph_3P)_2N$	81	31	46	2000 (m), 1902 (m, sh), 1878 (s), 1861 (s)	1590 (w)
[$CH_3CH_2C(=O)Fe(CO)_4$] $(Ph_3P)_2N$		76	72	2005 (m), 1905 (s), 1887 (vs), 1870 (vs)	1612 (w-m)
[$PhCH_2C(=O)Fe(CO)_4$] $(Ph_3P)_2N$		68		2010 (m), 1915 (m-s), 1893 (vs), 1868 (s)	1610 (m)
[$PhC(=O)Fe(CO)_4$] $(Ph_3P)_2N$		37		2000 (m), 1915 (sh), 1897 (vs), 1872 (s)	1565 (w-m)
[$CH_2=CHC(=O)Fe(CO)_4$] $(Ph_3P)_2N$	81	39		2002 (m), 1908 (s), 1885 (s), 1870 (s)	1560 (w)

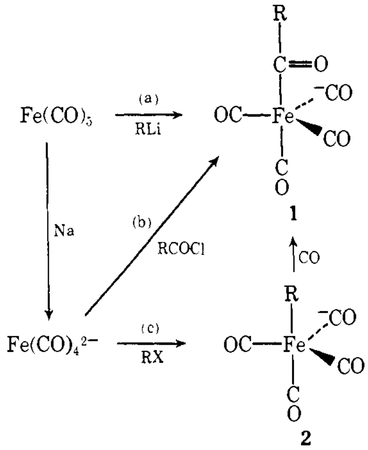
Table II. Yield and Infrared Data for Alkyltetracarbonylferrate Salts

Compound	Yield, %	Terminal CO ν_{CO}, cm^{-1}
[$PhCH_2CH_2Fe(CO)_4$] $(Ph_3P)_2N$	61	1987 (w-m), 1882 (sh), 1863 (vs)
[$PhCH_2Fe(CO)_4$] $(Ph_3P)_2N$	58	1998 (m), 1884 (s), 1860 (s)
[$CH_3CH_2Fe(CO)_4$] $(Ph_3P)_2N$	54	1988 (m), 1880 (s), 1855 (s)
[$NCCH_2Fe(CO)_4$] $(Ph_3P)_2N$	67	2010 (m), 1892 (vs), 1879 (s), ν_{CN} 2193 (w-m)
[$C_2H_5OC(O)CH_2Fe(CO)_4$] $(Ph_3P)_2N$	61	2000 (m), 1902 (s), 1878 (vs), ν_{CO_2Et} 1670 (m)
[$CH_3OCH_2Fe(CO)_4$] $(Ph_3P)_2N$	71	1994 (w-m), 1874 (vs), 1860 (s)

acyl tetracarbonylferrate(0) complexes are intermediates in these reactions. The isolation, characterization, and reactions of these alkyl and acyl carbonyl anions are described herein.

The acyl anions were prepared by three methods, a, b, and c (Scheme I). In method a addition of organolithium reagents to a terminal carbonyl on coordinatively saturated $Fe(CO)_5$ affords the highest yields of isolated acyl anion salts, but this method is less useful for organic synthesis since the strongly basic alkyllithium reagents will not tolerate most unmasked functional groups. Fischer previously employed method a to isolate tetraalkylammonium salts of the acetyl and benzoyl complexes.[3] As the counterion we have used the bis(triphenylphosphine)iminium cation. Ruff previously noted that this cation forms crystalline salts which are kinetically resistent to autoxidation with otherwise air-sensitive anions.[4] Method b involves reaction between acid chlorides and $Na_2Fe(CO)_4$. In method c alkyl bromides are treated with $Na_2Fe(CO)_4$ in the presence of CO. Method c, which is synthetically the most significant procedure, can be viewed as either an SN2 displacement at carbon or as an oxidative addition at iron.[5]

Scheme I



Examples of acyl tetracarbonylferrate(0) complexes prepared by methods a, b, and c are collected in Table I. The infrared spectra of these acyl salts are consistent with C_{3v} symmetry expected for trigonal-bipyramidal coordination about iron(0) with the bulkier acyl group occupying an apical position, **1**. Selection rules predict three ν_{CO} bands ($E + 2A_1$) and the highest frequency band is best attributed to the A_1 mode of the symmetric equatorial stretch.[6] In most cases the lowest ν_{CO} band is split in the solid state, but in solution a single band is observed in this frequency range. The low, 1550–1620 cm^{-1}, position of the acyl C–O stretch reflects the high electron drift into this group through backbonding. This suggests that the acyl oxygen should be basic and this is confirmed by Fischer's alkylation of this oxygen using the *hard* alkylating agent, triethyloxonium fluoroborate, to form a stable carbene complex.[7]

We have isolated the first examples of alkyltetracarbonylferrate(0) salts from the reaction of $Na_2[Fe(CO)_4]$ with alkyl bromides followed by treatment with bis(triphenylphosphine)iminium chloride (Table II).[8] The three ν_{CO} bands are again consistent with the expected C_{3v} symmetry, **2**, but the center of the ν_{CO} absorptions is shifted to lower frequency compared with the analogous acyl complexes as expected from the greater electron density on iron in the alkyl anions **2**. This is reflected in the greater nucleophilicity of the alkyl iron complexes.[2] The highly basic alkyl salts, **2**, are also more sensitive toward aerial oxidation except when electron-withdrawing groups are adjacent to the carbon–iron bond. The isolation of alkyl iron derivatives which contain organic functional groups such as $-CN$ and $-CO_2C_2H_5$ is remarkable and augurs well for

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(3) (a) E. O. Fischer, V. Keiner, and R. D. Fischer, *J. Organometal. Chem.*, **16**, P60 (1969); (b) E. O. Fischer and V. Keiner, *ibid.*, **23**, 215 (1970).

(4) *Cf.* J. K. Ruff, *Inorg. Chem.*, **7**, 1818 (1968); we thank Professor Ruff for a preprint of his synthesis of bis(triphenylphosphine)iminium chloride.

(5) J. P. Collman, *Accounts Chem. Res.*, **1**, 136 (1968).

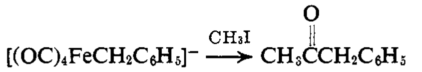
(6) D. M. Adams, "Metal-Ligand and Related Vibrations," St. Martin's Press, New York, N. Y., 1968, p 109.

(7) E. O. Fischer and C. G. Kreiter, private communication.

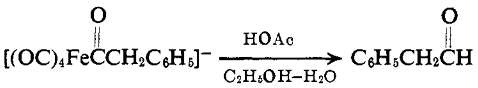
(8) Conversion of alkyl to acyl anions (under 1 atm of CO) goes to completion for simple alkyls but for benzyl or alkyls with electron-withdrawing substituents adjacent to the carbon–iron bond an equilibrium results which can be reached from either end.

the utilization of these reagents in selective organic reactions.

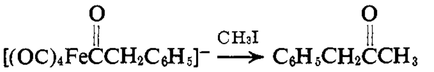
The isolation of these acyl and alkyl anions permitted us to demonstrate their role as intermediates in aldehyde and ketone syntheses, eq 1–3.[9]



$$[(OC)_4FeCH_2C_6H_5]^- \xrightarrow{CH_3I} CH_3\overset{O}{\overset{\|}{C}}CH_2C_6H_5 \quad (1)$$



$$[(OC)_4Fe\overset{O}{\overset{\|}{C}}CH_2C_6H_5]^- \xrightarrow[C_2H_5OH-H_2O]{HOAc} C_6H_5CH_2\overset{O}{\overset{\|}{C}}H \quad (2)$$



$$[(OC)_4Fe\overset{O}{\overset{\|}{C}}CH_2C_6H_5]^- \xrightarrow{CH_3I} C_6H_5CH_2\overset{O}{\overset{\|}{C}}CH_3 \quad (3)$$

Acknowledgment. This work was supported by the National Science Foundation (Grant No. GP20273X). We are also indebted to D. Clark, R. G. Komoto, and S. R. Winter for assistance.

[9] The products were identified by their infrared spectra and 2,4-DNP derivatives. Yields from reactions 1, 2, and 3 were 75, 86, and 73%, respectively.

[10] National Institutes of Health Postdoctoral Fellow.

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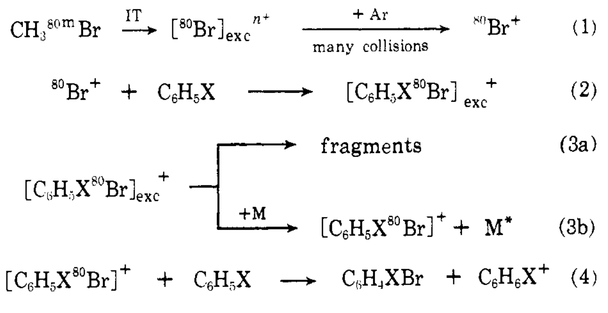
Gas-Phase Aromatic Substitutions by Brominium Ions from the Isomeric Transition of ^{80m}Br

Sir:

The use of labeled, gaseous ions, such as HeT^+ and R^+, resulting from the nuclear decay of suitable tritiated precursors provides a unique tool for the study of electrophilic reactions in gaseous systems at atmospheric pressure,[1–4] and seems to fill to a certain extent the gap between solution chemistry and mass spectrometric methods.

We have now extended the scope of the research to another electrophile, the gaseous brominium ion, which can be conveniently obtained *via* the isomeric transition (IT) of ^{80m}Br (T = 4.4 hr). The chemical consequences of the IT of ^{80m}Br are unusually well known, and represent a typical example of the nuclear phenomena, which can be broadly described as "inner shell ionization."[5] In particular, the IT of ^{80m}Br contained in molecules such as CH_3Br is known to cause their instantaneous Coulomb explosion, giving rise to ^{80}Br ions with a preferred charge of +7.[6] When the decay occurs in a sufficiently large excess of a rare gas, having an ionization potential (IP) intermediate between the first and the second IP of Br, the charge of the daughter ions can be rapidly reduced to unity by charge-exchange processes,[7] while the excess kinetic energy (some electron volts) resulting from the explosion is taken away by unreactive collisions. The thermal $^{80}Br^+$ ion eventually obtained represents a valuable gaseous electrophile, whose products can be easily traced due to their radioactivity.

This communication presents the preliminary results of a study on gas-phase bromination of benzene, toluene, and the halobenzenes by brominium ions, resulting from the IT of ^{80m}Br in $CH_3{}^{80m}Br$. The methyl bromide was prepared by neutron activation of CH_3Br,[8] purified by preparative glc, and allowed to decay in a gaseous system containing typically 95 mol % Ar, 2.5 mol % of the substrate, and 2.5 mol % of the $CH_3{}^{80m}Br$. After a reaction time of about 30 min, the products were rapidly separated with a 4-m Igepal CO-880 column at 120–150°, using a discontinuous radio gas chromatographic technique.[8,9] The yields of the products, *i.e.*, the ratio of their activity to the activity of the ^{80}Br daughter ions formed during the reaction, were calculated from the known initial activity of the $CH_3{}^{80m}Br$, the half-life of ^{80m}Br, and the reaction time, suitable corrections being allowed for the decay of the 17.6-min ^{80}Br. Half-life and γ-spectrometric measurements confirmed that the products were free from isotopic impurities, *e.g.*, ^{82}Br and the parent ^{80m}Br, indicating that their formation occurred exclusively *via* the daughter ions from IT. The isomeric distribution given in Table I was insensitive to the addition of radical (I_2, Br_2) and electron (SF_6) scavengers, providing evidence against a contribution from thermal Br atoms and radiolytic processes. In addition to the substitution products, $C_6H_5{}^{80}Br$ was also formed from all the substrates, its yields increasing in the order $C_6H_5F < C_6H_5CH_3 < C_6H_5Cl$ (*cf.* footnote *a* of Table I) and decreasing at the highest concentrations of the moderator. However, in contrast to homolytic substitution by hot halogen atoms,[9–11] the yields from halogen for hydrogen substitution are generally higher than those from halogen for halogen substitution. Competition experiments gave an apparent $k_{toluene}/k_{benzene}$ value[12] of about 2, while the reactivity ratio of the halobenzenes was close to unity.[13] The following reaction scheme is suggested for the formation of the aromatic products.[14]



$$CH_3{}^{80m}Br \xrightarrow{IT} [^{80}Br]_{exc}{}^{n+} \xrightarrow[\text{many collisions}]{+Ar} {}^{80}Br^+ \quad (1)$$

$$^{80}Br^+ + C_6H_5X \longrightarrow [C_6H_5X^{80}Br]_{exc}{}^+ \quad (2)$$

$$[C_6H_5X^{80}Br]_{exc}{}^+ \longrightarrow \text{fragments} \quad (3a)$$

$$[C_6H_5X^{80}Br]_{exc}{}^+ \xrightarrow{+M} [C_6H_5X^{80}Br]^+ + M^* \quad (3b)$$

$$[C_6H_5X^{80}Br]^+ + C_6H_5X \longrightarrow C_6H_4XBr + C_6H_6X^+ \quad (4)$$

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[1] For a review, *cf.* F. Cacace, *Advan. Phys. Org. Chem.*, **8**, 79 (1970).

[2] F. Cacace and S. Caronna, *J. Amer. Chem. Soc.*, **89**, 6848 (1967).

[3] F. Cacace and G. Perez, *J. Chem. Soc. B*, 2086 (1971).

[4] F. Cacace, R. Cipollini, and G. Ciranni, *ibid.*, 2089 (1971).

[5] For a review, *cf.* S. Wexler, *Actions Chim. Biol. Radiat.*, **8**, 107 (1965).

[6] S. Wexler and G. R. Anderson, *J. Chem. Phys.*, **33**, 850 (1960).

[7] In addition to compelling theoretical considerations, preliminary mass spectrometric data indicate that the charge of the $^{80}Br^+$ ions from the decay of $CCl_3{}^{80m}Br$ is effectively reduced to unity by the addition of Ar or Ne. No stable adduct could be formed from the reaction of multiply charged brominium ions with the substrate.

[8] For a review, *cf.* G. Stöcklin, "Chemie heisser Atome," Verlag Chemie, Weinheim, 1969.

[9] G. Stöcklin and W. Tornau, *Radiochim. Acta*, **6**, 86 (1966).

[10] G. Stöcklin and W. Tornau, *ibid.*, **9**, 25 (1968).

[11] K. Berei and G. Stöcklin, *ibid.*, **15**, 39 (1971).

[12] The toluene reactivity includes the contribution of the side chain (*cf.* Table I).

[13] Accurate data would require the knowledge of all the decomposition products, resulting from the fragmentation of the excited arenonium ions.

[14] A contribution from long-lived, excited states of the brominium ion cannot be completely ruled out.