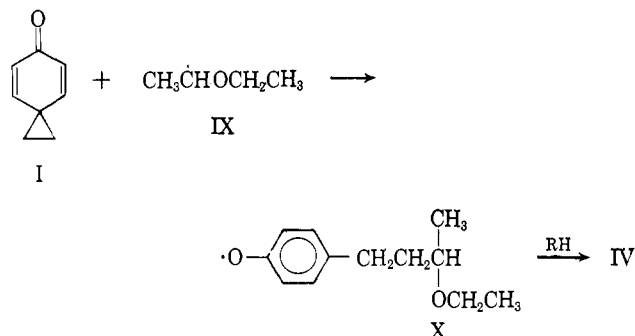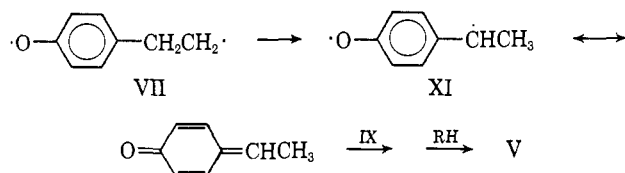the relatively stable radicals VIII and IX. Products II and III are generated by hydrogen abstraction and coupling of VIII and IX. While coupling of VII and IX, possibly after hydrogen abstraction by oxygen of VII, would ultimately give IV, this product could arise by a radical displacement on I (ground state) by IX, followed by hydrogen abstraction.[11] Formation of

V is formally a rearrangement reaction. The vibrational excitation of VII and the driving force for formation of XI may be sufficiently great that rearrange-

ment by 1,2-hydrogen migration occurs to an extent unexpected by analogy with the β-phenylethyl radical[13] or other model radical systems.[14] Coupling of XI and IX would then lead to V. Alternatively, hydrogen abstraction from the benzylic carbon of p-ethylphenol (II) gives a radical which would give V by coupling with IX.[15] Finally, isolation and preliminary characterization of some dimers and polymers give results in accord with this scheme.

Since the reactions which ensue on photolysis of I are due to n → π* excitation of a chromophore which is formally analogous to that of santonin, 4,4-diphenylcyclohexadienone, and other 2,5-cyclohexadienones, it is tempting to interpret our results as evidence for the formation of diradicals as primary intermediates on n → π* excitation of all such dienones, and that differences in the photochemistry arise in subsequent steps. However, it is possible that our results are quite irrelevant with respect to these other systems. Current experiments will hopefully resolve the points at issue.[16]

(11) Radical displacements, while rare, are known in cyclopropane chemistry.[12] This would be the first case of a carbon–carbon radical displacement reaction.

(12) D. E. Applequist, G. F. Fanta, and B. W. Henrikson, J. Am. Chem. Soc., 82, 2368 (1960).

(13) L. H. Slaugh, ibid., 81, 2262 (1959).

(14) C. Walling in ref. 10b, pp. 416–423.

(15) Recent incomplete studies on the ratio of IV to V as a function of concentration of I make it appear more likely that both products are derived from a common intermediate (such as VII) via reactions in a solvent cage.

(16) This work was supported in part by a grant from the Army Research Office (Durham).

(17) National Institutes of Health Predoctoral Fellow, 1963–1964.

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A 1,4-Chlorine Shift and an Estimate of the Rate Enhancement Owing to Chlorine Participation in the Addition of Trifluoroacetic Acid to 5-Chloro-1-hexene

Sir:

We have found that reaction of 5-chloro-1-hexene-5-d, 1, with trifluoroacetic acid gives 5-chloro-2-hexyl-2-d trifluoroacetate, 2, the product of a 1,4-chlorine shift, which may arise via a cyclic chloronium ion intermediate, as shown in eq. 1. Based on n.m.r. analysis
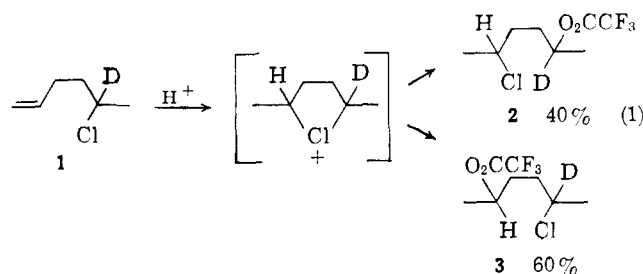
of the distilled products obtained in 52% yield from 1.48 g. of 1, 60% of "normal addition product," 3, is formed, along with 40% of 2. The corresponding reaction products from the nondeuterated chloride, 5-chloro-1-hexene, were identified as the expected diastereomeric 5-chloro-2-hexyl trifluoroacetates by elementary analysis,[1] infrared analysis, gas chromatography (two peaks attributable to diastereomers: 20-ft. Dow–Corning 550 silicone column, 100°), and n.m.r. analysis at 60 Mc. (CH₃CHCl, methyl doublet at δ 1.50 and poorly resolved sextuplet at δ 4.00; CH₃CHO₂CCF₃, methyl doublet at δ 1.33 and unresolved multiplet at δ 5.08, in the pure liquid containing a trace of tetramethylsilane). The n.m.r. spectra of the deuterated reaction products showed, in addition to methyl doublets of reduced intensity, broadened single peaks approximately in the middle of the doublets, attributable to the groups CH₃CDCl and CH₃CDO₂-CCF₃, in which the H–D coupling constant is small. The per cent of chlorine shift was calculated from the ratios of the areas of the doublet and "unsplit" peaks in each methyl region. Both measured ratios were within 2% of the value reported above, and these values could be approximately confirmed by integration of the low-field region of the spectrum.

A second series of experiments has enabled us to estimate the rate acceleration associated with chlorine participation in the addition of trifluoroacetic acid to 5-chloro-1-alkenes, and to show that the above-mentioned product distribution (eq. 1) may be the result of a competition between ordinary Markonikov addition and addition proceeding via a cyclic chloronium ion, which has a 50% probability of opening at C-2 or C-5 if secondary isotope effects are negligible. The reactivity of a series of ω-chloro-1-alkenes was determined (Table I) and the rate data was plotted (Fig. 1) in a form previously shown to give a straight line when the inductive rate depression falls off by a constant factor per methylene group.[2]

(1) Anal. Calcd. for C₈H₁₂ClF₃O₂: C, 41.30; H, 5.19. Found: C, 41.28; H, 5.17.

(2) (a) P. E. Peterson and C. Casey, Tetrahedron Letters, 1569 (1963). (b) In Fig. 1, Δ log k is the difference in the logarithms of the rate constants for the ω-chloro-1-alkenes and the corresponding unsubstituted alkenes. Reasonable values for errors in Δ log k, as indicated in Fig. 1, were calculated by assuming that ±5% error might be present in each rate constant.
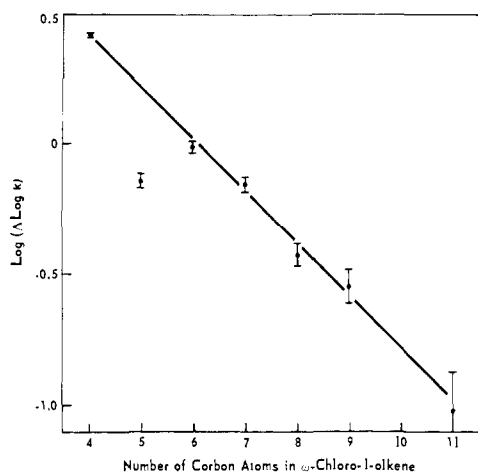
Fig. 1.—Plot of the rate data based on the assumption that the substituent effect changes by a constant factor per methylene group.

Based on the marked deviation of the point for 5-chloro-1-pentene from the line defined by the other rate constants, the rate of reaction of 5-chloro-1-pentene may be calculated to be seven to ten times faster than expected in the absence of chlorine participation. Since terminal and nonterminal substituents show similar rate effects,[2a,3] the per cent of 1,4-chlorine shift expected for the reaction shown in eq. 1 is 43–45.[4] The agreement with the value found, 40%, is fair.

TABLE I

RATES OF ADDITION OF TRIFLUOROACETIC ACID TO ω-CHLORO-1-ALKENES AT 60.0°[a]

Alkene	$k \times 10^6$ sec.$^{-1}$, 60°
4-Chloro-1-butene	2.85[b]
5-Chloro-1-pentene	217[c]
6-Chloro-1-hexene	160
7-Chloro-1-heptene	308
8-Chloro-1-octene	708
9-Chloro-1-nonene	868
11-Chloro-1-undecene	1283

[a] 0.125 M sodium trifluoroacetate was present to neutralize adventitious traces of strong acid. Alkene concentrations were 0.1 or 0.03 M. [b] Determined by Mr. G Thompson. [c] From ref. 3.

Previously a 1,4-chlorine shift was found in addition of trifluoroacetic acid to 5-chloro-1-pentyne[5] but not in addition of trifluoroacetic acid to 5-chloro-1-pentene. The present demonstration of a 1,4-chlorine shift in an alkene addition supports previous postulates[3,5] concerning the importance of cyclic halonium ion intermediates in alkene additions and demonstrates that halogen shifts are not a special feature associated with the possible intermediacy of vinyl cations in the reaction of alkynes.

(3) P. E. Peterson and G. Allen, *J. Am. Chem. Soc.*, **85**, 3608 (1963).

(4) Following the usual treatment for estimating anchimeric assistance, and using the averaged value, (7 + 10)/2 = 8.5, ($k_{\text{unassisted}}$ + k_{assisted}) $k_{\text{unassisted}}$ = 8.5. The fraction of assisted reaction presumed to proceed via a chloronium ion is k_{assisted}/k_{total} = 7.5/8.5 = 0.88. The per cent of chlorine shift is 50% × 0.88 = 44%.

(5) P. E. Peterson and J. E. Duddey, *J. Am. Chem. Soc.*, **85**, 2865 (1963).

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The Signs of Si^{29}–H^1 and Si^{29}–F^{19} Coupling Constants[1]

Sir:

Although it is well established theoretically[2] and experimentally[3] that the signs of directly bonded X–H[1] coupling constants are positive (with the exception of H–F), it is less certain that directly bonded X–Y coupling constants follow the same pattern. Recent MO calculations by Pople and Santry[2a] indicate that the X–Y coupling constants for first-row elements are likely to be negative if one of the nucleii is F^{19} and positive in all other cases in agreement with the limited experimental data available at present.[4]

In this communication we wish to report the signs for directly bonded Si^{29}–H^1 and Si^{29}–F^{19} coupling constants. These have been determined by carrying out {Si^{29}}H^1 field-sweep double resonance experiments on (CH$_3$)$_2$-SiHCl and (CH$_3$)$_3$SiF molecules, respectively. The procedure followed can be illustrated by considering the case of (CH$_3$)$_3$SiF in some detail. The proton spectrum for this compound, measured with a Varian DP-60 spectrometer, consists of a doublet centered at τ 9.80 ± 0.01, with $J_{\text{H}^1-\text{C}-\text{Si}-\text{F}^{19}}$ = 7.51 ± 0.05 c.p.s. Superimposed about the midpoints of the main proton signals are Si^{29} satellite doublets[5] with $J_{\text{H}^1-\text{C}-\text{Si}^{29}}$ = 7.09 ± 0.05 c.p.s. Although the Si^{29} spectrum was not recorded, the first-order spectrum would consist of two sets of decets ($J_{\text{H}^1-\text{C}-\text{Si}^{29}}$ = 7.09 c.p.s.) separated by $J_{\text{Si}^{29}-\text{F}^{19}}$ between their midpoints.

The Si^{29} radiofrequency field was applied at 11.215 Mc./sec. with a Rohde and Schwarz Type XUA frequency synthesizer, and frequencies were monitored with a Rohde and Schwarz Type FKM counter. The Si^{29} frequency was varied in small increments (5–10 c.p.s.), while repeatedly scanning the proton spectrum until the correct decoupling frequency was obtained. Since $J_{\text{Si}^{29}-\text{F}^{19}}$ >> $J_{\text{Si}^{29}-\text{C}-\text{H}^1}$, it is possible to irradiate near the frequency of one set of Si^{29} multiplets without perturbing transitions of the other set. The relative signs of $J_{\text{Si}^{29}-\text{F}^{19}}$ and $J_{\text{H}^1-\text{C}-\text{Si}-\text{F}^{19}}$ can therefore be determined by irradiating one of the Si^{29} multiplets and observing which pair of satellite lines collapses. For (CH$_3$)$_3$SiF, irradiation at the *lowest* Si^{29} frequency collapsed the *low-field* satellite, increasing the Si^{29} frequency by 280 c.p.s.; *i.e.*, $J_{\text{Si}^{29}-\text{F}^{19}}$ led to a collapse of the high-field satellite. Thus $J_{\text{Si}^{29}-\text{F}^{19}}$ and $J_{\text{H}^1-\text{C}-\text{Si}-\text{F}^{19}}$ have the same sign (note, γ for Si^{29} is negative). Since it is likely that the vicinal H^1–F^{19} coupling constant is positive,[6] it can be concluded that $J_{\text{Si}^{29}-\text{F}^{19}}$ is also positive. However, because of the negative magnetogyric ratio of Si^{29}, the reduced coupling constant[2a] given by $K = (2\pi/$

(1) This work was carried out while the author was a guest worker at the National Physical Laboratory, Basic Physics Division, Teddington, England.

(2) (a) J. A. Pople and D. P. Santry, *Mol. Phys.*, **8**, 1 (1964); (b) M. Karplus and D. M. Grant, *Proc. Natl. Acad. Sci. U. S.*, **48**, 1269 (1959); (c) M. Karplus, *J. Am. Chem. Soc.*, **84**, 2458 (1962); (d) N. Muller, *J. Chem. Phys.*, **36**, 359 (1962).

(3) (a) P. C. Lauterbur and R. J. Kurland, *J. Am. Chem. Soc.*, **84**, 3406 (1962); (b) F. A. L. Anet, *ibid.*, **84**, 3767 (1962); (c) S. L. Manatt, G. L. Juvinall, and D. D. Elleman, *ibid.*, **85**, 2664 (1963).

(4) (a) G. V. D. Tiers, *ibid.*, **84**, 3972 (1962); (b) J. H. Noggle, J. D. Baldeschwieler, and C. B. Colburn, *J. Chem. Phys.*, **37**, 182 (1962); (c) K. Brei and H. J. Bernstein, *ibid.*, **38**, 1216 (1963).

(5) Si^{29} natural abundance, 4.7%; $I = \frac{1}{2}$; $\mu = -0.55477$ nuclear magnetons.

(6) D. P. Evans, S. L. Manatt, and D. D. Elleman, *J. Am. Chem. Soc.*, **85**, 238 (1963).