

known liquid volume. When the trap had filled with liquid nitrosyl chloride (d^{-12} , 1.417) to a predetermined level, the contents were transferred under nitrogen to the olefin-solvent mixture which had been precooled to approximately -40° . The condensing trap was rinsed with cold solvent (-40°) to transfer all the nitrosyl chloride to the reaction flask. The reaction flask, equipped with a mechanical stirrer, a thermometer, and a condenser with drying tube, was allowed to come to the desired reaction temperature and was maintained at this temperature, with vigorous stirring, by adjustment of the Dry Ice-isopropyl alcohol bath. The cooling bath is necessary since in most cases the reaction is exothermic and a large heat capacity reservoir is needed to adequately control the temperature.

Addition of Nitrosyl Chloride to Cyclohexene. A. In Sulfur Dioxide at -30° .—A mixture of 10.15 ml (0.1 mol) of cyclohexene and 50 ml of sulfur dioxide was cooled to -40° and 4.62 ml (0.1 mol) of nitrosyl chloride was added by the general addition procedure. The mixture was stirred at -30° for 3 hr and then filtered to yield 12.55 g (85%) of slightly green solid, which was washed immediately with cold methanol to give a white solid: mp $139-144^\circ$; uv max (95% EtOH), 280.5 μ . Recrystallization from absolute EtOH gave a white solid (1): mp $152-153^\circ$ (lit.⁷ mp $152-153^\circ$); uv max (95% EtOH), 294.5 μ (ϵ 8000); nmr (CDCl_3), δ 1.85 (complex multiplet, 8 H), 4.27 (m, 1 H, CHCl), and 5.43 (m, 1 H, $\text{CH}-\text{N}=\text{N}$).

Anal. Calcd for $\text{C}_{12}\text{H}_{20}\text{Cl}_2\text{N}_2\text{O}_2$: C, 48.85; H, 6.78; Cl, 24.03; N, 9.50. Found: C, 48.90; H, 7.03; Cl, 23.72; N, 9.62.

B. In Carbon Tetrachloride at 20° .—A slight modification of the general method of addition of nitrosyl chloride was necessary in this case. The trap containing the condensed nitrosyl chloride was connected to the reaction flask by means of an addition tube extending below the surface of the reaction mixture, and the nitrosyl chloride was allowed to evaporate into the rapidly stirred reaction mixture at a rate so as to keep the temperature below 20° . After 45 min, the small amount of solid 1 (approximately 1.0 g) which had collected at the top of the solution was filtered, and the filtrate was concentrated to half its volume on a rotary evaporator. Gas chromatographic separation and infrared analysis showed the major components of the liquid mixture to be 1,2-dichloro-1-nitrosocyclohexane, 1-nitro-2-chlorocyclohexane, and 2-chlorocyclohexanone, with some 1,2-dichlorocyclohexane and two other minor unidentified components present.

C. In Carbon Tetrachloride at -30° .—Nitrosyl chloride (0.1 mol) was added by the general addition procedure to a solution of 0.1 mol of cyclohexene in 50 ml of carbon tetrachloride which had been precooled to -40° . The mixture was then brought to -30° and stirred vigorously for 5 hr, after which the light green paste was filtered and washed with cold carbon tetrachloride to give 4.43 g (30%) of a white solid: mp $136-144^\circ$; uv max 280.5 (95% EtOH). Recrystallization of this material from ethanol gave a solid, mp $142-145^\circ$, which exhibited infrared absorption (KBr) at 1193, 1227, and 1216 cm^{-1} (*trans*-nitroso dimer) and at 1555 cm^{-1} (nitro). Nmr analysis revealed the mixture to consist of 95% 1 and 5% 2.

Three recrystallizations of this mixture from ethanol led to pure 1: mp $152-153^\circ$; uv max (95% EtOH), 294.5 μ . A small amount of 2, still contaminated slightly with 1, was separated from the mother liquor.

D. In Trichloroethylene at -30° .—Under the same reaction conditions as described above, cyclohexene (0.1 mol) underwent reaction with nitrosyl chloride (0.1 mol) to give a white solid mixture which was shown by ir and nmr analyses to consist of approximately equal amounts of 1 and 2.

E. In Water at Room Temperature.—Utilizing the slightly modified method of addition of nitrosyl chloride as described in part B, cyclohexene reacted with nitrosyl chloride in water at room temperature to yield a solid mixture consisting of 65% 1 and 35% 2, as determined by ir and nmr analyses.

F. In Water in the Presence of Fluoride Ion.—A solution consisting of 24 g of potassium fluoride dissolved in 80 ml of distilled water was placed in a 250-ml, three-necked flask. To this was added 20.3 ml (0.2 mol) of cyclohexene, and nitrosyl chloride in slight excess of 0.2 mol was added slowly with vigorous stirring. A precipitate was formed almost immediately and was filtered to yield 4.75 g (15%) of a white solid, mp $157-159^\circ$ with decomposition. Recrystallization of this solid from acetone gave a pure sample, mp $168-169^\circ$, which was identified as *trans*-2,2'-dinitro-*trans*-azodioxycyclohexane (2) by its infrared and nmr spectra, its elemental analysis, and its ready conversion

into 2-nitrocyclohexanone by hydrolysis with levulinic acid:² ir (KBr), 1555 (nitro), 1451, 1390 (doublet), 1330, 1260 cm^{-1} (*trans*-dimer); nmr (deuterioacetone), δ 1.82 (complex multiplet, 8 H), 4.96 (m, 1 H, CHNO_2), and 5.57 (m, 1 H, $\text{CH}-\text{N}=\text{N}$).

Anal. Calcd for $\text{C}_{12}\text{H}_{20}\text{N}_2\text{O}_6$: C, 45.57; H, 6.33; N, 17.72. Found: C, 45.63; H, 6.43; N, 17.84.

Registry No.—1, 17350-60-6; 2, 17350-61-7; nitrosyl chloride, 2696-92-6; cyclohexene, 110-83-8.

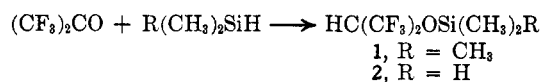
Perhalo Ketones. The Reaction of Perhalo Ketones with Silanes¹

R. E. A. DEAR

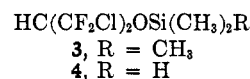
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Received April 18, 1968

Silanes are known to add to the carbonyl linkage of perhalo ketones to give alkoxy silanes.²⁻⁴ Janzen and Willis reported the preparation of alkoxy silanes 1 and 2, among others, by the ultraviolet irradiation of mixtures of hexafluoroacetone and alkylsilanes. These



workers found that, of the compounds studied, only trimethylsilane reacts with hexafluoroacetone in the absence of irradiation. We find that dimethylsilane will also react with hexafluoroacetone, to give good yields of 2, if the compounds are heated together at 50° for 24 hr. Trimethylsilane is more reactive in these additions and combines without the application of heat. Entirely analogous reactions were observed between the same silanes and 1,3-dichlorotetrafluoroacetone, giving products 3 and 4. These reactions were somewhat slower than those with hexafluoroacetone and here, too, dimethylsilane is less reactive than trimethylsilane. This indicates that the inductive effect of the additional methyl group renders the Si-H bond more polar in trimethylsilane.



It was also observed that under photolytic conditions^{2,5} the Si-H bond of trichlorosilane adds to hexafluoroacetone to give 5. We find that when trichlorosilane is heated with hexafluoroacetone for 70 hr at 50° , in the absence of irradiation, the reaction takes an entirely different course, and the Si-Cl bond adds to the carbonyl linkage giving 1,1,1,3,3,3-hexafluoro-

(1) This is paper XV in the series on Perhalo Ketones. For paper XV see L. G. Anello, A. K. Price, and R. F. Sweeney, *J. Org. Chem.*, **33**, 2692 (1968).

(2) A. F. Janzen and C. J. Willis, *Can. J. Chem.*, **43**, 3063 (1965).

(3) W. R. Cullen and G. E. Styan, *Inorg. Chem.*, **4**, 1437 (1965).

(4) G. W. Parshall, *ibid.*, **4**, 52 (1965).

(5) E. G. Howard, P. B. Sargent, and C. G. Krespan, *J. Amer. Chem. Soc.*, **89**, 1422 (1967).

TABLE I
 PHYSICAL PROPERTIES

| Compound | Structure | Bp, °C | n_D^{20} | Yield, % | Analysis, % | |
|----------|--|-----------------|------------|-------------------|----------------------------------|------------------------|
| | | | | | Calcd | Found |
| 1 | HC(CF ₃) ₂ OSi(CH ₃) ₃ | 90 ^a | 1.3161 | 80.6 | | |
| 2 | HC(CF ₃) ₂ OSi(CH ₃) ₂ H | 73 ^b | 1.3059 | 62.0 | | |
| 3 | HC(CF ₂ Cl) ₂ OSi(CH ₃) ₃ | 144 | 1.3776 | 73.0 | C, 26.33 H, 3.69 Cl, 25.69 | 26.39 3.61 25.77 |
| 4 | HC(CF ₂ Cl) ₂ OSi(CH ₃) ₂ H | 128 | 1.3724 | 72.3 | C, 23.18 H, 3.11 Cl, 27.37 | 23.10 3.14 27.19 |
| 6 | ClC(CF ₃) ₂ OSiCl ₂ H | 86 | 1.3386 | 62.6 ^c | C, 11.95 H, 0.33 Cl, 35.28 | 11.72 0.17 34.88 |
| 7 | [ClC(CF ₃) ₂ O] ₂ SiClH | 136 | 1.3248 | | C, 15.43 H, 0.22 Cl, 22.70 | 15.24 0.13 22.37 |

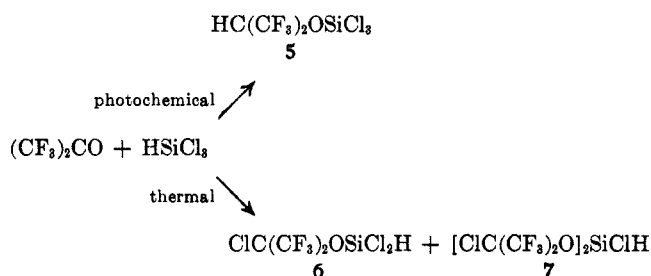
^a Lit.² bp 90° (748 mm). ^b Lit.² bp 72–73° (743 mm). ^c This represents a combined yield for 6 and 7 based on the silane consumed.

 TABLE II
 SPECTRAL DATA OF NEW COMPOUNDS

| Compound | Structure | Si-H stretching frequency, cm ⁻¹ | Chemical shifts, ppm ^a | Coupling constants, Hz |
|----------|--|---|--|--|
| 3 | HC(CF ₂ Cl) ₂ OSi(CH ₃) ₃ | ... | CH ₃ 0.25 (s) CH 4.38 (t of t) | $J_{\text{HCCF}_a} = 8$; $J_{\text{HCCF}_b} = 6$ $J_{\text{HCSiH}} = 3$; $J_{\text{HSiOCCF}} = 1$ |
| 4 | HC(CF ₂ Cl) ₂ OSi(CH ₃) ₂ H | 2185 | CH ₃ 0.34 (d) CH 4.33 (t of t) SiH 4.84 (m) | $J_{\text{HCCF}_a} = 8$; $J_{\text{HCCF}_b} = 5$ $J_{\text{HSiCH}} = 3$; $J_{\text{HSiOCCF}} = 1$ |
| 6 | ClC(CF ₃) ₂ OSiCl ₂ H | 2283 | SiH 5.96 (s) | |
| 7 | [ClC(CF ₃) ₂ O] ₂ SiClH | 2320 | SiH 5.62 (s) | |

^a s = singlet, d = doublet, t = triplet, m = complex multiplet, δ scale, with tetramethylsilane as internal standard.

2-chloroisopropoxydichlorosilane (6), bp 86°, and bis-(1,1,1,3,3,3-hexafluoro-2-chloroisopropoxy)chlorosilane (7), bp 136°.



The physical properties determined for the compounds discussed are summarized in Table I. The spectral data (Table II) obtained from compounds 1 and 2 were in good agreement with those previously described.² In the infrared spectra 4 exhibits a medium intensity Si-H stretching frequency at 2185 cm⁻¹, whereas the Si-H stretching frequencies in 6 and 7 appear at 2283 and 2320 cm⁻¹, respectively. By comparison, trichlorosilane absorbs at 2258 cm⁻¹. No C-H stretching frequencies were observed in 6 and 7. This may be contrasted with the data presented for 5,² which shows C-H stretching bands, but has no Si-H absorption.

The pmr spectra of the compounds were also examined. In 3 the methyl groups appear as a sharp singlet at 0.25 ppm (δ scale; downfield from tetramethylsilane), and the methine proton appears as a triplet of triplets centered at 4.38 ppm ($J_{\text{HCCF}_a} = 8$, $J_{\text{HCCF}_b} = 6$ Hz), a pattern which is typical of a lone proton adjacent to two nonequivalent chlorodifluoromethyl groups. The methine proton in 4 gives a similar pattern, cen-

tered at 4.33 ppm ($J_{\text{HCCF}_a} = 8$, $J_{\text{HCCF}_b} = 5$ Hz). The methyl groups appear as a doublet at 0.34 ppm ($J_{\text{HCSiH}} = 3$ Hz), and the proton bound to silicon gives a complex, partially resolved multiplet, showing evidence of coupling not only with the adjacent methyl protons, but also with the fluorine atoms present in the molecule. The multiplet is centered at 4.84 ppm ($J_{\text{HSiCH}} = 3$, $J_{\text{HSiOCCF}_a} = 1$, $J_{\text{HSiOCCF}_b} = 1$ Hz).

The pmr spectrum clearly distinguishes the structure of 6 from compound 5 of Janzen and Willis. While 5 has a methine proton adjacent to two CF₃ groups and displays a septet centered at 4.68 ppm,² 6 has no absorption in this region but has a singlet due to Si-H at 5.96 ppm. Compound 7 also has an Si-H singlet at 5.62 ppm. Trichlorosilane itself has an Si-H resonance at 6.25 ppm.⁶ The Si-H proton evidently becomes more deshielded as the number of chlorine atoms on silicon increases in this series.

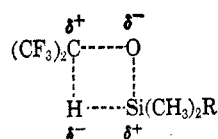
It was proposed originally^{2,3} that the thermal reaction between hexafluoroacetone and trimethylsilane proceeded by way of a nucleophilic attack of the carbonyl oxygen on the central silicon atom, followed by an intermolecular hydride transfer. This mechanism would be unlikely under the mild reaction conditions employed, since it is known that hexafluoroacetone is a very poor nucleophile, even toward reactive compounds such as phosphorus pentachloride.⁷ Recently Janzen and Willis⁸ rejected their original proposal and now suggest that the mechanism involves electrophilic attack by the carbonyl carbon on one of the hydrogen atoms attached to silicon, resulting in initial

(6) A value of τ 3.848 (δ 6.152) is quoted in the literature for a dilute solution spectrum: D. E. Webster, *J. Chem. Soc.*, 5132 (1960).

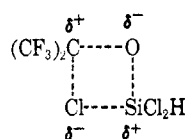
(7) B. S. Farah and E. E. Gilbert, *J. Org. Chem.*, **30**, 1241 (1965).

(8) A. F. Janzen and C. J. Willis, *Inorg. Chem.*, **6**, 1900 (1967).

formation of a hexafluoroisopropoxide anion $\text{HC}(\text{CF}_3)_2\text{O}^-$. However, the formation of a discrete anion, accompanied by the corresponding siliconium ion, is unnecessary. The results are explained equally well by a four-center transition state of the type



followed by formation of the C-H and Si-O bonds to give 1 and 2. The present work with hexafluoroacetone and trichlorosilane tends to support this idea since the production of 6 and 7 can be explained by an analogous electrophilic attack of the carbonyl carbon on the chlorine atom of the silicon-chlorine bond, with formation of a four-center transition state similar to that already described.



Any discrete anion formed would necessarily be the 2-chlorohexafluoroisopropoxide ion, a species which Janzen and Willis⁸ have rejected as being unlikely owing to the poor nucleophilicity of the chloride ion. A similar mechanism has been proposed for the reaction of hexafluoroacetone with alkoxy silanes.⁹ The small amount of dialkoxysilane 7 produced in the reaction results simply by the combination of 6 with another mole of ketone, by the pathway already outlined.

It thus appears that reactions between perhalo ketones and silanes may proceed by two distinct pathways, depending on the reaction conditions employed. In the liquid phase, in the absence of any radical initiator, the four-center mechanism as outlined above accounts for the products observed. Our results with hexafluoroacetone and trichlorosilane corroborate this suggestion. In the presence of ultraviolet light, a free-radical chain reaction mechanism seems most probable.¹⁰ In the case of the nonhalogenated silanes used in the experiments, both pathways lead to the same product, and no attempt has been made to distinguish between the two, although it is doubtful that a radical mechanism could be operative under the conditions employed here. Only in the case of a suitably substituted silane, such as trichlorosilane, are the two mechanisms readily resolved.

Experimental Section

Volatile materials were manipulated in a vacuum manifold system. The perhalo ketones are products of Allied Chemical Corp. and were used without further purification. All silanes were purchased from Peninsular ChemResearch, Inc. Elemental analyses were carried out by Schwarzkopf Microanalytical Laboratory, and nuclear magnetic resonance spectra were obtained on a Varian A-60 instrument at 60 MHz. Spectral data for new compounds are summarized in Table II.

In general, the reactions were carried out in glass Fisher-Porter Aerosol compatibility tubes, although some large-scale runs were made in a 300-ml stainless steel pressure reactor. Re-

actions were continued until the rate of pressure decrease was minimal. The reaction between hexafluoroacetone and trichlorosilane is given below as a typical experimental procedure.

Reaction of $(\text{CF}_3)_2\text{CO}$ and Cl_3SiH .—Trichlorosilane (16 g, 0.118 mol) was placed in a glass compatibility tube, which was then cooled to -78° . The free space over the silane was evacuated, and hexafluoroacetone (23.5 g, 0.141 mol) was introduced through a vacuum manifold system. The glass tube contained a small, plastic-covered magnetic stirring bar, and the liquid contents of the tube were stirred overnight at ambient temperature. No reaction was apparent so the tube was warmed to 45° . The autogenous pressure rose to 75 psig and gradually fell, over a 70-hr period, to 20 psig. Distillation of the contents of the tube gave 4.1 g of unreacted Cl_3SiH ; 13.3 g of $\text{ClC}(\text{CF}_3)_2\text{OSiCl}_2\text{H}$, bp 86° ; and 5.2 g of $[\text{Cl}(\text{CF}_3)_2\text{O}]_2\text{SiClH}$, bp 136° .

Registry No.—3, 17203-08-6; 4, 17222-09-2; 5, 4071-97-0; 6, 17203-10-0; 7, 17203-11-1.

Acknowledgment.—It is a pleasure to thank Dr. D. F. Harnish and Professor Robert West for fruitful discussions of these results. The pmr spectra were obtained by Mr. R. J. Tepper and Dr. B. B. Stewart.

Substituent Effects and Thermodynamic Consequences of Linear Free-Energy Relations

JOHN W. LARSON AND LOREN G. HEPLER

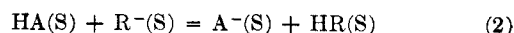
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There is now considerable empirical support for various linear free-energy relations as accurate and economical correlations of effects of substituents on organic molecules. Possibly the best known and most widely used linear free-energy relation is the Hammett equation that is written as in eq 1. Since we are

$$\log K = \rho\sigma \quad (1)$$

specifically concerned with application of this equation to acid-base equilibria in solution, K represents equilibrium constants for reactions of the type given in



where HR represents the parent or reference acid and HA represents the substituted acid of interest. The symbol (S) is used to denote that the preceding species is in solution. The constant σ is intended to depend only on the substituent, but ρ depends on the particular reaction under consideration and also on both the solvent and the temperature.

Since the empirical successes of the Hammett equation are well known, we turn to careful consideration of some of its thermodynamic implications. Taking the substituent constant σ to be independent of temperature, we differentiate eq 1 with respect to temperature to obtain eq 3 and 4. These equations

$$\Delta H^\circ = [2.3RT^2(\partial\rho/\partial T)]\sigma = -(\partial \ln \rho / \partial \ln T)\Delta G^\circ \quad (3)$$

$$\Delta S^\circ = 2.3R[\rho + T(\partial\rho/\partial T)]\sigma = -[(1/T) + (\partial \ln \rho / \partial T)]\Delta G^\circ \quad (4)$$

indicate that ΔH° and ΔS° values for reactions of the type in eq 2 should be proportional to σ and ΔG°

(9) R. A. Braun, *Inorg. Chem.*, **5**, 1831 (1966).

(10) C. G. Krespan and W. J. Middleton, *Fluorine Chem. Rev.*, **1**, 145 (1967).

(1) Some of the work reported here was done while both authors were at Carnegie Institute of Technology, Pittsburgh, Pa.