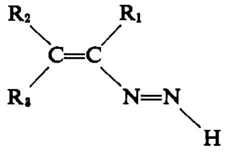
Alkenyldiazenes

Sir:

Kishner[1] discovered that reduction of α-substituted ketones with hydrazine led to alkenes. General agreement exists upon the intermediacy of alkenyldiazenes (1) in that reaction[2–4] and in other reactions which are closely related.[5–7] Disubstituted diazenes readily arise from the reaction of an α-substituted ketone and substituted hydrazines (methyl,[8] phenyl[9]).



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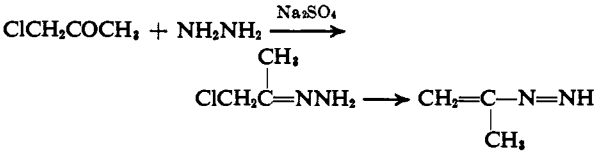
We now report a general method for the preparation of alkenyldiazenes involving formation of an α-halohydrazone and its conversion to the diazene with weak base. For example, chloroacetone (0.01 *M*) and hydrazine (0.05 *M*) in anhydrous, *oxygen-free* acetonitrile over sodium sulfate rapidly produce the α-halohydrazone, which yields 2-propenyldiazene after elimination (maximum concentration of product in 1 hr, yield 70%). Benzoic acid is added and the solution distilled to produce a yellow solution of 2-propenyldiazene (1, $R_1 = CH_3$; $R_2 = R_3 = H$) (eq 1).



$$\mathrm{ClCH_2COCH_3} + \mathrm{NH_2NH_2} \xrightarrow{\mathrm{Na_2SO_4}} \mathrm{ClCH_2}\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{C}}}\mathrm{{=}NNH_2} \longrightarrow \mathrm{CH_2{=}}\underset{\mathrm{CH_3}}{\underset{|}{\mathrm{C}}}\mathrm{{-}N{=}NH} \quad (1)$$

Spectroscopic data, as shown in Table I, provide strong support for the assigned structures. 2-Propenyldiazene disappears in a bimolecular reaction, unusual behavior which has been observed for all monosubstituted diazenes thus far studied.[10–14] The rate constant for bimolecular disappearance of 2-propenyldiazene (see Table I) is the same as that found for the analogous reaction of phenyldiazene.[10] We thus extend the generalization that the observed rate constant for the disappearance of monosubstituted diazenes exhibits only a mild dependence on the substituent (0.002–0.03 M^{-1} (sec^{-1}), the only exception being *t*-butyldiazene ($k_2 \sim 0.9\ M^{-1}\ \mathrm{sec}^{-1}$).[10–14]

Table I. Spectroscopic Maxima and Bimolecular Rate Constants for Alkenyldiazenes

Compound	$\pi \rightarrow \pi^*$ transition λ_{max}, mμ (ϵ_{max})	$n \rightarrow \pi^*$ transition λ_{max}, mμ (ϵ_{max})	k_2, M^{-1} sec^{-1} [a]
$CH_2{=}C(CH_3)N{=}NCH_3$ [b]	2320 (6060)	3860 (55)	
$CH_2C(CH_3)N{=}NH$ [c]	2300 (6500)	4100 (41) [d]	0.015
$CH_2{=}CHN{=}NH$ [c]	2210 (7200)	4030 (40) [d]	0.0017

[a] All rate constants are based on at least two determinations in CH_3CN at 25°. [b] In 95% ethanol.[8] [c] In CH_3CN. [d] These were determined through quantitative formation of diazenes from reactants.

The major product of the bimolecular decompositions in each case was the corresponding alkene, *i.e.*, RN=NH → RH, $\sim$70% yield, consistent with the mechanism already developed for phenyldiazene.[10] The structures of the alkenyldiazenes follow from (1) the method of preparation, (2) spectroscopic properties, (3) bimolecular disappearance, and (4) high sensitivity to oxygen.[10–13] Alkenyldiazenes represent a new class of conjugated dienes, readily accessible from convenient starting materials and possessing a number of unusual and potentially useful chemical properties. Investigations of the alkenyldiazenes are now under way and will be reported in due course.

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(1) N. Kishner, *J. Russ. Phys. Chem. Soc.*, **45**, 973 (1913).

(2) N. J. Leonard and S. Gelfand, *J. Am. Chem. Soc.*, **77**, 3269, 3272 (1955).

(3) P. S. Wharton, S. Dunny, and L. S. Krebs, *J. Org. Chem.*, **29**, 958 (1964).

(4) H. H. Szmant, *Angew. Chem. Intern. Ed. Engl.*, **7**, 120 (1968).

(5) I. Elphimoff-Felkin and M. Verrier, *Tetrahedron Letters*, 1515 (1968).

(6) W. Kirmse, B-G. von Bulow, and H. Schepp, *Ann.*, **691**, 41 (1966).

(7) B. Fuchs and M. Rosenblum, *J. Am. Chem. Soc.*, **90**, 1061 (1968).

(8) B. T. Gillis and J. D. Hagerty, *ibid.*, **87**, 4576 (1965).

(9) L. Caglioti, G. Rosini, and F. Rossi, *ibid.*, **88**, 3865 (1966).

(10) Phenyldiazene: P. C. Huang and E. M. Kosower, *J. Am. Chem. Soc.*, **90**, 2367 (1968).

(11) *t*-Butyldiazene: P. C. Huang and E. M. Kosower, *ibid.*, **89**, 3911 (1967).

(12) Aryldiazenes (4-methoxy, 4-bromo, 2-bromo, 4-nitro): E. M. Kosower, P. C. Huang, and T. Tsuji, *ibid.*, **91**, 2325 (1969).

(13) Cyclopropyldiazene: T. Tsuji and E. M. Kosower, unpublished results.

(14) Methyldiazene: M. N. Ackerman, J. L. Ellenson, and D. H. Robinson, *J. Am. Chem. Soc.*, **90**, 7173 (1968).

(15) On leave from the Department of Chemistry, Faculty of Engineering Science, Osaka University, Osaka, Japan.

(16) We are grateful for support from the Petroleum Research Fund, the National Institutes of Health, and the Army Research Office (Durham).

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Received January 27, 1969

Trichlorosilyl Hydrides of Transition Metals

Sir:

As we have earlier reported,[1] the reaction of iron pentacarbonyl with trichlorosilane at elevated temperatures affords *cis*-$(OC)_4Fe(SiCl_3)_2$ or $[(OC)_4FeSiCl_2]_2$, depending upon the conditions. In analogy with the reaction of iron pentacarbonyl with tin tetrachloride,[2] a reasonable intermediate would be $(OC)_4Fe(H)SiCl_3$, which would not be expected to survive the temperatures employed (>140°). Such an intermediate would resemble the recently reported $(OC)_4Fe(H)SiH_3$.[3] Accordingly, we explored the possibility that the intermediate would be formed under mild

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(1) W. Jetz and W. A. G. Graham, *J. Am. Chem. Soc.*, **89**, 2773 (1967).

(2) The product at 0° is *cis*-$(OC)_4Fe(Cl)SnCl_3$, which disproportionates to *cis*-$(OC)_4Fe(SnCl_3)_2$ on warming: R. Kummer and W. A. G. Graham, *Inorg. Chem.*, **7**, 1208 (1968).

(3) B. J. Aylett, J. M. Campbell, and A. Walton, *Inorg. Nucl. Chem. Letters*, **4**, 79 (1968).

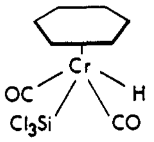
Table I. Properties of Trichlorosilyl Hydrides[a]

	Compound	Mp, °C	τ(M–H)[b]	γ(CO), cm^{-1} [c]
1	$(OC)_4Fe(H)SiCl_3$	<0	19.0	2124, 2069, 2058, 2053[d]
2	$C_6H_6(OC)_2Cr(H)SiCl_3$	114–114.5	20.5	1982, 1922
3	$C_5H_5(OC)_2Mn(H)SiCl_3$	82–83	19.7[e]	2028, 1977
4	$C_5H_5(OC)Fe(H)(SiCl_3)_2$	131–132	21.6	2025
5	$C_5H_5(OC)Co(H)SiCl_3$	31–33	23.3	2045

[a] Microanalysis and mass spectrometry support the formulation of all compounds except **1**; the thermal instability and air sensitivity of the latter has prevented us from obtaining meaningful results. For **3** and **4**, $[parent - Cl]^+$ is the heaviest fragment observed. [b] Nmr solvent is cyclohexane for **5**, acetonitrile for other compounds. [c] Infrared carbonyl stretching fundamentals; solvent is *n*-hexane except for **2**, for which low solubility required the use of dichloromethane. [d] Additional bands at 2000 and 2023 cm^{-1} due to $Fe(CO)_5$ grow as the spectrum is measured. [e] Broad.

conditions by ultraviolet irradiation of $Fe(CO)_5$–$HSiCl_3$ mixtures.

We report in this communication the isolation of the anticipated intermediate, *cis*-$(OC)_4Fe(H)SiCl_3$ (**1**) and the extension of this photochemical reaction to other metal carbonyl derivatives. Thus far, reactions with π-$C_6H_6Cr(CO)_3$, π-$C_5H_5Mn(CO)_3$, π-$C_5H_5Fe(CO)_2$-$SiCl_3$, and π-$C_5H_5Co(CO)_2$ have yielded compounds **2–5**. On the basis of these preliminary results, it is clear that a new and broadly applicable route has been opened to this important class of transition metal hydrides.



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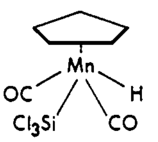

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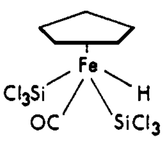

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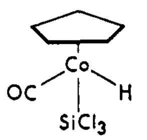

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The very volatile *cis*-$(OC)_4Fe(H)SiCl_3$ crystallizes from pentane at −78° and melts well below room temperature to an extremely air-sensitive liquid. Its reaction with tetrafluoroethylene was examined with the object of forming a more stable tetrafluoroethyl derivative; instead, the product from a reaction at room temperature is a yellow crystalline solid characterized by analysis and mass spectrum as $[(OC)_4FeSiCl_3]_2$. It is presumably related to the known compound $[(CO)_4RuSi(CH_3)_3]_2$.[4]

Compounds **2–5** are prepared under similar conditions,[5] and, with the exception of **5**, appear stable for long periods in the purified crystalline form. Solutions are much less stable. Fractional sublimation under vacuum is an important purification technique; the work-up procedures, in our opinion, are more exacting than those normally encountered in metal carbonyl chemistry. Yields range from an estimated 10% with **5** to >90% with **2**.

It is scarcely necessary to point out that all of these compounds conform to the 18-electron or effective atomic number rule. Formally, they are derived by replacing an electron-pair-donating carbonyl group with H and $SiCl_3$ as single-electron donors. This formal viewpoint may correspond closely to the mechanism as well. Presumably, a photon ejects a carbonyl group to form a coordinatively unsaturated or 16-electron intermediate, to which the Si–H bond adds.[6]

X-Ray crystallographic studies on some of the compounds are in progress.[7] Analogy with established structures[8] suggests an arrangement in which the metal occupies the apex of a distorted square pyramid, with ligands other than the ring forming the base. We have seen no evidence for the second isomer that is possible in principle for such a structure.[9]

Compound **4** was first obtained as a product of the thermal reaction between Cl_3SiH and $[\pi$-$C_5H_5Fe(CO)_2]_2$.[10] It is a very strong acid (pK_a estimated as 4 in acetonitrile) of which the anion forms stable salts. The acid strength of the other hydrides has not yet been determined.

Acknowledgment. We thank the National Research Council of Canada for financial support and for a bursary to W. J.

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(4) J. D. Cotton, S. A. R. Knox, and F. G. A. Stone, *Chem. Commun.*, 965 (1967).

(5) Reactions in this work were carried out using a Hanovia Type 30620 lamp placed a few inches from a water-cooled quartz reactor. The solvent was hexane.

(6) Oxidative addition of Si–H to certain square-planar d^8 compounds (which are 16-electron species according to the effective number rule) has been observed: F. de Charentenay, J. A. Osborn, and G. Wilkinson, *J. Chem. Soc., A*, 787 (1968), and references cited.

(7) Professor J. A. Ibers (Northwestern University) is determining the structure of **4**. The structures of **2** and **3** are being studied by Professor M. J. Bennett in this department.

(8) Specifically, those of the types π-$C_5H_5Mo(CO)_3R$ and π-$C_5H_5Mo(CO)_2LR$; *cf.* M. R. Chruchill and J. P. Fennessey, *Inorg. Chem.*, 6, 1213 (1967); 7, 953 (1968).

(9) The *trans* placement of basal ligands in the suggested structures **2–4** has not been established. The arrangement in π-$C_5H_5Mo(CO)_2[P(C_6H_5)_3]COCH_3$ is *trans*, however.[8] We have observed that the high-field proton of **4** is equivalently coupled to the *two* silicons (^{29}Si, $I = {}^1/_2$, 4.7%) with J(H–Fe–Si) = 20 cps. This is consistent with a *trans* geometry, but could also result from time averaging of other structures.

(10) W. A. G. Graham and W. Jetz, Abstracts, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, No. M82. Full details of our study of this reaction will shortly be submitted for publication.

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Received February 15, 1969

Polyhedral Carboranes Containing an Arsenic, Antimony, or Germanium Atom in the Cage

Sir:

Recently it was reported that distorted icosahedral boranes containing both a carbon and a phosphorus atom and isoelectronic with $B_{12}H_{12}^{2-}$ could be prepared in reasonable yield by the route described in the following equation.[1]

$$Na_3B_{10}H_{10}CH(C_4H_8O)_2 + PCl_3 \longrightarrow 1,2\text{-}B_{10}H_{10}CHP + 3NaCl + 2C_4H_8O$$

In principle other heavier nonmetal and metalloid elements should be inserted into the carborane frame-

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(1) J. L. Little, J. T. Moran, and L. J. Todd, *J. Am. Chem. Soc.*, **89**, 5495 (1967).