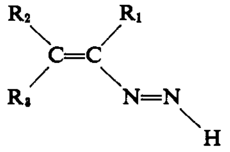
Alkenyldiazenes

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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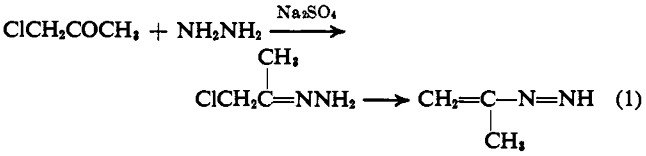
We now report a general method for the preparation of alkenyldiazenes involving formation of an α-halohydrazone and its conversion to the diazene with weak base. For example, chloroacetone (0.01 *M*) and hydrazine (0.05 *M*) in anhydrous, *oxygen-free* acetonitrile over sodium sulfate rapidly produce 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).



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

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 ($k_2 \backsim 0.9\ M^{-1}\ sec^{-1}$).[10-14]

The major product of the bimolecular decompositions in each case was the corresponding alkene, *i.e.*, RN=NH → RH, ∽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.

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.

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

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Takashi Tsuji,[15] Edward M. Kosower[16]
Department of Chemistry, State University of New York
Stony Brook, New York 11790

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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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