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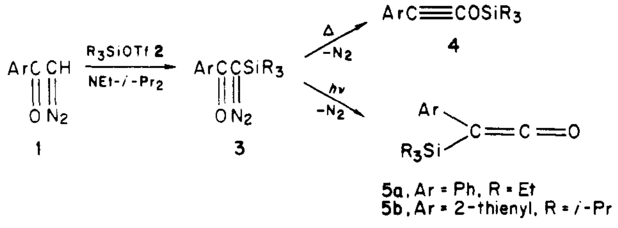
Preparation of 1-Aryl-2-siloxyalkynes from Silylated α-Diazo Carbonyl Compounds

Summary: Silylated α-diazo carbonyl compounds R$_3$SiC(N$_2$)C(O)Ar, prepared from a monosubstituted α-diazo carbonyl compound with trialkylsilyl triflates, rearrange to 1-aryl-2-siloxyalkynes with loss of N$_2$ at or above room temperature; this novel transformation is thought to be initiated by a C → O silyl shift yielding a diazoethene intermediate.

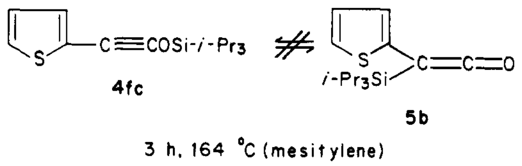
Sir: Silylated α-diazo carbonyl compounds are usually obtained by electrophilic diazoalkane substitution of monosubstituted α-diazo carbonyl compounds with a chlorosilane.[1] Recently, trimethylsilyl triflate (Me$_3$SiOTf), already known for its superior silylating power,[2] has been introduced for a smooth and effective trimethylsilylation of diazomethane, ethyl diazoacetate, and diazomethylphosphoryl compounds.[3,4] However, in our hands no clean reaction took place in the case of α-diazoacetophenone and Me$_3$SiOTf; the initially formed silylated diazo compound decomposed on workup.

As we have now found, 1-aryl(or heteroaryl)-2-diazo-1-ethanones 1 can be silylated smoothly with triethylsilyl triflate, *tert*-butyldimethylsilyl triflate, or triisopropyl triflate in the presence of a tertiary amine (see Table I). The formation of the silylated diazo compound 3 followed from the appearance of a new diazo stretching vibration in the IR spectrum. Simultaneously, a more or less intense band indicating a ν(C≡C) vibration was observed. It turned out that a thermal rearrangement of 3 with loss of N$_2$ was taking place, leading to a siloxyacetylene 4. In most cases, this rearrangement occurs already at room temperature, and no effort was then made to isolate 3. Compounds **3aA**, **3cA**, **3cC**, and **3fC**, being sufficiently stable, could be isolated and then rearranged to the siloxyacetylene in boiling benzene.

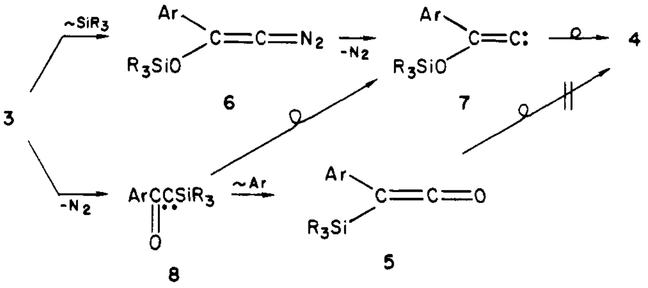
Typically, the following procedure for the synthesis of 4 was applied: The solution of silyl triflate 3 (10 mmol) in ether (5 mL) was added dropwise to a solution of diazo carbonyl compound 1[1] (10 mmol) and diisopropylethylamine (1.74 mL, 10 mmol) in ether (60 mL), kept at 0 °C. The mixture was then allowed to assume room temperature and was stirred for another 20 h. The precipitated ammonium triflate was filtered off and washed with ether. The filtrate was concentrated and benzene (50 mL) was added. After 2 h at reflux, the solvent was evaporated and the residue was separated by column chromatography (Merck Lobar column, LiChroprep Si60, 40–63 μm, eluent CHCl$_3$). The siloxyacetylenes 4 were further purified by Kugelrohr distillation.



Scheme I



Scheme II



The silylated diazo compounds 3 suffer protodesilylation extremely easily (e.g., **3cC** in CH$_3$OH gave **1c** in 86% isolated yield). Thus, with the trialkylammonium triflate around, it is understandable why the silylation reaction 1 → 3 could never be driven to completion.

To our knowledge, siloxyalkynes have been mentioned only once in the literature,[5] but their reactivity is not yet known. Compounds 4 with Si-*i*-Pr$_3$ or SiMe$_2$-*t*-Bu are thermally stable oils which were distilled without decomposition. The SiEt$_3$ derivatives, on the other hand, decomposed partly on column chromatography and extensively on attempted distillation. The possible interconversion siloxyacetylene/silyl ketene could not be observed, as was checked for the isomeric pair **4fC** and **5b** (Scheme I).

The siloxyalkynes are solvolyzed at room temperature by water–acetone or alcohols to give arylacetic acids or their esters, respectively. The C≡C stretching frequency of siloxyalkynes 4 compares well with that of alkynyl tosylates[6] (e.g., PhC≡COTs, 2260 cm^{-1}) but is distinctly different from isomeric yne ethers, e.g., PhOC≡CSi-*i*-Pr$_3$[7] (2190 cm^{-1}).

A preliminary picture of the rearrangement 3 → 4 is given in Scheme II. We think that the sequence is initiated by a C → O 1,3-silyl shift, for which there is much precedent.[8,9] The activation barrier for 3 is, however,

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(1) Regitz, M. "Diazoalkane"; Thieme; Stuttgart, 1977.

(2) Hergott, H. H.; Simchen, G. *Liebigs Ann. Chem.* **1980**, 1781.

(3) Martin, M. *Synth. Commun.* **1983**, *13*, 809.

(4) Regitz, M.; Allspach, T.; Gümbel, H. *J. Organomet. Chem.*, in press.

(5) Pirrung, M. C.; Hwu, J. R. *Tetrahedron Lett.* **1983**, *24*, 565.

(6) Stang, P. J.; Surber, B. W. *J. Am. Chem. Soc.* **1985**, *107*, 1452.

(7) Prepared according to: Himbert, G.; Henn, L. *Liebigs Ann. Chem.* **1984**, 1358. This compound is an oil which decomposed on attempted distillation.

(8) (a) Brook, A. G.; Bassindale, A. R.; "Molecular Rearrangements in Ground and Excited States"; De Mayo, P., Ed.; p 193; Academic Press: New York, 1980; Vol. 2. (b) Brook, A. G. *Acc. Chem. Res.* **1974**, *7*, 77.

(9) Colvin, E. "Silicon in Organic Synthesis"; Butterworths; London, 1981; p 33.

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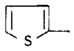
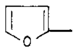
Table I. Preparation of 1-Aryl-2-silyl-2-diazoethanones 3 and 1-Aryl-2-siloxyalkynes 4 (1 → 3 → 4)

			$3^{a,b}$			$4^{a,c}$		
diazo compd 1, Ar =	R_3SiOTf 2, R_3Si =		yield, %	$\nu(C{=}N_2)$,^{d} cm^{-1}		yield,^{e} %	bp,^{f} °C/torr	$\nu(C{\equiv}C)$,^{d} cm^{-1}
1a, Ph	$SiEt_3$	**3aA**	87	2065	**4aA**	*g*		2258
	$SiMe_2$-*t*-Bu				**4aB**	70	150/0.006	2265
	Si-*i*-Pr_3				**4aC**	61	130/0.07	2260
1b, C_6H_4-4-CH_3	Si-*i*-Pr_3				**4bC**	56	120/0.05	2258
1c, C_6H_4-4-OCH_3	$SiEt_3$	**3cA**	58	2063	**4cA**	*h*		2260
	$SiMe_2$-*t*-Bu				**4cB**	53	145/0.005	2265
	Si-*i*-Pr_3	**3cC**	62	2060	**4cC**	65	175/0.45	2260
1d, C_6H_4-4-Br	Si-*i*-Pr_3				**4dC**	62	150/0.05	2260
1e, C_6H_4-3-Cl	Si-*i*-Pr_3				**4eC**	60	130/0.01	2260
	$SiMe_2$-*t*-Bu				**4fB**	68	160/0.005	2255
	Si-*i*-Pr_3	**3fC**	39^h	2060	**4fC**	71	150/0.01	2260
	Si-*i*-Pr_3				**4gC**	69	140/0.01	2261

[a] All isolated compounds except for the unstable alkynes **4aA** and **4cA** gave satisfactory elemental analyses. [b] Isolated by column chromatography (Merck Lobar column, LiChroprep Si60, eluent $CHCl_3$). [c] Compounds **4** are colorless to yellow oils. [d] IR spectrum from film, except for **3fC** (KBr pellet). [e] Yield refers to **1**. [f] Oven temperature for Kugelrohr distillation. [g] Only crude product obtained. [h] Yellow powder, mp 37 °C (from pentane).

much lower than normally found for the β-keto silane → siloxyalkene rearrangement,[10] probably due to the more polar C=O bond in the diazo ketone. The rearrangement leads to a diazoethene **6**. This elusive species has been postulated as an intermediate in other reactions[11] but was never isolated or trapped. It is assumed that **6** either reacts to **4** in a concerted fashion or that spontaneous loss of N_2 from **6** creates vinylidenecarbene **7**.[11b] Such species can be trapped if the migrating tendency of the β-substituents is low.[12] The presence of a β-aryl group (bearing no strongly electron-withdrawing substituents) prevents such trapping completely. In line with these known facts, thermolysis of **3cC** in the presence of cyclohexene gave only rearrangement product **4cC** but no [2 + 1]-cycloaddition product arising from a vinylidene carbene.

Another pathway would be thermal decomposition of **3** to give keto carbene **8** which then rearranges to **4** via vinylidene carbene **7** or ketene **5**. At least the latter route could be excluded. Silyl ketenes **5a,b** which were obtained by unsensitized irradiation of **3aA**, **3fC**[13] do not rearrange to a siloxyacetylene up to 164 °C (mesitylene, 3 h). The formation of a silyl ketene on photolysis of **3** is not in itself a proof of a carbene intermediate, since it is well-known that on direct photolysis of a diazo carbonyl compound, Wolff rearrangement can occur directly from the excited singlet state of the diazo compound.[14] On the other hand, the thermal stability of many α-diazo carbonyl compounds and of silyl diazo acetates does not lend support to the "thermal" decomposition **3** → **8** at room temperature. The detailed mechanistic aspects of the transformation **3** → **4** as well as the chemistry of siloxyalkynes are under active investigation.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft.

Registry No. **1a**, 3282-32-4; **1b**, 17263-64-8; **1c**, 6832-17-3; **1d**, 4203-30-9; **1e**, 7023-78-1; **1f**, 72676-21-2; **1g**, 21443-46-9; **2a**, 79271-56-0; **2b**, 69739-34-0; **2c**, 80522-42-5; **3aA**, 96845-66-8; **3cA**, 96845-67-9; **3cC**, 96845-68-0; **3fC**, 96845-69-1; **4aA**, 96845-70-4; **4aB**, 96845-71-5; **4aC**, 96845-72-6; **4bC**, 96845-73-7; **4cA**, 96845-74-8; **4cB**, 96845-75-9; **4cC**, 96845-76-0; **4dC**, 96845-77-1; **4eC**, 96845-78-2; **4fB**, 96845-79-3; **4fC**, 96845-80-6; **4gC**, 96845-81-7; **5a**, 96845-82-8; **5b**, 96845-83-9.

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[12] (a) Stang, P. J. *Acc. Chem. Res.* **1982**, *15*, 348; *Chem. Rev.* **1978**, *78*, 384. (b) Gilbert, J. C.; Weerasooriya, U.; Giamalva, D. *Tetrahedron Lett.* **1979**, 4619. (c) Gilbert, J. C.; Weerasooriya, U. *J. Org. Chem.* **1983**, *48*, 448.

[13] Irradiation of **3aA** (λ > 280 nm, 2 mmol in 90 mL of anhydrous benzene, 1.5 h) gave **5a** (37% yield after column chromatography): IR (neat) $\nu(C{=}C{=}O)$ 2080 cm^{-1}. Irradiation of **3fC** as before gave **5b** (94% yield; Kugelrohr distillation at 140 °C/0.25 torr); IR (neat) $\nu(C{=}C{=}O)$ 2085 cm^{-1}).

[14] (a) Ando, W. In "The Chemistry of Diazonium and Diazo Groups"; Patai, S., Ed.; Wiley: New York, 1978; Vol. I, p 467. (b) Meier, H.; Zeller, K.-P. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 32.

Catalytic "Homo-Reformatsky" Reaction. Ambident Chemical Reactivities of the Zinc Homoenolate of Propionate

Summary: Zinc halide catalyzed reaction of 1-alkoxy-1-siloxycyclopropane with carbonyl compounds gives 4-siloxy esters, while a related reaction with acid chlorides produces either 4-keto esters or (acyloxy)cyclopropanes.

Sir: Generation of nucleophilic metal homoenolates from siloxycyclopropanes[1–3] is an emerging new methodology for organic synthesis. We have previously demonstrated the feasibility of such an approach by the reactions of titanium[1] (1) and zinc[2] (2) homoenolates of alkyl propionates

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