Synthesis and Reactions of the First Allenyl Azo Compounds

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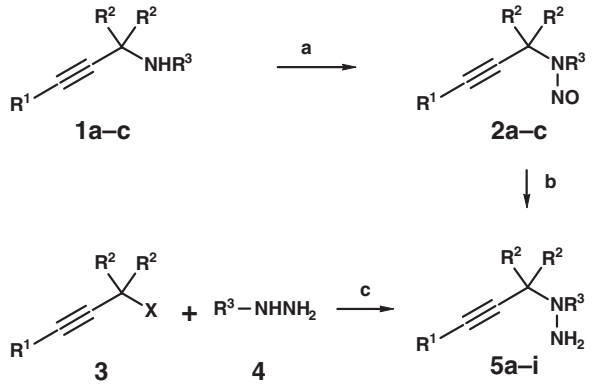
(Received November 29, 2002; CL-021021)

Several propargylhydrazines were prepared and then oxidized by manganese dioxide to generate short-lived 1,1-diazenes, which produced novel allenyl azo compounds (**8**) through [2,3] sigmatropic rearrangement. Isomerization of **8** or nucleophilic addition to the title compounds lead to hydrazones as well as pyrazole derivatives.

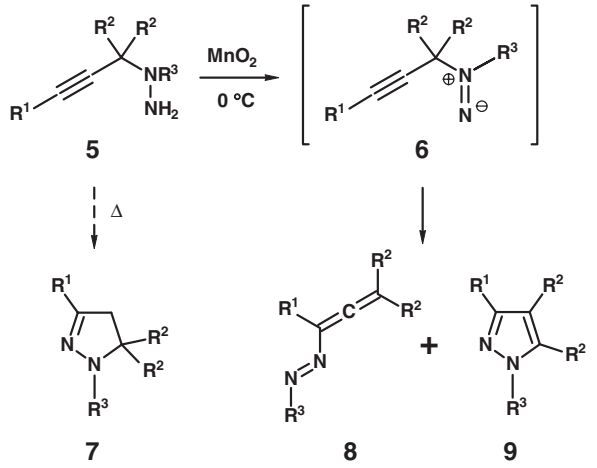
The chemistry of azoalkenes has been investigated extensively over the last decades owing to the interesting addition and cycloaddition reactions of these extremely reactive conjugated heterodienes.[1] Whereas numerous synthetic methods are known for the preparation of olefinic azo compounds,[1a,b] in which the double bond is conjugated with the azo group, up to now no report on allenyl azo compounds has been published. However, the known[2] [2,3] sigmatropic rearrangement of short-lived allylic 1,1-diazenes to allyl azo compounds can be modified not only to produce azoalkenes[3] but also in order to generate allenyl azo compounds for the first time.

Starting with secondary amines **1a–c**, we prepared the propargylhydrazines **5a–c** by nitrosation followed by reduction (Scheme 1). The hydrazines **5c–i** were synthesized by alkylation of **4**[3] using propargyl chlorides (for **5c**,**e**,**f**,**h**,**i**) or bromides (for **5d**,**g**). Treatment of **3** (R^1 = H, R^2 = Me, X = Cl) with **4** (R^3 = Me) under mild conditions was claimed to lead mainly to the isomeric product 1-(1,1-dimethyl-2-propynyl)-2-methylhydrazine and smaller amounts of a pyrazoline (**7c**) and a unsaturated hydrazone.[4] We found that the reaction of the same starting materials in the presence of copper powder gave **5c**[5] in 69% yield. The structure of **5c** was proved by the independent synthesis via **2c**.



Scheme 1. Synthesis of propargylhydrazines **5**, for the key of R^1, R^2, and R^3 see Table 1; reagents and conditions: a) AcOH, H_2O, $NaNO_2$, 0 °C, 92% **2a**, 94% **2b**, 81% **2c**; b) $LiAlH_4$, Et_2O, 36 °C, 42% **5a**, 37% **5b**, 25% **5c**; c) 0–20 °C, 5–24 h, Et_2O or without solvent; copper powder and H_2O or EtOH in the case of **5c**,**h**,**i**; 69% **5c**, 75% **5d**, 70% **5e**, 61% **5f**, 45% **5g**, 50% **5h**, 54% **5i**.

On oxidation with activated manganese dioxide, the propargylhydrazines **5** were converted into new allenes **8** and unwanted pyrazoles **9** (Scheme 2). If yellow mercury(II) oxide was used to transform **5** to **8** via **6**, yields were lower. While the stability of **8c**,**h**,**i** allowed the isolation in good yields and purity (Table 1), the instability of allenyl azo compounds with R^2 = H, especially in the case of **8a** and **8b**, gave rise to significantly lower yields. Nevertheless, **8c**, **8d**, and **8f** were isolated with good purity by preparative gas chromatography. Oxidation of **5g** furnished only **8g** and **9g**, and thus, rearrangement of **6g** to produce allyl propargyl diazene (4,5-diazaocta-1,4-dien-7-yne) was not



Scheme 2. Synthesis of allenyl azo compounds **8** via [2,3] sigmatropic rearrangement of short-lived 1,1-diazenes **6**, for the key of R^1, R^2, and R^3 see Table 1.

Table 1. Oxidation[a] of propargylhydrazines **5** to produce allenyl azo compounds **8** and pyrazoles **9**

5	R^1	R^2	R^3	Yield[b] of **8**/%	Yield[b] of **9**/%
a	H	H	Ph	53–77	
b	Me	H	Ph	51	
c	H	Me	Me	92	
d	Me	H	Me	34–44	15–26
e	CH_2N_3	H	Me	24	24
f	H	H	Me	59–65	16–21
g	H	H	$CH_2CH{=}CH_2$	47	10
h	H	Me	$(CH_2)_3CH{=}CH_2$	88	
i	H	Me	CH_2CH_2OH	95	

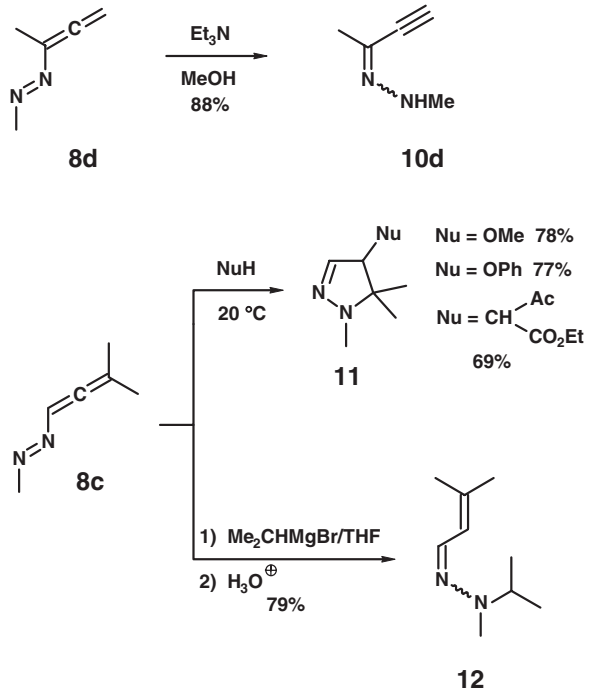
[a]The oxidations are performed using an excess of activated manganese dioxide in CH_2Cl_2 or chloroform at 0 °C and a reaction time of 35–45 min.
[b]Yields based on ^{1}H NMR standard for **8a**,**b**,**d**–**g** and **9d**–**g**, yields referred to isolated **8c**,**h**,**i**.

observed.

All allenyl azo compounds **8** were unequivocally spectroscopically characterized.[6] In the case of **8d–f**, distinctive long-range coupling with $^{7}J = 1.5$–1.7 Hz was observed in the ^{1}H NMR spectra. The *E* configuration of **8** was established by comparison of the physical and spectroscopic data with those of other azo compounds[3] and particularly by the very small low-field shifts of the ^{1}H NMR signals of **8** in the presence of Eu(fod)$_3$. On photolysis, **8** yielded at best only traces of the stereoisomer with a *Z*-configurated azo group. Instead, the expected hydrocarbons, e.g. pent-2-yne and 3-methylbuta-1,2-diene from **8d** or but-2-yne and buta-1,2-diene from **8f**, were generated. Azo compounds **8d** and **8f** tend to cyclize to furnish **9d** and **9f** in quantitative first-order reactions when heated in a solution in benzene or chloroform to 30 °C. Interestingly, the analogous reactions of **8c**,**h**,**i**, which imply the migration of a methyl group to afford **9c**,**h**,**i**, required prolonged reflux of a very dilute solution of the azo compounds in benzene (yield 86–90%).[7]

On heating or distillation at higher temperature, the hydrazines **5c**,**f**,**i** were partially isomerized to dihydropyrazoles **7**. However, these heterocycles are not intermediates in the transformation **5** → **9** as shown in control experiments starting with **7** and activated MnO_2.

In concentrated solution, or especially in the presence of a base like NEt_3, prototropic rearrangement to give hydrazones, for instance **8d** → **10d**, was the main reaction of allenyl azo compounds (Scheme 3). On treatment with an excess of nucleophiles such as alcohols, phenols, or ethyl acetoacetate, **8c** led to ring closure products **11**, even at room temperature. On the other hand, the reaction of **8c** with isopropylmagnesium bromide provided the hydrazone **12** on 1,4-addition. Simple azoalkenes also prefer 1,4-addition of Grignard reagents to generate hydrazones. However, in this case, the nucleophile did not attack the nitrogen but the β-carbon atom.[1a,8]



Scheme 3. Reactions of allenyl azo compounds.

This work is Part 13 of the series 'Rearrangement reactions'. The research was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

Dedicated to Prof. Peter Welzel on the occassion of this 65th birthday.

References and Notes

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5 Compound **5c**: Colorless solid, mp 60–62 °C. ^{1}H NMR ($CDCl_3$): δ 1.33 (s, CMe_2), 2.29 (s, C≡CH), 2.42 (s, NMe), 2.99 (br. s, NH_2). ^{13}C NMR ($CDCl_3$): δ 28.0 (q, C*Me*$_2$), 43.0 (q, NMe), 58.3 (s, *C*Me$_2$), 72.6 (d, $J = 248$ Hz, C≡*C*H), 83.5 (d, $J = 48$ Hz, *C*≡CH). ^{15}N NMR (C_6D_6): δ −301.1 (NMe), −296.4 (NH_2). The external standard CH_3NO_2 (δ = 0) was used.

6 Selected data for allenyl azo compounds. Compound **8c**: Yellow liquid. ^{1}H NMR ($CDCl_3$): δ 1.87 (d, $^{5}J = 2.4$ Hz, CMe_2), 3.78 (s, NMe), 6.79 (sept, $^{5}J = 2.4$ Hz, C=CH). ^{13}C NMR ($CDCl_3$): δ 20.4 (q, C*Me*$_2$), 56.3 (q, NMe), 104.1 (s, *C*Me$_2$), 115.7 (d, *C*H=C=C), 207.2 (CH=*C*=C). IR ($CDCl_3$): 2978, 2958, 2916, 1954 cm^{-1}. GC MS (EI) *m*/*z* (%): 110 (M^+, 13), 109 (10), 67 (26), 43 (78), 41 (100). Compound **8d**: Yellow liquid. ^{1}H NMR ($CDCl_3$): δ 1.81 (t, $^{5}J = 2.9$ Hz, CMe), 3.83 (t, $^{7}J = 1.7$ Hz, NMe), 5.35 (qq, $^{5}J = 2.9$ Hz, $^{7}J = 1.7$ Hz, CH_2). ^{13}C NMR ($CDCl_3$): δ 12.8 (q, C*Me*), 56.6 (q, NMe), 80.5 (t, CH_2), 123.7 (s, *C*Me), 215.3 (s, C=*C*=C). IR ($CDCl_3$): 2966, 2914, 1976, 1946 cm^{-1}. GC MS (EI) *m*/*z* (%): 96 (M^+, 23), 95 (19), 81 (5), 53 (26), 43 (100). Compound **8f**: Yellow liquid. ^{1}H NMR ($CDCl_3$): δ 3.87 (t, $^{7}J = 1.7$ Hz, NMe), 5.51 (dq, $^{4}J = 6.0$ Hz, $^{7}J = 1.7$ Hz, CH_2), 7.02 (t, $^{4}J = 6.0$ Hz, CH=C). ^{13}C NMR ($CDCl_3$): δ 56.6 (q, NMe), 82.7 (t, CH_2), 117.7 (d, *C*H=C=C), 214.7 (s, C=*C*=C). IR ($CDCl_3$): 1935 cm^{-1}. UV (pentane): λ_{max} 378 nm ($\varepsilon \approx 50$), 230 nm ($\varepsilon \approx 10000$). GC MS (EI) *m*/*z* (%): 82 (M^+, 4), 43 (100), 39 (33).

7 For example, refluxing of a 0.003 molar solution of **8c** in benzene for 12 h gave **9c** with 90% yield.

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