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Communications

Synthesis of Allylazo Compounds by Reactions of Aryldiazonium Salts with Allylsilanes

Herbert Mayr*,† and Klaus Grimm

Institut für Chemie der Medizinischen Universität zu Lübeck, Ratzeburger Allee 160, D-2400 Lübeck, Germany

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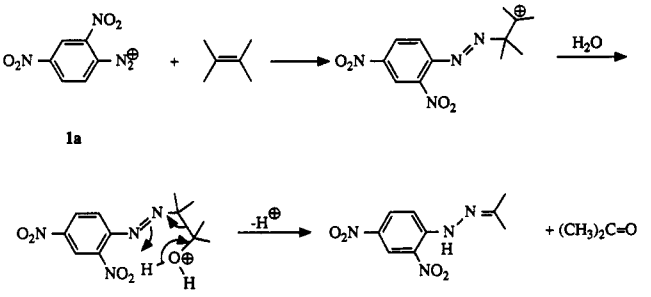
Summary: Aryldiazonium tetrafluoroborates react with allylsilanes to yield allylazo compounds. If the allylic carbon attached to the azo group carries hydrogen, tautomerization with formation of hydrazones takes place.

The coupling of aryldiazonium ions with arylamines and phenols, discovered by Griess in 1858,[1] has been one of the most important reactions in industrial chemistry for more than a century.[2] Among the aliphatic C-nucleophiles previously reported to react with diazonium ions, CH-acidic compounds,[3a] enol ethers,[3b] enamines,[3c] and 1,3-dienes[3d] are the most important ones. Marxmeier and Pfeil have found that the 2,4-dinitrobenzenediazonium ion **1a** also reacts with ordinary alkenes, often with cleavage of the original CC double bond as shown in Scheme I.[4]

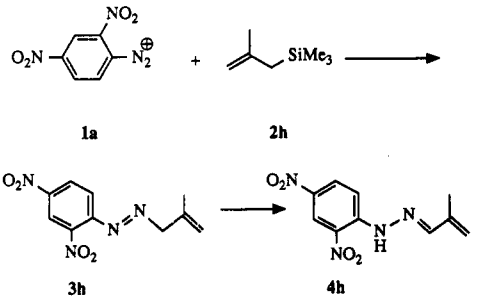
Though allylsilanes have been combined with a manifold of electrophiles,[5] reactions with diazonium ions have not yet been reported. Since the nucleophilicity of allyltrimethylsilane is similar to that of those alkenes,[6] which are known to be susceptible to electrophilic attack by **1a**, the electrophilicity of **1a** should also be sufficient for a reaction with allylsilanes.

Combination of the γ,γ-disubstituted allylsilanes **2a–2g** with 2,4-dinitrobenzenediazonium tetrafluoroborate **1a** in acetonitrile gives the allylazo compounds **3a–3g** in 38–94% yields (Table I).[7] This reaction thus provides a straightforward access to allylazo compounds, which are of interest as precursors to allyl radicals.[8] Representatives of this class of compounds have previously been synthesized by treatment of sulfamides (from allylamines and *N*-sulfonylaniline) with NaOCl and NaOH[8g] or by sigmatropic rearrangements of diazenes, which have been generated by oxidation of *N*-allyl-*N*-arylhydrazines.[9]

Scheme I



Scheme II



The reaction of methallyltrimethylsilane **2h** with **1a** BF_4^- initially yields the crystalline allylazo compound **3h**, which

† Present address: Institut für Organische Chemie der Technischen Hochschule Darmstadt, Petersenstr. 22, W-6100 Darmstadt, Germany.

(1) Griess, P. *Liebigs Ann. Chem.* **1858**, *106*, 123.

(2) (a) Szele, I.; Zollinger, H. *Top. Curr. Chem.* **1983**, *112*, 1. (b) Hegarty, A. F. In *The Chemistry of Diazonium and Diazo Groups*; Patai, S., Ed.; Wiley: Chichester, 1978; p 511. (c) Schündehütte, K. H. *Methoden der Organischen Chemie (Houben-Weyl-Müller)*; Thieme: Stuttgart, 1965; Vol. X/3, p 213. (d) Saunders, K. H.; Allen, R. L. M. *Aromatic Diazo Compounds*; Edward Arnold: London, 1983.

(3) (a) Parmerter, S. M. *Org. React.* **1959**, *10*, 1. (b) Terent'ev, A. P.; Jagorsvkii, V. A. *Zh. Obshch. Khim.* **1956**, *26*, 211. (c) Crary, J. W.; Quayle, O. R.; Lester, C. T. *J. Am. Chem. Soc.* **1956**, *78*, 5584. (d) Huisgen, R.; Bronberger, F. *Tetrahedron Lett.* **1984**, *25*, 57. (e) Huisgen, R.; Bronberger, F. *Tetrahedron Lett.* **1984**, *25*, 61.

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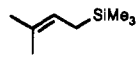
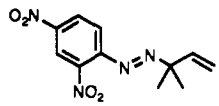
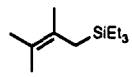
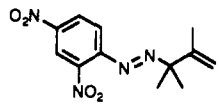
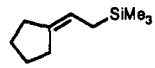
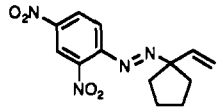
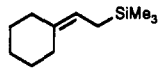
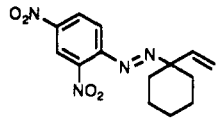
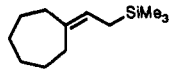
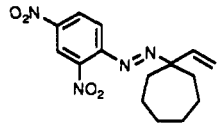
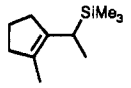
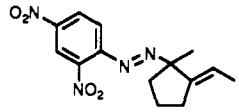
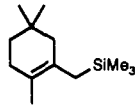
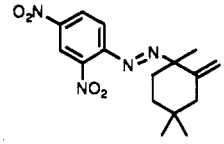
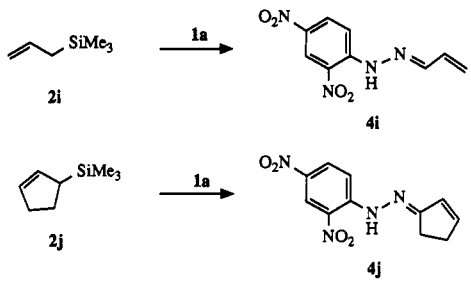
Table I. Allylazo Compounds from γ,γ-Disubstituted Allylsilanes 2 and 2,4-Dinitrobenzenediazonium Tetrafluoroborate 1a

	allylsilanes 2	products 3	(% yield)	^{13}C NMR chemical shifts[a]
a			84	24.46 (q), 74.75 (s), 115.01 (t), 141.32 (d)
b			69	19.68 (q), 24.07 (q), 76.85 (s), 112.79 (t), 147.13 (s)
c			38[b]	23.92 (t), 35.29 (t), 86.53 (s), 115.21 (t), 139.67 (d)
d			59	22.27 (t), 25.60 (t), 33.94 (t), 76.66 (s), 117.06 (t), 140.08 (d)
e			41[b]	22.57 (t), 30.34 (t), 35.90 (t), 80.59 (s), 115.19 (t), 141.34 (d)
f			59	15.10 (q), 22.94 (t), 22.97 (q), 29.34 (t), 39.09 (t), 82.95 (s), 120.18 (d), 144.78 (s)
g			94	18.51 (t), 25.72 (q), 29.19 (q), 31.25 (q), 36.76 (s), 37.54 (t), 40.60 (t), 77.17 (s), 111.40 (t), 159.63 (s)

[a] Aryl-C: C-1 δ = 149.96–150.43 (s), C-2 δ = 144.51–144.81 (s), C-3 δ = 120.24–120.51 (d), C-4 δ = 147.01–147.22 (s), C-5 δ = 128.30–128.42 (d), C-6 δ = 120.39–121.05 (d). [b] Unidentified hydrazones were also formed.

Scheme III



has been stored in the dark at −20 °C for several months. At room temperature, rearrangement to the hydrazone **4h** is detectable after several hours. This tautomerization is very fast in chloroform solution (not purified from traces of HCl) or during chromatography on silica gel. Analogously, the reaction of **2i** and **2j** with **1a** yields the hydrazones **4i** and **4j** as stable final products. Allylsilanes with one or two hydrogen atoms in γ-position thus can

Table II. Relative Reactivities of the Allylsilanes 2a–2h toward (p-$H_3COC_6H_4$)PhCH$^+$ and Their Ability To React with Diazonium Ions

		reaction with		
	k_{rel}[a]	1a	1b	1c
2i	1	+	−	−
2j	6.60	+	−	−
2c	~7	+	+	−
2d	~7	+	+	−
2e	~7	+	+	−
2a	7.92	+	+	−
2h	508	+	+	−
2f	~10^3	+	+	−
2g	~10^3	+	+	+
2b	1675	+	+	+

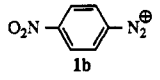
[a] From ref 6d; estimates marked by the ~ sign are based on k_{rel} values of structurally analogous compounds.

(4) Marxmeier, H.; Pfeil, E. *Chem. Ber.* **1964**, *97*, 53.
(5) (a) Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer-Verlag: Berlin, 1983. (b) Schinzer, D. *Synthesis* **1988**, 263. (c) Fleming, I. In *Comprehensive Organic Chemistry*; Barton, D., Ollis, W. D., Eds.; Pergamon Press: Oxford, 1979; Vol. 3, p 541. (d) Sakurai, H. *Pure Appl. Chem.* **1985**, *57*, 1759. (e) Colvin, E. *Silicon in Organic Synthesis*; Butterworths: London, 1981.
(6) (a) Mayr, H.; Schneider, R.; Irrgang, B.; Schade, C. *J. Am. Chem. Soc.* **1990**, *112*, 4459. (b) Mayr, H. *Angew. Chem.* **1990**, *102*, 1415; *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1371. (c) Hagen, G.; Mayr, H. *J. Chem. Soc., Chem. Commun.* **1989**, 91. (d) Hagen, G.; Mayr, H. *J. Am. Chem. Soc.* **1991**, *113*, 4954.
(7) Typical Procedure. Allylsilane **2b** (0.530 g, 2.67 mmol) was added to a suspension of 2,4-dinitrobenzenediazonium tetrafluoroborate (0.500 g, 1.77 mmol) in dry acetonitrile. The mixture was stirred until the diazonium salt dissolved. After addition of water, the mixture was extracted with two 10-mL portions of CH_2Cl_2. The organic layers were dried over $CaCl_2$ and evaporated. After purification of the residue by column chromatography (silica gel, CH_2Cl_2/pentane, 70/30) product **3b** was obtained and recrystallized from pentane: Orange plates (0.340 g, 69%), mp 55–56 °C.

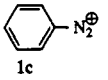
(8) (a) Luedtke, A.; Meng, K.; Timberlake, J. W. *Tetrahedron Lett.* **1987**, *28*, 4255. (b) Adams, J. S.; Burton, K. A.; Andrews, B. K.; Weisman, R. B.; Engel, P. S. *J. Am. Chem. Soc.* **1986**, *108*, 7935. (c) Rossi, M.; Golden, D. M. *J. Am. Chem. Soc.* **1979**, *101*, 1230. (d) Crawford, R. J.; Takagi, K. *J. Am. Chem. Soc.* **1972**, *94*, 7406. (e) Crawford, R. J.; Hamelin, J.; Strehlke, B. *J. Am. Chem. Soc.* **1971**, *93*, 3810. (f) Al-Sader, B. H.; Crawford, R. J. *Can. J. Chem.* **1970**, *48*, 2745. (g) Porter, N. A.; Iloff, P. M. *J. Chem. Soc., Chem. Commun.* **1971**, 1575.
(9) Baldwin, J. E.; Brown, J. E.; Höfle, G. *J. Am. Chem. Soc.* **1971**, *93*, 788.

oxidatively be desilylated by treatment with aryldiazonium ions.

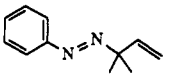
Preliminary experiments showed that among the allylsilanes used in this work all but **2i** and **2j** also react with the less electrophilic *p*-nitrobenzenediazonium ion **1b**. The highly alkylated allylsilanes **2b** and **2g** even react with the unsubstituted benzenediazonium ion **1c** to give **3b′** and **3g′** in 51 and 74% yield, respectively. In accord with our previous report that allylstannanes are more nucleophilic than structurally analogous allylsilanes by several orders of magnitude,[6d] tri-*n*-butylprenylstannane also reacted with the parent benzenediazonium ion **1c** to afford 49% of **3a′**. Though the correlation between reactivities toward carbenium and diazonium ions does not seem to be perfect, Table II shows that the nucleophilicity scale developed with respect to diarylcarbenium ions[6] also allows one to roughly predict the feasibility of electrophilic attack of diazonium ions at allylsilanes.



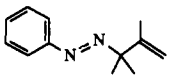
1b



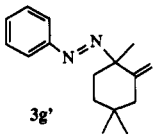
1c



3a′



3b′



3g′

Registry No. **1a**, 345-12-0; **1b**, 456-27-9; **1c**, 369-57-3; **2a**, 18293-99-7; **2b**, 64545-12-6; **2c**, 83438-58-8; **2d**, 63922-76-9; **2e**, 138061-12-8; **2f**, 138061-13-9; **2g**, 138061-14-0; **2h**, 18292-38-1; **2i**, 762-72-1; **2j**, 14579-08-9; **3a**, 138061-15-1; **3a′**, 31928-42-4; **3b**, 138061-16-2; **3b′**, 138061-17-3; **3c**, 138061-18-4; **3d**, 138061-19-5; **3e**, 138061-20-8; **3f**, 138061-21-9; **3g**, 138061-22-0; **3g′**, 138061-23-1.

(*R*)-1-Acetyl-5-isopropoxy-3-pyrrolin-2-one: A Versatile Chiral Dienophile from (*S*)-Malic Acid

Wim-Jan Koot, Henk Hiemstra,* and W. Nico Speckamp*

Department of Organic Chemistry, University of Amsterdam, Nieuwe Achtergracht 129, 1018 WS Amsterdam, The Netherlands

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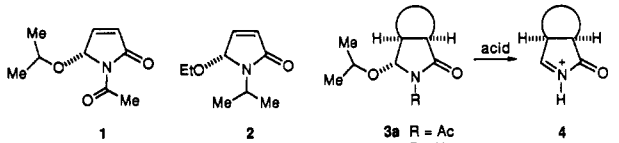
Summary: The title compound, readily prepared from (*S*)-malic acid, reacts as a Diels–Alder dienophile with several 1,3-dienes with excellent regio- and stereoselectivity without loss of enantiomeric purity. The synthesis of an enantiomerically pure intermediate in a projected synthesis of gelsemine is detailed.

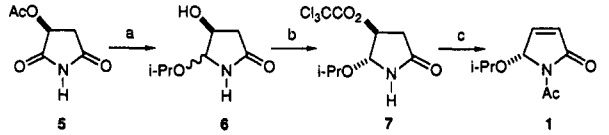
Of the various ways to control the absolute stereochemistry of an intermolecular Diels–Alder reaction, the approach involving the use of an enantiomerically pure dienophile has proven to be most practicable.[1] In this paper we wish to present the synthesis and utility of the chiral dienophile (*R*)-1-acetyl-5-isopropoxy-3-pyrrolin-2-one (**1**), which in essence can be viewed as an enantiomerically pure synthetic equivalent of maleimide.[2]



1 **2** **3a** R = Ac, **3b** R = H **4**

The choice for the structural features present in **1** was eventually made, when we had found that other Δ^3-pyrrolin-2-ones such as **2**[3] were unsuitable for our purposes. The isopropoxy function at C-5 in **1** is meant to direct 1,3-dienes to react at the opposite face of the molecule to give **3a**.[4] The significance of an alkoxy function at C-5 becomes apparent after removal of the *N*-acetyl function, as **3b** is expected to allow the introduction of a variety of substituents via *N*-acyliminium intermediate **4**.[5] The presence of the *N*-acetyl function in **1** is required to prevent racemization and enhance the reactivity and regiochemical bias of the dienophile.[6]

Scheme I[a]



5 **6** **7** **1**

[a] Reagents and conditions: (a) (i) $LiBH_4$ (1.0 equiv), THF, −20 → 0 °C, (ii) H_2SO_4 in i-PrOH (pH = 3), 0 °C → reflux, 55%; (b) $(Cl_3CCO)_2O$ (1.1 equiv), DMAP (1.1 equiv), Et_2O, −60 °C → rt, 86%; (c) Ac_2O/pyridine, DMAP (cat.), 0 °C → rt, 85%.

The synthesis of (*R*)-**1** is detailed in Scheme I. (*S*)-3-Acetoxysuccinimide (**5**), readily prepared on large scale from (*S*)-malic acid,[7] was regioselectively reduced with lithium borohydride in THF at −20 °C. The crude reaction mixture was acidified with sulfuric acid. The solvent THF was then substituted for 2-propanol and the resulting mixture heated at reflux for 18 h to effect both isopropanolysis and transesterification, to give **6** as a 1:4

(1) For reviews, see: (a) Paquette, L. A. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic: New York, 1984; Vol. 3, Chapter 7. (b) Oppolzer, W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 876.

(2) For recent alternative approaches, see: (a) Arai, Y.; Matsui, M.; Koizumi, T.; Shiro, M. *J. Org. Chem.* **1991**, *56*, 1983. (b) Baldwin, S. W.; Greenspan, P.; Alaimo, C.; McPhail, A. T. *Tetrahedron Lett.* **1991**, *32*, 5877. For a chiral synthetic equivalent for maleic anhydride, see: (c) Feringa, B. L.; de Jong, J. C. *J. Org. Chem.* **1988**, *53*, 1125. (d) de Jong, J. C.; Jansen, J. F. G. A.; Feringa, B. L. *Tetrahedron Lett.* **1990**, *31*, 3047.

(3) The study of **2** originated from our work on the synthesis of the indole alkaloid peduncularine and will be described in a full paper; see: Klaver, W. J.; Hiemstra, H.; Speckamp, W. N. *J. Am. Chem. Soc.* **1989**, *111*, 2588.

(4) For Diels–Alder additions to Δ^3-pyrrolin-2-ones with carbon substituents at C-5, see: (a) Vedejs, E.; Campbell, J. B., Jr.; Gadwood, R. C.; Rodgers, J. D.; Spear, K. L.; Watanabe, Y. *J. Org. Chem.* **1982**, *47*, 1534. (b) Stork, G.; Nakahara, Y.; Nakahara, Y.; Greenlee, W. J. *J. Am. Chem. Soc.* **1978**, *100*, 7775. (c) Ohfune, Y.; Tamita, M. *J. Am. Chem. Soc.* **1982**, *104*, 3511. (d) Harkin, S. A.; Singh, O.; Thomas, E. J. *J. Chem. Soc., Perkin Trans. 1* **1984**, 1489. (e) Ackermann, J.; Matthes, M.; Tamm, C. *Helv. Chim. Acta* **1990**, *73*, 122. (f) Meyers, A. I.; Busacca, C. A. *Tetrahedron Lett.* **1989**, *30*, 6973.

(5) For a review, see: Hiemstra, H.; Speckamp, W. N. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds; Pergamon: Oxford, 1991; Vol. 2, Chapter 4.5.

(6) (a) Vedejs, E.; Gadwood, R. C. *J. Org. Chem.* **1978**, *43*, 376. (b) Baker, J. T.; Sifniades, S. *J. Org. Chem.* **1979**, *44*, 2798. (c) Schmidlin, T.; Tamm, C. *Helv. Chim. Acta* **1980**, *63*, 121.

(7) (a) Chamberlin, A. R.; Chung, Y. L. *J. Am. Chem. Soc.* **1983**, 105, 3653. (b) Hart, D. J.; Yang, T.-K. *J. Org. Chem.* **1985**, *50*, 235.

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