

Figure 1. Pseudo-first-order rates observed for 1a-e with excess diazoacetophenone.

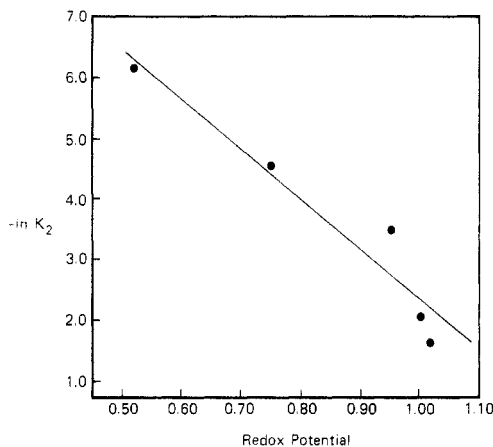
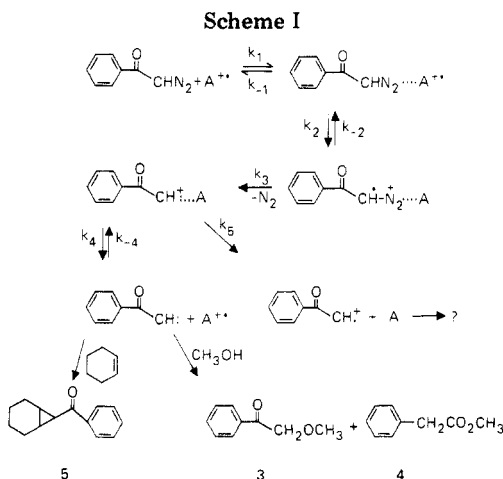


Figure 2. Relationship of second-order rate constant of the reaction of 1a-e and 2 to redox potentials of 1a-e.



cations are very reactive with a variety of functional groups including carbonyl, epoxy, and olefinic compounds. We are currently investigating these reactions at greater length as well as looking into the synthetic exploitation of these reagents as selective oxidants.

**Registry No.** 1a, 78065-12-0; 1b, 78065-13-1; 1c, 78065-14-2; 1d, 78090-05-8; 1e, 78065-15-3; 2, 3282-32-4.

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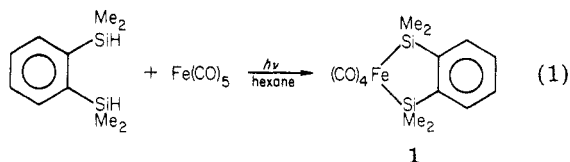
## A Disilylated Iron Carbonyl Complex as Reagent for the Conversion of Nitriles into Aldehyde-Enamines

**Summary:** A readily available disilylated iron carbonyl complex converted nitriles into aldehyde-enamines. This chemical transformation is proved to be useful for the reduction of nitriles into aldehydes and for the protection of nitriles.

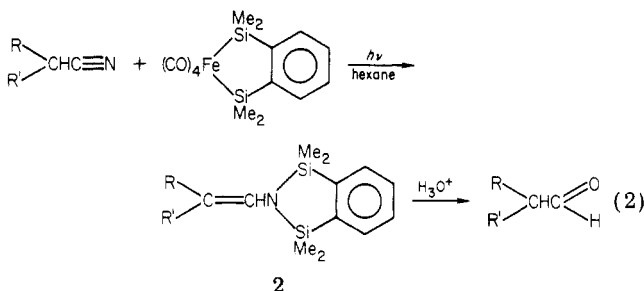
**Sir:** Our current interest in the use of organometallic compounds in organic synthesis has led us to investigate the reactivity of organosilyl transition-metal complexes.<sup>1</sup> These compounds are potential reagents for organic syntheses.<sup>2</sup>

In a previous communication, we mentioned the formation of a silylated vinylamine by photolysis of silylated iron carbonyl complexes in the presence of nitriles.<sup>1</sup> We report herein the use of a readily available iron carbonyl complex to effect this new chemical transformation and some of its possible uses in organic synthesis.

Complex 1, originally prepared by Fink,<sup>3</sup> was easily obtained from 1,2-bis(dimethylsilyl)benzene<sup>4</sup> and iron pentacarbonyl (eq 1).



Exposing hexane solutions of equimolecular amounts of nitrile and complex 1 to UV light for several hours afforded the disilylated enamines 2 in good yields (eq 2).<sup>5</sup>



These enamines are very stable and did not hydrolyze under neutral conditions. However, hydrolysis with dilute HCl led to the corresponding aldehydes in good yields.

As illustrated in Table I, a wide range of nitriles were converted into aldehyde-enamines. Alkyl and benzyl

(1) Corriu, R. J. P.; Moreau, J. J. E. *J. Chem. Soc., Chem. Commun.* 1980, 278.

(2) Johnson, D. L.; Gladysz, J. A. *J. Am. Chem. Soc.* 1979, 101, 6433.

(3) We found dozen-gram quantities of complex 1 were best obtained by using the photochemical reaction with  $\text{Fe}(\text{CO})_5$  rather than using the reaction with  $\text{Fe}_2(\text{CO})_9$  (Fink, W. *Helv. Chim. Acta* 1976, 59, 606). In a typical preparation, 6 mL ( $45 \times 10^{-3}$  mol) of iron pentacarbonyl and 8.8 g ( $45 \times 10^{-3}$  mol) of 1,2-bis(dimethylsilyl)benzene were dissolved in 600 mL of dry degassed hexane. The solution was irradiated at room temperature for 15 h, using an immersed 450-W high-pressure mercury lamp in a quartz reaction vessel. The solvent was evaporated under reduced pressure, and the brown residue was dissolved in 30 mL of degassed *n*-pentane; crystallization at  $-78^\circ\text{C}$  afforded 11.0 g of complex 1 (68%) as off-white air-stable crystals.

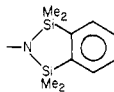
(4) Fink, W. *Helv. Chim. Acta* 1974, 57, 1010; Bourgeois, P.; Calas, R. *J. Organomet. Chem.* 1975, 84, 165.

(5) The reaction of acetonitrile with complex 1 illustrates the standard procedure: complex 1 (3.09 g,  $8.6 \times 10^{-3}$  mol) and acetonitrile (0.35 g,  $8.6 \times 10^{-3}$  mol) were dissolved in 200 mL of dry degassed hexane. The solution was irradiated at room temperature for 30 h, using an immersed high-pressure 450-W mercury lamp in a quartz reaction vessel. The reaction mixture was filtrated, and the solvent was removed under reduced pressure. Distillation of the residue afforded 1.4 g (70%) of the disilylated vinylamine [bp (18 mm) =  $95^\circ\text{C}$ ].

Table I. Conversion of Nitriles into Disilylated Enamines and Hydrolysis to Aldehydes<sup>a</sup>

entry	nitrile	reaction time, h	enamines	<i>E:Z</i> <sup>b</sup>	isolated yield, %	aldehydes	% yield <sup>c</sup>
1	CH <sub>3</sub> CN	30			70	CH <sub>3</sub> CHO	65
2	CH <sub>3</sub> CH <sub>2</sub> CN	30		65:35	85	CH <sub>3</sub> CH <sub>2</sub> CHO	82
3	(CH <sub>3</sub> ) <sub>2</sub> CHCN	30			80	(CH <sub>3</sub> ) <sub>2</sub> CHCHO	68
4	PhCH <sub>2</sub> CN	21		55:45	95	PhCH <sub>2</sub> CHO	79
5	Ph <sub>2</sub> CHCN	20			78	Ph <sub>2</sub> CHCHO	84
6	NC(CH <sub>2</sub> ) <sub>4</sub> CN	34		18:82	70	NC(CH <sub>2</sub> ) <sub>4</sub> CHO	79
7		22		50:50	50		
8	MeOCH <sub>2</sub> CN	43		40:60	70		
9	EtOOCCH <sub>2</sub> CN	6		100:0	83	EtOOCCH <sub>2</sub> CHO	73
10		76		<i>e</i>	60		
11		30		56:44	75		

<sup>a</sup> Reactions were carried out by irradiating a hexane solution of a 1:1 mixture of nitrile and complex 1, using a high-pressure 450-W mercury lamp in a quartz reaction vessel. After complete reaction, as monitored by IR spectroscopy, the solvent was removed, and the enamines were isolated by distillation from the residue. <sup>b</sup> *E:Z* ratio was determined by NMR spectroscopy at 100 MHz. <sup>c</sup> Isolated as pure recrystallized 2,4-dinitrophenylhydrazone. <sup>d</sup>

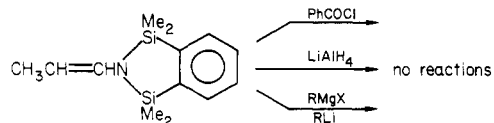


<sup>e</sup> NMR spectroscopy indicated the presence of two isomers in a 7:3 ratio; *E* and *Z* structures have not been assigned.

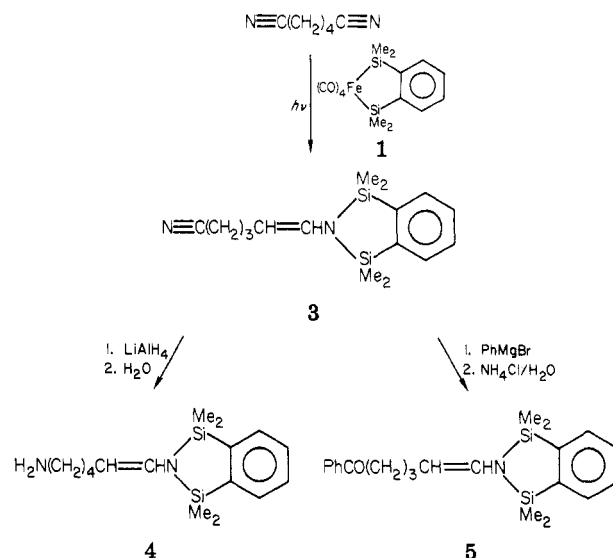
cyanides gave a 70–95% yield of enamines as a mixture of *E* and *Z* isomers, which upon hydrolysis yielded the aldehydes (cf. entries 1–5). Complex 1 thus appears as an interesting reagent for the reduction of nitriles into aldehydes, for which only a few methods are available.<sup>6</sup>

The synthetic utility of such a reduction is well illustrated by the reaction of complex 1 with dinitriles. Adiponitrile was easily converted to the monoenamine, and subsequent hydrolysis gave the cyanoaldehyde (cf. entry 6). Also of interest is the reaction with  $\alpha$ -cyanotoluonitrile for which reduction occurred only for the cyano group having  $\alpha$  hydrogen atoms (cf. entry 7). Nitriles containing other functional groups were also selectively converted to functional enamines (cf. entries 8–11). However, with keto nitriles, good yields of the enamines were obtained only for a protected carbonyl group.

The disilylated enamines 2 appeared as a new functional group since they exhibited different reactivity compared to carbon enamines. The propenylamine, obtained from propionitrile, failed to react with benzoyl chloride under the usual reaction conditions. An electronic interaction between silicon and nitrogen can account for this weak nucleophilic character. Moreover, the silicon–nitrogen bond is very stable. No cleavage occurred with nucleophiles such as LiAlH<sub>4</sub> and Grignard or lithium reagents.



## Scheme I. Protection of Nitriles as Disilylated Enamines



Owing to the stability of the silicon–nitrogen bonds, disilylated enamines could be used as a protecting group for nitriles as exemplified in Scheme I.

The cyano enamine 3 obtained from adiponitrile was reduced to the amino enamine 4 by LiAlH<sub>4</sub>. Similarly, phenylmagnesium bromide reacted with the nitrile function, which led to the keto enamine 5. In both cases, mild hydrolysis did not affect the enamine function.

Complex 1 constitutes an attractive reagent which effects a unique chemical transformation of nitriles into disilylated enamines. These enamines can be used both for new functionalization and protection of nitriles. We are cur-

(6) Backeberg, O. G.; Staskun, B. *J. Chem. Soc.* 1962, 3961, and references therein; Malek, J.; Cerny, M. *Synthesis* 1972, 217; Fry, J. L. *J. Chem. Soc., Chem. Commun.* 1974, 45.

rently investigating the chemical reactivity of these new enamine reagents derived from nitriles and their synthetic uses.

**Registry No.** 1, 56977-62-9; 2 (R = R' = H), 78108-63-1; 2-(E) (R = CH<sub>3</sub>; R' = H), 78108-64-2; 2-(Z) (R = CH<sub>3</sub>; R' = H), 78108-65-3; 2-(E) (R = R' = CH<sub>3</sub>), 78108-66-4; 2-(E) (R = Ph; R' = H), 78108-67-5; 2-(Z) (R = Ph; R' = H), 78108-68-6; 2 (R = R' = Ph), 78108-69-7; 2-(E) (R = 2-cyanophenyl; R' = H), 78108-70-0; 2-(Z) (R = 2-cyanophenyl; R' = H), 78108-71-1; 2-(E) (R = MeO; R' = H), 78108-72-2; 2-(Z) (R = MeO; R' = H), 78108-73-3; 2-(E) (R = COOEt; R' = H), 78108-74-4; 2-(E) (R = 2-methyl-1,3-dioxolan-2-yl; R' = Ph), 78108-75-5; 2-(Z) (R = 2-methyl-1,3-dioxolan-2-yl; R' = Ph), 78108-76-6; 2-(E) (R = 6-(1,4-dioxaspiro[4.5]decyl)methyl; R' = H), 78108-77-7; 2-(Z) (R = 6-(1,4-dioxaspiro[4.5]decyl)methyl; R' = H), 78108-78-8; 3-(E), 78108-79-9; 3-(Z), 78108-80-2; 4, 78108-81-3; 5, 78108-82-4; acetonitrile, 75-05-8; propanenitrile, 107-12-0; 2-methylpropanenitrile, 78-82-0; benzeneacetonitrile, 140-29-4;  $\alpha$ -phenylbenzeneacetonitrile, 86-29-3; hexanedinitrile, 111-69-3; 2-cyano-benzeneacetonitrile, 3759-28-2; methoxyacetonitrile, 1738-36-9; cyanoacetic acid, ethyl ester, 105-56-6; 2-methyl- $\alpha$ -phenyl-1,3-dioxolane-2-acetonitrile, 78108-83-5; 1,4-dioxaspiro[4.5]decane-6-propanenitrile, 78108-84-6; acetaldehyde, 75-07-0; propanal, 123-38-6; 2-methylpropanal, 78-84-2; benzeneacetaldehyde, 122-78-1;  $\alpha$ -phenylbenzeneacetaldehyde, 947-91-1; 6-oxohexanenitrile, 3523-02-2; 3-oxopropanoic acid, ethyl ester, 34780-29-5; acetaldehyde 2,4-DNP, 1019-57-4; propanal 2,4-DNP, 725-00-8; 2-methylpropanal 2,4-DNP, 2057-82-1; benzeneacetaldehyde 2,4-DNP, 2074-04-6;  $\alpha$ -phenylbenzeneacetaldehyde 2,4-DNP, 10479-11-5; 6-oxohexanenitrile 2,4-DNP, 13050-18-5; 3-oxopropanoic acid, ethyl ester 2,4-DNP, 2003-74-9.

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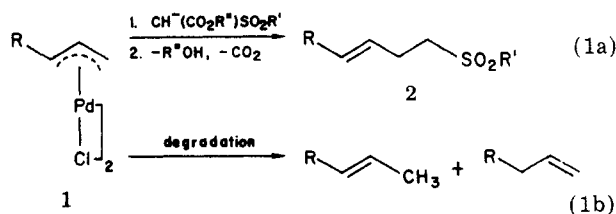
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### Regio- and Stereoselective Anti-Markovnikov Hydro-sulfonation of Conjugated Dienes via $\pi$ -Allylpalladium Complex: Synthesis of (Z)- $\Delta^3$ -Alkenyl Sulfones

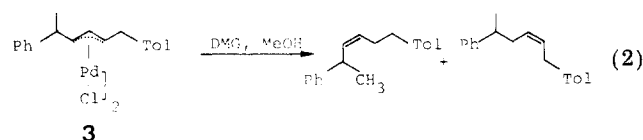
**Summary:** Butadienes of type 4 may be converted to products of type 7 by means of palladium chloride.

**Sir:** Stereocontrolled di- and trisubstituted olefin synthesis is still a problem of pressing concern in organic synthesis. Palladium chemistry has made a great contribution to this problem.<sup>1</sup> The reactions via  $\pi$ -allylpalladium intermediates, however, are generally limited to the syntheses of *E* olefins, reflecting the thermodynamically favored syn geometry.<sup>2</sup> Typical examples are illustrated in eq 1. The



(1) (a) Trost, B. M.; Runge, T. A.; Jungheim, L. N. *J. Am. Chem. Soc.* 1980, 102, 2840. (b) Trost, B. M.; Fortunack, J. M. *Ibid.* 1980, 102, 2841. (c) Trost, B. M.; Vincent, J. E. *Ibid.* 1980, 102, 5680. (d) Trost, B. M.; Curran, D. P. *Ibid.* 1980, 102, 5699. (e) Trost, B. M.; Schmuft, N. R.; Miller, M. J. *Ibid.* 1980, 102, 5979. (f) Overman, L. E.; Knoll, F. M. *Ibid.* 1980, 102, 865. (g) Negishi, E.; Valente, L. F.; Kobayashi, M. *Ibid.* 1980, 102, 3298. (h) Tsuji, J.; Shimizu, I.; Suzuki, H.; Naito, Y. *Ibid.* 1979, 101, 5070. (i) Larock, R. C.; Biefling, B. *J. Org. Chem.* 1978, 43, 1468. For a review, see: Trost, B. M. *Tetrahedron* 1977, 33, 2615.

alkylation of 1 with sulfonylacetate anion provides (*E*)- $\Delta^3$ -sulfone derivatives 2. Degradation with CH<sub>3</sub>ONa-C-H<sub>3</sub>OH,<sup>3</sup> NaCN-CH<sub>3</sub>OH,<sup>4</sup> or reducing agents (NaBH<sub>4</sub>,<sup>5</sup> LiAlH<sub>4</sub>,<sup>6</sup> HCO<sub>2</sub>H-pyridine)<sup>7</sup> also gives rise to *E* olefins, but in these cases comparable amounts of mixtures of regioisomers are produced, predominately the more substituted ones. In sharp contrast to these, we have found that treatment of the  $\pi$ -allylpalladium complex (3) with 2 equiv of dimethylglyoxime (DMG; in CH<sub>3</sub>OH in the presence of an appropriate amount of pyridine to dissolve 3 at ambient temperature overnight) provides *Z* olefins as a mixture of regioisomers [(*Z*)-1-*p*-tolyl-5-phenylhex-3-ene and (*Z*)-1-*p*-tolyl-5-phenylhex-2-ene in a ratio of 1:2 in virtually quantitative yield (eq 2)].<sup>8</sup> Interestingly, this reaction is



clearly accompanied by the inversion of configuration around the allylic moiety of 3.<sup>9</sup> We expected that the above stereoselectivity, coupled with the regioselectivity as observed in the anti-Markovnikov hydro-sulfonation of 1,3-dienes,<sup>10</sup> might be applied to the preparation of useful synthons, (*Z*)- $\Delta^3$ -sulfones 7 (Scheme I). Indeed, this proved to be the case, and (*Z*)- $\Delta^3$ -sulfones 7 were prepared in high regio- and stereoselectivities, independent of the configuration of the starting 1,3-dienes.<sup>11</sup> Results are summarized in Table I, which covers dienes with various structural features. The reaction consists of two steps: preparation of  $\pi$ -allylpalladium complexes 5 and 6 and degradation of these with DMG, as typified in the following example (entry 1). A mixture of 1,3-pentadiene (cis-trans mixture, 3 mmol), PdCl<sub>2</sub> (2 mmol), and sodium neophylsulfinate (4 mmol) in 20 mL of acetic acid was heated at 50 °C for 4 h with magnetic stirring. After the usual extractive workup with EtOAc (NaHCO<sub>3</sub>-H<sub>2</sub>O) and evaporation of the solvent, the yellow residue of 5a and 6a (R<sup>1</sup> = CH<sub>3</sub>, R<sup>2</sup> = R<sup>3</sup> = H) was dissolved in CH<sub>3</sub>OH<sup>12</sup> and treated with DMG (4 mmol). After the mixture was stirred overnight at ambient temperature and the CH<sub>3</sub>OH evaporated, the yellow solid residue was washed several times with benzene-hexane. Purification of the extracts by column chromatography (silica gel, benzene-EtOAc

(2) In some instances, *Z* olefins are prepared by kinetically controlled reactions using *Z*-allylic acetates as starting materials. Trost, B. M.; Verhoeven, T. R. *J. Org. Chem.* 1976, 41, 3215.

(3) (a) Faller, J. W.; Laffey, K. J. *Organomet. Chem. Synth.* 1972, 1, 471. (b) Christ, D.-C. H.; Hüttel, R. *Angew. Chem.* 1963, 75, 921. (c) Schenach, T. A.; Caserio, F. F., Jr. *J. Organomet. Chem.* 1969, 17. (d) Hüttel, R.; Kochs, P. *Chem. Ber.* 1968, 101, 1043.

(4) Dunne, K.; McQuillin, F. J. *J. Chem. Soc. C* 1970, 2196.

(5) (a) Bullpitt, M. L.; Kitching, W. J. *Organomet. Chem.* 1972, 46, 21. (b) Hutchins, R. O.; Learn, K.; Fulton, R. P. *Tetrahedron Lett.* 1980, 21, 27.

(6) Jones, D. N.; Knox, S. D. *J. Chem. Soc., Chem. Commun.* 1975, 165.

(7) Tsuji, J.; Yamakawa, T. *Tetrahedron Lett.* 1979, 613.

(8) Both isomers showed *J* = 11-12 Hz for the olefinic protons in the <sup>1</sup>H NMR (100 MHz) and no =CH out of plane bending around 960 cm<sup>-1</sup> in the IR (ascribable to trans-disubstituted olefins).

(9) The syn geometry of 3 (as a solution in CDCl<sub>3</sub> or CD<sub>3</sub>OD) is apparent from the coupling pattern (triplet, *J* = 11.5 Hz) of the proton attached to the central carbon of allylic moiety. Robinson, S. D.; Shaw, B. L. *J. Chem. Soc.* 1963, 4806.

(10) Tamaru, Y.; Kagotani, M.; Yoshida, Z. *J. Chem. Soc., Chem. Commun.* 1978, 367.

(11) *E* and *Z* mixtures of dienes were used without separation.

(12) It is crucial to dissolve 5 (and/or 6) completely before addition of DMG, otherwise the reaction loses its selectivity to give intractable mixtures, which mainly consist of 7 and/or 8 and their regio isomers, dienylyl neophyl sulfones, and starting dienes. In cases where 5 showed very poor solubility in CH<sub>3</sub>OH, a sufficient amount of pyridine (2-5 equiv to 5) or CH<sub>2</sub>Cl<sub>2</sub> was added to dissolve the 5.